Effect of ball milling energy on rheological and thermal properties of amaranth flour

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Abstract Pearled amaranth grains obtained by abrasive milling were processed by planetary ball milling to produce amaranth flours. The influence of milling energy on rheological and thermal behavior of amaranth flour dispersions and stability during 24 h storage at 4 °C were investigated based on a factorial design. The rheological behavior of flour dispersions (4 % and 8 % w/v) was determined using a rotational viscometer, while gelatinization degree was determined by differential scanning calorimetry as a measure of structural changes. The power law model was found to be suitable in expressing the relationship between shear stress and shear rate. Flour dispersions showed a pseudoplastic behavior. However this character decreased with the storage being dependent on flour concentration and milling energy. A decrease of the consistency index and an increase of the flow behavior index were observed as a result of the increasing milling energy. Gelatinization enthalpy decrease showed the loss of crystalline structure due to ball milling. Amaranth flour dispersions presented increasing stability during storage. It was observed, that the stability changed with the concentration of amaranth flours. Thus, more stable dispersions were obtained as the

flour concentration increased. The highly milled sample was the most stable sample during the storage.

Keywords Ball milling · Amaranth · Pseudoplastic behavior · Viscosity

Introduction

Over many years the traditional grains has been essential food for mankind. Recently the use of pseudocereals such as amaranth and quinoa has increased as a good raw material for the production of pasta, breakfast food, extruded and expanded products; bread and bakery goods and soup, because of its nutritional, processing and storing characteristics (Bodroza-Solarov et al. 2008). Several researchers achieved good results in the preparation of pasta and baked goods by mixing amaranth flour and cassava starch (Fiorda et al. 2013; Sanz-Penella et al. 2013).

The knowledge of rheological properties of flour dispersions is important to control the process conditions, design flow systems and estimate texture of foods. In the same way, the effect of temperature on rheological properties might be documented because a wide range of temperatures is encountered during the process and storage of food dispersions containing starches (Rao 1999a). Therefore, studies on rheological properties of flour dispersions are very important for the purpose of producing products with the desirable qualities. Wang et al. (1999) and Bhattacharya (Bhattacharya and Bhattacharya 1994, Bhattacharya and Bhattacharya 1996) have studied the rheological properties of rice and maize flour dispersions, respectively. They found that under steady shear, the rheological properties of dispersions depend on concentration, temperature and variety. Consequently, the modification

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of the rheological properties in flour could increase its industrial use.

In a recent paper, the effect of planetary ball-milling on amaranth flour characteristics such as particle size distribution, hydration properties and crystallinity degree was investigated using X-ray diffraction and FT-IR spectroscopy. It was found that ball-milling treatment could cause crystallinity loss in starch structure (Roa et al. 2014). It is expected that high homogenization and particle size reduction provided by the planetary ball mill have an influence on rheological behavior of flour dispersions. However, till preset no attempt has been made to study rheological properties of amaranth flour which was modified by high impact milling.

The objectives of this study were (i) to determine the rheological and thermal properties of amaranth flour dispersions affected by milling energy, using a rotational viscometer and a DSC technique; (ii) to identify the effects of the concentration and milling energy on apparent viscosity and the stability of flour dispersion during 24 h of refrigerated storage.

Materials and methods

Material

Amaranth grains (*Amaranthus cruentus*) used in this study were harvested on the west of Buenos Aires by Cereales Naturales S.R.L (Lomas del Mirador, Argentina). The grains were screened to remove foreign matter and stored in sealed containers at room temperature previous to their use. The moisture content of amaranth grain was 10.5 ± 0.1 g/100 g (AOAC 2000).

Amaranth flour

Amaranth fraction was first obtained by abrasive milling using a laboratory mill Suzuki MT-95 (Suzuki, Sao Pablo, Brazil) with a rotational speed of 2800 rpm. This mill device separates pearled amaranth (starchy fraction yield, 70 %) and bran (lipid-protein fraction yield, 28 %). Milling conditions involved 100 g of milling load and 90 min of milling time (Roa et al. 2013). Pearled amaranth (164 g) was then milled in a planetary ball mill model PM-100 (Retsch, Haan Mettman, Germany) with one stainless steel milling cylinder (500 mL). The amaranth sample and five times weight stainless steel balls (25 balls = 820 g, $\Phi = 10$ mm) were placed into the stainless steel container up to about two thirds of their capacity. The mill was rotated horizontally at constant milling speed of 400 rpm at four levels of energy (0.92–1.63–2.87–6.52 kJ/g of sample) obtaining the amaranth flours. The ball milling was changed in rotational direction every 30 s. Milling energy values were selected as a milling variable from the operative menu. Control tests were performed for each energy

level in order to discount the energy consumption without sample. Milled samples were sifted in a Testing Equipment, model Zonytest through sieves (ASTM standard, USA) n° 60 (250 μ m), n° 80 (177 μ m) and n° 200 (74 μ m). The residue (74 μ m) contained the flour and was selected for different analysis.

Particle size

Particle size distribution of amaranth flour was measured by static light scattering (SLS) using a Mastersizer 2000 device equipped with a Hydro 2000MU as dispersion unit, from Malvern Instruments Ltd. (Malvern Instruments Ltd., Worcestershire, UK). Five scans were recorded for each sample. Sample dispersion was calculated in term of Span (Eq. 1) as function of diameters Dv_{10} , Dv_{50} and Dv_{90} stand for 10 %, 50 % and 90 % of total volume at particles distribution, assuming a spherical shape. Where, Dv_{10} , Dv_{50} , and Dv_{90} are values calculated by the software using the Rayleigh theory. Mean and standard deviation values of triplicates are reported.

$$\text{Span} = \frac{Dv_{90} - Dv_{10}}{Dv_{50}} \quad (1)$$

Thermal properties

Thermal properties of amaranth flour were determined by DSC analysis using a DSC 822 (Mettler-Toledo model, Schwerzenbach, Switzerland) with an empty pan as reference. Thermal parameters were recorded in triplicate. Amaranth flour (3 mg, dry weight basis) was placed in a 40- μ L aluminum pan, and distilled water was added to give a sample-to-water weight ratio of 1 to 3. The pan was sealed, and the sample was allowed to equilibrate overnight at 4 °C before analysis. In the DSC, the sample was held at 30 °C for 1 min followed by heating from 30 °C to 95 °C at a rate of 10 °C/min. Gelatinization temperatures, onset (T_o), peak (T_p) and endset (T_e), together with gelatinization enthalpy (ΔH) were recorded in triplicate.

Preparation of amaranth flour dispersion

Amaranth flour dispersions (4 % and 8 % w/v) were prepared by mixing amaranth flour with distilled water. These concentrations were selected based on previous tests performed with flour dispersions from 2 % to 10 % w/v. For present study two systems were selected to evaluate the effect of ball milling energy: a fluid slurry similar to a beverage (4 % w/v) and other with higher consistency, similar to a “cream soup” (8 % w/v). For preparation, the dispersions were moderately stirred for 30 min at room temperature, and heated at 95 °C in a water

Fig. 1 Particle size distribution of amaranth flours as function of milling energy

bath for 30 min with mild agitation provided by a magnetic stirrer. To the end of the heating period, the cooked amaranth flour dispersion was cooled at 25 °C and immediately transferred to the rheometer cup for the measurements of rheological properties. In order to evaluate the stability of the dispersions with time, they were stored at 4 °C for 24 h and then measurements of viscosity were repeated.

Rheological measurements

Flow properties of heated amaranth flour dispersions were determined using a rotational viscometer (Brookfield DV-LVT; Brookfield Engineering Laboratories, Inc., Middleboro, U.S.A) with coaxial cylinder probes. Measurements were made at several rotational speeds corresponding to a percentage torque ranging from 10 to 100 %. For low viscosities, an UL/Y adapter with UL spindle was used. The sample chamber with jacket was connected to a constant temperature bath in order to determine flow characteristics at constant temperature of 25 °C. Rheological tests were triplicated.

The data obtained were fitted to the power law:

$$\sigma = K\dot{\gamma}^n \quad (2)$$

Where σ is the shear stress (Pa) and $\dot{\gamma}$ is the shear rate (s^{-1}). The rheological parameters determined were the consistency

Fig. 2 Apparent viscosity of amaranth flour dispersions (4 % w/v) at 25 °C as function of shear rate for different levels of milling energy

index (K ; Pa s^n) and the flow behavior index (n ; dimensionless). Using magnitudes of K and n , apparent viscosity ($\mu_a = \sigma/\dot{\gamma}$) at specific shear stress can be calculated.

Statistical analysis

Significance of the effect of ball milling energy on rheological and thermal parameters of modified amaranth flour were evaluated by one-way ANOVA (significance level $\alpha = 0.05$ %) with Tukey post-test using Prism 5 (GraphPad Software Inc., San Diego, CA, USA). In some cases, p value was calculated by a non-parametric t test in order to deeper analyse differences between samples.

Results and discussion

Amaranth flour

Amaranth flour used in this study was characterized in previous investigations according to some of its functional properties (Roa et al. 2014). For the actual approach the particle size distributions of amaranth flours are presented in Fig. 1 as a function of the grinding energy delivered during ball milling. Table 1 resumes the characteristics parameters obtained from each particle size distribution. It can be appreciated that median particle size (D_{50}) range from 880 μm (0 kJ/g control) up

Table 1 Particle size distribution characteristics and thermal parameters of amaranth flours obtained by planetary ball milling as function of milling energy

Milling energy (kJ/g)	Median diameter D_{50} (μm)	Span (dimensionless)	T_{onset} ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)	T_{endset} ($^{\circ}\text{C}$)	ΔH (J/g)
0.0	929.7 ± 76.4^a	0.247 ± 0.026^c	65.18 ± 1.17^a	73.48 ± 0.20^a	80.82 ± 1.18^a	7.91 ± 0.15^a
0.92	201.0 ± 3.3^b	2.032 ± 0.029^b	67.52 ± 0.74^a	74.51 ± 0.11^a	80.32 ± 0.23^a	7.04 ± 0.09^b
1.63	150.4 ± 0.5^c	2.104 ± 0.004^a	64.85 ± 5.51^a	74.26 ± 0.85^a	80.22 ± 0.11^a	5.43 ± 0.01^c
2.87	121.7 ± 0.6^d	1.909 ± 0.011^c	67.84 ± 1.14^a	74.29 ± 0.43^a	79.69 ± 0.22^a	3.39 ± 0.23^d
6.52	68.0 ± 0.5^e	1.874 ± 0.014^d	49.27 ± 0.78^b	57.07 ± 0.20^b	79.10 ± 0.0^a	0.34 ± 0.01^e

Different letters indicate significant differences ($p < 0.05$) on each column. Mean and standard deviation values of triplicates are reported

Fig. 3 Apparent viscosity of amaranth flour dispersions (8 % w/v) at 25 °C as function of shear rate for different levels of milling energy

to 70 μm (6.52 kJ/g) while the Span value changed from 2.05 (0.92 kJ/g) to 1.87 (6.52 kJ/g) stating that the samples were more homogeneous with the increasing energy.

Thermal properties

The crystalline order in starch granule is often a basic factor to influence functional properties. Collapse of crystalline order within the starch granules, generates irreversible changes in properties, such as granule swelling, pasting, loss of optical birefringence, loss of crystalline order, uncoiling and dissociation of the doubles helices, and starch solubility (Tester 1997; Singh and Singh 2003; Roa et al. 2014).

Starch gelatinization is the transition of the semi-crystalline structure in native starch granules, to an amorphous structure. This transition occurs on a heating of an aqueous suspension of starch granules. Starch transition temperatures and gelatinization enthalpies by DSC have been extensively investigated by many authors (Chen et al. 2003; Dhital et al. 2010; Dhital et al. 2011; Han et al. 2007; Campanella et al. 2002; Morrison and Tester 1994).

Table 1 reports the values of the gelatinization temperatures (T_{onset} , T_{peak} , T_{endset}) and enthalpy of gelatinization for the flour samples subjected to different ball-milling energies. Enthalpy values decreased significantly compared to those of the control sample from 7.91 ± 0.15 J/g up to 0.34 ± 0.01 J/g. A very significant reduction in gelatinization

enthalpy from 14.0 J/g to 0.13 J/g and from 6.8 J/g to 0.9 J/g was observed by Han et al. (2007) and (Loubes et al. 2012) respectively, after of rice starch or rice flour processing in a planetary ball mill; while Sanguanpong et al. (2003) and Martinez-Bustos et al. (2007) reported that milled native cassava starch was highly amorphous due to the loss of crystallinity in ball milling. Therefore, high impact milling caused a decrease of enthalpy gelatinization, producing a disruption of crystalline regions and double helix content, due to the slight depolymerization of amylose and the breakdown of amylopectin, decreasing the ability to gelatinize.

The onset temperature ($49.27 \text{ }^{\circ}\text{C} \pm 0.78 \text{ }^{\circ}\text{C}$) and the wide gelatinization range ($T_{\text{endset}} - T_{\text{onset}} = 29.83 \text{ }^{\circ}\text{C}$) of the highly treated sample, was significantly different from those shown in Table 1. This behavior is due to a decrease on the crystallinity degree (Roa et al. 2014), which causes an unstable structure and makes the granule less resistant. Another reason is due to irregularly shaped granules produced after ball-milling. A decrease of thermal parameters with an increase of milling time was also reported by Han et al. (2007) and Huang et al. (2007), who studied the effect of milling time on thermal parameters of rice starch and cassava starch respectively. While Singh and Singh (2003) and Kaur et al. (2002) reported lower transition temperatures due to irregular shape of potato starch granules.

Rheological properties

The effect of milling energy on the viscosity of the flour dispersions, as function of shear rate, is shown in Figs. 2 and 3 at different starch concentrations. The apparent viscosity decreased with the increasing shear rate, implying that all the samples behaved as shear thinning systems. The highest viscosity values were obtained at lowest shear rate, and the lowest at highest shear rate. Similar behaviour was observed by Ibanoglu and Ibanoglu (1999) and Manohar et al. (1998) when they studied semi liquid breakfast food.

The data of apparent viscosity at different shear rates was used to determine the behavior of consistency coefficient and flow index, by power law model (Eq. 2). Consistency

Table 2 Consistency index (Eq. 2) of amaranth flour dispersions at 25 °C as function of flour concentration and storage time¹

Milling energy (kJ/g)	Consistency index (K) Flour dispersion 4 % (0 h) ¹	Consistency index (K) Flour dispersion 4 % (24 h) ¹	Consistency index (K) Flour dispersion 8 % (0 h) ¹	Consistency index (K) Flour dispersion 8 % (24 h) ¹
0.0	172.0 $\pm$ 18.0 ^a	56.21 $\pm$ 3.07 ^c	5845 $\pm$ 590 ^a	3773 $\pm$ 102 ^b
0.92	158.7 $\pm$ 14.3 ^{ab}	53.23 $\pm$ 3.19 ^c	4899 $\pm$ 159 ^a	3462 $\pm$ 141 ^{bc}
1.63	128.9 $\pm$ 3.7 ^{ab}	37.52 $\pm$ 0.48 ^d	4736 $\pm$ 96 ^a	3277 $\pm$ 66 ^{cd}
2.87	125.8 $\pm$ 2.9 ^b	34.54 $\pm$ 1.57 ^d	3856 $\pm$ 214 ^b	3079 $\pm$ 65 ^d
6.52	57.9 $\pm$ 7.7 ^c	24.24 $\pm$ 1.72 ^e	606.3 $\pm$ 28.3 ^c	678 $\pm$ 15 ^e

Different letters indicate significant differences ($p < 0.05$) on each concentration. Mean and standard deviation values of triplicates are reported

Table 3 Flow behavior index (Eq. 2) of amaranth flour dispersions at 25 °C as function of flour concentration and storage time¹

Milling energy (kJ/g)	Flow index (<i>n</i>) Flour dispersion 4 % (0 h) ¹	Flow index (<i>n</i>) Flour dispersion 4 % (24 h) ¹	Flow index (<i>n</i>) Flour dispersion 8 % (0 h) ¹	Flow index (<i>n</i>) Flour dispersion 8 % (24 h) ¹
0.0	0.47 ± 0.01 ^b	0.46 ± 0.09 ^b	0.28 ± 0.05 ^d	0.60 ± 0.04 ^a
0.92	0.48 ± 0.04 ^b	0.43 ± 0.02 ^b	0.36 ± 0.02 ^{cd}	0.58 ± 0.02 ^a
1.63	0.49 ± 0.04 ^b	0.42 ± 0.09 ^b	0.39 ± 0.01 ^c	0.56 ± 0.02 ^a
2.87	0.51 ± 0.01 ^b	0.40 ± 0.07 ^b	0.48 ± 0.02 ^b	0.55 ± 0.05 ^a
6.52	0.64 ± 0.04 ^a	0.30 ± 0.08 ^c	0.56 ± 0.02 ^a	0.48 ± 0.02 ^b

Different letters indicate significant differences ($p < 0.05$) on each concentration. Mean and standard deviation values of triplicates are reported

coefficient (K) and flow index (n) values on time (0 h – 24 h) are given in the Tables 2 and 3 respectively.

All processed samples (4 % - 8 %) at time (0 h) showed an increase in value of n as the milling energy increased. This behavior is due to the ball milling, which produced the breakage of the intra and intermolecular associative bonding system in the starch network, increasing the starch solubility and affecting the process of hydration and swelling of the starch granule. Hasjim et al. (2012) showed similar results when they studied rice milling using hammer and cryogenic milling.

The flour solutions 8 % showed a significant increase in flow index (n) during storage at 4 °C for 24 h (i.e. samples from 0.0 kJ/g to 2.87 kJ/g). This decrease in pseudoplastic behavior was probably induced by rearrangement of amylose, which increased free-water of system during storage. However, the highly milled sample (6.25 kJ/g), showed a lower flow behavior index ($n = 0.48$) after storage compared to flow behavior index ($n = 0.56$) before storage. This indicates that it was the most stable sample after storage.

The K values increased as the concentration increased, due to a higher presence of amylose and amylopectin which facilitates network starch formation (Autio and Eliasson 2009). This ability is lost with increasing grinding due to the changes caused on structure of starch granule. Therefore, the consistency index value decreased as the milling energy increased (Table 2). However, the highly milled samples showed higher stability during storage. This stability is reflected in lower variation on K value before and after storage.

Conclusions

This study showed that ball milling processing achieved particle size reduction, causing rupture of starch granule, loss in the gelatinization enthalpy and an increasing solubility. These features induced the decreasing pseudoplastic behavior and a higher stability of the soups during storage. The stability of modified amaranth starch represents a technological advantage in the development of liquid food in comparison with the native starch; since it avoids or delays the phase separation

in the product. The decrease in viscosity of soups with shear rate levels would facilitate the flow and exchange of heat during the process, generating low energy demand for the process. The ball milling is a simple process that presents minimal environmental problems and is easy to operate. By selecting appropriate operation conditions, ball milling can provide amaranth fractions with some special functional properties that may be of potential use in the food industry. To conclude, a more suitable performance to develop liquid food could be obtained using amaranth flour by the application of ball milling procedure.

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