
Volume 57, Issue 1, June 2014
ISSN 0023-6438
ELSEVIER
LWT -
Food Science and Technology
An official publication of the
Swiss Society of Food Science and Technology
and
International Union of Food Science and Technology
SGLWT SOSSTA
IUFoST
Available online at www.sciencedirect.com
ScienceDirect
www.elsevier.com/locate/lwt

LWT - Food Science and Technology 57 (2014) 320–328

Contents lists available at ScienceDirect

LWT - Food Science and Technology

journal homepage: www.elsevier.com/locate/lwt

Thermo-mechanical rice flour modification by planetary ball milling

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ARTICLE INFO

Article history:
Received 16 March 2013
Received in revised form
15 August 2013
Accepted 19 December 2013

Keywords:
Particle size
Thermal properties
Crystallinity
Damaged starch
Planetary ball milling

ABSTRACT

Planetary ball milling is presented as an alternative way to improve the native flour properties by physical modification. A grinding protocol was developed by combination of grinding and pause stages. The effect of rotational speed (450–650 rpm) and milling time (10–20 min) on flour properties were determined using RSM method. The effect of milling conditions on flour attributes was significant. With increasing milling speed and time a significant increase in damaged starch, water-absorption and solubility indexes was observed. Changes in functional attributes, intrinsically related to structural and morphological properties of rice flour, were satisfactorily correlated with crystallinity loss, specific surface area and gelatinization degree. Modified rice flours presented pre-gelatinized characteristics which can offer new opportunities for flour applications, for example as ingredient for instant meal product. Flour modification can be controlled by selecting milling conditions. The distinctive characteristic of the planetary ball mill was the fast speed with which the modified flour was obtained which presented intermediate characteristics in relation with native and amorphous state.

1. Introduction

Rice flour is a valuable food product which has a wide variety of applications including baby food, traditional Asian food, gluten-free rice bread and other food products for gluten-sensitive individuals (Yeh, 2004). Furthermore, rice flour is also considered a suitable material in the field of biodegradable and edible films (Dias, Müller, Larotonda, & Laurindo, 2011).

Three methods are used to prepare rice flour: wet, semi-dry and dry milling. Even though wet milling minimizes starch damage of rice flour, it causes some loss of nutrients in the process water. Due to high costs and environmental concerns, dry or semi-dry methods have been used to produce rice flour similar in quality to that obtained by wet-milling (Champagne, 2004).

The usual machinery for flour manufacture (wet and dry) includes hammer, roller and attrition mills. Pin, ball, blade, and cryogenic mills are also used. These mills differ in the effective operating forces and the extent of frictional heat generation during grinding. Cryogenic milling was recently developed in order to avoid frictional heat (Mahasukhonthachat, Sopade, & Gidley, 2010).

The different types of mills and grinding methods significantly affect the physicochemical and functional properties of rice flour such as swelling power, solubility, gelatinization temperatures and enthalpy values (Chen, 1995; Chen, Lu, & Lii, 1999; Nishita & Bean, 1982; Yang, 1994).

In recent years, researchers have focused their attention on the physical methods to modify the functional properties of flours and starches. Hydrothermal treatment (Cham & Suwannaporn, 2010; Wu, Chen, Li, & Wang, 2010) was successfully applied to expand the usefulness of rice flours. The effects of ball milling on structure and porosity of starch granule, starch conversion to an amorphous state, starch fragmentation and crystallinity loss have been recently reported in the literature (Anzai, Hagiwara, Watanabe, Komiyama, & Suzuki, 2010; Han, Chang, & Kim, 2007; Liu, Ma, Yu, & Xue, 2011; Martínez-Bustos, López-Soto, San Martín-Martínez, Zazueta-Morales, & Velez-Medina, 2007).

Planetary ball mill, a novel technology, which is increasingly being used in mechanochemistry as a method for carrying out chemical synthesis and obtaining nano powders by means of dry or wet milling (Charkhi, Kazemian, & Kazemeini, 2010; Fukumori et al., 1998; Zhang et al., 2009), is actually very little used in the food industry. The limited information found is related to waste recovery in the food industry to produce mechanically activated powder or to obtain amorphous and porous or materials by means of high energy milling (Tsai et al., 2008). These millings are frequently associated to long grinding time (several hours). However, the effects achieved by means of short grinding times have not been sufficiently explored.

In this study, the potential of planetary ball milling to obtain modified rice flour was investigated. In an attempt to control thermo-mechanical damage an adequate grinding protocol was

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http://dx.doi.org/10.1016/j.lwt.2013.12.048

developed. A factorial design based on milling time and rotational speed was established using a constant ball-to-rice mass ratio. Changes in particle size distribution, damaged starch level, absorption index, swelling power, rice flour crystallinity and thermal properties of rice flour were observed as function of grinding conditions. The correlations among ball-milling attributes were also investigated.

2. Materials and methods

2.1. Materials

Long-grain milled rice with 23.7 g/100 g amylose content (dry basis) and 13.2 g/100 g moisture content (dry basis) was purchased at a local market. The grains were hand-cleaned to remove any foreign material before their storage in plastic bags at 4 °C prior to their use. The proximate composition of rice grain was determined by standard methods: starch (AACC, 1995, 76-01 method); protein (AOAC, 1995, 976.05 method); fat (AOAC, 1995, 920.39 method) and ash (AOAC, 1995, 923.03 method).

2.2. Dry milling of rice

A high impact planetary ball mill (model PM100, Retsch Co., Germany) with a milling speed range of 100–650 rpm was used for pulverization of the milled rice. The direction of movement of the sun wheel is opposite to that of the grinding jars in the ratio of 1:2. Milled rice grains (200 g) were put into the jar (500 mL) containing eight zirconium oxide beads (30 mm diameter). The latter is the ball-to-powder mass ratio recommended by the manufacturer.

A factorial design was employed comprising two factors: rotational speed (450, 550, 650 rpm) and grinding time (10, 15, 20 min). A rotational speed range was established in order to obtain convenient particle size and to limit milling times. A grinding time range was established in order to avoid overheating of the flour sample. Experimental design with triplicate at the central point is shown in Table 1. Each milling test was conducted in duplicate.

Rice flour obtained from milled rice grain (25 g), with 30 s milling time in a Butt mill (Decalab Fbr®, Buenos Aires, Argentina) was used as the control sample.

2.3. Moisture and damaged starch

The moisture in rice flour was determined by following the AACC (44–15A) standard method (AACC, 1995). Damaged starch was assayed by the AACC standard method (76-30A) using a damaged starch assay kit (Megazyme International Ireland Ltd., Ireland). The results were reported as g/100 g flour (dry basis).

2.4. Particle size distribution

Particle size distribution of flour samples were also measured by static light scattering (SLS) using a Mastersizer 2000 device equipped with a Hydro 2000 MU as dispersion unit, from Malvern Instruments Ltd (Malvern Instruments Ltd, Worcestershire, UK). The pump speed was settled at 1800 rpm. Deionized water was used as dispersing reagent, and the refractive index and absorptivity of it was 1.53, and 0.001 respectively. The values of Dv10, Dv50, Dv90 and a measure of dispersion called *Span* (Charkhi et al., 2010) were reported.

Table 1
Experimental design and values of damaged starch (DS) and moisture content (MC).

Experiment number	Rotational speed (rpm)	Milling time (min)	MC[b] (g/100 g)	DS[b] (g/100 g)
	Experimental (Coded[a])	Experimental (Coded[a])		
1	450 (−1)	10 (−1)	12.83 ± 0.01	9.7 ± 0.2
2	450 (−1)	15 (0)	12.51 ± 0.02	11.8 ± 0.1
3	450 (−1)	20 (1)	12.29 ± 0.05	13.0 ± 0.4
4	550 (0)	10 (−1)	12.45 ± 0.02	12.3 ± 0.4
5[c]	550 (0)	15 (0)	12.43 ± 0.01	13.3 ± 0.2
6	550 (0)	20 (1)	12.41 ± 0.06	14.0 ± 0.1
7	650 (1)	10 (−1)	11.74 ± 0.01	14.2 ± 0.4
8	650 (1)	15 (0)	11.54 ± 0.03	15.5 ± 0.4
9	650 (1)	20 (1)	11.27 ± 0.01	16.6 ± 0.2

[a] A linear relationship among experimental and coded factors was used.
[b] Dry basis.
[c] Central point by triplicate.

$$\text{Span} = \frac{\text{Dv90} - \text{Dv10}}{\text{Dv50}} \tag{1}$$

Dv10 and Dv90 represent the particle diameters that cumulative volume of particles are 10% and 90%, respectively and Dv50 is the median for a volume distribution. The specific surface area (SSA), calculated by the software from the diameter D (4.3) (Raphaelides & Georgiadis, 2006) were also reported. The particle sizes are reported as the average and standard deviation of ten readings made on a sample.

2.5. Hydration properties

Water absorption index (WAI) was determined using the method of Chiang and Yeh (2002). Swelling power (SP) and water soluble index (WSI) were obtained by the procedure of Vandeputte, Derycke, Geeroms, and Delcour (2003). Water solubility, swelling power, and water absorption index were calculated as follows:

$$\text{WAI}\ (\text{g/g}) = \frac{\text{weight of sediment}}{\text{weight of dry sample solids}} \tag{2}$$

$$\text{WSI}\ (\text{g/100 g}) = \frac{\text{weight of dry supernatant}}{\text{weight of dry sample solids}} \times 100 \tag{3}$$

$$\text{SP}(\text{g/g}) = \frac{\text{weight of sediment}}{\text{weight of dry sample solids} - \text{weight of dry supernatant}} \tag{4}$$

All values were expressed on a dry weight basis and they were the average of two determinations.

2.6. X-ray diffractometry

The X-ray diffraction patterns of rice flour samples were measured using a diffractometer (XRD model PW1730/10, Philips, Netherlands) under the following conditions: Copper target tube, settled at 30 kV and 30 mA, scanning regions of the diffraction angle

$2\theta = 0–60°$, and scanning velocity 4.0°/min. The crystallinity degree was expressed as a percentage and calculated from the crystalline and amorphous areas obtained in each diffraction pattern as:

$$\mathrm{CD}\ (\%) = \frac{\mathrm{Ic}}{(\mathrm{Ia}+\mathrm{Ic})} \times 100 \tag{5}$$

where Ia = amorphous area on the X-ray diffractogram, Ic = crystallized area on the diffractogram (Zhang, Zhao, & Xiong, 2010).

2.7. Thermal properties

A DSC analysis was conducted using a calorimeter (DSC model 822, Mettler-Toledo, Schwerzenbach, Switzerland). Approximately 4.0 mg of flour sample was weighed in an aluminum pan after which distilled water was added to obtain a starch-to-water ratio of 1:3 (g/g). The sealed pan was equilibrated for 24 h before analysis. Scans were run at a heating rate of 10 °C/min from 30 °C to 100 °C using an empty pan as reference. Gelatinization temperatures, onset (T_o), peak (T_p) and endset (T_e), together with gelatinization enthalpy (μH) were recorded in triplicate. The gelatinization degree was calculated as percentage using:

$$\mathrm{GD}\ (\%) = \left(1 - \frac{\Delta H}{\Delta H_c}\right) \times 100 \tag{6}$$

where ΔH is the gelatinization enthalpy of rice flour samples and ΔH_C is the gelatinization enthalpy of the control sample expressed in J/g (dry basis).

2.8. Statistical analysis

A response surface methodology (RSM) was applied to analyze the effect of process factors (milling speed and milling time) on rice flour characteristics. The studied responses (Y_K, $K = 1,\ldots p$) were matched to the coded factors (x_i, $i = 1,\ldots n$) by the following polynomial model associated with the experimental design (Khuri & Cornell, 1987):

$$Y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{\substack{i=1 \\ i<j}}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^{n} a_{ij} x_i x_j \tag{7}$$

The coefficients a_0, a_i and a_{ii} represent the constant, linear and quadratic effects respectively, and a_{ij} represents the interaction effect of factors x_i and x_j. A linear relationship between coded and processing factors was adopted (Khuri & Cornell, 1987).

The Statgraphics Plus® software package (version 5.1, Statistical graphics Corporation, USA) was used to perform the statistical analysis.

3. Results and discussion

3.1. Preliminary milling tests

Grain composition was determined in duplicate, the results expressed in wet basis were: moisture (11.7 g/100 g), starch (79.5 g/100 g), fat (0.5 g/100 g), protein (7.8 g/100 g; N × 5.75), and ash (0.4 g/100 g).

To select the jar and ball material, stainless steel and zirconium oxide accessories were tested. The effect of jar and bead material on particle size distribution of rice flour was analyzed. A more dispersed particle size distribution was obtained with the use of stainless steel accessories. The lower hardness of this material (544 HV) as compared to zirconium oxide (1200 HV) also caused a significant contamination of rice flour by abrasion effect. As consequence, zirconium accessories were selected.

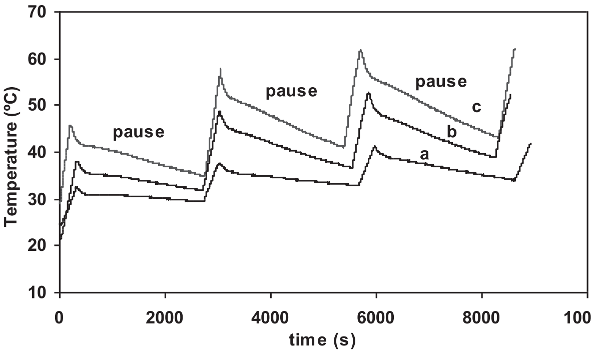

Fig. 1. Grinding protocol: effect of milling speed on sample temperature. 450 rpm (a), 550 rpm (b), 650 rpm (c). Grinding periods of 5 min followed by pause interval of 40 min.

Preliminary tests were also performed to determine the grinding protocol of rice grains. A special device (PM GrindControl Retsch Co., Germany) was used to monitor rice temperature in order to avoid product overheating. Fig. 1 shows the selected grinding protocol at different rotational speeds, which also includes grinding periods of 5 min followed by pause intervals of 40 min. Grinding was performed with direction reversal every 30 s to prevent the ball slipping. Such grinding cycle ensures temperature control of the rice sample. It was observed that temperature reached higher values with increasing milling time at fixed milling speed. The highest values of temperature were 42 °C, 53.1 °C and 62.3 °C at 450, 550 and 650 rpm respectively. Moisture content decreases (~10%) as milling speed increases from 450 to 650 rpm (Table 1).

3.2. Damaged starch

Table 1 shows the experimental data of damaged starch percentage as function of milling conditions. It was observed that values of damage starch resulted greater than the control value (2.7 ± 0.3 g/100 g). Milling speed as well as milling time significantly affected damaged starch. Damaged starch reached 16.6 g/100 g at 650 rpm and 20 min of milling time. This value represents six times the control value. Damaged starch values within the range 4.86–9.19 g/100 g have been reported by Lu and Lin (2001) using the conventional milling procedures (hammer mill, attrition grinders). The thermo-mechanical modification of rice flour can be accurately followed by means of damaged starch content.

Table 2 shows the effect of milling conditions on damaged starch determined by RSM, in terms of codified milling speed (x_1) and

Table 2
Effects of milling conditions on damaged starch, parameters of size distribution and water absorption index in terms of codified variables: grinding speed (x_1) and milling time (x_2).

Coefficient		DS (g/100 g)	Dv50 (μm)	Span	WAI (g/g)
Constant	a_0	13.175	93.8	1.285	2.949
Linear	a_1	2.575*	−45.0*	0.358*	0.255*
	a_2	1.438*	−44.5*	0.062*	0.211*
Quaratic	a_{11}	0.188NS	−7.0	0.198	0.009NS
	a_{22}	0.01NS	93.8	1.285	0.02NS
Interaction	a_{12}	−0.263NS	−1.0	0.148	0.125*
Correlation	r^2	0.9795	0.9965	0.9820	0.9625

*Significant at $p < 0.05$; NS: non significant coefficient; –, eliminated coefficient. DS: damaged starch, Dv50: median diameter, Span: measure of distribution dispersion, WAI: water absorption index.

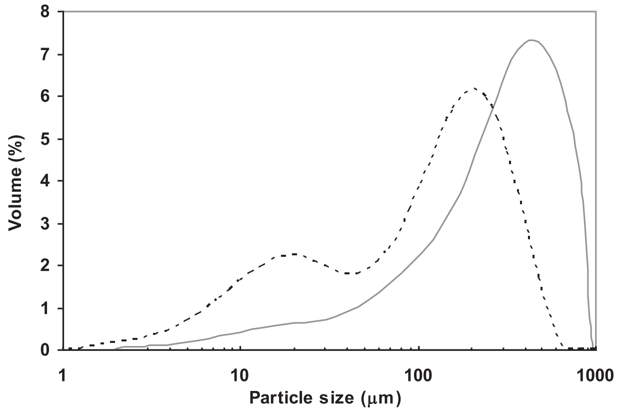

Fig. 2. Volume size distribution by static light scattering (SLS). Control sample (—); Central point of experimental design (– –).

milling time (x_2). Equation (7) provided a satisfactory fit of experimental data of damaged starch ($R^2 = 0.98$). The linear effects of both factors on damaged starch were significant. The minimum value of DS (9.7 g/100 g) was obtained by milling at 450 rpm during 10 min.

3.3. Determination of particle size distribution

Modified rice flours presented a bimodal distribution in comparison with control sample as it can be appreciated in Fig. 2 for flour sample obtained at 550 rpm and 15 min (central point of experimental design) with peak values at 20 and 209 μm. The parameters of particle size distribution are shown in Table 3 in terms of Dv10, Dv50, Dv90 and span values as function of selected milling conditions. It was observed that modified rice flours presented lower values of particle size parameters in contrast with the control; whereas the contrary effect was found for the span values. The different diameters (Dv10, Dv50 and Dv90) decreased with increasing milling speed and time. This result reflects the ascendant relevance of fine fraction (20 μm peak value) as milling conditions became more severe. RSM was applied to analyze the effect of milling conditions (factors) on parameters of particle size distribution: Dv50 and span (Table 2). The responses studied were suitably explained by a second-order model (Eq. (7)) and acceptable fitting ($R^2 \geq 0.98$) was obtained for the studied responses. It was found that milling speed (linear effect) and milling time (linear effect) affected the values of Dv50 and span. However, an increase in milling time led to lower values of Dv50 and simultaneously to lower homogeneity (higher span values) as a consequence of bimodal distribution of particle size generated by ball milling. Some authors have reported particle agglomeration as consequence of the high energy involved in planetary ball milling (Fukumori et al., 1998) or hammer milling (Suksomboon & Naivikul, 2006). In contrast, no agglomeration was found by SLS method in the present work. Probably as a consequence of short periods of grinding applied.

Table 3
Size characteristics of rice flour at different milling condition.

Experiment number	Dv10[a] (μm)	Dv50 (μm)	Dv90 (μm)	Span[b]
Control	52.06 ± 2.93a	322.23 ± 3,91a	712.78 ± 5,89a	2.05 ± 0.03a
1	17.06 ± 0.67b	262.80 ± 8.12b	669.18 ± 13.68b	2.48 ± 0.05c
3	15.54 ± 0.31c	187.71 ± 3.38d	455.32 ± 6.64e	2.34 ± 0.03b
4	15.01 ± 0.43c	244.08 ± 6.85c	634.27 ± 10.51c	2.54 ± 0.06c
6	12.44 ± 0.28d	131.11 ± 3.62f	352.70 ± 6.98f	2.60 ± 0.09c
7	12.77 ± 0.50d	174.78 ± 8.36e	519.20 ± 18,93d	2.90 ± 0.12d
9	9.11 ± 0.13e	96.26 ± 4.17g	331.77 ± 7.74g	3.35 ± 0.09e

Values followed by the same online letter within a column do not differ significantly ($p < 0.05$).

[a] Dv10 and Dv90 represent the particle diameters that cumulative volume of particles are 10% and 90%, respectively, Dv50, median diameter.

[b] Size dispersion index.

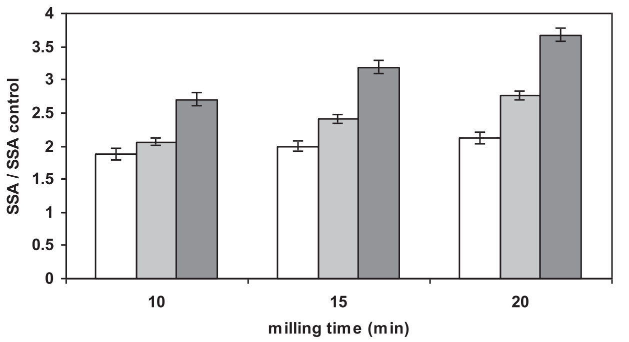

Fig. 3. Values of relative specific surface area as function of milling conditions. 450 rpm (□); 550 rpm (▨); 650 rpm (■).

The values of relative specific surface area (RSSA = SSA/SSA$_{\text{control}}$) are shown in Fig. 3 as function of milling conditions. A significant effect of milling conditions on specific surface area was observed. The values of specific surface area (SSA) were 0.066 and 0.181 m^2/g for control and central point respectively. The flour modifications achieved in this work resulted moderated in comparison with the SSA of starch nanoparticles (SSA = 1.64 m^2/g) reported by Szymońska, Targosz-Korecka, and Krok (2009).

3.4. Water absorption index

Values of index are shown in Fig. 4 as function of milling conditions. The effect of milling factors on WAI can be observed in Table 2. The analysis was performed by RSM and satisfactory results were obtained using Eq. (7) ($R^2 = 0.96$). There were significant effects of milling speed (linear), milling time, and interaction between milling speed and process time on WAI. This index increased as both factors were increasing, being the effect of milling speed more marked at 20 min milling time. The maximum (3.55 g/g) and minimum (2.62 g/g) values of WAI were obtained at 650 rpm (20 min) and 450 rpm (10 min) respectively.

In this study, WAI varied between 2.6 and 3.5 g/g. These values are greater than those of the control (2.3 g/g). Lower values of WAI (2.1–2.9 g/g) were reported by Chiang and Yeh (2002) for rice flour obtained by means of a wet-milling procedure instead of dry milling.

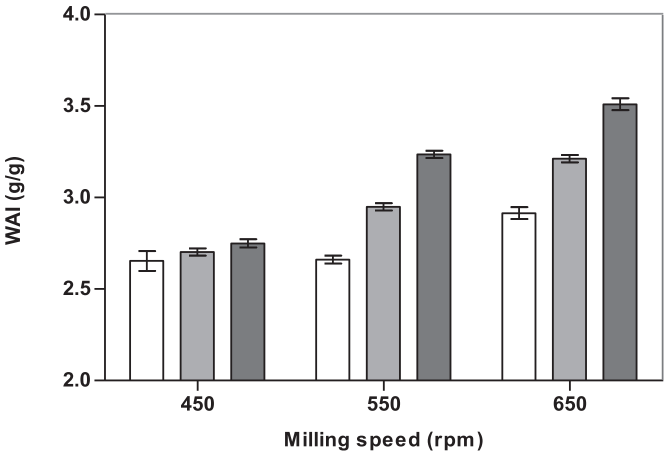

Fig. 4. Values of water absorption index as function of milling conditions. 10 min (□); 15 min (▨); 20 min (■).

3.5. *Swelling power and water solubility index*

The resulting data of SP and WSI for the different milling conditions are shown in Figs. 5 and 6 respectively. As it can be observed, that SP values of modified rice flour at constant temperature resulted higher than control value at the same temperature. However, in the case of WSI, the comparison between control and modified flours values depended on the temperature used.

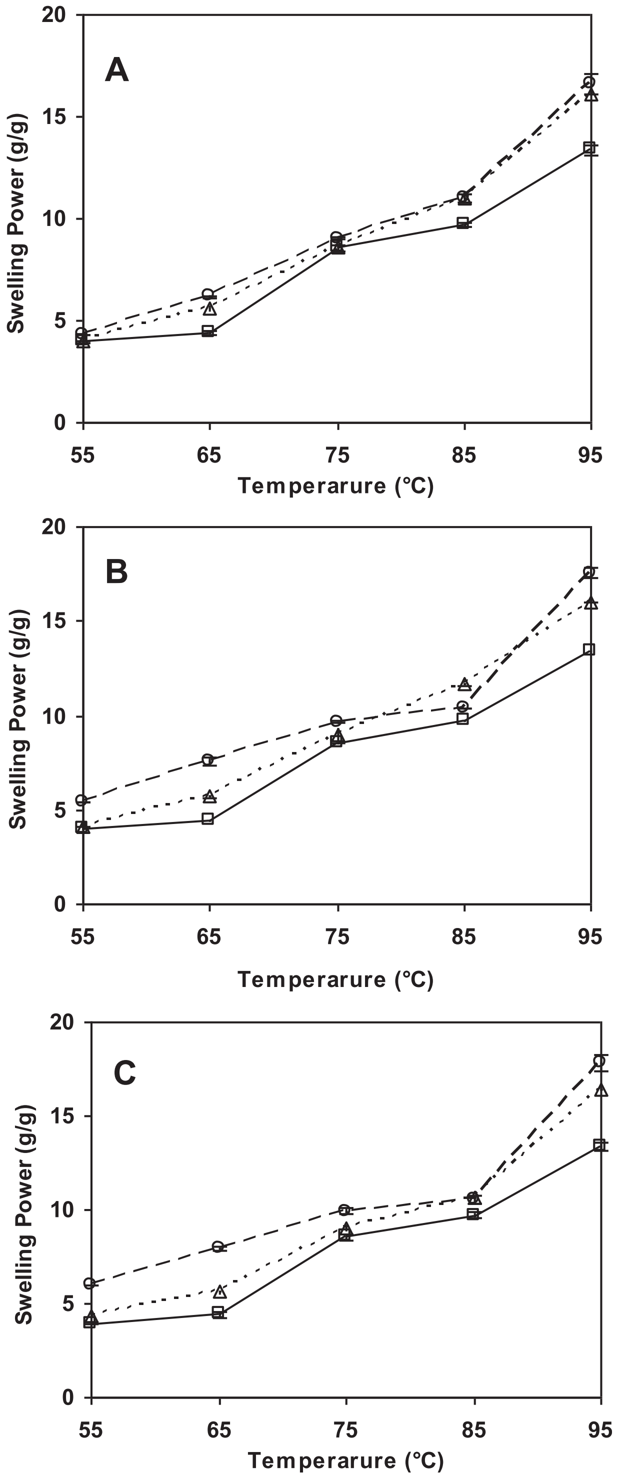

Fig. 5. Effect of milling time on swelling power (SP) at different milling speeds: 450 rpm (A), 550 rpm (B), 650 rpm (C); Control (□), 10 min (△), 20 min (○).

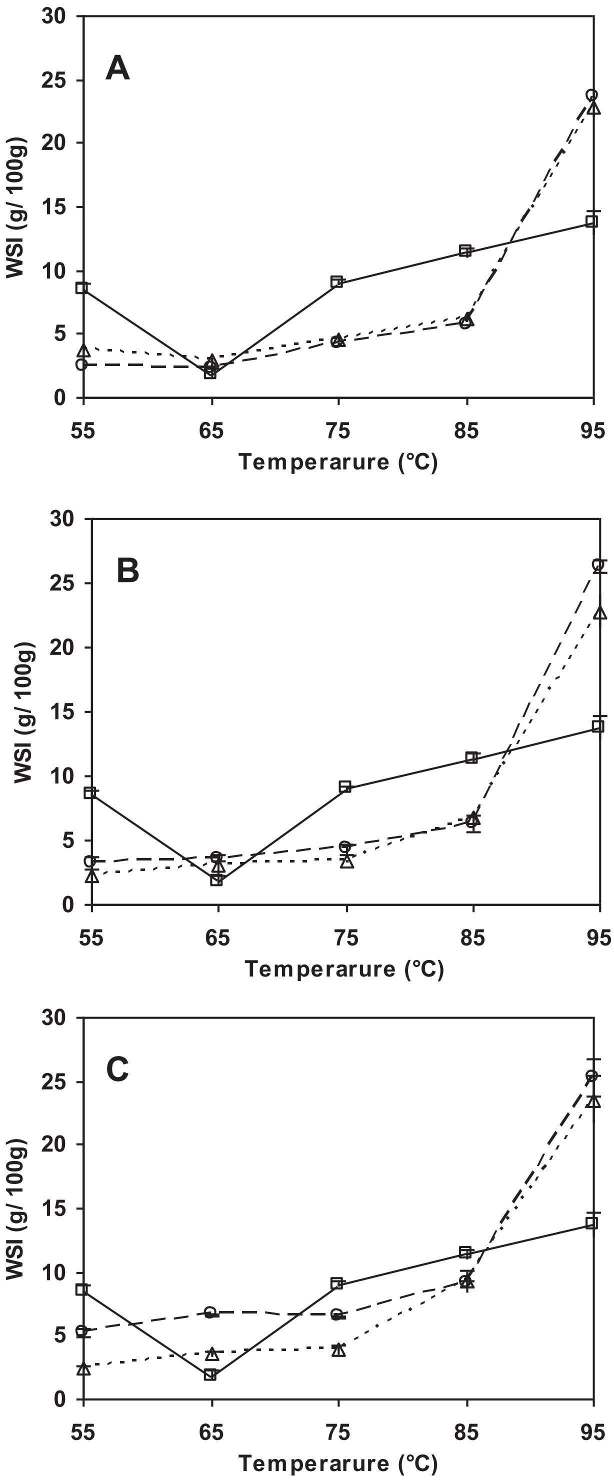

Fig. 6. Effect of milling time on water solubility index (WSI) at different milling speeds: 450 rpm (A), 550 rpm (B), 650 rpm (C); Control (□), 10 min (△), 20 min (○).

Swelling power increased with milling time at fixed rotational speed (Fig. 6). A considerable change in the slope of curves can be observed from 75 °C to 95 °C, possibly due to starch gelatinization. The non-waxy rice restricted the swelling and resulted in the presence of a network structure from amylose molecules that could hold the starch molecules together (Tester & Morrison, 1990).

The positive effect of grinding time on SP was again observed above 85 °C. Similar results were found in the literature related to

Table 4
Effects of milling conditions on swelling power (SP) in terms of coded factors: milling speed (x_1) and milling time (x_2).

Coefficient		SP–55 °C	SP–65 °C	SP–75 °C	SP–85 °C	SP–95 °C
Constant	a_0	4.8	6.65	9.48	11.05	16.77
Linear	a_1	0.52*	0.46*	0.33*	−0.22NS	0.23NS
	a_2	0.55*	0.8*	0.28*	−0.25NS	0.65*
Quadratic	a_{11}	−0.13NS	−0.32NS	−0.31*	−0.24NS	0.12NS
	a_{22}	–	–	−0.03NS	0.12NS	–
Interaction	a_{12}	0.32*	0.44*	0.11NS	−0.03NS	0.08NS
Correlation	r^2	0.9838	0.9695	0.8953	0.5108	0.9071

*Significant at $p < 0.05$; NS: non significant coefficient; –, eliminated coefficient. SP: swelling power at different temperatures.

rice starch of similar amylose content (Li & Yeh, 2001). The slope change shifts to higher temperatures as speed increases. Possibly, the differences were caused by damaged starch produced during the grinding process (Chen et al., 1999). This observation is consistent with the higher levels of damaged starch (see Table 1) caused by the use of higher rotational speed.

WSI, determined as a proximate measure of soluble starch (soluble proteins must be considered in flour samples), is associated to amylose content due to its higher solubilization in comparison with amylopectin (Wang et al., 2010). Solubility increased as the test temperature increased (Fig. 6). It was found that SP–85 °C (Fig. 5) and WSI–85 °C (Fig. 6) does not reflect the effect of milling conditions probably due to the transitions that occur at this temperature, which may be associated with gelatinization and pasting of the studied system. Therefore, it is more convenient to select SP and WSI tests at temperatures far from this transition temperature for the purpose of detecting the influence of milling conditions on the functional properties of flour.

RSM was applied to quantify the effect of grinding on the parameter SP and WSI. The results are shown in Tables 4 and 5 respectively.

The proposed polynomial model (Eq. (7)) provided a satisfactory fit ($R^2 > 0.89$) in all cases except for SP–85 °C. In this latter case, the effect of grinding conditions was not significant due to gelatinization. It is observed that the correlation coefficient (R^2) decreased as the temperature approached transition temperature. Table 4 shows that milling speed affected the SP values below 85 °C while it was not significant at 85 °C or 95 °C. Milling time effect on SP values was significant except in the case of SP–85 °C. The interaction effect between factors was only significant for SP–55 °C and SP–65 °C.

When performing the same RSM analysis for WSI, a satisfactory fit by equation (7) can be observed, which is in all cases $R^2 > 0.83$. Significant and positive effects of milling speed and processing time on WSI values can also be noted (Table 5) with the exception of WSI-85 °C where only the effect of speed milling was significant. Interaction effect was appreciable for WSI–55 °C, WSI-65 °C and WSI–75 °C.

Table 6 shows the maximum and minimum SP values corresponding to optimum milling conditions. A similar analysis was performed using WSI (not shown here). However, SP was selected due to its better performance.

Table 5
Effects of milling conditions on water solubility index (WSI) in terms of codified factors: grinding speed (x_1) and milling time (x_2).

Coefficient		WSI–55 °C	WSI–65 °C	WSI–75 °C	WSI–85 °C	WSI–95 °C
Constant	a_0	2.76	3.31	3.82	6.49	24.53
Linear	a_1	0.39*	1.21*	0.36*	1.57*	0.58*
	a_2	0.42*	0.49*	0.53*	−0.18NS	0.98*
Quadratic	a_{11}	0.72*	0.55NS	1.01*	1.08*	−0.72NS
	a_{22}	–	0.02NS	–	–	−0.04NS
Interaction	a_{12}	0.97*	0.94*	0.74*	0.09NS	0.24NS
Correlation	r^2	0.9216	0.9081	0.9353	0.8871	0.8319

*Significant at $p < 0.05$; NS: non significant coefficient; –, eliminated coefficient. WSI: water solubility index.

Table 6
Predicted maximum and minimum SP values as function of milling conditions.

SP index		SP (g/g)	Speed (rpm)	Time (min)
SP–55 °C	max	6.05	650	20
	min	3.91	450	10
SP–65 °C	max	8.03	650	20
	min	5.51	450	10
SP–75 °C	max	9.93	612	20
	min	8.69	450	10
SP–95 °C	max	17.86	650	20
	min	16.07	487	10

It is clear that the sensitivity of SP to detect the influence of milling conditions is affected by the temperature at which tests were performed. Using SP–95 °C information is lost because only the effect of grinding time is detected. At 85 °C it is impossible to detect the effect of any grinding conditions. When testing at SP–75 °C, the effect of grinding conditions was detected. However, due to the quadratic influence of grinding speed, no distinction is noted between 612 and 650 rpm. In contrast SP–55 °C and SP–65 °C provide a sensitive detection of the effect of milling conditions (SP–65 °C is slightly more sensitive). They can be considered as the most suitable SP indexes to characterize the rice flour obtained.

3.6. Thermal properties

Rice flour samples obtained from different milling conditions were analyzed by DSC and thermal parameters were determined, as shown in Table 7. Enthalpy values were significantly lower than those of the control sample (7.4 ± 0.2 J/g) due to the milling effect on rice components. Gelatinization temperatures of control were 70.2 ± 0.6 °C (onset), 73.8 ± 0.5 °C (peak) and 82.2 ± 0.8 °C (endset). These temperatures were comparatively higher than those shown in Table 7.

The decrease of enthalpy and temperature of gelatinization, observed after severe grinding, have been associated to a loss of shorter range crystalline order and double helix content due to slight depolymerization of amylose and breakdown of amylopectin in the damaged starch granules (Martínez-Bustos et al., 2007).

A diminution of thermal parameters with an increase of milling time and speed was also reported by Han et al. (2007) and Huang, Lu, Li, and Tong (2007), who studied the effect of milling time on thermal parameters of rice starch and cassava starch respectively.

A very significant reduction in gelatinization enthalpy (from 14 J/g to 0.13 J/g) and peak temperature (from 75.14 °C to 63.88 °C) was observed by Han et al. (2007) after 30 min of rice starch processing in a planetary ball mill at 300 rpm. The reduction in thermal parameters was comparatively smaller in this study possibly due to the pause periods programmed between milling stages.

Table 7
Thermal parameters of rice flour by DSC method.

Experiment number	T_o (°C)	T_p (°C)	T_e (°C)	ΔH (J/g d.b.)	GD (%)
1	67.8 ± 0.5	72.9 ± 0.6	78.1 ± 0.6	4.7 ± 0.2	36
2	67.9 ± 0.5	73.5 ± 0.8	78.4 ± 0.5	3.9 ± 0.4	47
3	67.9 ± 0.7	73.6 ± 0.6	78.7 ± 0.8	3.2 ± 0.2	57
4	68.3 ± 0.8	73.2 ± 0.7	77.9 ± 0.5	3.5 ± 0.1	53
5[a]	66.3 ± 0.6	72.4 ± 0.8	77.4 ± 0.5	3.1 ± 0.3	58
6	64.3 ± 0.5	71.5 ± 0.5	76.9 ± 0.9	2.6 ± 0.2	65
7	69.0 ± 0.6	72.7 ± 0.5	77.7 ± 0.7	3.1 ± 0.2	58
8	67.1 ± 0.7	71.8 ± 0.4	76.5 ± 0.5	2.0 ± 0.1	73
9	65.1 ± 0.7	70.9 ± 0.8	75.2 ± 0.6	0.9 ± 0.1	88
Control	62.0 ± 0.5	67.1 ± 0.5	72.2 ± 0.6	6.8 ± 0.2	0

[a] Central point by triplicate.

Table 8
Effects of milling conditions on DSC in terms of codified variables: grinding speed (x_1) and milling time (x_2).

Coefficient		T_o (°C)	T_p (°C)	T_e (°C)	ΔH (J/g d.b.)
Constant	a_0	66.3	72.37	77.41	3.07
Linear	a_1	0.40NS	−0.77*	−0.967*	−0.97*
	a_2	−1.30*	−0.47*	−0.483*	−0.77*
Quaratic	a_{11}	1.17NS	0.2NS	0.033NS	−0.1NS
	a_{22}	–	–	−0.017NS	0.01NS
Interaction	a_{12}	−1.01*	−0.625*	−0.775*	−0.17NS
Correlation	r^2	0.9236	0.9304	0.9998	0.9577

*Significant at $p < 0.05$; NS: non significant coefficient; –, eliminated coefficient. Gelatinization temperatures: T_o, T_p, T_e, onset, peak and endset respectively. ΔH: gelatinization enthalpy.

It should be noted that, using other physical methods of flour modification, different effects to this work were found. The extrusion always causes complete starch gelatinization (Hagenimana, Ding, & Fang, 2006; Menegassi, Pilosof, & Arêas, 2011). The hydrothermally treated flour presents the characteristic annealing effect (delay of the gelatinization event) which is opposite to that observed in this study (advancement of gelatinization) as it was reported in the literature (Lai, 2001).

To assess the effect of milling conditions on thermal parameters, an RSM analysis was performed. The results are shown in Table 8. Results show that Eq. (7) provides a good fit of experimental data ($R^2 > 0.92$). It can be observed that milling speed and milling time have a significant negative effect on gelatinization temperatures and gelatinization enthalpy. However, the effect of milling speed at onset temperature is not significant. The interaction effect was only significant for gelatinization temperatures. The influence of milling time on peak temperature was more marked at 650 rpm while the effect of milling speed was more evident at 20 min of milling.

Predicted values (Eq. (6)) of gelatinization degree (GD) varied from 36% to 88% changing milling conditions from 450 rpm (10 min) to 650 rpm (20 min).

The high level of gelatinization detected by DSC analysis would reflect the significant level of starch granule damage due to the energy released during the grinding of the sample even when a grinding protocol was used to prevent excessive heating of the product.

3.7. X-ray diffractometry

Fig. 7 shows the results of the X-ray diffraction analysis for rice flour corresponding to the extremes of experimental range and control sample. They show an A-type XRD pattern with strong reflection peaks at 2θ about 15°and 23°, and an unresolved doublet at 17°, 18° 2θ, typical for cereal starches (Shih, King, Daigle, An, & Ali, 2007; Zhang et al. 2010).

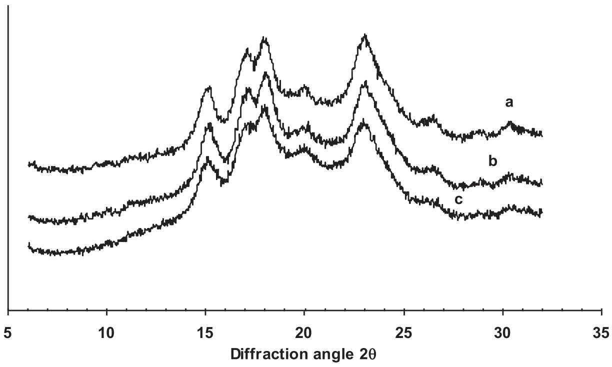

Fig. 7. X-ray diffraction patterns of control and modified rice flours as function of selected milling conditions. Control (a), 450 rpm – 10 min (b), 650 rpm – 20 min (c).

As shown in Fig. 7, the diffraction peaks weakened gradually as milling conditions increased, in other words, the proportion of crystalline states decreased; the non-crystalline states increased.

The reduction of crystallinity degree (Eq. (5)), among 10 and 20 min were: 32–31%, 30–28% and 29–24% for 450 rpm, 550 rpm and 650 rpm respectively. The crystallinity degree of control sample was 37%.

The crystallinity change obtained in this work was moderate in comparison with an others results in the literature. Liu et al. (2011) reported the transition from polycrystalline state to amorphous state of maize starch using a planetary ball mill at 500 rpm and for milling times higher than two hours. In this case the XRD patterns together with FT-IR and 13C CP/MAS NMR spectra showed a reduction of crystallinity and content of double helices of starch chains.

The results seem to reaffirm findings from the DSC analyses that the structure of rice flour changes under the milling conditions, being the crystalline loss (relative to control sample) of about 14–35% according to milling conditions.

3.8. Correlations between flour properties

The following significant correlations (p-value < 0.03) were found by means of Pearson's correlation analysis. Damaged starch was correlated with WAI ($r = 0.86$), CD ($r = -0.93$), ΔH ($r = -0.97$) and RSSA ($r = 0.92$). Water absorption index was correlated with ΔH ($r = -0.92$), CD ($r = -0.96$) and RSSA ($r = 0.96$). RSSA was correlated with ΔH ($r = -0.95$) and CD ($r = -0.98$). Crystallinity degree was correlated with ΔH ($r = 0.98$, p-value $= 0.0006$).

The results showed the high correlation coefficients between flour properties. Damaged starch, a conventional measure of starch modification, was positively correlated to WAI and RSSA while it was inversely related with crystallinity degree and gelatinization enthalpy. The relationships between DS and WAI; and DS and ΔH can be appreciated in Fig. 8A and B respectively. Chiang and Yeh (2002) reported a similar relationship between DS and WAI for rice flour obtained by wet-milling procedure. However, as a consequence of the usage of a planetary ball mill, the values of damaged starch corresponding to this work were higher. In addition, based on the approximately linear relationship shown in Fig. 8B, gelatinization enthalpy became a reliable parameter to measure damaged starch content.

The typical functional property, WAI, was highly correlated to ΔH and CD. These parameters give information related to the mobility of polymer chains and the disruption of molecular order, which are dependent on flour composition and structure. Moreover, WAI was positively correlated to RSSA, a parameter related to morphological aspect of flour particles. As it was expected, the significant increase of the surface area favored the interactions between powder surface and water molecules.

4. Summary and conclusions

The variation of milling conditions resulted in changes of functional properties. A considerable difference between functional properties of control and modified rice flours was found. Such functional changes can not be explained by temperature increment during dry milling (Section 3.1), which was insufficient to reach gelatinization temperature. However, the rice flour components suffered thermo-mechanical damage as a consequence of operating forces in planetary ball milling.

Modified rice flours presented a wide range of functional properties, from native to 88% gelatinized rice flour which may be

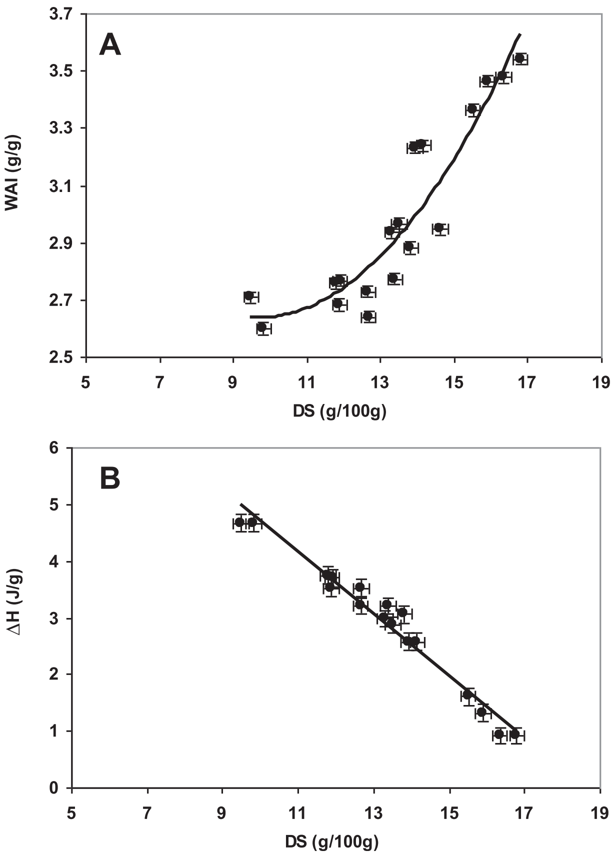

Fig. 8. Relationship among values of damaged starch (DS) and quality parameter: (A) water absorption index (WAI) and (B) gelatinization enthalpy (ΔH). Predicted values (—) based on the following expressions: $\text{WAI} = 0.02\ \text{DS}^2 - 0.38\ \text{DS} + 4.50$ ($r^2 = 0.87$) and $\Delta H = -0.543\ \text{DS} + 10.137$ ($r^2 = 0.97$).

used as an ingredient for instant meal product. Furthermore, it was found that absorption and swelling capacity as well as solubility were significantly enhanced by the thermo-mechanical modification applied in this study.

Crystallinity loss reached a maximum value of 35%, which is far from a complete amorphization. The changes in the functional properties obtained in this study differ from those obtained by other physical methods most frequently used (extrusion, hydrothermal processing). The modifications here obtained can be considered moderated in comparison with those obtained in extruded flour, which is characterized by a complete gelatinization. In contrast to hydrothermally treated flour, the one produced in this work did not evidence annealing effect, but it conversely exhibited advancement of peak temperature, together with the enthalpy decrease as increasing time or milling speed.

The significant correlations between gelatinization enthalpy, crystallinity degree and relative specific surface area (RSSA); point out the importance of these parameters to describe the thermo-mechanical modifications, which are intrinsically related to structural and morphological properties of rice flour. However, further studies on rheological and aggregation properties of rice flour will be required to better understand the incidence of SSA on flour modifications.

The distinctive characteristic of the planetary ball mill was the fast speed with which the modified flour was obtained which presented intermediate characteristics in relation with native and amorphous state. Results revealed that, by the application of an appropriate milling protocol, based on combinations of grinding and pause interval; it is possible to control thermo-mechanical damage.

Acknowledgments

The authors acknowledge the financial support from PME-2006-01685 and Secretaría de Ciencia y Técnica de la Universidad de Buenos Aires (Project UBACyT 20020110200357).

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