Pasting behaviour of high impact ball milled rice flours and its correlation with the starch structure

Maria Ana Loubes^{1,2} · Luciana Carla González^{1,2} · Marcela Patricia Tolaba^{1,2}

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Abstract The effects of rotational speed and milling time on pasting profile, particle size and morphology, damaged starch and gelatinization enthalpy of modified rice flours were analysed by response surface methodology to investigate the relationships among functional attributes and starch structure. Morphological changes were corroborated by scanning electron microscopy. Peak time (Pt), pasting temperature (PT), peak and final viscosities from rapid visco-analysis showed a significant decrease with increasing of milling severity. The reduction in final viscosity (FV up to 4770 mPa s), particularly for the refined flour fraction (volume median diameter, D50 < 140 µm), evidenced the poor capacity of damaged starch to bind water during heating step. In comparison with native flour, the modified flours presented higher values of damaged starch (DS 5.94–16.46%), and viscosities as well as lower values of gelatinization enthalpy (ΔH 4.67–0.71 J/g), Pt and PT denoting a lower resistance to shear stress and cooking. Such behavior is desirable in mixture design to enhance flour particles dispersion and to facilitate the interaction among food ingredients. Structural changes of starch were strongly associated to pasting behavior as it can be appreciated from the significant correlations founded: FV–DS, setback viscosity (SB)–DS, SB–D50, SB– ΔH . Planetary ball milling is a novel green method to obtain

physically modified rice flours with distinctive characteristics regarding native flours, which could be well controlled by selecting suitable milling conditions. More studies should be required to expand the applications of the modified rice flours, in food and non-food products, with specific functional requirements.

Keywords Planetary ball mill · RVA profile · Particle size · Damage starch · Thermal behavior

Introduction

In the last years, rice flour has acquired relevance due to its gluten-free character, which is fundamental to the treatment of celiac disease. Rice flour is also selected due to its low sodium and fat contents as well as its considerable amounts of digestible carbohydrates. Rice flour has become more popular in developed countries and its market is continuously expanding (Yeh 2004).

The properties of rice flour obtained by traditional dry milling have been discussed in the literature (Chen et al. 1999; Chiang and Yeh 2002; Yeh 2004; Wu et al. 2010). The visco-amylographic technique was successfully used to study pasting properties of rice flour and starch from waxy and non-waxy rice grains as well as to investigate the effect of milling conditions on rheological attributes of end products such as rice bread or rice pasta (Kaur et al. 2016; Singh et al. 2006; Wang et al. 2000; Hemavathy and Bhat 1994). Although rice bread and rice noodle are based on a mixture of rice flour and a gluten substitute, each particular product requires a specific flour granulometry and functionality. Flour functionality depends on process conditions and milling equipment and it can be substantially improved by suitable modification (Wu et al. 2010).

✉ Marcela Patricia Tolaba
mtolaba@di.fcen.uba.ar

¹ Faculty of Exact and Natural Sciences, Industry Department, University of Buenos Aires, Buenos Aires, Argentina

² Institute of Food Technology and Chemical Processes (ITAPROQ), CONICET - University of Buenos Aires, Intendente Güiraldes 2160, Ciudad Universitaria, C1428EGA Buenos Aires, Argentina

Heo et al. (2013) have evaluated the effect of dry and wet milling on the properties of rice flour to analyze which are the more convenient flours to produce rice noodles. Chiang and Yeh (2002), who investigated the effect of soaking on wet milling of rice, reported that the moisture content after soaking appeared to be a key factor for the loosening of the structure of rice kernels, which resulted in the production of small particle flours with little starch damage.

Recently, high impact milling was revealed as an efficient method for the physical modification of flours and starches (Han et al. 2007; Huang et al. 2007; Martinez-Bustos et al. 2007; Roa et al. 2014). Few grinding protocols were developed to better control of rice flour modification by using hammer mill (Hasjim et al. 2013) and planetary ball mill (Loubes and Tolaba 2014). Nevertheless, they are yet scarce and, more studies are needed to clarify the relationships between milling conditions and properties of modified flours or starches in order to design a suitable milling protocol to satisfy specific functional requirements.

The objective of this work was to analyze the influence of planetary ball milling conditions on structural and pasting properties of rice flour by the Response Surface method. As control native rice flour was adopted. The pasting profile was evaluated by using the Rapid Visco Analyzer (RVA). Thermal behavior, particle size distribution and damaged starch content of modified rice flours were also determined as function of milling speed and process time.

In addition, a correlation analysis between the different flour attributes was performed in order to achieve a better understanding of the structural changes produced by high impact milling.

Materials and methods

Material

A local variety of long-grain paddy rice, IRGA 417, harvested in 2014 was provided by the Experimental Station of INTA (National Institute of Agricultural Technology, Concepción del Uruguay, Entre Ríos, Argentina); with 28.4% db (dry basis) amylose content, determined according to Morrison and Laignelet (1983). Samples were husked and polished using a Suzuki MT-95 laboratory miller. The degree of polishing, calculated as the percentage of rice bran respect to brown rice, was 13% approximately.

The proximate composition of polished rice, determined in triplicate using standardized AOAC methods (2000),

was: 12% db moisture, 80.1% db total starch, 6.9% db protein, 0.3% db lipid, 0.2% db fiber and 0.5% db ash.

Milling process

High impact milling of rice was performed in a planetary ball mill (PM100, Retsch GmbH, Haan, Germany) with a ratio of 1: – 2 corresponding to opposite rotation of sun wheel respect to grinding jar. Polished rice grains (200 g) were put into the jar (500 ml) containing zirconium oxide beads (30 mm diameter) being the ball to rice mass ratio of 3.35:1 w/w. The milling protocol involved grinding periods (5 min with change of rotational direction every 30 s) followed by pause intervals (40 min) to avoid overheating of sample (Loubes and Tolaba 2014). Table 1 shows the experimental design in terms of rotational speed (450–650 rpm) and grinding time (10–40 min). The range of milling speed was selected to avoid a long time in obtaining modified flours of fine granulometry. Each milling test was conducted in duplicate.

Amorphous rice flour was obtained by the same grinding protocol at 650 rpm and 2 h of milling time. Crystallinity loss (100%) was checked by X-ray diffraction.

Control sample (native flour) was obtained by grinding rice grain (25 g) during 30 s in a butt mill (Decalab, Buenos Aires, Argentina).

Particle size analysis

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 agent, and processing data refractive index (1.53) and absorption parameter (0.001) of the dispersed phase was used. Five scans were recorded for each sample and the average value of the median diameter (D50) and dispersion index (Span) obtained from a volume distribution were reported (Loubes and Tolaba 2014).

$$Span = (D90 - D10)/D50 \quad (1)$$

Damaged starch

The damaged starch content (DS) in the flour samples was determined in accordance with the approved method 76-30A of AACC (2000) using a damaged starch assay kit (Megazyme International Ltd., Wicklow, Ireland). The results were reported as a percentage of flour weight on a dry basis. Three replicates were made for each sample.

Table 1 Experimental design and characteristic milling responses of control and modified rice flours

Milling speed (rpm) (x ¹)	Milling time (min) (x ²)	D50 (μm)	DS (% db)	ΔH (J/g db)	PV (mPa s)	FV (mPa s)	BD (mPa s)	SB (mPa s)	PT (°C)	Pt (min)
450 (– 1)	10 (– 1)	262.80 ± 8.12 ⁱ	5.94 ± 0.04 ^b	4.67 ± 0.28 ^f	4449 ± 197 ^e	8920 ± 190 ^{g,h}	344 ± 103 ^b	4814 ± 95 ^{f,g}	85.4 ± 0.1 ^g	5.70 ± 0.04 ^{c,d}
450 (– 1)	20 (– 0.3)	187.71 ± 3.38 ^g	6.06 ± 0.1 ^b	3.21 ± 0.57 ^{b,d}	6037 ± 42 ^h	8954 ± 45 ^h	2071 ± 20 ^g	4988 ± 17 ^h	79.5 ± 0.6 ^b	5.63 ± 0.04 ^{b,c}
450 (– 1)	30 (0.3)	135.05 ± 5.11 ^e	6.91 ± 0.2 ^c	3.24 ± 0.28 ^d	6352 ± 13 ⁱ	8880 ± 13 ^{g,h}	2301 ± 10 ^h	4828 ± 107 ^{f,g,h}	76.8 ± 0.1 ^a	5.70 ± 0.04 ^{c,d}
450 (– 1)	40 (1)	99.07 ± 2.71 ^c	10.00 ± 0.06 ^f	2.23 ± 0.57 ^{c,d}	5265 ± 85 ^f	7977 ± 42 ^e	1744 ± 74 ^f	4456 ± 31 ^e	79.9 ± 0.1 ^{b,c}	5.80 ± 0.01 ^{d,e,f}
550 (0)	10 (– 1)	244.08 ± 6.85 ^h	7.39 ± 0.18 ^{c,d}	3.67 ± 0.28 ^{d,e}	5045 ± 89 ^f	8995 ± 126 ^h	839 ± 27 ^d	4789 ± 64 ^{f,g}	84.2 ± 0.6 ^{e,f,g}	5.57 ± 0.04 ^b
550 (0)	20 (– 0.3)	131.11 ± 3.62 ^e	8.39 ± 0.17 ^e	2.58 ± 0.42 ^d	5969 ± 55 ^{g,h}	8739 ± 18 ^{f,g,h}	2117 ± 103 ^g	4886 ± 30 ^{f,g,h}	80.5 ± 0.7 ^{b,c}	5.70 ± 0.04 ^{c,d}
550 (0)	30 (0.3)	107.87 ± 3.09 ^d	10.82 ± 0.06 ^g	1.91 ± 0.28 ^{b,c}	5799 ± 263 ^{g,h}	8488 ± 255 ^f	2120 ± 151 ^g	4809 ± 143 ^{f,g}	78.7 ± 1.7 ^b	5.73 ± 0.1 ^{c,d,e}
550 (0)	40 (1)	75.37 ± 4.02 ^{a,b}	14.44 ± 0.14 ⁱ	1.48 ± 0.42 ^b	4071 ± 8 ^d	6457 ± 30 ^c	1331 ± 11 ^e	3717 ± 10 ^c	82.4 ± 0.8 ^{d,e}	5.90 ± 0.04 ^{f,g}
650 (1)	10 (– 1)	174.78 ± 8.36 ^f	7.66 ± 0.44 ^d	3.06 ± 0.28 ^{b,d}	5704 ± 89 ^g	9005 ± 8 ^h	1453 ± 85 ^e	4754 ± 4 ^f	83.5 ± 0.6 ^{e,f}	5.57 ± 0.04 ^b
650 (1)	20 (– 0.3)	96.26 ± 4.17 ^c	11.79 ± 0.23 ^h	0.92 ± 0.14 ^a	5082 ± 45 ^f	7877 ± 34 ^e	1701 ± 45 ^f	4496 ± 33 ^e	81.5 ± 0.1 ^{c,d}	5.73 ± 0.01 ^{c,d,e}
650 (1)	30 (0.3)	80.87 ± 3.65 ^b	14.84 ± 0.4 ⁱ	0.74 ± 0.28 ^a	4653 ± 44 ^e	6941 ± 136 ^d	1671 ± 44 ^f	3959 ± 134 ^d	80.4 ± 0.8 ^{b,c}	5.83 ± 0.04 ^{e,f}
650 (1)	40 (1)	72.51 ± 2.73 ^a	16.46 ± 0.38 ^j	0.71 ± 0.14 ^a	2984 ± 112 ^b	4770 ± 191 ^b	676 ± 62 ^c	2469 ± 141 ^b	85.1 ± 0.6 ^{f,g}	5.97 ± 0.04 ^g
Amorphous		76.45 ± 1.92 ^{a,b}	17.03 ± 0.3 ^j	—	556 ± 7 ^a	373 ± 8 ^a	426 ± 5 ^b	243 ± 7 ^a	—	4.72 ± 0.1 ^a
Control		322.23 ± 3.91 ^j	2.70 ± 0.30 ^a	6.82 ± 0.28 ^g	3668 ± 315 ^c	8619 ± 376 ^{f,g}	— 7 ± 8 ^a	4944 ± 68 ^{g,h}	87.4 ± 1.7 ^h	7.00 ± 0.01 ^h

Mean ± SD values followed by different letters in a column are significantly different ($p \leq 0.05$)

PV Peak viscosity, FV final viscosity, BD breakdown, SB setback, PT initial pasting temperature, Pt peak time

^aA linear relationship among experimental and coded factors was used

— not detected

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 aluminium pan; distilled water was then added to achieve a starch to water mass ratio of 1:3 w/w. The sealed pan was equilibrated for 24 h at room temperature before analysis. The samples were heated from 30 to 100 °C at 10 °C/min, using an empty pan as reference.

Gelatinization temperature (peak temperature, T_p) and enthalpy (ΔH) were recorded in triplicate. Values of enthalpy were expressed in J/g (db) and gelatinization degree (GD) as a percentage (Loubes and Tolaba 2014).

$$GD = (1 - \Delta H / \Delta H_{\text{control}}) \times 100 \quad (2)$$

Scanning electron microscopy

Rice flour sample was mounted on a circular aluminum stud with double-sided sticky tape, sputter coated with gold, and examined and photographed in a FESEM-Carl Zeiss Model Supra 40 field emission scanning electron microscope (Carl Zeiss, Darmstadt, Germany) at an accelerating voltage of 3 kV.

Pasting profile

Pasting properties of flour samples were determined with a Rapid Visco Analyser (RVA-4), using the RVA General Pasting Method (Newport Scientific Pty. Ltd., Warriewood, Australia). The RVA parameters were obtained from flour–water suspensions. Flour samples (3.5 g) were transferred into a canister and approximately 25 ± 0.1 ml distilled water were added. The slurry was heated to 50 °C, while stirring at 960 rpm for 10 s for thorough dispersion of flour. The slurry was held at 50 °C for 1 min, and then heated up to 95 °C at a heating rate of 10 °C/min and a stirring rate of 160 rpm. It was held at 95 °C for 1.8 min, and finally cooled to 50 °C at a cooling rate of 12 °C/min and holding at 50 °C for 1.4 min. Initial pasting temperature (PT), peak viscosity (PV), peak time (Pt), final viscosity (FV), breakdown (BD), and setback (SB), were obtained from the pasting curve. Analyses were performed in duplicate.

Statistical analysis

Significance of the effect of milling conditions on rice flour attributes were evaluated by one-way ANOVA (significance level $\alpha = 0.05\%$) with Fisher (LSD) post-test using Statgraphics Centurion (version XVI, Statistical graphics Corporation, USA) statistical software. Regression and

correlation analyses between rice flours properties as well as response surface methodology (RSM) were made through the same software. RSM was applied to analyze the effect of milling speed and milling time on pasting characteristics, particle size, damaged starch and thermal properties of rice flour. A significance level ($p < 0.05$) was set and the studied responses (Z_K , $K = 1, \dots, p$) were matched to the coded factors (x_1 : milling speed, x_2 : milling time) by the following polynomial model associated to experimental design (Khuri and Cornell 1987):

$$Y = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i=1}^n a_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=2}^n a_{ij} x_i x_j \quad (3)$$

The coefficients a_0 , a_i and a_{ii} represent the constant, linear and quadratic effects, respectively, and a_{ij} represents the interaction effects of coded factors (x_i and x_j). A linear codification of factors was used based on coded levels of experimental design.

Results and discussion

Particle size, damage starch content and gelatinization properties of modified rice flours

Modified rice flours presented bi-modal particle size distributions while control sample showed a mono-modal distribution with a mode of 417 μm . As milling time increased D50 values decreased (Table 1). In contrast, there was an increase of Span values from 2.05 ± 0.01 (native flour) to 3.79 ± 0.05 (amorphous flour) as a consequence of milling progress. The median diameter of amorphous rice flour was similar to that of rice flour obtained at 650 rpm and 40 min; therefore the powder activation reached in the present work is in accordance with literature reports (Liu et al. 2011; He et al. 2014).

Modified rice flours presented damaged starch contents up to six times higher than that of the control (Table 1). In comparison with other milling methods reported in the literature (Ngamnikom and Songsermpong 2011), the pulverizing effect of planetary ball mill was higher because it affected the starch granular structure (Tran et al. 2011). Starch damage during high impact milling has been associated to disruption of characteristic composite structure of rice starch granule (Zhongkai et al. 2002). Figure 1a shows the relationship between the damaged starch content and the particle size of rice flour. It can be appreciated that there was a significant increase of damaged starch content at diameter value below 150 μm , which correspond to the size of the composite starch granule. In accordance with this result, there was an increase of the micro-granular flour

Fig. 1 Relationship between milling properties. **a** Damaged starch content (DS) and median diameter (D50) of particle size distribution, **b** DS and volume fraction (Fv) of micro-granular starch (diameter < 5 μm), **c** D50 and gelatinization enthalpy (ΔH). Experimental (bullet) and predicted values (solid line)

fraction (diameter < 5 μm) from damaged starch content of 8% db (Fig. 1b).

As regards thermal properties, the modified rice flours presented peak temperatures within 68.6–73.6 °C, whereas the peak temperature of control was 67.1 °C. Similar peak gelatinization temperatures were reported by Singh et al. (2007) for rice varieties with medium or high amylose content. In contrast, gelatinization enthalpies in the present work were lower than those corresponding to low or medium amylose content (Singh et al. 2006). In the case of amorphous rice flour, the DSC endotherm could not be

detected as in literature reports for ultra-pulverized starches (Huang et al. 2007). The gelatinization enthalpies of modified rice flours (Table 1) were significantly lower than that of control ($p < 0.05$). A similar thermal behavior was observed by Han et al. (2007) and Huang et al. (2007) by increasing milling speed and time during physical modification of rice or tapioca starches.

Effects of milling conditions

The influence of processing conditions on the median diameter (D50), damaged starch content (DS), dispersion index of particle size distribution (Span) and gelatinization enthalpy (ΔH) of modified rice flours were analyzed by RSM. The studied responses were correctly simulated ($r^2 \geq 0.95$) by Eq. (3) in terms of coded milling factors. Figure 2a–d shows the predicted surfaces as well as the corresponding fitted equations. Both milling factors significantly affected ($p < 0.05$) all the studied responses. The quadratic effect of time can be easily appreciated in the Fig. 2a, b. The interaction effect was significant in the case of D50 and DS. As a result of the interaction, the influence of milling speed on D50 (negative effect) was more significant at low milling times. In contrast, its incidence on DS (positive effect) was appreciable at high milling times. The Span values (Fig. 2c) presented a linear increase with increasing values of milling speed or time. This shows that there was a reduction of flour homogeneity associated to the growth of fines.

Figure 2d shows the significant effects (negative and linear) of milling speed and time on gelatinization enthalpy; which evidences what a huge thermo-mechanical modification can be obtained by planetary ball milling. Such degree of gelatinization (up to 89.6% for 650 rpm and 40 min) has been associated with changes in crystalline starch structure (Chen et al. 2003; Dhital et al. 2011). In fact, damaged starch at the surface of flour particles confers them increasing heat transfer and water absorption capacities during starch gelatinization (Marshall 1992; Tran et al. 2011; Karlsson and Eliasson 2003).

In addition, the following significant correlations ($p < 0.01$) were found by the Pearson's correlation analysis. Gelatinization enthalpy was correlated with D50 ($r = 0.95$) and damaged starch content ($r = -0.90$), in accordance with Hasjim et al. (2013), who reported similar results for rice flour obtained in a hammer mill. The linear relationship between ΔH and D50 showed in Fig. 1c and the correspondence of D50 with damaged starch (Fig. 1a) evidence that thermal properties depend on flour particle size and on damage level of granular structure.

Fig. 2 Predicted surfaces as function of coded milling speed (x_1) and milling time (x_2): **a** Median diameter of particle size distribution (D50), **b** damage starch content (DS), **c** dispersion index of particle size distribution (span), **d** Enthalpy of starch gelatinization (ΔH)

Scanning electron microscopy

Polyhedral starch granules of control flour which exhibit high sphericity can be appreciated in Fig. 3a. With the intensification of dry milling process, flat particles were visualized (Fig. 3b). After 2 h of milling at 650 rpm crushed particles forming flakes were found (Fig. 3c). In comparison with control, the flakes presented a rough surface, low sphericity and higher size due to the melting of some granules. Such result is in accordance with the static light scattering analysis carried out in the present work.

The increase of particle size was also reported by Chen et al. (2003) in rice starch and He et al. (2014) in corn starch after 60 min and 5 h respectively of high energy milling. These authors did not detect any deformation of the starch granule probably due to the temperature control by the refrigerant gas injection. In contrast, Tran et al. (2011) observed the flattening of particles in rice flour which was obtained by hammer milling, even though an increase in size was not reported.

The observed changes in the morphology of starch granule suggests that glycosidic bonds were broken during planetary ball milling, increasing the proportion of free hydroxyl groups and the formation of new hydrogen bonds within the amorphous starch region (Chen et al. 2003).

This characteristic would favor entanglement to form a network with capacity to retain the gas generated during the manufacture of gluten free bread. Therefore, the action of the gluten substitute could be enhanced by adding modified rice flour to bread formulation.

Pasting behavior of modified rice flours

Figure 4 shows the RVA profiles of native rice flour and modified rice flours (selected samples). The RVA profiles of modified rice flours (curves 2 and 3) show the capacity of planetary ball milling to change the pasting behaviour of native flour (curve 1). The magnitude of this change is at least comparable to that observed between waxy and non-waxy rice varieties (Singh et al. 2007; Kaur et al. 2016). However, if amorphous flour (curve 4) is compared with native flour (curve 1) the great potential of high impact grinding is demonstrated. The pasting parameters of control and modified rice flours are summarized in Table 1 as function of milling conditions.

Modified rice flours presented values of initial PT between 76.8 and 85.4 °C, while the corresponding values of gelatinization peak temperature ranged within 68.6–73.6 °C. This result agrees with literature reports about initial PT as a measure in excess of the gelatinization temperature (Bao 2008; Hasjim et al. 2013).

Fig. 3 Scanning electron microscopy images of rice flours (selected samples). **a** Control sample, **b** 40 min at 650 rpm, **c** amorphous sample

Fig. 4 RVA pasting profile of control and selected samples of modified rice flours as function of milling conditions. Control sample (1), 450 rpm and 10 min (2), 650 rpm and 40 min (3), amorphous sample (4), temperature evolution (5)

Modified flours showed PT values lower than that of control. Probably, this was caused by their fine granulometry which facilitated the water diffusion and heat transfer during the heating step (Marshall 1992). Likewise, Zhang et al. (2010) reported a reduction of PT from 79 to 72 °C for rice starch processed 1 h at 450 rpm in a planetary ball mill.

The pasting profile of amorphous rice flour was flat, PT value could not be detected and PV was negligible. A similar result was reported by Han et al. (2007) who found a complete crystallinity loss in rice starch processed 30 min (without pause interval) at 300 rpm in a planetary ball mill.

PV reflects the swelling extent or water-binding capacity of starch, which can be related to end product quality (Manaois 2009). Modified rice flours showed PV values higher than that of control, with the exception of the flour sample obtained at 650 rpm and 40 min (Table 1). Besides, the Pt of modified flours was lower than that of control. The lowest Pt value was found for the amorphous rice flour.

The absence of a sharp peak in the case of control can be partially attributed to its greater cellular wall integrity, which difficult the breakage of swollen starch granules (Hasjim et al. 2013). In contrast, modified flours presented well defined and higher peak viscosities in accordance to its more disrupted starch-protein matrix, which enhance starch granule swelling (Hemavathy and Bhat 1994; Han et al. 2007). However, the excessive milling, as in the case of amorphous flour, produced the drastic reduction of PV. Such behavior has been associated to the destruction of the starch structure and the consequent higher water permeability and loss of thermal stability in supra-molecular structures (Zhang et al. 2010).

Breakdown viscosity measures the facility to disrupt the swollen granules and it reveals the organization level in starch structure (Adebawale and Lawal 2003). The higher BD values observed in modified flours suggest a resistance to the cooking process and to shear stress lower than that of the control sample. Such behavior is desirable in mixture design to enhance the dispersion of flour particles and to facilitate the interaction among food ingredients. In fact, the aptitude of modified rice flour to enhance the rice noodle performance was recently probed (Loubes et al.

Table 2 Effects of milling conditions on RVA pasting parameters in terms of coded factors: milling speed (x_1) and milling time (x_2)

Coefficients of Eq. (3)	PV (mPa s)	FV (mPa s)	BD (mPa s)	SB (mPa s)	PT (°C)	Pt (min)
a_0	5781	8560	2184	4860	79.1	5.71
a_1	− 460*	− 767*	− 120*	− 427*	1.1*	0.03*
a_2	− 446*	− 1221*	178*	− 597*	− 1.1*	0.14*
a_{11}	−	− 254*	− 107NS	− 206*	−	0.02NS
a_{22}	− 1195*	− 704*	− 1049*	− 558*	4.3*	0.03NS
a_{12}	− 851*	− 806*	− 509*	− 463*	1.7*	0.07*
r^2	0.9323	0.9750	0.9426	0.9637	0.9286	0.8628

PV Peak viscosity, FV final viscosity, BD breakdown, SB setback, PT initial pasting temperature, Pt peak time

*Significant at $p < 0.05$; NS non significant coefficient; −: eliminated coefficient

2016). The interaction of flour particles with gum used as gluten substitute was favored by the low size of flour particles which were activated by planetary ball milling.

During the cooling stage, all the samples showed a significant increase of FV. SB viscosity is an indicator of end product texture and it is related with syneresis or weeping during freeze–thaw cycles (Manaois 2009).

Significant correlations ($p < 0.01$) of SB with different flour properties: SB–D50 ($r = 0.96$), SB– ΔH ($r = 0.91$) and SB–DS ($r = -0.80$) were found. The results point out that the increase of starch degradation was the main factor in determining the SB of rice flours obtained by planetary ball milling.

A significant correlation ($p < 0.01$) between FV and damaged starch content ($r = -0.88$) was also found, as well as a non-linear relationship between FV and D50, which was satisfactorily fitted by a cubic equation ($FV = -3477 + 84.9 \text{ D50} - 0.852 \text{ D50}^2 + 0.001 \text{ D50}^3$, $R^2 = 0.87$). It was observed that the viscosity falls abruptly for particle size lower than 140 μm . These results are in accordance with Hasjim et al. (2013), who suggested that such relationships evidence a lesser capacity of damaged starch granules to bind water during heating at 95 °C.

Effects of milling conditions on pasting properties

Each pasting parameter was adequately explained ($r^2 > 0.86$) by a second order model Eq. (3) in terms of milling speed and time (Table 2). Both factors significantly ($p < 0.05$) affected the studied responses. Peak temperature and viscosities (PV, FV, BD and SB) were negatively affected by milling speed (linear effect) and time (quadratic effect). The interaction effect (negative) reflected, particularly at high level of milling time, a considerable reduction of viscosities as milling speed increased.

In contrast, a positive interaction effect was found for PT and Pt. Pt exhibited linear dependence on both studied factors and the maximum predicted values of viscosities correspond to milling speed of 450 rpm and milling times

of 28 min (PV) and 21 min (FV). The minimum values of PV (2829 mPa s) and FV (4809 mPa s) were obtained by severe milling conditions (650 rpm–40 min), under which the Pt was shorter (14%) than that of the control sample.

Conclusion

The pasting properties of flours from IRGA 417 rice obtained by planetary ball mill were dependent on the milling conditions. The amorphous flour exhibited a null aptitude to form paste. However, modified rice flours presented, in comparison with control, a distinctive pasting behaviour with higher values of breakdown (up to 2301 mPa s) and PV (up to 73% higher than control) and a significant reduction in pasting time (up to 20% lower than control) and temperature (up to 12% lower than control). Pasting characteristics of modified rice flours were associated to flour granulometry and evidenced the changes in starch structure during high impact milling. Modified flours showed, due to their pre-gelatinized character and the variable content of damaged starch (5.94–16.46% db), a wide spread of RVA parameters which can be obtained by selecting the suitable milling conditions.

The present work indicated that, planetary ball milling is a useful method to expand the applications of physically modified rice flour in food and non-food products.

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