RESEARCH ARTICLE

High-impact wet-milling: Effects of steeping conditions on rice starch attributes

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Planetary ball wet-milling of rice was evaluated in comparison with traditional wet-milling. The effect of alkali and surfactant concentrations on starch recovery and purity, crystallinity loss, pasting profile, and gel stability were investigated based on the Doehlert design. Particle size, crystallinity degree, and water absorption capacity were not affected by steeping conditions although they differ from those of native starch due to the thermo-mechanical damage associated to high-impact milling. Ball wet-milling allows significant reductions of alkali level and steeping time (from 24 to 1 h) and a high-quality starch is produced due to "in situ" steeping during ball milling. From the response surface method was found that combinations of alkali–surfactant affected the pasting properties and syneresis of starch. Isolated starches presented an advance in peak time and higher values of peak viscosity, breakdown, and initial pasting temperature in comparison with control. A wide range of peak viscosity (4360–7030 cP) could be obtained by selecting a convenient steeping condition. The freeze–thaw stability of starch gels was dependent of surfactant level. These results can be used to improve the manufacture and the selection criteria of rice starch with desirable properties.

Keywords:
Ball milling / Crystallinity degree / Hydration properties / Pasting profile / Starch gel stability

1 Introduction

The isolation method of rice starch differs from those of corn starch, wheat starch, or potato starch because of the differences in the nature and composition of their proteins. As rice proteins are soluble in alkali, alkaline solution (0.3–0.5% w/v NaOH) is used in the traditional rice wet-milling. Such method gives a good starch recovery and low protein content, approximately 1% at lab-scale process [1, 2]. Starch extraction requires, depending on rice variety, from 10 to 24 h of steeping at 25°C, which increases the chance of microbial contamination [1]. A steeping solution to grain mass ratio of 2:1 or higher is used, making it an expensive treatment of alkaline effluents [3, 4].

Different strategies have been proposed to enhance the performance of rice starch isolation, which include steeping with surfactants [5, 6], enzymes [4, 7], the application of high-intensity ultrasound, or combinations of these strategies [6, 8].

The anionic surfactants, as sodium dodecyl sulfate (SDS), induce the formation of protein–SDS complexes promoting changes in the tertiary and quaternary protein structure, which favor protein extraction [9, 10].

The use of enzymes that act on proteins and cellular walls, leads to high starch recovery and purity, as well as lower

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Abbreviations: BD, breakdown; **FV,** final viscosity; **MV,** minimum viscosity; **PT,** pasting temperature; **Pt,** peak time; **PV,** peak viscosity; **SB,** setback

damaged starch content. However, Lumdubwong and Seib [4] have pointed out that the enzymatic treatment is more expensive than traditional wet-milling.

Wet-milling assisted by high-intensity ultrasound produces significant reductions of chemical additives, steeping time, and cost of runoff treatment [6]. Nevertheless, this technology, which is currently costly, also increases the damaged starch content [6, 8].

The replacement of whole or broken polished rice grain by rice flour has also been proposed in order to shorten the steeping time [11]. High-impact mills, which have recently been accessible on the market, can be used for dry or wet-milling and to produce a high level of pulverization [12, 13]. They are offered as a potential tool for starch isolation and could be useful to obtain native or pre-gelatinized rice starches according to process conditions.

The aim of this study was to evaluate the ability of planetary ball mill to enhance the starch isolation in comparison with traditional rice wet-milling. The effects of surfactant (SDS) and alkali (NaOH) concentrations on starch recovery, protein content of starch, pasting profile, and stability of starch gels during a freeze–thaw cycle were investigated by means of RSM. Particle size, crystallinity degree, and water absorption of rice starch were also evaluated.

2 Materials and methods

2.1 Materials

Long grain polished rice (Molinos Río de la Plata S.A., Buenos Aires, Argentina) with 23.7 g/100 g db (dry basis) amylose content and moisture content of 10.3% wb (wet basis) was purchased at a local market. Amylose content was determined according to Morrison and Laignelet [14]. The proximate composition was determined in triplicate using standardized AOAC methods [15]: 79.5% db total starch, 7.8% db protein, 0.5% db lipid, 0.3% db fiber, and 0.4% db ash.

Analytical grade NaOH from Sigma Chemical Co. (St. Louis, MO, USA) and food-grade sodium dodecyl sulfate from J.T. Baker Co. (Phillipsburg, NJ, USA) were used.

2.2 Starch isolation by planetary ball wet-milling

Polished rice (111 g) was processed with 134 g of steeping solution in a planetary ball mill (PM100, Retsch GmbH, Haan, Germany) with zirconium jar (500 mL) and balls (diameter: 5 mm). A grain to ball mass ratio of 1:5 (g:g) was adopted in accordance with Loubes [16]. Seven combinations of NaOH (0, 0.025, 0.05, 0.075, 0.1 w/v%) and SDS (0.3, 0.9, 1.5 w/v%) were performed in accordance with the Doehlert design (Table 1). All combinations were conducted in duplicate but the central point was obtained by triplicate. Alkali concentration range was limited by that of traditional wet-milling (0.1 w/v% NaOH) to evaluate the synergistic effect of surfactant addition on starch recovery and properties. Concentration range of surfactant was set, based on literature reports [5, 6]. The homogenate was obtained by milling 15 min at 550 rpm with change of rotational direction every 30 s. The milling protocol involved grinding periods (5 min) followed by pause intervals (30 min) accounted as "in situ" steeping time. The resulted slurry was centrifuged for 10 min at 1400×*g* (Rolco 350 T, Rolco SRL, Buenos Aires, Argentina), the supernatant was discharged and the protein was hand isolated with a spatula. This procedure was repeated three times by the addition of distilled water in order to obtain a high-quality starch. Isolated starch was then neutralized with HCl (1N),

Table 1. Experimental design and responses of wet-milling tests

	SDS concentration (w/v %)	NaOH concentration (w/v %)		
Sample	Experimental (Coded[a])	Experimental (Coded[a])	Starch recovery[b] (% starch, db)	Protein content of starch[b] (%, db)
1	0.3 (−0.866)	0.025 (−0.5)	68.87	0.66
2	0.3 (−0.866)	0.075 (0.5)	73.63	0.91
3	0.9 (0)	0 (−1)	70.19	0.84
4[c]	0.9 (0)	0.05 (0)	67.57	0.76
5[c]	0.9 (0)	0.05 (0)	68.01	0.8
6[c]	0.9 (0)	0.05 (0)	67.12	0.72
7	0.9 (0)	0.1 (1)	73.68	0.92
8	1.5 (0.866)	0.025 (−0.5)	64.96	0.91
9	1.5 (0.866)	0.075 (0.5)	62.11	0.77
Control	0	0.1	69.56	1.03

a) A linear codification was adopted.
b) Average value from duplicates.
c) Central point of the experimental design by triplicate.

centrifuged, and freeze dried (ALPHA 1-4 LD2, Martin Christ Gefriertrocknungsanlagen GMB, Osterode am Harz, Germany) 48 h at −56°C and 0.04 mbar. Dried rice starch was stored at 20°C in a sealed container.

2.3 Starch isolation by traditional wet-milling

The method proposed by Chiang and Yeh [17] was adopted to obtain the control sample.

Polished rice (100 g) was soaked 24 h at 35°C using 200 mL of alkaline solution (0.1% w/v, NaOH). At the end of steeping time, the solution was discharged and the residue was wet-milled (Waring blender, Waring Products Division, New Hartford, USA) 2 min at high speed with the addition of 200 mL of fresh steeping solution. Then, the homogenate was centrifuged and processed following the procedure previously described.

2.4 Starch recovery and starch quality

The amount of isolated starch was divided by the total starch content of polished rice grain and percentage of starch recovered was determined. Protein content of starch was determined by Kjeldahl method [15] using a factor of 5.95. Both tests were conducted in triplicate.

FT-IR spectra of isolated starch and SDS were obtained in a FT-IR spectrometer model spectrum 400 (PerkinElmer, Inc., Shelton, CT, USA) with a DTGS detector. All the powders were studied in a MIRacle single-reflection attenuated total reflectance (ATR) accessory (PIKE Technologies, Inc., Madison WI, USA) with a single-reflection diamond/ZnSe crystal at an incident angle of 45°. The spectrum of each sample was obtained by taking the average of 64 scans at a resolution of 4 cm^{-1}, at 25°C. The spectra were acquired between 600 and 4000 cm^{-1}. A background spectrum was recorded in air (without sample) prior to each spectrum measurement. The average of the triplicates for each sample was reported. Spectral analysis was performed using the Spectrum software version 6.3.5 (PerkinElmer, Inc.).

2.5 Particle size analysis

Particle size distribution of starch samples were 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, Malvern, UK). The pump speed was 1800 rpm, deionized water was used as dispersing agent, and 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) obtained from a volume distribution was reported.

2.6 Crystallinity degree

The X-ray diffraction patterns of rice starch samples were measured using a diffractometer (Philips X'Pert MPD, PANalytical B.V., Almelo, The Netherlands), operating with Cu k radiation (0.1542 nm) at 40 kV and 35 mA. The scanning region of the diffraction angle (2θ, θ being the Bragg angle) was 6–32° with a scanning speed of 0.03°/2 s. The crystallinity degree was expressed as a percentage and calculated from the crystalline area (I_c) and amorphous area (I_a) obtained in each diffraction pattern as [18]:

$$CD(\%) = (I_c \times 100)/(I_a + I_c) \quad (1)$$

2.7 Water absorption index (WAI)

The method of Anderson et al. [19] with modifications was adopted. Starch (2 g) was mixed with 30 mL of distilled water for 30 s using a vortex mixer, and then heated for 30 min in a water bath at 30°C. The heated solution was centrifuged (1000×*g*) for 10 min The sediment was weighed to determine:

$$\text{WAI (g/g)} = \text{wet sediment weight/dry sediment weight} \quad (2)$$

2.8 Pasting properties

Pasting properties of starch samples were determined with a Rapid Visco Analyser (RVA-4), using the RVA General Pasting Method (Newport Scientific Pty. Ltd., Warriewood, Australia). The starch sample (3.5 g) was 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), minimum viscosity (MV), final viscosity (FV), breakdown (BD), and setback (SB) were obtained from the pasting curve.

2.9 Freeze–thaw stability of starch gels

Starch samples (20 g) were suspended in distilled water (5% w/w, db) and shook in a Vortex model AV11 (Decalab SRL, Buenos Aires, Argentina) for 10 s. They were then heated 20 min at 95°C with continuous stirring. The gelatinized samples were cooled and stored 1 wk at −20°C. At the end of freezer storage, the samples were thawed 5 h at 25 ± 2°C. Samples were shook (15 s) and centrifuged 10 min at 2250×*g*. Finally, the mass of exuded

water was measured by triplicate and syneresis (expressed as percentage) was calculated as:

$$\text{Syneresis } (\%) = \frac{\text{supernatant weight}}{\text{gel weight}} \times 100 \quad (3)$$

2.10 Statistical analysis

The significance of the effect of steeping conditions on starch milling attributes and different starch properties were evaluated by one-way ANOVA (significance level $\alpha = 0.05\%$) and Fisher (LSD) post-test.

The response surface method (RSM) was applied to analyze the effect of SDS and NaOH concentrations on starch recovery, protein content of starch, pasting profile behavior, and starch syneresis. The studied responses (Z_K, $K = 1,\ldots p$) were matched to the coded factors (x_1:SDS, x_2:NaOH) by the following polynomial model associated to experimental design [20]:

$$Y = a_0 + \sum_{i=1}^{n} a_i x_i \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=2_{i<j}}^{n} a_{ij}\, x_i x_j \quad (4)$$

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. All statistical analyses were accomplished using Statgraphics Centurion (version XVI, Statistical graphics Corporation, USA) statistical software.

3 Results and discussion

3.1 Starch recovery and purity

Rice starches isolated by high-impact wet-milling with different alkali–surfactant combinations presented in all the cases a better quality (protein content lower than $0.92 \pm 0.03\%$, db) than that of control from traditional alkaline wet-millling (Table 1). The comparison between FT-IR spectra of isolated starches and pure SDS (not shown here) evidenced that the surfactant could be completely eliminated by the proposed wet-milling method. Table 1 also shows that starch recovery was affected by the steeping conditions; several combinations NaOH–SDS produced values of starch recovery higher than that of the control ($69.6 \pm 0.4\%$, db).

Planetary ball wet-milling requires 1.2 g of steeping solution per 1.0 g of rice, which is significantly lower than the values reported ($\geq$2.0 g/g) in research publications concerning traditional rice starch isolation [4, 7, 17].

In comparison with traditional wet-milling, a significant reduction (from 24 to 1 h) of steeping time was also obtained by means of the proposed method, for which "in situ" steeping takes place during high-impact milling. In contrast, Wang and Wang [6], who obtained a rice starch recovery of 81% based on lab-scale wet-milling assisted by the combination of surfactant and high-intensity ultrasound, required a lower steeping time (<1 h) than that of the present work. As regards starch recovery, Lumdubwong and Seib [4] also reported a very high value (95%) from a steeping solution with 1.1% w/v of alkaline protease. However, the enzymatic process is 2.3 times more expensive than traditional wet-milling.

Although a high wet-milling performance can be reached by these sophisticated and expensive methods, the proposed method produced rice starch of comparable purity. Skerritt et al. [21] and Baldwin [22] have pointed out that 50°C or over are required to remove high-molecular-weight proteins (59–149 kDa) by means of surfactant solution (SDS 1–2% w/v). The pulverizing power of the planetary ball mill, which reached 52°C, probably facilitated the surfactant diffusion within the grain structure and produced a fast and effective starch–protein disaggregation.

The effects of the surfactant (x_1) and alkali (x_2) concentrations on starch recovery and protein content of starch were satisfactorily simulated ($R^2 \geq 0.95$) by Equation (4). Both response surfaces are shown in Figs. 1 and 2, respectively, with the corresponding mathematical Equation (4). The interaction effect among factors was significant for both studied responses as it can be demonstrated in the figures.

The maximum predicted starch recovery (79.8%, db) occurred with 0.3% w/v SDS and 0.1% w/v NaOH, while the minimum protein content of starch (0.64 g/100 g, db) takes place using 0.3% w/v SDS in the absence of alkali. These predicted responses were experimentally corroborated.

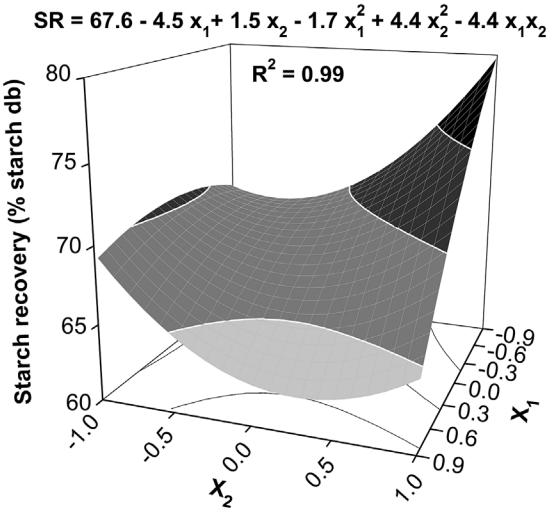

Figure 1. Predicted surface response for starch recovery as function of SDS (x_1) and NaOH (x_2) coded concentrations.

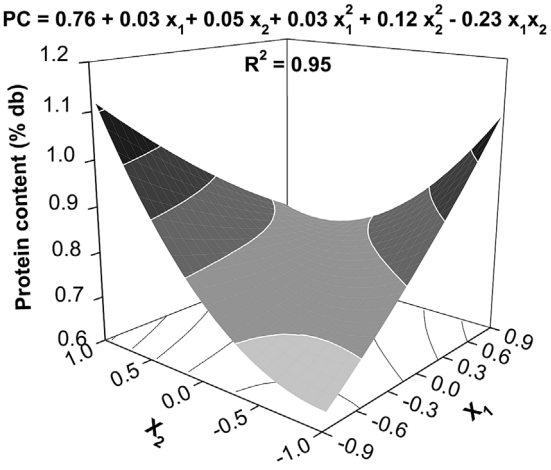

Figure 2. Predicted surface response for protein content of starch as function of SDS (x_1) and NaOH (x_2) coded concentrations.

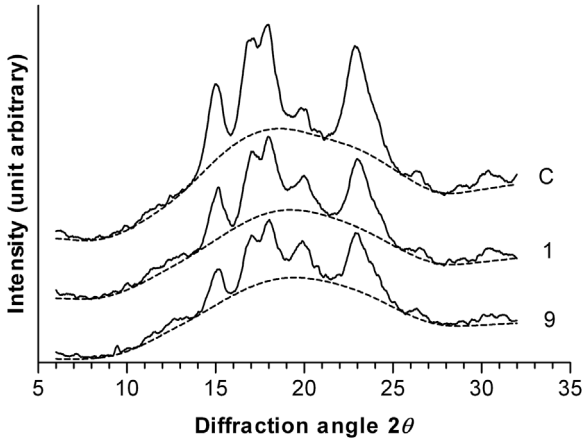

Figure 3. X-ray diffraction patterns of control and isolated starches as function of selected steeping conditions. C, control; sample 1:0.3% w/v SDS and 0.025% w/v NaOH, sample 9:1.5% w/v SDS and 0.075% w/v NaOH.

A multiple optimization was also performed by maximizing the starch recovery and, at the same time, minimizing the protein content of starch. The resulting optimum steeping in the planetary ball mill was 0.30% w/v SDS and 0.067% w/v NaOH (desirability = 0.97). The predicted responses were tested, and the results were a starch recovery of 72.1% (db) and protein residue of 0.82 g/100 g (db).

3.2 Particle size, crystallinity, and water absorption of rice starch

From RSM analysis, no significant effects ($p < 0.05$) of SDS–NaOH combinations on particle size, crystallinity, and water absorption index were observed.

Isolated starches presented a mono modal distribution with a peak at 5.75 μm, which is similar to the control value (5.01 μm) and to that reported by Li et al. [23]. Taking into consideration the size (2–5 μm) of starch granule [24], it seems that high-impact milling produces fragmentation at level of starch granule.

Figure 3 shows the XRD spectra of isolated starches (selected samples) and control. Control showed a crystallinity degree of 32.5% and a characteristic A-type diffraction pattern with reflection peaks at 2θ about 15° and 23°, and an unresolved doublet at 17° and 18° 2θ, which is typical of rice starch [25]. In contrast, the XRD profiles of isolated starches (samples 1 and 9) presented a crystallinity degree of 22.3% in average and a V-type diffraction pattern (characteristic peak at 20° 2θ), which is normally associated to the formation of a lipid–amylose complex [26]. The reduction of crystallinity degree can be attributed to the thermo-mechanical damages produced by high-impact milling and the internal modification of molecular organization of starch, which is caused by the action of chemical additives [27].

WAI values of isolated starches was 2.33 ± 0.10 g/g (db) in average while control value was 2.04 ± 0.01 g/g (db). This result substantiates the thermo-mechanical effect of planetary ball mill on crystalline structure [13]. However, the adopted milling conditions (15 min at 550 rpm) were not as severe as to induce higher changes on the WAI such as those obtained by extrusion [28] or hydrothermal treatment of starches [26].

3.3 Pasting properties

Pasting profile of control sample and isolated rice starches as function of alkali–surfactant combination are shown in Fig. 4 and the corresponding pasting parameters are listed in Table 2. It can be recognized that, in comparison with control sample, the obtained starches (curves 1–9), showed greater

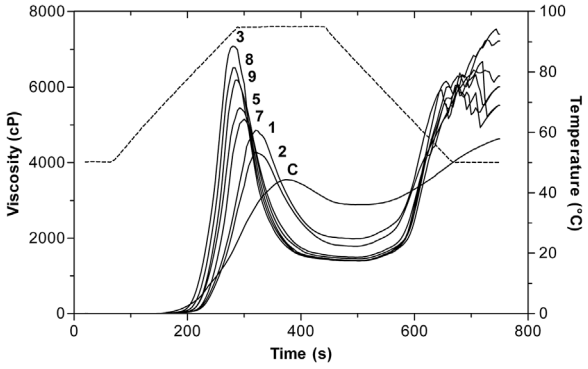

Figure 4. Effect of steeping conditions on pasting profile of isolated starches. C, control; T, temperature evolution; sample N°: 1 (0.3% w/v SDS and 0.025% w/v NaOH), 2 (0.3% w/v SDS and 0.075% w/v NaOH), 3 (0.9% w/v SDS and 0.0% w/v NaOH), 5 (0.9% w/v SDS and 0.05% w/v NaOH), 7 (0.9% w/v SDS and 0.1% w/v NaOH), 8 (1.5% w/v SDS and 0.025% w/v NaOH), 9 (1.5% w/v SDS and 0.075% w/v NaOH).

Table 2. Pasting parameters and syneresis of rice starch as function of steeping conditions

Sample	PV (cP)	MV (cP)	BD (cP)	PT (°C)	Pt (min)	Syneresis (%)
1	4836 ± 27^{c}	1961 ± 33^{e}	2876 ± 6^{c}	80.9 ± 0^{g}	5.3 ± 0.05^{d}	40.4 ± 0.6^{e}
2	4358 ± 102^{b}	1777 ± 4^{d}	2581 ± 106^{b}	81 ± 0^{g}	5.37 ± 0.05^{d}	41.7 ± 2.2^{e}
3	7029 ± 82^{i}	1485 ± 10^{c}	5544 ± 72^{j}	76 ± 0.1^{b}	4.70 ± 0.05^{a}	23.5 ± 2.1^{d}
4*	5334 ± 40^{e}	1458 ± 2^{bc}	3877 ± 37^{e}	79.5 ± 0.5^{ef}	5 ± 0^{c}	18.3 ± 1.4^{abc}
5*	5442 ± 15^{e}	1444 ± 10^{abc}	3998 ± 5^{f}	78.3 ± 0^{d}	4.83 ± 0.05^{b}	16.1 ± 1.1^{ab}
6*	5688 ± 13^{f}	1445 ± 9^{bc}	4244 ± 4^{g}	78.4 ± 0^{d}	4.87 ± 0^{b}	14.0 ± 3.1^{a}
7	5114 ± 49^{d}	1393 ± 11^{a}	3721 ± 37^{d}	80 ± 0.1^{f}	5 ± 0^{c}	21.1 ± 2.4^{cd}
8	6597 ± 124^{h}	1417 ± 26^{ab}	5181 ± 98^{i}	77.2 ± 0.5^{c}	4.63 ± 0.05^{a}	18.6 ± 1.4^{bc}
9	6208 ± 37^{g}	1393 ± 16^{a}	4816 ± 53^{h}	78.8 ± 0.6^{de}	4.8 ± 0^{b}	17.8 ± 0.6^{abc}
Control	3555 ± 18^{a}	2904 ± 25^{f}	651 ± 8^{a}	75.2 ± 0^{a}	6.23 ± 0.05^{e}	24.8 ± 3.4^{d}

PV, peak viscosity; MV, minimum viscosity; BD, breakdown; PT, initial pasting temperature; Pt, peak time.
Mean ± SD values followed by different letters in a column are significantly different ($p \leq 0.05$).
*Central point of the experimental design.

values of peak viscosity (up to 86% higher), breakdown and initial pasting temperature. In contrast, peak time and minimum viscosity values resulted up to 26 and 52%, respectively, lower than those observed in the control starch.

Wang and Wang [7] found significant increases of peak viscosity and breakdown in relation to the traditional wet-milling. These authors attributed such differences to the extremely low levels of protein and damaged starch reached by protease digestion.

The increase of peak viscosity and breakdown values was also obtained by increasing the surfactant concentration in rice starches isolated by wet-milling assisted by high-intensity ultrasound [6].

In the present work, a clear relationship among the residual protein content and peak viscosity was not observed. Nevertheless, when the starch samples with more than 0.90/100 g (db) protein content were excluded from the analysis, significant correlations were found between protein content (PC) and the following pasting parameters: breakdown (PC–BD, $r = 0.82$, $p < 0.05$), initial pasting temperature (PC–PT, $r = -0.91$, $p < 0.01$), and peak time (PC–Pt, $r = -0.91$, $p < 0.01$).

Furthermore, a sharp shape of peak viscosity, especially for concentrations above 0.3% w/v SDS (curves 3–9) can be observed (Fig. 4). Such profile suggests the presence of starch granules with more uniform expansion and break properties [29]. The control sample reached 4633 ± 5 cP of final viscosity and 1078 ± 8 cP of setback. The final viscosity of isolated starches were higher than those of the control (Fig. 4). However, they could not be accurately determined due to signal noise at the end of the trial which can be associated to the gel hardness.

Table 3 shows the significant effect of steeping conditions on pasting parameters determined by RSM in terms of codified surfactant (x_1) and alkali (x_2) concentrations. Equation (4) provides a satisfactory match of experimental

Table 3. Effect of steeping conditions on pasting parameters and syneresis of rice starch

Coefficients of Equation (4)	PV (cP)	MV (cP)	BD (cP)	PT (°C)	Pt (min)	Syneresis (%)
Constant						
a_0	5488	1445	4039	78.7	4.9	16.1
Linear						
a_1	1042*	−268*	1310*	−1.7*	−0.36*	−13.3*
a_2	−783*	−65*	−718*	1.6*	0.14*	−0.8NS
Quadratic						
a_{11}	−179NS	256*	−432*	1.3*	0.18*	16,1*
a_{22}	583*	–	593*	−0.8NS	−0.05NS	6.2*
Interaction						
a_{12}	–	92*	–	0.9NS	0.06NS	–
Correlation						
R^2	0.95	0.99	0.96	0.9	0.96	0.95

PV, peak viscosity; MV, minimum viscosity; BD, breakdown; PT, initial pasting temperature; Pt, peak time; NS, non significant coefficient; –, eliminated coefficient.
*Significant at $p < 0.05$.

pasting behavior ($R^2 > 0.90$). Both factors significantly affected ($p < 0.05$) the values of peak, minimum, and breakdown viscosities. The increase of SDS concentration caused an increase of peak viscosity and breakdown. In contrast, such responses decreased as alkali concentration was increased. Regarding minimum viscosity, no change was observed at 1.5% w/v SDS by varying alkali concentration but, at 0.3% w/v SDS there was a considerable reduction of minimum viscosity by increasing NaOH concentration.

The initial pasting temperature and peak time were affected by alkali (positive linear effect) and surfactant (negative non-linear effect), but the interaction effect among these factors was negligible.

3.4 Freeze–thaw stability of starch gels

A starch paste is freeze–thaw stable if it releases little or no exudates when subjected to freeze–thaw cycles [30]. The syneresis values of gels corresponding to control sample and isolated rice starches are listed in Table 2 as functions of steeping conditions. It can be observed that isolated starches produced similar or lower syneresis values than control with the exception of those obtained at the lowest level of surfactant.

After thawing, the control gel presented a rough surface and a sponge-like structure. In contrast, the isolated starches presented a smooth surface and a solid-like structure which contributed to a more accurate and rapid syneresis determination.

Other authors [31] also reported the formation of sponge-like structure in native rice starch gels with rather high amylose content. Regarding literature reports, the syneresis percentages observed in the present study were lower than those found by Deetae et al. [31] for non-waxy rice starch (28.7% syneresis) but, they were not as low as the syneresis of waxy rice gels [32].

The effect of alkali–surfactant combinations on syneresis percentage was calculated by RSM and is presented in Table 3. Freeze–thaw stability depended significantly on the steeping conditions ($p < 0.05$). The surfactant level was the main factor that influenced the gel stability. Syneresis values decreased as the surfactant concentration increased. A minimum syneresis of 13.3% was obtained at 1.19% w/v SDS and 0.05% w/v NaOH. These results suggest that rice starches isolated by a suitable combination of alkali and surfactant could replace chemically modified starches [33] due to their ability to provide improved stability to freezing-thawing.

4 Conclusions

High-quality rice starch could be obtained by planetary ball wet-milling. In comparison with traditional wet-milling, the proposed method would reduce significantly the amount of steeping solution and the alkali concentration from 0.1 to 0.067% w/v as well as the milling time from 24 to 1 h due to "in situ" steeping at high-impact. It is expected that this result will positively impact the cost of effluent treatment as well as environmental concerns.

In comparison with the control, the isolated starches showed similar particle size, a slight higher water absorption capacity, a significant reduction of crystallinity degree, and a V-type diffraction pattern.

In regard to pasting properties, starches isolated by high-impact wet-milling presented higher values of peak viscosity, initial pasting temperature, and breakdown than those of the control. Starch viscosity can be manipulated within a wide range by selecting suitable steeping conditions.

Starch gels stability during freeze–thaw treatment was dependent on surfactant level. Due to its low syneresis values, they may have a potential use in frozen products.

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