International Journal of Food Science +Technology

International Journal of Food Science and Technology 2018

Original article

Functional and thermorheological properties of rice flour gels for gluten-free pasta applications

Patrícia Fradinho,* Isabel Sousa & Anabela Raymundo

LEAF – Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda 1349-017 Lisboa, Portugal

(Received 30 July 2018; Accepted in revised form 8 October 2018)

Summary Based on the European Commission directives on circular economy, this work explores the functional and thermorheological properties of rice flour from broken kernels, a by-product from the rice industry, in order to evaluate its possible use in food applications, back into the value chain. Chemical and hydration properties of two rice varieties (Guiana – *Indica* spp, Ariete – *Japonica* spp) were accessed, as well as the impact of the rice variety on the texture and viscoelasticity of rice flour gels (6–26%). Both rice varieties presented statistically different physicochemical properties (protein, lipid and amylose contents), and hydration properties that support the distinct texture and rheology behaviour of gels obtained. Rheology results suggested the formation of a gel-network structure with high frequency dependence, especially at lower rice concentrations. Texture results suggest that both rice varieties could be suited for development of gluten-free products that require pre-gelatinised starch, such as pasta. The effect of gelatinised rice flour (10–25%) and gelatinised flour/rice flour ratio (40:60, 50:50, 60:40) on the physical properties and cooking quality of pasta were assessed. Better overall cooking quality and texture properties were obtained for the formulation with 20% gelatinised rice flour and 50:50 rice gel:rice flour ratio.

Keywords Amylose, broken rice, gelatinization, rheology, swelling power, waste valorisation.

Introduction

Rice is a major cereal crop worldwide and one of the three important commodities in terms of food security. European countries are responsible for the production of 4.5 million ton of paddy rice, accounting for a self-sufficiency rate of about 65%. Although Portugal produces only 6% of the total rice produced in Europe, the portuguese are the top European rice consumers, with around 16 kg per capita per year (INE, 2016). Most of the rice (*Oryza sativa*) produced in Portugal is botanically classified as ssp. *Japonica*, commercially known as *carolino*, very well adapted to portuguese environmental conditions and traditionally used in culinary preparations. However, *Indica* varieties have a high expression in terms of consumption, due to the demand for exotic rices (e.g. basmati, thai) and pre-prepared convenient meals. With a total production of about 190 000 tons of paddy rice, it only covers 70–75% of Portugal needs but it is self-sufficient in *carolino* rice consumption.

In recent years, a growing interest to maximise the uses of the agricultural by-products for different purposes has been observed. During rice de-husking and polishing, considerable quantities of by-products are produced, including broken rice, which accounts for about 15% of the milling rice. This by-product is an important raw material in fermentation industries such as breweries and distilleries. Nevertheless, it can also be further milled into flour and used to develop gluten-free added-value foods . Several studies have been published on the development of sweet cookies (Tavares *et al*., 2016), snacks (Paiva *et al*., 2012), syrup (Spinosa *et al*., 2016) and noodles (Ahmed *et al*., 2015) using broken rice flour.

The development of gluten-free foods is on today's agenda. Rice flour is the most suitable commodity for bakery applications due to its bland taste, white colour, digestibility and hypoallergenic properties. However, rice protein lacks the functionality of gluten to promote a viscoelastic dough structure. Therefore, bakery product's properties need to be modified by appropriate structure and texture forming ingredients or additives, including various hydrocolloids (Lazaridou *et al*., 2007; Crockett *et al*., 2011), proteins (Sozer, 2009) and emulsifiers (Lai, 2001).

The approach proposed in the present work is to optimise the specific thermal properties of starch to improve

*Correspondent: E-mail: pfradinho@isa.ulisboa.pt

doi:10.1111/ijfs.14001

dough viscoelastic characteristics, as reported by Padalino *et al.* (2013) and Marti *et al.* (2011) to produce gluten-free pasta with suitable technological quality.

Flours from different rice varieties differ in the gelatinisation behaviour and viscoelastic properties. Since starch is the main component of rice flour and greatly responsible for the cooking quality of rice, most studies (e.g. Singh *et al.*, 2006, 2007; Kong *et al.*, 2015) are focused on rice starches physicochemical and thermal properties, mainly from *Indica* rice varieties. However, other components present in the rice flour (protein, lipid and non-starch polysaccharides) take part in the gel formation, either facilitating or hindering the gelatinisation/retrogradation processes (Puncha-arnon & Uttapap, 2013). During gelatinisation process, an amylose-lipid complex is formed, restricting the expansion of starch granules during gelatinisation or retarding amylopectin retrogradation (Tester & Morrison, 1990; Yu *et al.*, 2012). Several studies have been conducted with rice starches isolated from rice flour (e.g. Kong *et al.*, 2015; Jang *et al.*, 2016), however, there are few studies available about the thermorheological properties of rice flour (Torres *et al.*, 2014). The present approach is focused on using broken rice by-product from the rice industry, following the European Commission strategy on Circular Economy, transforming wastes into high value-added products, and increasing globalised market for secondary raw materials (European Commission, 2015).

The main objective of the present work is to analyse the physicochemical, hydration and thermorheological properties of rice flour gels produced from broken rice's milling of Ariete, the most common portuguese *Japonica* variety, and Guiana rice (*Indica* variety), in order to evaluate their application in the development of gluten-free products, namely fresh pasta.

Materials and methods

Raw materials

Broken rice kernels from *O. sativa* ssp. *Indica* and *Japonica*, namely from Guiana and Ariete varieties, respectively, were provided by portuguese rice company Novarroz – Produtos Alimentares SA. Both rice varieties were milled and sieved to a size particle less than 180 μm in a Pulverisette 14 Premium (Fritsch) and kept at room temperature in a closed container protected from light.

Commercial rice flour Ceifeira (Dacsa Atlantic SA, lot 2545/17) was also used for the development of the gluten-free pasta.

Chemical composition of rice flours

Rice flours were analysed for its moisture according to AACC method 44-15.02 (AACC International, 1999a) and ash NP 518 (1986), based on gravimetric methods. Crude protein was determined by the micro Kjeldhal method according to the ISO20483 (2006) official method for cereals and pulses. The determined total nitrogen content was multiplied by a conversion factor of 5.95 (FAO, 2003) to obtain the flour's protein content. The rice flour's fat content was determined according to the procedure used for cereals and derived products in the Portuguese standard method NP 4168 (1991). Carbohydrate content was calculated by difference to 100% of main constituents (moisture, ash, protein and fat).

Amylose content and amylose/amylopectin ratio of rice samples were determined enzymatically using the K-AMYL 06/2015 Assay Kit (Megazyme International Ireland Ltd., Wicklow, Ireland). Amylose is expressed as a percentage of total starch. All chemical analyses were carried out at least in triplicate and expressed as the mean value ± standard deviation.

Hydration properties of rice flours

The swelling power (SP) of Guiana and Ariete rice flours was determined using the method developed by Leach *et al.* (1959) for starches, with slight modifications. This method involves the suspension of rice flour (w_{sample}) in excess water, with gentle stirring to keep it in suspension, followed by incubation at 20, 50, 70 and 90 °C (within the range of temperatures involved in the starch gelatinisation process), for 30 min and centrifugation at 10 000 ***g*** for 10 min. Swelling power was determined from the weight of the sediment ($w_{sediment}$) according to eqn (1):

$$\mathrm{SP}\,(\mathrm{g\ g^{-1}, dry\ basis}) = w_{sediment}/(w_{sample} - w_{residue}) \quad (1)$$

The water absorption index (WAI) and solubility (*S*) of rice flours were assessed by the method described by Anderson (1982), applying the same range of temperatures as for SP. Both parameters were determined according to eqns (2) and (3):

$$\mathrm{WAI}\,(\mathrm{g\ g^{-1}, dry\ basis}) = w_{sediment}/w_{sample} \quad (2)$$

$$\mathrm{S}\,(\%, \mathrm{dry\ basis}) = (w_{residue}/w_{sample}) \times 100 \quad (3)$$

Rice flour gel preparation

Rice flour suspensions from Guiana and Ariete varieties were prepared, ranging from 4.5% to 26.0% (w/w, dry basis). Flour was dispersed in water, under mechanical stirring (IKA Labortechnik, EURO-STD, Staufen, Germany) at 350 r.p.m. and heated at 90 °C during 30 min, in a water bath, according to previously optimised conditions (Torres *et al.*, 2014). The mixtures were poured into glass containers (35 mm height, 32 mm diameter) and left at 5 °C for 24 h to ensure full maturation.

Pasta preparation

In this study, commercial rice flour made from the milling of broken kernels from *Indica* and *Japonica* varieties was used. The flour composition in terms of rice varieties and their proportion was not provided by the manufacturer.

To assess the optimum pasta formulation, rice flour gel (10–25% d.b) was prepared according to procedure previously described. After cooling, rice flour gel was mixed with rice flour at 40:60, 50:50, 60:40 ratios, in a food processor (Bimby TM31; Vorwerk, Wuppertal, Germany) for 3 min at room temperature. Then, the dough was covered in aluminium foil and allowed to equilibrate for 15 min at 25 °C in an air oven, before measurements. Then, the dough was sheeted (2 mm diameter) and laminated as tagliatelle using a bench top pasta machine (Atlas 150, Marcato, Italy).

Rheology measurements

Rice flour suspensions (6–26%, w/w, d.b) from Ariete and Guiana varieties were dispersed under magnetic stirring (200 r.p.m.) at room temperature for 5 min, and immediately poured into the bottom plate of a 35 mm serrated parallel plate sensor (PP35) on the rheometer (MARS III; Haake, Karlsruhe, Germany), to promote gelatinisation *in situ*, avoiding further perturbations of the matrix. The temperature control was performed us Haake ing an UTC-Peltier system and the gap was set at 0.5 mm, according to Torres *et al.* (2014). Edges of samples were coated with liquid paraffin, to prevent moisture losses during tests.

Stress sweep tests were conducted on suspensions and on samples submitted to thermal treatment to ensure that all measurements were carried out within the viscoelastic region. Temperature, time and frequency sweep tests were performed inside this region at 1 Hz. Aqueous flour suspensions were held 5 min at 20 °C, between the plates, before testing. Small amplitude oscillatory shear measurements (SAOS) were performed to study the viscoelastic behaviour of the samples. First, the suspensions were heated from 20 to 90 °C at 2 °C min^{-1} and time sweep tests were conducted at 90 °C for 30 min. After thermal treatment, samples were cooled down to 5 °C at 2 °C min^{-1}. The maturation was performed at this temperature, during 30 min at 1 Hz, followed by the frequency sweep at 5 °C, with oscillation frequencies over the range 0.01–100 Hz. Each formulation was tested at least in duplicate.

The viscoelastic behaviour of dough formulations was performed in a controlled stress rheometer (MARS III; Haake) coupled with a UTC – Peltier system, using a serrated parallel plate system with 20 mm diameter and 2 mm gap. Frequency sweep tests at 20 °C were performed from 0.01 to 100 Hz, within the linear viscoelastic region. Each formulation was tested at least in triplicate.

Instrumental texture analysis

The texture profile analysis (TPA) of all rice flour gels and doughs was performed using a TA-XTplus Texture Analyser (Stable Micro Systems, Godalming, UK) in penetration mode, using a 10 mm acrylic probe.

The dough was moulded in acrylic discs (61.5 mm diameter and 18 mm height) and rested for 15 min before the probe plunged 8 mm at 1 mm s^{-1}. On the other hand, the gels were let to equilibrate at 20 °C for 30 min before a 15 mm perforation at 1 mm s^{-1}.

From the force vs. time texturograms, the parameters which discriminate the sample's texture were firmness and adhesiveness. Firmness (N) was considered as the maximum resistance to the penetration and was calculated as the height of the force peak. Adhesiveness ($-N$.s) is a characteristic of sticky materials and can be defined as the resistance of the material when the probe is recessing. This parameter is recorded as the negative area of the first cycle (Bourne, 2002). These determinations were conducted at 20 $\pm$ 1 °C in a temperature controlled room and were replicated at least eight times.

The firmness of cooked pasta samples prepared according to 2.5 was measured following AACC method 66-50.01 (AACC International, 1999b). Pasta firmness was determined by measuring the cutting force required to cut three cooked tagliatelle strips using a blade set with guillotine (HDP/BSG) that cut the sample at 0.17 mm s^{-1}. The thickness of the samples was measured to determine the cutting distance of each sample: 1.5–2.8 mm. Each formulation was replicated at least eight times.

Pasta stickiness is defined as the maximum peak force required to separate the probe from the sample surface (peak height) and the area under the peak as the work of adhesion Smewing (2009). Three tagliatelle strips were centrally aligned under a circular probe (44 mm diameter) on a raised platform and were retained within a circular slot (48 mm diameter) made in a base plate. The samples were compressed for 2 s with an applied force of 9.807 N at 0.5 mm s^{-1}. At least ten replicates were performed of each pasta formulation. The precision of the stickiness measurement decreases as elapsed time increases. Therefore, the time for stickiness measurement was set at 15 min after draining.

Cooking quality evaluation of pasta

The optimum cooking time was defined empirically by cooking the tagliatelle samples in boiling distilled water for 1 min. The swelling index (Padalino *et al.*, 2013) of cooked pasta was determined by weighing 10 g of the sample, before and after cooking, and then drying it at 103 ± 2 °C until constant weight, and is determined by eqn (4).

$$\text{Swelling}\,(\text{mLg}^{-1}) = (\rho_{\text{water}} \times V_{\text{water absorbed during cooking}})/m_{\text{dry sample}} \quad (4)$$

Pasta water absorption is defined as the weight increase of pasta before and after cooking, and was determined as percent weight gain with respect to the weight of uncooked pasta. The samples were cooked, rinsed with water and allowed to drain for 5 min. The water absorption was then determined by eqn (5).

$$\text{Water absorption}\,(\%) = [(m_{\text{cooked sample}} - m_{\text{raw sample}})/m_{\text{raw sample}}] \times 100 \quad (5)$$

Cooking loss (Zhu *et al.*, 2010) is defined by the amount of solids lost into the cooking water, and was determined by evaporating the 100 mL of water used for cooking 10 g of dough, and is expressed according to eqn (6).

$$\text{Cookingloss}\,(\%) = (m_{\text{residue after evaporation}}/m_{\text{sample}}) \times 100 \quad (6)$$

At least three measurements were performed for each analysis.

Statistical analysis

Experimental data were analysed using Statistica 10 (StatSoft Inc, Tulsa, OK, USA) by means of *t*-test and analysis of variance (one-way ANOVA) using the *Post Hoc* Comparison Tukey test, with 95% confidence ($P < 0.05$). Pearson correlation analysis was also conducted ($P < 0.05$) to determine the relationships between the physicochemical and hydration properties of the samples. To assess possible relationships between protein content, lipid content, SP (at 90 °C) and amylose (dependent variable) content of rice a multiple linear regression was performed.

Results and discussion

Chemical composition of rice flours

The chemical composition of rice samples is presented in Table 1.

As expected, carbohydrates are the main constituent of rice flour. In the traditional wheat semolina pasta, proteins play an important role in structure building through the establishment of a gluten network, and starch granules act as inner fillers. However, in a gluten-free matrix, starch assumes the major responsibility for functional properties, particularly its amylose content. According to the classification of rice based on amylose content (Juliano, 1998), Ariete (*Japonica*) variety is ranked as low amylose rice (10–20% amylose) and Guiana (*Indica*) is intermediate amylose (20–25% amylose). Other authors have reported amylose values between 4.1–16.4% (Singh *et al.*, 2006) and 18.3–27.9% (Mariotti *et al.*, 2009) for *Indica* rice varieties; and 10.5% for Giza (*Japonica*) (Ahmed *et al.*, 2015) and 19.9% *Japonica* (Singh *et al.*, 2000). Santos *et al.* (2013) reported amylose values between 9.4% and 15.2% for portuguese *Japonica* varieties. According to the results from Table 1, amylose content is highly dependent on the rice variety, and significantly higher ($P < 0.05$) for Guiana rice. The differences in physicochemical parameters of both rice varieties, mainly amylose content, could support the different technological behaviour of these rice varieties, as discussed later on.

Protein content is higher in Guiana (*Indica*) than in Ariete (*Japonica*) and both values are similar to those found by Singh *et al.* (2000) for other rice varieties. Most studies dealing with starch pasting properties are performed with isolated starch with residual protein content. Since protein content has an important impact on pasting properties, it is natural that the high protein values could help to explain the possible differences in the behaviour of the studied rice gels, when compared to gels obtained from isolated starch.

Hydration properties

The swelling index is an indicator of the water absorbed by the flour (mainly by starch and proteins) during cooking, which will be used for the gelatinisation of starch and the hydration of protein. The hydration properties of rice flour (Fig. 1) are related to physicochemical characteristics such as amylose and protein contents, and consequently to the gel formation (Lai, 2001), an important property in the food industry to define the range of application of the biopolymers.

Table 1 Chemical composition of Guiana and Ariete rice flours

Rice sample	Protein % (w/w, d.b)	Lipids* % (w/w, d.b)	Ash % (w/w, d.b)	Carbohydrates % (w/w, d.b)	Moisture (% w/w)	Amylose* (% w/w)	AM/AP
Guiana	7.4 ± 0.4	1.8 ± 0.1	0.6 ± 0.0	89.7	12.5 ± 0.1	22.4 ± 1.5	1/3.5
Ariete	6.4 ± 0.5	2.8 ± 0.7	0.6 ± 0.0	90.2	13.1 ± 0.2	16.4 ± 1.6	1/5.1

AM/AP, amylose/amylopectin ratio.
Samples marked with * showed significant differences ($P < 0.05$, *t*-test) for each parameter.

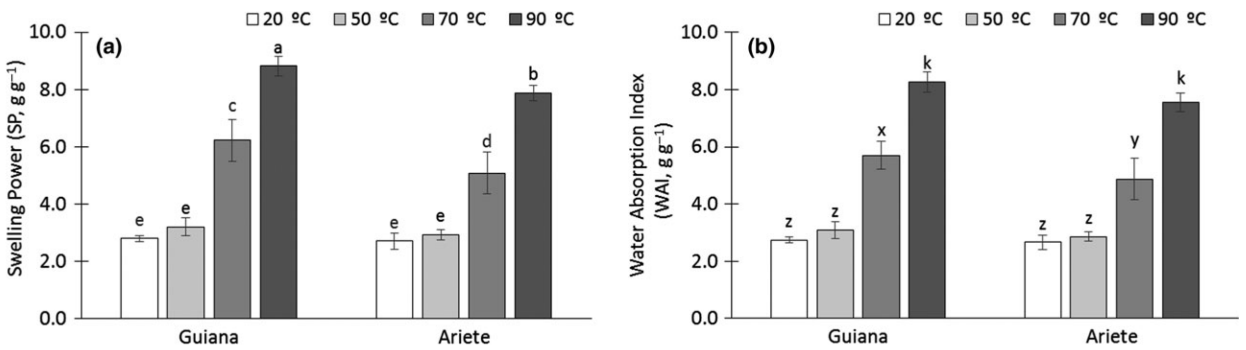

Figure 1 Impact of temperature of the Guiana (*Indica*) and Ariete (*Japonica*) rice flours on swelling power (a) and water absorption index (b). Samples marked with different letters showed significant differences ($P < 0.05$, one-way ANOVA *post-hoc* Tukey test) for each parameter.

Both rice varieties exhibited different gelatinisation behaviour, since at 20 °C (room temperature) there is no significant difference ($P < 0.05$) in SP, but at 70 and 90 °C, corresponding to the gelatinisation process, Guiana (*Indica*) exhibits significantly ($P < 0.05$) higher SP values. Differences in SP can resulted from differences in amylose content, viscosity pattern and weak internal organisation as a consequence of negatively charged phosphate groups within the rice starch granules (Singh *et al.*, 2006). Water absorption results from both rice varieties showed that only at 70 °C Guiana is significant ($P < 0.05$) more prone than Ariete to absorb water. Flours with high water absorption should have more hydrophilic constituents, such as polysaccharides (Kaushal *et al.*, 2012). Since the carbohydrate content is similar for both samples, the results can be explained by the amylose content of the studied samples.

The swelling behaviour of cereal starch is related to its pasting and rheological properties. This parameter has been reported as a property mainly related with the amylopectin content. Ariete presented a higher amylopectin (Table 1) content but lower SP than Guiana (at 70 °C) and this can be explained by its significantly lower amylose content (Ariete: 16.4%, Guiana: 22.4%). Although amylopectin swells to a greater extent along with protein and lipids as individual components, in combination with amylose there is a resistance to swelling (Fabian *et al.*, 2011). Amylose acts both as a diluent and as an inhibitor of swelling of the starch granules, especially in the presence of lipids (Tester & Morrison, 1990). In fact, amylose and lipid content are strongly negatively correlated ($r = -0.948$, $P < 0.05$).

The results of the multiple linear regression model were significant ($P < 0.001$, adj $R^2 = 0.999$) indicating that approximately 99.9% of the variance in the amylose results is explained by protein, lipids and SP (at 90 °C) according to the following correlation expression (7):

$$\text{Amylose} = 35.52 + 2.96\,\text{Protein} - 4.65\,\text{Lipid} - 2.71\,\text{SP} \quad (7)$$

As shown in Fig. 1a, SP of both rice flours increased with temperature, and have a steeper increase near the gelatinisation temperature. WAI (Fig. 1b) presents a similar pattern to SP. Guiana rice flour shows higher values in both parameters.

These results show a temperature-dependency of both swelling and WAI for both rice varieties, following polynomial eqns (8–11).

$$\text{SP}_{\text{Gu}} = 0.001T^2 - 0.070T + 3.610, R^2 = 1 \quad (8)$$

$$\text{SP}_{\text{Ar}} = 0.002T^2 - 0.122T + 4.447, R^2 = 0.999 \quad (9)$$

$$\text{WAI}_{\text{Gu}} = 0.001T^2 - 0.077T + 3.640, R^2 = 0.987 \quad (10)$$

$$\text{WAI}_{\text{Ar}} = 0.002T^2 - 0.091T + 3.857, R^2 = 0.997 \quad (11)$$

There was a significant correlation between SP and WAI (eqns 12 and 13) which is often reported by other authors (Wang & Seib, 1996; Peries *et al.*, 2016).

$$\text{SP}_{\text{Gu}} = -0.014\,\text{WAI}^2 + 1.179\,\text{WAI} - 0.292, \text{R}^2 = 1 \quad (12)$$

$$\text{SP}_{\text{Ar}} = -0.010\,\text{WAI}^2 + 1.182\,\text{WAI} - 0.347, \text{R}^2 = 1 \quad (13)$$

As expected, solubility (S) results increased with temperature, following a polynomial relation (eqns 14 and 15):

$$S_{\text{Gu}} = 0.001T^2 + 0.027T + 0.937, R^2 = 0.971 \quad (14)$$

$$S_{\text{Ar}} = 0.002T^2 - 0.077T + 2.457, R^2 = 0.998 \quad (15)$$

A strong positive correlation ($r = 0.965$, $P < 0.05$) was also found between solubility (at 50 °C) values and amylose content, since amylose linear chain is more water soluble than amylopectin. In this sense, a flour with higher amylose content should be more easily used for making pre-gelatinised flours, which would of great interest for pasta making.

Rheology characterisation of rice gels

The empirical rheology method performed by the amylograph is the standard test accepted for determination of the gelatinisation properties of flour/starch. However, several authors (Singh *et al.*, 2006; Mariotti *et al.*, 2009) have been using fundamental rheology methods since they use smaller size samples, better precision and the ability to study different temperature profiles (Pojić *et al.*, 2013).

As expected for a gel, an increase in the linear elastic modulus with rice flour concentration is observed (Fig. 2), which reflects an increase in the gel structure level as more gel linkages are formed. As the temperature increases, a sharp increase in G' is observed, which corresponds to the gelatinisation temperature range. For both rice varieties starch gelatinisation occurs between 52.6 and 78.2 °C and is dependent on rice content, since this parameter increases with the increase of rice concentration. For lower rice concentrations, there is a steeper increase in G' with heating temperature, while for rice flour concentrations above 17.5%, the temperature does not have such a marked influence on G'. Moreover, for Ariete rice variety (Fig. 2b) this behaviour is noticed even at 9% rice concentration.

Since water influences both the flexibility and the molecular mobility of starch molecules, in a more concentrated gel, water molecules seem to have less mobility as they are close packed and more extensively hydrogen bonded to relatively large and immobile starch molecules (Lu *et al.*, 2011). At these high rice flour concentrations, there is not enough available water for the swelling of all starch granules. So, as a consequence, amylose is not completely leached and no steep increase in the G' is observed.

Gelatinisation temperature is not only related to amylose content, it also depends on granular architecture, molecular weight distribution and amylopectin fine structure (Sodhi & Singh, 2003). For all rice concentrations tested, Ariete rice variety presents higher gelatinisation temperature than Guiana. Although this study focus only two rice varieties, Mariotti *et al.* (2009) also reported a significative correlation between gelatinisation temperature and amylose content.

Although the gelatinisation temperature varies with rice concentration, Peak Temperature is almost identical (85.2–87.6 °C) for all concentrations at both rice flours. Similar pattern but different temperature ranges were obtained by Spigno & De Faveri (2004) for starch contents between 10% and 80%.

During the cooling process (data not shown), an increase of viscoelastic parameter G' with rice flour content is noticed as expected, meaning that a slight reinforcement due to more linkages between molecules of the gel structure is observed on cooking. This behaviour is in agreement with the formation of a continuous network by the solubilised amylose molecules that link swollen starch granules by hydrogen bonds. The maturation kinetics (data not shown) of all rice concentrations showed a rapid gel maturation (G' and G'' remain constant) just after a few minutes of maturation. This feature brings a technological advantage for future use of pre-gelatinised rice flour in gluten-free products.

The rheology behaviour of Guiana and Ariete gels after maturation is depicted in Fig. 3.

For all rice concentrations studied from both rice varieties, G' is always higher than G'', indicating the existence of a three-dimensional network formed by carbohydrate and protein macromolecules that trap the water molecules and starch granules. As expected for gel systems the structure is reinforced with intermolecular linkages with the increase of rice flour, therefore viscoelastic parameters increase with concentration. However, from 17.5% rice content there is

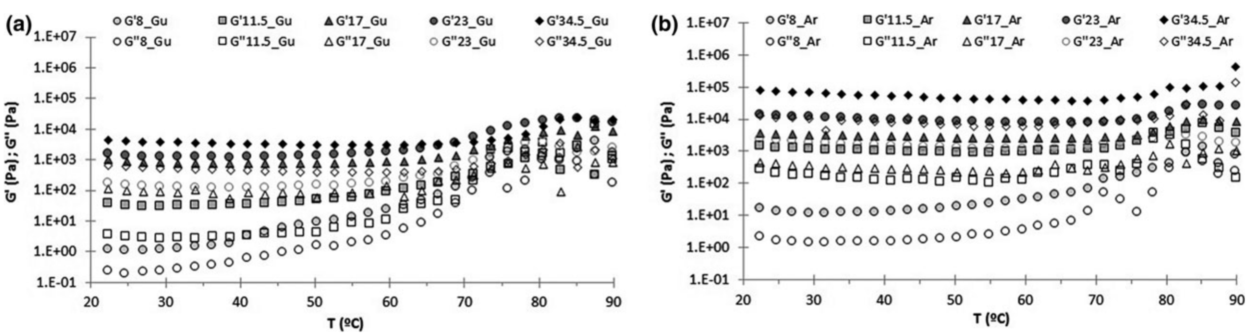

Figure 2 Evolution of viscoelastic moduli during heating (2 °C min^{-1}) of Guiana (a) and Ariete (b) rice flours at 6%, 9%, 13%, 17.5% and 26% rice content (closed symbols-G'; open symbols-G'').

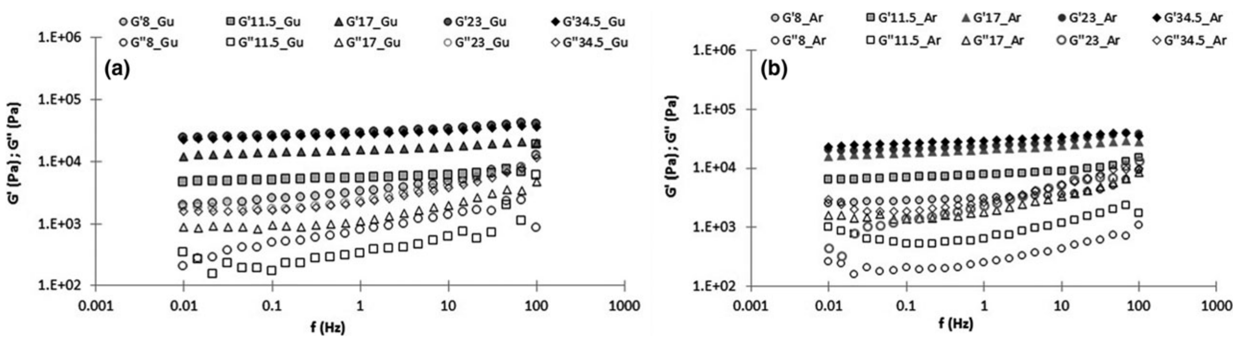

Figure 3 Mechanical spectra of (a) Guiana and (b) Ariete rice flour gels (closed symbols-G'; open symbols-G'') at different concentrations (6–26% w/w, d.b).

little increase in the viscoelastic moduli especially for Ariete variety. This phenomenon is related with close packing of the molecules due to the tight association between starch molecules in high starch concentrations as discussed earlier.

At low rice concentrations (6% and 9%) G'' tends to exhibit a minimum, which has been related to the formation of physical entanglements among polymeric molecules, that reinforce the three-dimensional network (Ferry, 1980). Especially at lower rice contents, both viscoelastic moduli increase with the frequency, with a stronger dependency for G''. This results in a weak gel-like behaviour of the rice pastes, as previously reported by Mariotti *et al.* (2009) for flours from several rice varieties.

Texture of rice flour pastes

For the suspension prepared with 4.5% (w/w) rice flour no gel formation was observed. Consequently, this concentration was not used for further studies. According to Lu *et al.* (2011) for starch concentrations lower than 5%, the leached-out amylose and swollen granules are not high enough to interact themselves to form a matrix. In the present study, 6% (w/w) is probably the critical gelation concentration.

The texture of rice flour pastes was evaluated by a TPA penetration test, and the resulting firmness and adhesiveness parameters were determined and presented in Fig. 4.

For both rice varieties, gel firmness and adhesiveness are nearly constant until 13% rice flour concentration. Texture results show that for rice content above this concentration, both texture parameters suffered a steeper increase ($P < 0.05$) associated with the reduced mobility of water molecules, as discussed previously. This could indicate a maximum rice flour concentration for future use in food applications, since high adhesiveness values bring technological constraints and undesirable features in pasta development. Therefore, 17.5% should be close to the maximum rice concentration usable, although other ingredients added in the pasta making process (e.g. other flours, hydrocolloids) would also contribute to the adhesiveness of the final product.

It is also observed that considering the same rice flour concentration in Guiana and Ariete, there is a statistical difference ($P < 0.05$) between firmness and adhesiveness values of the two rice varieties for 17.5% and 26.0% rice content, respectively. These results are in agreement with the ones reported by Lu *et al.* (2011) for different varieties of both rice subspecies. These results are consistent with the rheology study previously discussed in Section Rheology characterisation of rice gels.

As referred by Jang *et al.* (2016), these textural properties of starch gels are dependent on the amylose and protein contents. Pearson correlation was performed between physicochemical properties of flours and texture parameters of gels to verify if a correlation between these properties can be applied. In a review published by Marti & Pagani (2013) several studies are mentioned that report the high correlation between high amylose (25–33%) rice and the sensory acceptance of the pasta produced. Therefore, the ideal starch for gluten-free (GF) pasta products should have a marked tendency to retrograde: this property is useful to give rigidity to cooked pasta, and to reduce both the stickiness of the pasta surface and the cooking loss. However, other studies (e.g. Ahmed *et al.*, 2015) are in favour of low amylose content. A *Japonica* rice (Giza variety) was selected as the best for the development of gluten-free products due to its high water holding capacity, peak viscosity and above all low amylose (11.6%).

Optimisation of pasta formulation

As observed in this study, Guiana rice variety showed statistically ($P < 0.05$) higher amylose content than Ariete, which could be more suited for GF pasta applications. However, due to industrial constrains related with low market demand for rice flour, broken

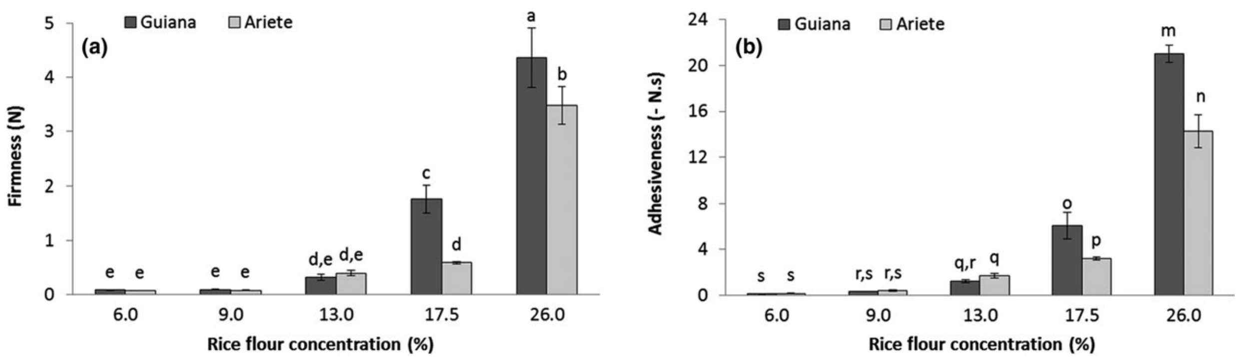

Figure 4 Texture parameters (a – firmness; b – adhesiveness) of rice gels (6–26% w/w, d.b). Different letters indicate significant differences ($P < 0.05$, one-way ANOVA *post-hoc* Tukey test) for the same parameter.

kernels are milled all together, independently of rice variety. Therefore, rice flour available in the portuguese market is a blend of both *Indica* and *Japonica* rice varieties, in random proportions.

For this reason, the optimisation of pasta formulation was performed using a commercial rice flour with the following chemical composition: 6.0 (±0.6)% protein, 0.8 (±0.1)% lipids, 11.5 (±1.7) % amylose, 1/7.7 AM/AP (amylose/amylopectin ratio).

Several formulations of rice pasta were tested according to the procedure described in Section Pasta preparation. However, not all of them are suitable for pasta formation (Fig. 5).

The optimisation of pasta formulation was performed taking into account the formulations 10% _40:60, 15%_40:60, 15%_50:50, 20%_50:50, 25% _50:50, 25%_60:40. Both dough and pasta made from these formulations were characterised in terms of their physical, rheological and cooking quality parameters. From a processing point of view, the best doughs which revealed to be less sticky and easier to handle, were: 20%_50:50 and 25%_50:50.

Physical properties of uncooked pasta dough

The rheological behaviour of dough formulations prepared with different proportions of rice gel is depicted in Fig. 6.

Viscoelastic behaviour of the doughs shows a weak gel-like structure, with a slight frequency dependence. For all gluten-free pasta analysed, a similar trend was observed regardless of dough composition.

To quantify the impact of different combinations of gelatinised rice flour and rice flour on the elastic modulus, the variation of G' with dough composition is represented in Fig. 7, at three frequency values (0.1, 1 and 10 Hz) obtained from the respective mechanical spectra. It is observed that a higher gel concentration leads to a more structured dough, whereas higher rice gel ratio leads to a less structured dough. This behaviour is consistent with the doughs texture profile (Fig. 8).

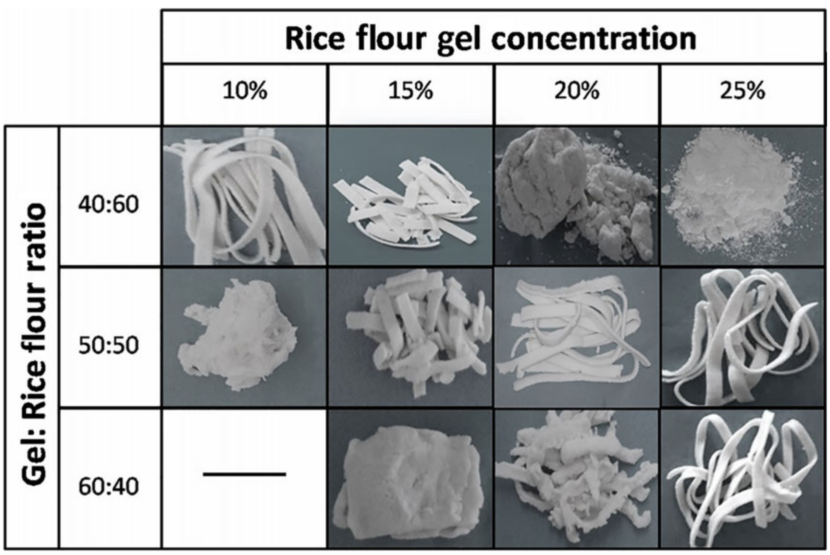

Figure 5 Dough formulations produced with 10–25% rice flour and different gel:rice flour ratios (40:60, 50:50 and 60:40).

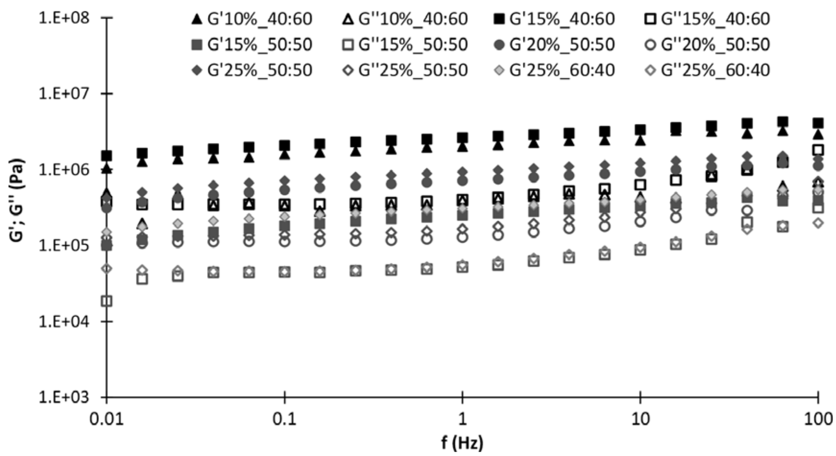

Figure 6 Mechanical spectra of dough formulations: 10%_40:60, 15%_40:60, 15%_50:50, 20%_50:50, 25%_50:50, 25%_60:40 (% rice flour gel_rice gel:rice flour ratio).

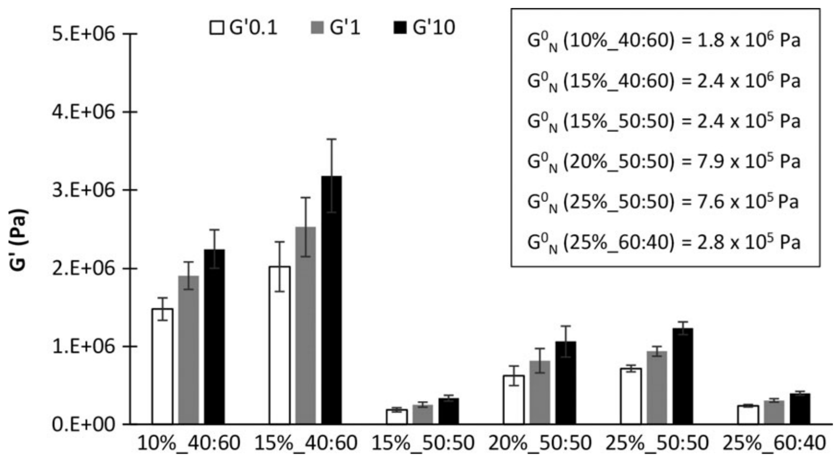

Figure 7 *G′* at 0.1 (□), 1 (▫) and 10 Hz (■) of dough with 10–25% rice flour gel concentration and different gel:rice flour ratios (40:60, 50:50 and 60:40).

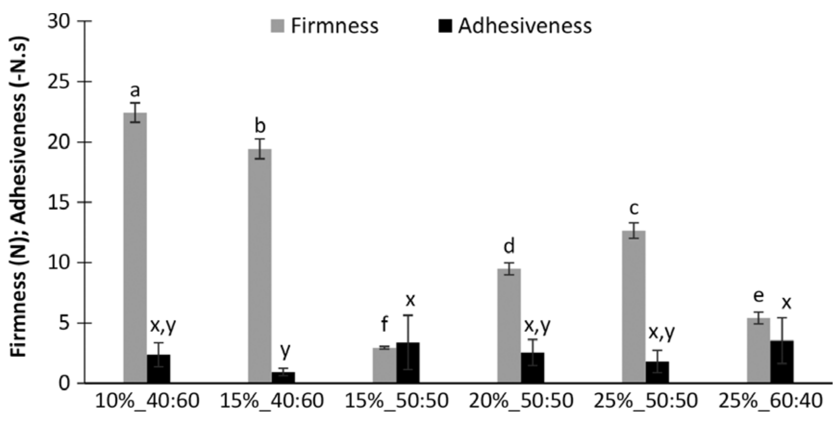

Figure 8 Texture parameters of dough formulations. Different letters indicate significant differences ($P < 0.05$, one-way ANOVA *post-hoc* Tukey test) for the same parameter.

In the texture tests all dough formulations showed statistically different firmness values. It is noteworthy that firmness is more dependent on the rice gel:flour ratio (40:60, 50:50, 60:40) than on rice flour concentration (10–25%). Considering the same rice gel:flour ratio (e.g. 50:50), a significant increase in firmness is observed for different rice gel concentrations (e.g. 15%, 20%, 25%). It is also observed that increasing gel:flour ratio, for the same gel concentration (25%_50:50 and 25%_60:40), a significantly decrease in firmness is observed.

Cooked pasta quality

The cooking behaviour, which is a critical step for quality perception of pasta, includes the evaluation parameters presented in Table 2.

Cooking loss is commonly used to predict the pasta cooking quality and is an indicator of the capability of the starch-protein matrix to retain its physical integrity during cooking. Traditionally, the loss of solids represents a measure of pasta quality, expressing its resistance to disintegration upon boiling: low amounts of solids into the cooking water indicate a high pasta cooking quality (Pagani *et al.*, 2007). According to Schmiele *et al.* (2013) good quality wheat pasta should present a maximum cooking loss of 6%. However, unlike durum wheat pasta, due to the lack of gluten, the characteristics of GF pasta depend heavily upon the functional properties of the starch, since in the present study functions as almost the only structural network of the final GF product, since protein play a minor role due to its low content (6%) in the flour used.

Water absorption is related with the pasta yield after cooking (Zhu *et al.*, 2010), and the swelling index is an indicator of the water uptake by starch and proteins during cooking, as a measure for gelatinisation and protein hydration (Padalino *et al.*, 2013).

Comparing uncooked and cooked pasta, there is no correlation ($P < 0.05$) in firmness neither in adhesiveness values (Fig. 9). This can be explained considering that the uncooked dough is a partially gelatinised product, so the thermal modifications suffered by the starch during cooking are not so pronounced comparing to what happens in wheat pasta.

Using optimisation criteria for each parameter: cooking loss, stickiness and adhesiveness were minimised, while swelling, water absorption and firmness were maximised, the pasta with the best characteristics was the 20%_50:50.

Generally, the ideal starch for GF pasta products should have a marked tendency to retrograde, property generally observed in high amylose cereals and pulses, this assures good cooking behaviour in terms of texture and low cooking loss, even after prolonged cooking (Marti & Pagani, 2013). However, the commercial flour used in this study, with low amylose content, showed to be suitable for the production of a good quality GF pasta, with low stickiness and cooking losses.

Table 2 Cooking quality parameters of pasta formulations prepared with gelatinised rice flour

Pasta formulation	Swelling power (mL g^{-1})	Water absorption (%)	Cooking loss (%)
10%_40:60	0.79 ± 0.09^{b}	$47.76 \pm 5.43^{y,z}$	1.57 ± 0.38^{n}
15%_40:60	0.96 ± 0.05^{a}	55.74 ± 2.30^{x}	5.50 ± 0.47^{m}
15%_50:50	0.50 ± 0.05^{d}	26.92 ± 2.99^{w}	1.48 ± 0.30^{n}
20%_50:50	$0.73 \pm 0.01^{b,c}$	41.24 ± 0.32^{z}	1.05 ± 0.12^{n}
25%_50:50	$0.85 \pm 0.03^{a,b}$	$49.09 \pm 1.18^{x,y}$	1.60 ± 0.40^{n}
25%_60:40	0.64 ± 0.03^{c}	33.72 ± 1.82^{w}	1.40 ± 0.37^{n}

Samples marked with different letters, showed significant differences ($P < 0.05$, one-way ANOVA *post hoc* Tukey test) for each parameter.

Conclusions

The use of flour from broken rice kernels constitutes a valuable raw material with good gelling abilities for food applications. Based upon physicochemical and hydration properties, texture and rheology measurements of the respective gels, both Guiana and Ariete rice varieties presented suitable characteristics for food applications.

Using the present results for a specific food application like production of fresh gluten-free pasta, the maximum rice concentration for pasta making should be around 17.5%, although incorporation of other ingredients could interfere with this value. This critical concentration seems to be independent of the amylose content of rice (16.4% Ariete and 22.4% Guiana).

Based on cooking quality and texture parameters of all pasta formulations, the optimal formulation is the one with 20% rice gel and a 50:50 gel:flour ratio.

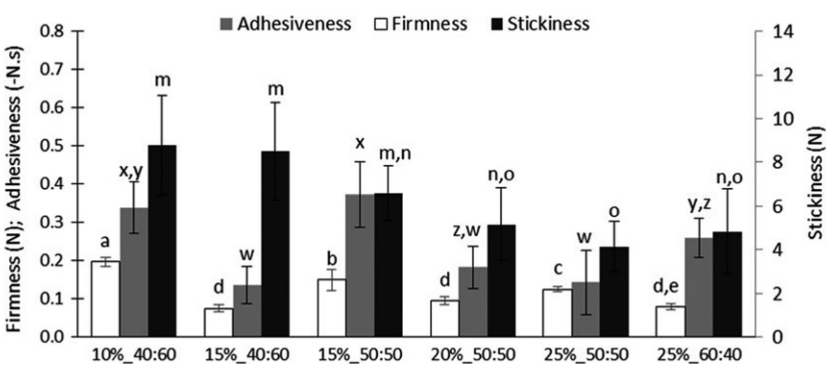

Figure 9 Texture parameters of cooked pasta formulations prepared with gelatinised rice flour. Different letters indicate significant differences ($P < 0.05$, one-way ANOVA *post-hoc* Tukey test) for the same parameter.

Since this product is designed for celiac consumers with a different sense of taste than of non-celiac, a sensory analysis should be performed with a consumer panel of celiac people.

Acknowledgments

This work was supported by COMPETE program: QREN – 'Arroz +' Project n.38749 and by national funds from Fundação para a Ciência e a Tecnologia (Portugal) through the research unit UID/AGR/04129/2013 (LEAF). Patrícia Fradinho acknowledges her PhD grant from Universidade de Lisboa (Ref. C0144M). The authors express their gratitude to Rita Soares for her contribution to this work.

References

AACC International (1999a). *Approved Methods of Analysis*. 11th edn. Method 44-15.02 – Moisture: Air-Oven Methods. Reapproval November 3, 1999. St. Paul, MN: AACC International.

AACC International (1999b). *Approved Methods of Analysis*. 11th edn. Method 66-50.01 – Pasta and Noodle Cooking Quality. St. Paul, MN: AACC International.

Ahmed, J., Al-Jassar, S. & Thomas, L. (2015). A comparison in rheological, thermal, and structural properties between Indian Basmati and Egyptian Giza rice flour dispersions as influenced by particle size. *Food Hydrocolloids*, **48**, 72–83.

Anderson, R.A. (1982). Water absorption and solubility and amylograph characteristics of roll-cooked small grain products. *Cereal Chemistry*, **59**, 265–269.

Bourne, M. (2002). *Food Texture and Viscosity*. 2nd edn. London: Academic Press.

Crockett, R., Ie, P. & Vodovotz, Y. (2011). How do xanthan and hydroxypropyl methylcellulose individually affect the physicochemical properties in a model gluten-free dough? *Journal of Food Science*, **76**, E274–E282.

European Commission (2015). Closing the loop – an EU action plan for the circular economy. Brussels, COM(2015)614.

Fabian, C., Ayucitra, A., Ismadji, S. & Ju, Y.-H. (2011). Isolation and characterization of starch from defatted rice bran. *Journal of the Taiwan Institute of Chemical Engineers*, **42**, 86–91.

FAO (2003). *Food Energy – Methods of Analysis and Conversion Factors*. Pp. 93. FAO, Food and Nutrition Paper 77. Rome: Food and Agriculture Organization of the United Nations.

Ferry, J.D. (1980). *Viscoelastic Properties of Polymers*. 3rd edn. New York: John Wiley & Sons Inc.

INE (2016). Instituto Nacional de Estatística (Statistics Portugal). Available online at: https://www.ine.pt/xportal/xmain?xpgid=ine_main&xpid=INE

ISO20483 (2006). Cereals and pulses – determination of the nitrogen content and calculation of the crude protein content – Kjeldahl method. International Organization for Standardization.

Jang, E.-H., Su-Jin Lee, S.-J., Hong, J.-Y. *et al.* (2016). Correlation between physicochemical properties of japonica and indica rice starches. *LWT – Food Science and Technology*, **66**, 530–537.

Juliano, B.O. (1998). Varietal impact on rice quality. *Cereal Foods World*, **43**, 207–222.

Kaushal, P., Kumar, V. & Sharma, H.K. (2012). Comparative study of physicochemical, functional, antinutritional and pasting properties of taro (*Colocasia esculenta*), rice (*Oryza sativa*) flour, pigeonpea (*Cajanus cajan*) flour and their blends. *LWT – Food Science and Technology*, **48**, 59–68.

Kong, X., Zhu, P., Sui, Z. & Bao, J. (2015). Physicochemical properties of starches from diverse rice cultivars varying in apparent amylose content and gelatinisation temperature combinations. *Food Chemistry*, **172**, 433–440.

Lai, H.M. (2001). Effects of rice properties and emulsifiers on the quality of rice pasta. *Journal of the Science of Food and Agriculture*, **82**, 203–216.

Lazaridou, A., Duta, D., Papageorgiou, M., Belc, N. & Biliaderis, C.G. (2007). Effects of hydrocolloids on dough rheology and bread quality parameters in gluten-free formulations. *Journal of Food Engineering*, **79**, 1033–1047.

Leach, H.W., McCowen, I.D. & Schoch, T.J. (1959). Structure of the starch granule. I. Swelling and solubility patterns of various starches. *Cereal Chemistry*, **36**, 534–544.

Lu, S., Chen, J.-J., Chen, Y.-K., Lii, C.-Y., Lai, P. & Chen, H.-H. (2011). Water mobility, rheological and textural properties of rice starch gel. *Journal of Cereal Science*, **53**, 31–36.

Mariotti, M., Sinelli, N., Catenacci, F., Pagani, M.A. & Lucisano, M. (2009). Retrogradation behaviour of milled and brown rice pastes during ageing. *Journal of Cereal Science*, **49**, 171–177.

Marti, A. & Pagani, M.A. (2013). What can play the role of gluten in gluten free pasta? *Trends in Food Science and Technology*, **31**, 63–71.

Marti, A., Pagani, M.A. & Seethraraman, K. (2011). Understanding starch organisation in gluten-free pasta from rice flour. *Carbohydrate Polymers*, **84**, 1069–1074.

NP 4168 (1991). *Cereais e derivados – Determinação do teor de matéria gorda total*. Lisboa: Instituto Português da Qualidade.

NP 518 (1986). *Cereais e Leguminosas – Determinação do teor de cinza. Processo por incineração a 550 °C*. Lisboa: Instituto Português da Qualidade.

Padalino, L., Mastromatteo, M., De Vita, P., Ficco, D.B.M. & Del Nobile, M.A. (2013). Effects of hydrocolloids on chemical properties and cooking quality of gluten-free spaghetti. *International Journal of Food Science and Technology*, **48**, 972–983.

Pagani, M.A., Lucisano, M. & Mariotti, M. (2007). Traditional Italian products from wheat and other starchy flours. In: *Handbook of Food Products Manufacturing* (edited by Y.H. Hui). Pp. 327–388 Hoboken, NJ: John Wiley & Sons Inc.

Paiva, A.P., Barcelos, M.F.P., Pereira, J.A.R., Ferreira, E.B. & Ciabotti, S. (2012). Characterization of Food bars manufactured with agroindustrial by-products and waste. *Ciência e Agrotecnologia*, **36**, 333–340.

Peries, C.M., Wijesekara, K.B. & Navarathne, S.B. (2016). Effect of freezing and hot water soaking on the functional properties of rice flour derived from four Sri Lankan traditional rice varieties. *Procedia Food Science*, **6**, 68–72.

Pojić, M., Hadnađev, M. & Hadnađev, T. (2013). Gelatinization properties of wheat flour as determined by empirical and fundamental rheometric method. *European Food Research and Technology*, **237**, 299–307.

Puncha-arnon, S. & Uttapap, D. (2013). Rice starch vs. rice flour: differences in their properties when modified by heat–moisture treatment. *Carbohydrate Polymers*, **91**, 85–91.

Santos, T., Lemos, D., Brites, C., Guiné, R.P.F. & Correia, P.R. (2013). Contribuição para a caracterização de cultivares de arroz. Proceeding from the VII Congresso Ibérico de Agroingeniería y Ciencias Hortícolas, Ref. N°C0048: Madrid, Spain.

Schmiele, M., Jaekel, L.Z., Ishida, P.M.G., Chang, Y.K. & Steel, C.J. (2013). Massa alimentícia sem glúten com elevado teor proteico obtida por processo convencional. *Ciência Rural*, **43**, 908–914.

Singh, V., Okadome, H., Toyoshima, H., Isobe, S. & Ohtsubo, K. (2000). Thermal and physicochemical properties of rice grain, flour and starch. *Journal of Agriculture and Food Chemistry*, **48**, 2639–2647.

Singh, N., Kaur, L., Sandhu, K.S., Kaur, J. & Nishinari, K. (2006). Relationships between physicochemical, morphological, thermal, rheological properties of rice starches. *Food Hydrocolloids*, **20**, 532–542.

Singh, N., Nakaura, Y., Inouchi, N. & Nishinari, K. (2007). Fine structure, thermal and viscoelastic properties of starches separated from Indica rice cultivars. *Starch/Stärke*, **59**, 10–20.

Smewing, J. (2009). Pasta-the invariable variables. *Food Science and Technology Today*, 1–4.

Sodhi, N.S. & Singh, N. (2003). Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. *Food Chemistry*, **80**, 99–108.

Sozer, N. (2009). Rheological properties of rice pasta dough supplemented with proteins and gums. *Food Hydrocolloids*, **23**, 849–855.

Spigno, G. & De Faveri, D.M. (2004). Gelatinization kinetics of rice starch studied by non-isothermal calorimetric technique: influence of extraction method, water concentration and heating rate. *Journal of Food Engineering*, **62**, 337–344.

Spinosa, W.A., Júnior, V.S., Galvan, D., Fiorio, J.L. & Gomez, R.J.H.C. (2016). Syrup production via enzymatic conversion of a byproduct (brokenrice) from rice industry. *Acta Scientiarum. Technology Maringá*, **38**, 13–22.

Tavares, B.O., Silva, E.P., Silva, V.S.N., Soares Júnior, M.S., Ida, E.I. & Damiani, C. (2016). Stability of gluten free sweet biscuit elaborated with rice bran, broken rice and okara. *Food Science and Technology*, Campinas, **36**, 296–303.

Tester, R.F. & Morrison, W. (1990). Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose, and lipids. *Cereal Chemistry*, **67**, 551–557.

Torres, M.D., Fradinho, P., Raymundo, A. & Sousa, I. (2014). Thermorheological and textural behaviour of gluten-free gels obtained from chestnut and rice flours. *Food and Bioprocess Technology*, **7**, 1171–1182.

Wang, L. & Seib, P.A. (1996). Australian salt-noodle flours and their starches compared to US wheat flours and their starches. *Cereal Chemistry*, **73**, 167–175.

Yu, S., Ma, Y., Menager, L. & Sun, D.-W. (2012). Physicochemical properties of starch and flour from different rice cultivars. *Food and Bioprocess Technology*, **5**, 626–637.

Zhu, F., Cai, Y.-Z. & Corke, H. (2010). Evaluation of Asian salted noodles in the presence of *Amaranthus* betacyanin pigments. *Food Chemistry*, **118**, 663–669.