Quality Indicators of Rice Based Gluten-free Bread-like Products: Relationships between Dough Rheology and Quality Characteristics

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ABSTRACT

The design of gluten-free bread-like products involves the study of gluten-free dough rheology and the resulting baked product characteristics, but little information has been obtained connecting dough and baked product properties. The aim of this study was to determine quality predictors of gluten-free bread like products at dough level by defining possible correlations between dough rheological properties and both instrumental parameters and sensory characteristics of the those products. Diverse rice based gluten-free doughs were defined and rheologically characterized at dough level and the technological and sensorial quality of the resulting baked products was investigated. Dough Mixolab® parameters, bread-like quality parameters (moisture content, specific volume, water activity, colour, and crumb texture), and chemical composition significantly (P<0.05) discriminated between the samples tested. In general, the highest correlation coefficients (r>0.70) were found when quality instrumental parameters of the baked products were correlated with the dough Mixolab® parameters, and lower correlation coefficients (r<0.70) were found when sensory characteristics were correlated with dough rheology or instrumental parameters. Dough consistency during mixing (C1), amplitude and dough consistency after cooling (C5) would be useful predictors of crumb hardness; and C5 would be also predictor of perceived hardness of gluten-free bread-like products.

Key words: Rice flour; Gluten-free; Wheat free; Dough behaviour; Bread quality

1) INTRODUCTION

Gluten-free breads are products initially designed for people who have intolerance to some specific peptides comprised in the gluten proteins (Catassi & Fasano, 2008). Nevertheless, there is an increasing number of people interested in wheat free foods motivated by health concern or because they want to avoid wheat in the diet. Particularly, gluten from wheat, rye, barley, triticale, and some varieties of oats (Comino et al., 2011) must be eliminated from the diet of individuals suffering from celiac disease.

Cereal products, especially breads, are basic components of the diet in many countries due to their sensory characteristics or/and nutritional quality. However, the manufacture of bread-like products without gluten results in major technological problems for bakers. In fact, many gluten-free products available on the market are often of poor technological quality, exhibiting low volume, poor color, and crumbling crumb, besides great variation in the nutrient composition, with low protein and high fat contents (Matos & Rosell, 2011). A range of bread-like gluten-free products has been designed to provide coeliac disease sufferers or wheat free diet eaters with bread substitutes. The term gluten-free bread is generally used for referring to a gluten-free bakery product that is eaten as bread substitute, but has different characteristics than wheat bread, because of that, the term gluten-free bread-like products was preferred in this manuscript. The gluten-free bread recipes contain mainly rice or maize flours combined with potato, maize or wheat starches (Gujral & Rosell, 2004; Gallagher et al., 2004; Demirkesen et al., 2010; Matos & Rosell, 2011).

Rice flour is one of the most suitable cereal flours for preparing gluten-free products due to its several significant properties such as natural, hypoallergenic, colorless, and bland taste. In addition, it has also hypoallergenic proteins, and low content of sodium and fat and high amount of easily digested carbohydrates (Gujral & Rosell, 2004). The relatively small amount of prolamin in rice, forces to use some sort of gum, emulsifier, enzymes or dairy products, together with rice flour, for obtaining some viscoelastic properties (Demirkesen et al., 2010). Several studies had reported the use of rice flour for making good-quality gluten-free bread-like products (Kadan et al., 2001; McCarthy et al., 2005; Ahlborn et al., 2005; Moore et al., 2006; Lazaridou et al., 2007; Marco & Rosell, 2008 a,b; Pruska-Kędzior et al., 2008; Sciarini et al., 2010; Demirkesen et al., 2010). Those studies were mainly focused on bread instrumental and/or sensory characteristics.

Scarce information has been presented about the rheological characteristics of the gluten-free doughs, which greatly vary in consistency, going from batter to dough. Gluten free dough is referred to a semisolid system that can be manually handled, whereas when very high water content is added in the recipe, the rheological properties of the dough resemble a semiliquid system named batter. Some studies reported information about gluten-free dough behavior using rheometers. Pruska et al. (2008) compared the rheological properties of gluten-free dough formulations (maize flour, maize starch, rice flour) concluding that they can be defined as physical gels of different viscoelasticity and structural networking. Rice flour based dough or even protein enriched rice flour dough behaves as a viscoelastic solid with storage modulus (G′) higher than loss modulus (G″) (Gujral & Rosell 2004; Marco & Rosell, 2008b). The incorporation of resistant starch increases storage (G′) and loss (G″) moduli of gluten-free doughs, increasing their elastic behaviour (Korus et al., 2009). Other researches have studied the rheological properties of different gluten-free doughs by extrusion and penetration tests using a Texture Analyzer (Moore et al., 2006; Sciarini et al., 2010; Onyango et al., 2011) and the average force after reaching a plateau was used as indicator of batter firmness or consistency. Rapid Visco Analyzer (Kim & Yokoyama, 2011) and Viscoamylograph (Sciarini et al., 2010) also gave information about the pasting properties of the batters. Additionally, mixing and pasting behaviour of different rice flour based doughs were studied using the Mixolab® (Marco & Rosell, 2008a).

Nevertheless, the information about dough or batter rheological properties has rarely been exploited when designing or developing gluten-free bread like products, neither it has been used for predicting bread characteristics. The main objective of this study was to define predictors of the quality of gluten-free bread-like products at dough level. With that aim, different gluten-free rice based doughs were defined to cover a range of gluten-free doughs with different rheological features, and in consequence, to obtain gluten-free bread like products with diverse technological and sensorial quality. The Mixolab® was used to obtain a complete characterization of the gluten-free dough behaviour by recording the mechanical changes during mixing and heating simulating the mechanical work as well as the heat conditions that might be expected during the baking process. Different correlations between rheological dough properties and quality parameters of gluten-free bread-like products were established.

2) MATERIALS AND METHODS

Materials

Commercial gluten-free blend (corn starch, whole egg powder, sugar, xanthan gum and salt) was generously donated by Huici-Leidan SA (Huarte, Spain). Commercial rice flour, supplied by Harinera Los Pisones (Zamora, Spain), had moisture and protein contents of 11.5g/100g and 6g/100g, respectively. Soybean protein isolate was from Trades SA (Barcelona, Spain). The soybean protein isolate had moisture, protein, lipid, ash and carbohydrates (calculated by difference) contents of 6.9, 80.8, 0.2, 3.6 and 8.5 g/100g, respectively. Composition of the different ingredients was determined following the ICC Standard Methods (1994). Corn starch, potato starch, skim milk powder and whole egg powder were obtained from EPSA, (Valencia, Spain). HPMC (Methocel K4M) was obtained from Dow Chemical (Pittsburg, USA). Xanthan gum food grade from Jungbunzlauer (Ladenburg, Germany) has an apparent viscosity of 6.0 mPas at 24ºC. Pectin (GENU®pectin 150 USASAG type Baking, PKelco) was provided by Puratos (Groot-Bijgaarden, Belgium). Vegetal seed oil, compressed yeast, commercial sugar and salt were purchased from local market. All reagents were of analytical grade.

Mixolab® Measurements

Mixing and pasting behaviour of the gluten-free flour blends were studied using the Mixolab® (Chopin, Tripette et Renaud, Paris, France), which allows mixing the dough under controlled temperature and also a temperature sweep until 90ºC followed by a cooling step. It measured in real time the torque (expressed in Nm) produced by passage of dough between the two kneading arms, thus allowing the study of its physico-chemical behaviour. All ingredients used on each formulation (Table 1), with the exception of yeast, were introduced into the Mixolab® bowl and mixed. The settings used in the test were 8 min for initial mixing, temperature increase at 2.3 ºC/min until 90 ºC, 7 min holding at 90 ºC, temperature decrease at 4ºC/min until 50ºC, and 5 min holding at 50ºC; and the mixing speed during the entire assay was 80 rpm. Three replicates were carried out for each formulation. The following parameters were obtained from the recorded curve: initial consistency (C1), stability (min) or elapsed time at which the torque produced is kept constant, minimum torque (Nm) or the minimum value of torque produced by dough passage subjected to mechanical and thermal constraint (C2), peak torque (Nm) or the maximum torque during the heating stage (C3), the minimum torque during the heating period (Nm) (C4) and the torque obtained after cooling at 50ºC (C5). Additionally, derived parameters were calculated: cooking stability range (C4-C3) and cooling setback or gelling (C5-C4). Detailed description of physical changes that occurred along Mixolab® measurement (mixing, pasting and gelling) was gathered by Rosell et al. (2007). Recently, detailed information about Mixolab® parameters has been reported by Marco & Rosell (2008a) and Rosell et al. (2010).

Breadmaking Process

Different gluten-free rice formulations were initially selected to cover a range of gluten-free doughs with different rheological features, and in consequence, gluten-free bread like products with diverse technological and sensorial quality. Bread formulations were based on reported recipes (Marco & Rosell, 2008a; McCarthy et al., 2005; Kadan et al., 2001; Moore et al., 2006; Pruska-Kędzior et al., 2008; Ahlborn et al., 2005; Sciarini et al., 2010; Demirkesen et al., 2010), which were modified according to preliminary rheological results. Seven formulations were used to obtain gluten-free bread-like products (BF), one was based on corn starch (commercial blend) and in the other, rice flour was the major ingredient, present individually or blended with potato or corn starch. They contained different ingredients (starches, proteins, other hydrocolloids) widely used in the design of gluten-free bread type products. The formulations used are showed in Table 1, which were based on the following: 1000g of corn starch (F1); 1000g of rice flour (F2, F3); 1000g of blend of rice flour + corn and potato starches (F4, F5, F6); and 1000g of blend of rice flour + potato starch (F7). Gluten-free batters or doughs were prepared in a spiral mixer (AV18/2, Vimar Industries 1900, S.L., Sabadell, Spain) by mixing all or part of the flour and the other ingredients with the water determined in preliminary test (Table 2). Dough pieces (400g) or batters (400g) were placed into regular metallic, lard coated pans and proofed in a cabinet at 85% relative humidity during the time (min) and temperature (ºC) detailed in Table 2. The batter or dough pieces were baked in an electric convection oven (Eurofours, Gommegnies, France) as described in Table 2. After baking, loaves were removed from the pans and kept at room temperature for 2 hours to cool down. Loaves packed in polyethylene bags to prevent drying were stored at 24 ºC for 24 hours and then used for bread quality assessment. Four loaves were obtained from each formulation. Duplicates were carried out in different days.

Quality Assessment of Gluten-free Bread-like Products

Instrumental quality parameters

The moisture content of gluten-free bread-like samples was determined following the ICC (1994). Volume was determined by the rapeseed displacement method. Specific volume (cm^3 /g) of the individual loaf was calculated by dividing volume by weight. Water activity of samples was measured using an Aqua Lab Series 3 (Decagon devices Pullman, USA) at 22ºC. The colour of the crumb samples was measured at three different locations by using a Minolta colorimeter (Chromameter CR-400/410, Konica Minolta, Tokyo, Japan) after standardization with a white calibration plate (L^*= 96.9, a^*= -0.04, b^*=1.84). The colour was recorded using CIE-$L^*a^*b^*$ uniform colour space (CIE-Lab) where L^* indicates lightness, a^* indicates hue on a green (-) to red (+) axis, and b^* indicates hue on a blue (-) to yellow (+) axis. Data from three slices per sample were averaged.
The crumb hardness was measured on uniform slices of 10mm thickness. Three slices from the centre of each loaf were used for texture evaluation. Texture profile analysis (TPA) was performed using a universal testing machine TAXT2i (Stable Micro Systems, Surrey, UK) equipped with a 30-Kg load cell and 25-mm aluminium cylindrical probe. Crumb characteristics were assessed using a texture analyser (TAXT2i texture analyser Stable Micro Systems, Surrey, UK). The settings used were a test speed of 2.0 mm/s with a trigger force of 5 g to compress the middle of the bread crumb to 50% of its original height at a crosshead speed of 1mm/s. Values were the mean of at least three replicates.

Chemical Composition

The chemical composition of the samples was determined according to ICC corresponding standard methods (ICC, 1994), namely, the moisture content (ICC standard 110/1), fat (ICC 136), proteins (N x 6.25) (ICC 105/2) and ash (ICC 104/1). Total carbohydrates were determined by difference subtracting 100 g minus the sum of protein, ash and fat expressed in grams/100 grams FAO (2003). Determinations were carried out in triplicate.

Sensorial Analysis

A descriptive sensory analysis was performed for evaluating the sensory characteristics of the gluten-free bread-like products. Sensory analysis was carried out with ten trained panellists under normal lightening conditions and at room temperature. The range of time that the test panellist had participated in descriptive analysis and scale rating of a wide range of bread products varied from 3 to 20 years. Samples were presented in slices (1cm thick) on plastic dishes coded and served in a randomised order. Preliminary training test was performed to define the best descriptors for characterizing the product. Panellists were sat in a round table and after evaluating the sample, an open discussion was initiated to define the best descriptors for characterizing the product. Evaluation included perception at first glance of the bread slice (crust and crumb included) and mastication with the molar teeth up to swallowing. The attributes assessors finally agree were, appearance (by observing the product slice), odour, colour, taste, texture attributes during chewing and springiness (ability to regain original shape after pressing down the crumb with the middle finger). The descriptors for each attributes were appearance (visually liking or disliking), odour (scale goes from high when typical of bread or bakery products to low, uncharacteristic of bakery products), colour (scales goes from high yellow/beige to low when brown or grey), taste (scale goes from high when typical taste of bread or bakery products to low, uncharacteristic of bakery products), texture attributes during chewing (scales goes from hard-soft, crumbly-cohesive). Attribute intensity was scored on a scale varying from 1 to 5. Samples were considered acceptable if their mean score for overall acceptance was above 3.0 (neither like nor dislike).

Statistical Analysis

For each quality parameter, a one way analysis of variance (ANOVA) was applied using Statgraphics Plus V 7.1 (Statistical Graphics Corporation, UK). Fisher's least significant differences (LSD) test was used to assess significant differences ($P<0.05$) among samples that might allow discrimination among them. Additionally, Pearson correlation analysis was applied to establish possible relationships between the rheological dough properties and both instrumentals and sensorial quality parameters of the gluten-free bread-like products.

3) RESULTS AND DISCUSSION

Mixing and Pasting Properties of Gluten-free Doughs

Figure 1 show the curves obtained from the Mixolab® corresponding to the seven gluten-free dough formulations evaluated. Plots reflected the dough changes due to both the mixing force and the temperature. The patterns obtained during mixing, overmixing, pasting and gelling greatly varied with the mixture composition, which was expected considering the complex blend of ingredients (Table 1). The presence of different proteins and starches modifies protein-protein interactions and also the starch gelatinization and the gelling processes (Rosell et al., 2007; Marco & Rosell, 2008a; Rosell et al., 2010). All Mixolab® parameters significantly ($P<0.05$) discriminated among the formulated dough tested (Table 3). During the mixing and overmixing, significant variation was observed in the dough maximum consistency, time to reach that consistency and the stability (Table 3). Some formulations yielded mixtures with dough consistencies (with C1 higher than 0.5 Nm), whereas F3, F4, F5 and F7 led to mixtures with batter consistencies (C1 lower than 0.3 Nm) that were difficult to handle. F6 showed the highest C1 value and the lower time to C1 value, indicating that this dough reached major consistency in minor time, likely due to its major amount of proteins (egg, milk). Regarding stability, F7 showed the highest value followed by F1, while F5 presented the lower dough stability value. The amplitude, indicative of the role of water in the lubrication during mixing (Rosell & Collar, 2009) showed also significant differences, and thus different extensional properties of the evaluated doughs. The simultaneous mechanical shear stress and temperature led to a minimum torque that has been related to protein unfolding or protein weakening (Rosell et al., 2007). The values for C2 were quite low compared with the ones detected for wheat dough (0.4-0.5 Nm). That result might be ascribed to the protein thermal properties rather than to the amount of proteins, since some gluten-free doughs had very high protein content (F4 and F6). As temperature increases, starch gelatinization occurs and therefore viscosity increases, which is detected as an increase in torque (Rosell et al., 2007). As was expected F1 showed the highest C3 value, likely due to its highest starch content, specifically corn starch (Table 1). In the case of F2 and F3 (only with rice flour as starch source), a delayed peak corresponding to starch gelatinization was observed, derived from the high gelatinization temperature of the rice starch. It should be remarked that two gelatinization peaks were observed in F4, F5 and F6. Those peaks resulted from the presence of different starches (rice, corn and potato) with diverse pasting temperatures, being 65.4ºC for potato starch, 69.9ºC for corn starch and 70.2ºC for rice flour. Furthermore, it must be taken into account that hydrocolloids like xanthan gum, HPMC or pectin, contained in the doughs can retain water, competing with the starch for the available water, limiting the starch granule swelling and, therefore promoting a delay in the pasting process (Rosell et al., 2011).

During temperature holding at 90ºC, a reduction in consistency occurred, which is related to the physical breakdown of the starch granules. F1 showed the highest value, likely due to the high content of corn starch in this dough.

After cooling, F1 presented the highest C5 value followed by F6 and F5. The cooling process was accompanied by an enhancement of dough consistency associated to starch gelling, due to amylose chains crystallization, which is greatly dependent on the starch type and the presence of gelling additives or ingredients with water binding ability (Rosell et al., 2007; Rosell et al., 2010). Regarding the secondary parameters, all doughs showed very low cooking stability range (C4-C3); whereas the cooling setback (C4-C5) was only significantly higher for F1 and F6 (Table 3). High setback value suggests that dough presents high retrogradation tendency and, consequently the baked product prepared from this dough would undergo high staling rate over storage.

Some studies have been published about the effect of gelling agents and proteins on the mechanical properties of wheat dough due to dual mixing and temperature constraint using the Mixolab® (Collar et al., 2007; Marco & Rosell, 2008a, Rosell & Collar, 2009; Rosell et al., 2010). Those studies concluded that the effect of gelling or thickening agents on the mechanical properties greatly depends on the nature of the added polymer and the type of interaction among them. Moreover, the addition of proteins to wheat or rice flour also led to changes on the mechanical and baking properties, depending on the protein source (Bonet et al., 2006; Marco & Rosell, 2008a).

Bread Quality Assessment

Gluten-free bread-like products (BF1-BF7) obtained from the formulated doughs (F1-F7) presented important crumb differences regarding colour, appearance, shape, size and volume. The values obtained for specific volume, crumb colour, moisture content, water activity, height/width ratio and hardness are showed in Table 4. All instrumental quality parameters tested significantly (P<0.05) discriminated among samples. Specific volume values ranged from 1.44 to 3.03 cm^3/g, except for BF2 (4.48 cm^3/g) and BF7 (5.07 cm^3/g), which showed the highest values of specific volume. In general, values of specific volume obtained in this study agree with previous reports (Hathorn et al., 2008, Marco & Rosell, 2008a; Sabanis et al., 2009, Sciarini et al., 2010).
The $L*$, $a*$ and $b*$ values for crumb colour showed significant (P<0.05) differences among gluten-free bread-like products (Table 4). The lower values of $L*$ (lightness) were obtained for BF4 and BF6, which had in common the presence of xanthan gum, and proteins blend (soybean protein in BF4 or skim milk powder and whole egg powder in BF6). Likely, soybean proteins and egg powder could be responsible of decreasing lightness, since BF7, containing only skim milk powder as protein source showed the highest $L*$ value. Regarding $a*$, all showed negative (green hue) values, with exception of BF6. The $b*$ scale showed positive value (yellow hue) for all samples evaluated. BF6 exhibited significantly higher $b*$ value than the other samples, derived from the original yellow pigment of the egg powder added as ingredient in this formulation.
Significant differences (P<0.05) in crumb moisture and water activity were found among the different gluten-free bread-like samples (Table 4). Differences in water activity and moisture content could be attributed to differences in the recipes. In fact, BF6 showed the lowest water activity and moisture content, which can be ascribed to the presence of whole egg powder in the formulation. The highest moisture content was observed in BF4 that contained soy protein, which agrees with results of Marco & Rosell (2008a) when incorporating soybean proteins to gluten-free breads. Overall, the crumb moisture contents were lower than those reported by other researchers (Sabanis et al., 2009; Marco & Rosell 2008a; Matos & Rosell, 2011).
Wide variation in the crumb hardness (1.3 N to 147.5 N) was observed among the gluten-free bread-like samples (Table 4). These results reflect large differences depending on type of formulation used for obtaining the experimental gluten-free baked products. Frequently, gluten-free bread-like products due to their complex formulation,

mainly based in carbohydrates (Matos & Rosell, 2011), present high crumb hardness when compared to standard wheat bread.

Table 5 shows the macronutrients compositions of the seven gluten-free bread specialities evaluated in this study. Analysis of data collected using ANOVA showed that all chemical composition significantly (*P*<0.05) discriminated between the baked samples. Protein and fat content ranged between 3.30-14.97 g/100g, and 0.20-9.57 g/100g, respectively. In regard to protein content, it was high in the gluten-free bread-like samples BF4 and BF6 which contained more proteins, while BF6 and BF7 were the specialties with higher fat content. Total carbohydrate was the major component in gluten-free bread-like products based on flours and/or starches. These results agree with those recently reported by Matos & Rosell (2011) who evaluated in detail the chemical composition of many types of gluten-free bread like products.

Sensory analysis of the different types of gluten-free bread-like samples is presented in Table 6. According to ANOVA results, these bread-like products differed significantly (*P*<0.05) in crumb appearance, taste, colour, springiness, hardness and crumbliness. Conversely, no significant differences were observed in odour. The highest score for crumb appearance, colour and perceived hardness was obtained for BF3 and BF5. Additionally, the best taste was perceived in BF3, and BF5 received the highest score for springiness, indicating major elasticity. In general, BF3, which did not contain any additional protein source, was scored high for most of the sensorial attributes evaluated, including hardness and crumblines. On the contrary, BF6 was scored low for most of the sensory attributes evaluated. It seems that the addition of whole egg powder as unique source of proteins affected negatively the sensory perception of this product. The results obtained from sensory test clearly revealed great variability on sensory quality of the gluten-free bread-like products tested.

Relationships among the Rheological Properties of Formulated Doughs and the Instrumental and Sensory Characteristics of the Gluten-free Bread-like Products

Relationship among the rheological properties of formulated doughs recorded from Mixolab®, and the product instrumental and sensory characteristics were analyzed. Table 7 illustrates the broad range of correlations found between parameters obtained during the heating and cooling cycles with the Mixolab® and the instrumental quality parameters (specific volume, water activity, moisture content and TPA-hardness) of the bread-like baked products. Water activity and moisture content were highly significant and negatively correlated with C1, amplitude and gelling (C5-C4) parameters. Specific volume showed high and negative correlation with cooking stability range (C4-C3) and C5 parameters, which are associated to the cooling stage of the Mixolab®. Presumably, high dough or batter consistencies limit the expansion during proofing, reducing the specific volume. Nevertheless, a positive correlation between apparent viscosity and loaf volume ($r = 0.83$, $P<0.05$) and also between porosity and loaf volume values ($r = 0.81$, $P <0.05$) in gluten-free breads has been reported by Sabanis et al., (2009). There were good correlations between TPA-hardness values and Mixolab® parameters. The relationships between the TPA-hardness and C1, amplitude, C5 and gelling (C5-C4) parameters were found to be particularly highly significant ($P <0.001$) and positive. This could indicate that the TPA-hardness values are strongly correlated ($r >0.70$) with parameters characterising both protein and starch cooling behaviours. It is important to remark that wheat dough viscosity characteristics determined with the Rapid Viscoanalyzer (RVA) have been also correlated with wheat bread texture parameters (Collar 2003). The pasting profile during cooking and cooling of wheat dough has been highly correlated with bread staling kinetic parameters. Particularly, peak viscosity, pasting temperature, and setback during cooling can be considered predictors at dough level of bread firming behaviour during storage of wheat bread. Regarding gluten-free doughs, pasting behaviour of corn flour has been significantly correlated with dough textural parameters. Specifically, springiness and stickiness parameters were positively associated to gelatinisation and retrogradation phenomena (Brites et al., 2010).

Table 8 showed correlation coefficients and significance levels found among Mixolab® parameters, instrumental quality parameters and sensory characteristics obtained from formulated dough and the prepared gluten-free bread like products. Particularly, all sensory characteristics evaluated (appearance, colour, springiness, hardness and crumblines) showed significant negative correlations with b^* (hue on a yellow axis), although correlation coefficients only indicated strong linear relationship between b^* and perceived colour and perceived hardness. It seems that crumb structure has strong influence on the b^* parameter. Additionally, hardness perceived revealed high ($P <0.001$) and positive correlation with specific volume ($r = 0.7149$) and high negative correlations with b^* ($r = -0.7945$), TPA-hardness ($r = -0.7646$) and C5 ($r = -0.7005$) Mixolab® parameter.

Hardness is a very important sensory characteristic when assessing bread quality. In this study, as it was mentioned, perceived hardness showed negative correlation with b^* and TPA-hardness. Apparently, the colour perception is closely related to crumb structure since breads presenting hue yellowness and packed crumb structure could be rated lowly. It has been reported that smaller loaves were denser and had tightly packed crumb structure, resulting in higher crumb firmness (Sabanis et al., 2009); this drives to think that bread with compact crumb could be perceived as hard. Sabanis et al. (2009) reported a negative correlation between crumb firmness and loaf volume (r = -0.89, P >0.05).

In general, many relationships were found (Table 8), however the correlation coefficients were higher between dough properties and instrumental bread parameters (r >0.70) than among instrumental parameters and sensory characteristics (r <0.70).

4) CONCLUSIONS

The patterns obtained during mixing, overmixing, pasting and gelling greatly varied depending on the gluten-free dough or batter composition. All Mixolab® parameters significantly (P<0.05) discriminated among the doughs evaluated. Additionally, differences found in the rheological dough properties from Mixolab® were mainly associated with the presence/ absence of protein and starch sources in the dough. Instrumental quality parameters evaluated in the gluten-free bread-like products significantly (P <0.05) discriminated among the samples.

Several relationships were found among the rheological properties of formulated gluten-free dough/batter, the instrumental quality parameters and sensory characteristics of the bread-like products. In general, the highest correlation coefficients (r >0.70) were obtained between the Mixolab® rheological properties at dough level and the instrumental quality parameters of the fresh baked products. Conversely, lower correlation coefficients (r <0.70) were found when correlations were established with sensory characteristics. Particularly, dough/batter consistency during mixing (C1), amplitude and dough consistency after cooling (C5) would be useful predictors of TPA crumb hardness of baked product; and C5 would be also predictor of perceived hardness of gluten-free bread-like products.

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REFERENCES

Ahlborn GJ, Pike OA, Hendrix SB, Hess WM & Huber CS (2005) Sensory, mechanical, and microscopic evaluation of staling in low-protein and gluten-free breads. Cereal Chemistry, 82, 328-335.

Bonet A, Blaszczak W & Rosell CM (2006) Formation of homopolymers and heteropolymers between wheat flour and several protein sources by transglutaminase-catalyzed cross-linking. Cereal Chemistry, 83, 655-662.

Brites C, Trigo MJ, Santos C, Collar C & Rosell CM (2010). Maize-based gluten-free bread: Influence of processing parameters on sensory and instrumental quality. Food Bioprocess Technology, 3, 707-715.

Catassi C, & Fasano A (2008) Celiac disease. In: Arent EA, Dal Bello F (eds) Gluten-Free Cereal Products and Beverages, pp 1-27. Elsevier, London/San Diego.

Collar C (2003) Significance of viscosity profile of pasted and gelled formulated wheat doughs on bread staling. European Food Research Technology, 216, 505-513.

Collar C, Bollain C & Rosell CM (2007) Rheological behaviour of formulated bread doughs during mixing and heating. Food Science and Technology International, 13, 99-107. DOI: 10.1177/1082013207078341.

Comino I, Real A, de Lorenzo L, Cornell H, López-Casado MA, Barro F, Lorite P, Torres MI, Cebolla A, & Sousa C (2011) Diversity in oat potential immunogenicity: basis for the selection of oat varieties with no toxicity in coeliac disease. Gut, 60, 915-922. DOI:10.1136/gut.2010.225268.

Demirkesen I, Mert B, Sumnu G & Sahin S (2010) Rheological properties of gluten-free bread formulations. Journal of Food Engineering, 96, 295-303.

FAO. Food and Nutrition Paper 77 (2003) Food energy-methods of analysis and conversion factors. FAO. Rome: Food and Agriculture Organization of the United Nation. ISSN 0254-4725.

Gallagher E, Gormley TR & Arendt EK (2004) Recent advances in the formulation of gluten-free cereal-based products. Trends in Food Science and Technology, 15, 143-152.

Gujral HS & Rosell CM (2004) Improvement of the breadmaking quality of rice flour by glucose oxidase. Food Research International, 37, 75-81.

Hathorn CS, Biswas MA, Gichuhi PN & Bowell-Benjamin AC (2008) Comparison of chemical, physical, micro-structural, and microbial properties of breads supplemented with sweet potato flour and high-gluten dough enhancers. LWT-Food Science and Technology, 41, 803-815.

ICC. International Association for Cereal Chemistry (ICC) (1994) Standard No 110/1, 105/2, 104/1, 136.

Kadan RS, Robinson MG, Thibodeaux DP & Pepperman AB (2001) Texture and other physicochemical properties of whole rice bread. Journal of Food Science, 66, 940-944.

Kim Y & Yokoyama W (2011) Physical and sensory properties of all-barley and all-oat breads with additional hydroxypropyl methylcellulose (HPMC) and β-glucan. Journal of Agricultural and Food Chemistry, 59, 741-746.

Korus J, Witczak M, Ziobro R & Juszczak L (2009) The impact of resistant starch on characteristics of gluten-free dough and bread. Food Hydrocolloids, 23, 988–995.

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

Marco C & Rosell CM (2008a) Breadmaking performance of protein enriched, gluten-free breads. European Food Research and Technology, 227, 1205-1213.

Marco C & Rosell, CM (2008b) Functional and rheological properties of protein enriched gluten-free composite flours. Journal of Food Engineering, 88, 94-103.

Matos ME & Rosell CM (2011) Chemical composition and starch digestibility of different gluten-free breads. Plant Food for Human Nutrition, 66, 224-230. DOI: 10.1007/s11130-011-0244-2.

McCarthy DF, Gallagher E, Gormley TR, Schober TJ & Arendt EK (2005) Application of response surface methodology in the development of gluten-free bread. Cereal Chemistry, 82, 609-615.

Moore MM, Heinbockel M, Dockery P, Ulmer HM & Arendt EK (2006) Network formation in gluten-free bread with application of transglutaminase. Cereal Chemistry, 83, 1, 28-36.

Pruska-Kędzior A, Kędzior Z, Gorący M, Pietrowska K, Przybylska A & Spychalska K (2008) Comparison of rheological, fermentative and baking properties of gluten-free dough formulations. European Food Research Technology, 227, 1523-1536.

Rosell CM, Collar C & Haros M (2007) Assessment of hydrocolloid effects on the thermo-mechanical properties of wheat using the Mixolab®. Food Hydrocolloids, 21, 452-462.

Rosell CM & Collar C (2009) Effect of temperature and consistency on wheat dough performance. International Journal of Food Science & Technology, 44, 493-502.

Rosell CM, Santos E & Collar C (2010) Physical characterization of fiber-enriched bread doughs by dual mixing and temperature constraint using the Mixolab®. European Food Research Technology, 231, 535-544

Rosell CM, Yokoyama W & Shoemaker C (2011) Rheology of different hydrocolloids-rice starch blends. Effect of successive heating-cooling cycles. Carbohydrate Polymers, 84, 373-382. DOI:10.1016/j.carbpol.2010.11.047.

Sabanis D, Lebesi D & Tzia C (2009) Effect of dietary fibre enrichment on selected properties of gluten-free bread. LWT-Food Science and Technology, 42, 1380–1389.

Sciarini LS, Ribotta PD, León AE & Pérez GT (2010) Influence of gluten-free flours and their mixtures on batter properties and bread quality. Food Bioprocess Technology, 3, 577–585. DOI: 10.1007/s11947-008-0098-2.

Figure Captions

Figure 1. Plots obtained with different gluten-free doughs/batters when recording the rheological behaviour by using Mixolab® device.

Table 1 Gluten-free dough formulations

Ingredients	F1	F2	F3	F4	F5	F6	F7
Commercial GF blend, g	1000	-	-	-	-	-	-
Rice flour, g	-	1000	1000	350	400	696	500
Corn starch	+	-	-	225	200	130	-
Potato starch	-	-	-	300	400	174	500
Fresh yeast, g	50	30	28	20	50	22	50
Salt, g	-	18	24	17	15	17	20
Sugar, g	10	30	120	10	60	78	50
Vegetal oil, g	-	60	56	-	30	52	60
Skim milk powder, g	-	-	-	-	-	39	100
Whole egg powder, g	+	-	-	-	-	174	-
Soy protein, g	-	-	-	125	-	-	-
Xanthan gum, g	+	-	-	10	-	16	-
HPMC, g	-	40	28	-	-	4	22
Pectin, g	-	-	-	-	50	-	-
Water (mL)	600	1100	1060	1050	900	565	790

+ Ingredient present in the commercial blend

Table 2 Breadmaking process conditions for each gluten-free dough formulations

Breakmaking		F1	F2	F3	F4	F5	F6	F7
Mixing	Procedure	Mix all ingredients	a) Mix 500g rice flour with 550ml boiling water for 5min, cool down till 35ºC. b) Add the rest of ingredients	a) Mix water, rice flour and oil b) Mix other dry ingredients c) Mix (a+b)	a)Mix yeast in a solution of sugar and water b)Add the rest of ingredients	Mix all ingredients	a)Mix yeast in a solution of sugar and water b) Add slowly xanthan gum and HPMC during 3min mixing c) Add rest of ingredients	a)Mix yeast with water and then oil b) Mix dry ingredients for 1 min c) Mix a+b
	Time (min)	5	5	10	10	3	5 (then hold 10 min), 3	2
Fermentation	Time (min)	45	60	40	30	40	50	35
	Temperature (ºC)	30	30	35	30	35	30	40
Baking	Time (min)	25	60	45	45	30	50	25
	Temperature (ºC)	210	175	190	190	200	190	230

Table 3 Rice-based dough characteristics during mixing and heating determined by using the Mixolab®

Dough Codes	Time to C1, min	C1, Nm	Stability, min	Amplitude, Nm	C2, Nm	C3, Nm	C4, Nm	C5, Nm	Cooking stability range,C4-C3, Nm	Gelling, C4-C3, Nm
F1	1.37±0.05 bc	0.88±0.10 d	2.49±0.30 e	0.07±0.01 b	0.33±0.01 b	3.07±0.03 e	2.99±0.04 d	3.64±0.6 e	-0.08±0.00 d	0.65±0.05 d
F2	1.79±0.03 c	0.56±015 c	0.51±0.08 b	0.07±0.00 b	0.22±0.01 b	0.87±0.01 b	0.65±0.06 ab	0.84±0.08 a	-0.22±0.00 b	0.19±0.02 a
F3	1.01±0.10 ab	0.14±0.20 ab	1.29±0.15 d	0.01±0.00 a	0.01±0.00 a	0.69±0.05 a	0.56±0.07 a	0.74±0.07 a	-0.13±0.00 c	0.18±0.02 a
F4	1.70±0.11 c	0.05±0.18 a	1.00±0.21 c	0.01±0.00 a	0.02±0.01 a	0.77±0.03 ab	0.70±0.04 b	1.00±0.05 b	-0.08±0.00 d	0.30±0.05 b
F5	0.75±0.19 a	0.14±0.15 ab	0.09±0.13 a	0.04±0.02 ab	0.01±0.00 a	1.05±0.07 c	1.03±0.05 c	1.45±0.04 c	-0.02±0.00 e	0.42±0.05 c
F6	0.67±0.21 a	1.77±0.13 e	0.48±0.03 b	0.29±0.01 c	0.23±0.01 b	1.30±0.06 d	1.07±0.03 c	2.61±0.07 d	-0.23±0.01 b	1.54±0.06 e
F7	1.03±0.15 ab	0.26±0.09 b	5.46±0.27 f	0.02±0.01 a	0.00±0.00 a	1.15±0.05 c	0.57±0.03 a	1.00±0.06 b	-0.58±0.02 a	0.43±0.04 c
p-value	0.0024	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000

Values are means ± standard deviation. Different letters within a column mean significant differences *(P*<0.05).
C1: initial consistency; C2: minimum torque; C3: maximum torque during the heating; C4: minimum torque during the heating period; C5: torque obtained after cooling at 50ºC.

Table 4 Instrumental quality parameters of the gluten-free bread-like products

Samples codes	Specific Volume, cm^3/g	Crumb colour parameters *L**	*a**	*b**	Moisture content, %	Water activity	TPA-Hardness, N
BF1	1.91 ± 0.05 b	78.31 ± 0.76 d	-2.59 ± 0.17 a	14.47 ± 0.79 d	37.17 ± 0.07 c	0.96 ± 0.00 c	84.90 ± 3.07 c
BF2	4.48 ± 0.02 f	72.17 ± 1.01 c	-1.21 ± 0.20 bc	7.13 ± 1.02 b	37.97 ± 0.04 d	0.96 ± 0.00 c	1.33 ± 0.33 a
BF3	3.03 ± 0.04 e	73.79 ± 2.87 c	-0.89 ± 0.16 cd	6.30 ± 0.25 b	37.40 ± 0.17 c	0.95 ± 0.00 b	2.30 ± 0.30 a
BF4	2.52 ± 0.04 d	62.24 ± 0.81 a	-0.80 ± 0.15 d	12.15 ± 0.54 c	43.53 ± 0.32 f	0.97 ± 0.00 d	36.27 ± 2.93 b
BF5	2.41 ± 0.04 c	65.77 ± 0.27 b	-1.22 ± 0.02 bc	5.06 ± 0.12 a	39.30 ± 0.08 e	0.97 ± 0.00 d	7.53 ± 0.46 a
BF6	1.44 ± 0.03 a	63.40 ± 0.62 a	1.72 ± 0.43 e	21.89 ± 0.37 e	25.67 ± 0.30 a	0.92 ± 0.00 a	147.50 ± 11.12 d
BF7	5.07 ± 0.08 g	81.50 ± 0.09 e	-1.53 ± 0.04 bc	6.47 ± 0.15 b	33.33 ± 0.06 b	0.95 ± 0.00 b	5.43 ± 0.51 a
P- value	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Values are means ± standard deviation. Different letters within a column mean significant differences ($P<0.05$).
TPA-Hardness: Crumb hardness measured with a texturometer.

Table 5 Proximate composition of the gluten-free bread-like products.

Sample Codes	Protein, g/100g, dm	Fat, g/100g, dm	Minerals, g/100g, dm	Total Carbohydrate* g/100g, dm
BF1	3.30 ± 0.00 a	0.97 ± 0.02 b	1.37 ± 0.12 bc	64.87 ± 0.16 g
BF2	7.57 ± 0.12 e	3.40 ± 0.01 d	1.13 ± 0.08 a	55.57 ± 0.08 c
BF3	7.10 ± 0.04 c	3.70 ± 0.00 e	1.31 ± 0.00 b	54.57 ± 0.18 b
BF4	14.97 ± 0.00 g	0.20 ± 0.02 a	1.47 ± 0.03 c	43.90 ± 0.31 a
BF5	3.63 ± 0.03 b	1.87 ± 0.01 c	1.03 ± 0.06 a	58.20 ± 0.06 f
BF6	12.33 ± 0.03 f	9.57 ± 0.00 g	1.46 ± 0.01 c	56.17 ± 0.29 d
BF7	7.43 ± 0.03 d	4.77 ± 0.04 f	1.41 ± 0.14 bc	57.43 ± 0.17 e
P- value	0.0000	0.0000	0.0001	0.0000

(*)Total Carbohydrate (dm) by difference: 100 – (weight in grams [protein + fat + ash] in 100 g of food) (FAO. 2003).

Values are means ± standard deviation. Different letters within a column mean significant differences ($P<0.05$).

Table 6 Sensorial analysis of the gluten-free bread like products

Sample Codes	Crumb appearance	Taste	Odour	Colour	Springiness	Hardness	Crumblines
BF1	2.67 ± 1.21 bc	1.33 ± 0.52 a	2.17 ± 1.17	3.00 ± 0.89 bc	1.50 ± 1.22 a	1.50 ± 1.22 a	1.67 ± 0.82 a
BF2	2.67 ± 0.52 bc	2.50 ± 0.84 b	3.17 ± 0.75	3.67 ± 1.03 bc	1.33 ± 0.52 a	3.83 ± 0.75 b	3.67 ± 1.37 bc
BF3	4.50 ± 0.55 d	3.67 ± 1.14 c	3.33 ± 1.48	4.33 ± 0.45 c	2.00 ± 0.71 ab	4.17 ± 0.84 b	4.00 ± 1.00 c
BF4	1.33 ± 0.89 a	1.17 ± 0.45 a	1.83 ± 0.84	2.67 ± 0.89 ab	3.00 ± 1.87 bc	2.00 ± 1.22 a	1.33 ± 0.55 a
BF5	4.50 ± 0.55 d	2.50 ± 0.55 b	3.33 ± 1.03	4.33 ± 0.82 c	3.33 ± 1.03 c	3.67 ± 0.52 b	2.17 ± 0.75 ab
BF6	1.83 ± 1.17 ab	2.50 ± 0.84 b	2.33 ± 1.21	1.67 ± 0.82 a	1.17 ± 0.41 a	1.50 ± 0.84 a	1.50 ± 0.84 a
BF7	3.17 ± 0.41 c	3.33 ± 1.21 bc	2.83 ± 1.33	3.67 ± 1.21 bc	2.33 ± 1.37 abc	4.33 ± 1.21 b	3.00 ± 0.63 bc
P-value	0.0000	0.0000	0.1218	0.0002	0.0089	0.0000	0.0000

Values are means ± standard deviation. Different letters within a column mean significant differences ($P<0.05$)

Table 7 Correlation matrix between instrumental quality parameters of gluten-free bread-like products and dough/batter rheological parameters determined with the Mixolab®

	Instrumental quality parameters			
Mixolab® parameters	Specific volume	Water activity	Moisture content	TPA-Hardness
Time to C1		0.5101*	0.5422*	
C1	-0.4816*	-0.7833***	-0.8193***	0.8969***
Stability	0.5579**			
Amplitude	-0.5151*	-0.7768***	-0.8113***	0.8671***
C2				0.5916**
C3				0.4880*
C4	-0.5112*			0.4868*
C5	-0.6594**			0.7849***
Cooking stab range C4-C3	-0.7016***		0.4749*	
Gelling C5-C4	-0.5906**	-0.8013***	-0.8355***	0.9287***

Correlations indicated by *r* values. ****P*-value <0.001, ***P*-value <0.01, **P*- value <0.05.
C1: initial consistency; C2: minimum torque; C3: maximum torque during the heating; C4: minimum torque during the heating period; C5: torque obtained after cooling at 50ºC.

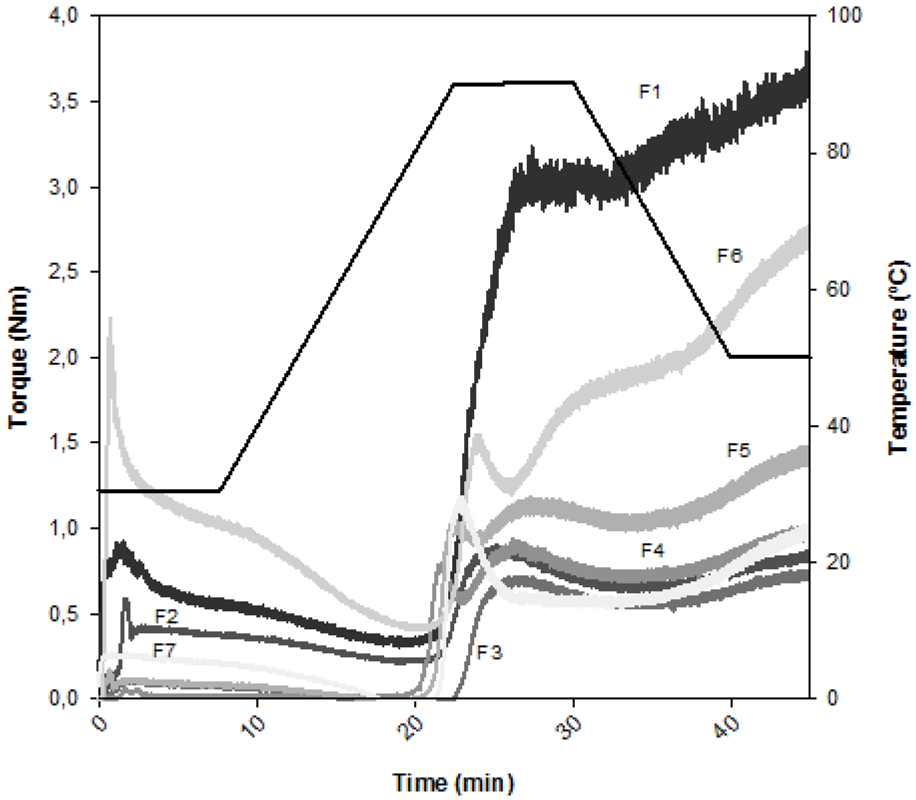
Table 8 Correlation matrix between sensory characteristics and instrumental parameters at dough and baked product level

	Sensorial characteristics				
Instrumental parameters	Crumb appearance	Colour	Springiness	Hardness	Crumblines
Mixolab® parameters					
C1			-0.6494**	-0.571**	
Amplitude			-0.5182*	-0.5444*	
C2			-0.6232**	-0.5332*	
C3				-0.5179*	
C4				-0.5639**	
C5				-0.7005***	-0.5584**
Gelling C5-C4				-0.5913**	-0.5217*
Quality parameters					
Specific volume				0.7149***	0.6242**
*L**					0.4852*
*a**		-0.4737*			
*b**	-0.6073**	-0.7636***	-0.4398*	-0.7945***	-0.6071**
Water activity			0.5362*		
Moisture content			0.5403*		
TPA-Hardness	-0.4904*		-0.4375*	-0.7646***	-0.6102**

Correlations indicated by *r* values. ****P*-value <0.001, ***P*-value <0.01, **P*- value <0.05.

C1: initial consistency; C2: minimum torque; C3: maximum torque during the heating; C4: minimum torque during the heating period; C5: torque obtained after cooling at 50ºC.

Figure 1.


Torque (Nm)
Temperature (ºC)
Time (min)
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3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
100
80
60
40
20
0
0
10
20
30
40
F1
F6
F5
F4
F2
F7
F3