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Optimization of rheological properties of gluten-free pasta dough using mixture design

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A B S T R A C T

The rising demand of gluten-free products for celiac people has led to important technological research on the replacement of the gluten matrix in the production of high quality gluten-free foods. The objective of this work was to evaluate the effect of composition (hydrocolloids, water, and proteins) on the rheological and textural properties of gluten-free dough used for producing pasta based on corn-starch and corn flour. Extensibility and rheological properties of gluten-free pasta dough were studied. Rising protein or gum contents produced a marked increase of deformation at break. However protein content was negatively correlated with breaking force. The increase in gums content produced an increase in storage and loss moduli (G', G''). G' was always larger than G'' with a small increase of both moduli with frequency. The mechanical relaxation spectrum was predicted from dynamic oscillatory data using the broadened Baumgaertel–Schausberger–Winter model. Application of a mixture design allowed finding the optimal composition to achieve the desirable textural properties using response surface methodology. A formulation containing 35.5% water, 2.5% gums, 4.7% proteins, 42.8% corn-starch, 10.7% corn flour, 1% NaCl, and 2.8% sunflower oil led to the highest values of G', breaking force, and extensibility according to the optimization analysis performed.

1. Introduction

Celiac disease is a form of enteropathy affecting the (small) intestine in genetically predisposed children and adults, precipitated by the ingestion of gluten-containing foods (Hall et al., 2009). When people with celiac disease consume gluten, their immune system generates antibodies against this protein, causing damage to the tiny hair-like projections in the small intestine. Therefore, this can lead to the inability to absorb nutrients and inadequate nutrition. The mainstay of treatment for celiac disease is life-long adherence to a gluten-free (GF) diet. For the majority of patients, the introduction of a GF diet results in full clinical and histological remission and has been associated with improvements in quality of life. Specifically the storage proteins (prolamins) in wheat (gliadin), rye (secalin) and barley (hordein) have to be avoided (Hall et al., 2009).

Rising demands for GF products parallels the apparent or real increase in celiac disease, or other allergic reactions/intolerances to gluten consumption (Lazaridou et al., 2007). Consequently, there is still a need to find substances that could improve the quality of this type of product. Replacement of the gluten network to produce GF products is a major technological challenge, gluten being the essential structure-building protein. Thus, substances that imitate the viscoelastic properties of gluten are always required in GF products (Mariotti et al., 2011).

Noodles prepared from rice flour are the most popular Asian pasta, widely consumed in Southeast Asian countries. Gluten-free pasta studies mainly involved rice flour alone or in combination with other non-gluten cereals and/or additives (Huang et al., 2001; Marti et al., 2010; Sozer, 2009). In order to produce GF pasta with similar appearance and texture as conventional pasta obtained from wheat flour, it is a usual methodology to obtain pregelatinized starch through heat and cool stages, thus forming a rigid network based on the retrograded starch (Cabrera-Chávez et al., 2012; Mariotti et al., 2011).

Development of fresh gluten-free pasta could also be possible including hydrocolloids in the formulation. It has been observed that the film-forming properties act as a lubricant inside the batter and protect the other formulation ingredients from being damaged by mixing, particularly starch granules (Alamprese et al., 2007, 2009; Yu and Ngadi, 2004).

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Xanthan gum, locust bean gum, alginates and carboxymethyl cellulose (CMC) are common stabilizers used in food technology to provide viscosity, improve firmness, giving body and mouthfeel to the end product. Through their ability to bind water, gums can increase the rehydration rate of pasta upon cooking or soaking (Yu and Ngadi, 2004). Nonstarch polysaccharides such as xanthan gum (XG) and locust bean gum (LBG) have very significant viscoelastic properties and might be used to mimic the properties of gluten to form the elastic texture of pasta. The synergistic interaction between these two polysaccharides in solutions often leads to an increase in solution viscosity or the formation of gels. This subject has attracted the interest of many researchers during the last two decades due to its effectiveness in reducing production costs and enhancing rheological properties (Mao and Rwei, 2006). It is known that xanthan in aqueous solutions adopts a rigid, ordered conformation as a double-stranded helix. On heating, it undergoes an order-disorder transition from helix to random coil. At moderate concentrations, xanthan undergoes self-association to form a "weak gel", which flows under a steady stress. When mixed LBG, XG forms a true gel via the cross-links between segments of LBG and XG (Mao and Rwei, 2006).

Even when gluten-free bread formulations containing hydrocolloids and proteins have been investigated for several decades (Anton and Artfield, 2008; Gallagher et al., 2003; Mezaize et al., 2009), there are few works related with other types of gluten-free dough production (Huang et al., 2001; Lorenzo et al., 2008, 2009; Sozer, 2009).

Response surface methodology (RSM), as an effective tool for development and optimizing processes, is usually employed when many factors and interactions affect the desired response and provides an adequate representation of most continuous response surfaces over a relatively broad factor domain (Myers and Montgomery, 2002). Designing an experiment to fit a response surface model typically involves selecting among several candidate designs. A particular group of designs corresponds to experiments with mixtures, very commonly involved in product development whenever a multicomponent system is concerned. In a mixture experiment, the independent factors are proportions of different components of a blend where the proportions of the different factors must sum to 100% (Cornell, 2002). When a mixture design is employed, the purpose of the experiment is to model the blending surface either to predict the response for any combination of the ingredients or to determine the influence on the response of each component individually and in combination with the other components (Cornell, 2002).

The rheological characterization of pasta dough provides important information for food technologists, allowing ingredient selection strategies to design, improve, and optimize the final product. Rheological studies become particularly useful when predictive relationships for rheological properties of foods can be developed, starting from the molecular architecture of the constituent species. When conducted in the linear range, dynamic tests allow the specific expression of well-defined rheological parameters, such as the storage modulus (G') and the loss modulus (G''). In the case of gluten-free doughs, when frequency sweep tests were conducted in the linear domain, G' was greater than G'' and a rather low dependence of both moduli on frequency has been observed by several authors (Lazaridou et al., 2007; Moreira et al., 2011; Sivaramakrishnan et al., 2004).

The objectives of this work were: a) to evaluate the effect of the addition of mixtures of xanthan/locust bean gums, dry egg/dry egg-white, and water, on the linear viscoelastic and textural properties of gluten-free dough used for pasta production using corn starch and corn flour as the main ingredients, b) to obtain and model the relaxation mechanical spectrum from small amplitude oscillatory data to interpret structural features of the material and c) to predict the optimum formulation of fresh pasta dough in terms of the industrial handling requirements considering as the target conditions the characteristics of a wheat dough.

2. Materials and methods

2.1. Materials

Corn starch (12.5% moisture, 0.3% protein) was obtained from Droguería Saporiti (Buenos Aires, Argentina); corn flour (7% moisture and 8% protein) from Herboeste (Buenos Aires, Argentina). Dry egg (2% moisture, 42% proteins) and dry egg-white (3.3% moisture, 95% proteins) from Tecnovo SA (Entre Ríos, Argentina), food-grade commercial xanthan (XG), and locust been gums (LBG) (Sigma Chemical Co., St. Louis, MO), analytical grade NaCl, sunflower oil (Molinos Río de La Plata SACIFI, Buenos Aires), and cold distilled water were used.

Moisture content of flour and starch was determined according to AACC 44-40 (2000); dry matter of dry egg and dry egg-white was analyzed according to AOAC 17-006 (1984). Protein contents were analyzed by Kjeldahl using a conversion factor of 6.25.

A dough pasta (control sample) formulated with 300 g commercial wheat flour (14% moisture and 9% protein (Molino Cañuelas, Buenos Aires, Argentina) and 149.5 g of fresh egg was prepared in order to obtain a reference rheological behavior.

2.2. Pasta dough sample preparation

Basic pasta dough formula consisted in 42.8% of corn starch, 10.7% corn flour, 1% NaCl, and 2.8% sunflower oil (Barron, 2006), with different amounts of water, egg proteins, and gums added.

The protocol of Lorenzo et al. (2008, 2009) was followed to prepare the gluten-free dough. Dry ingredients were premixed for 1 min in a commercial food processor (Universo, Rowenta, Germany) at 400 rpm (setting #2). With the processor still running, the lipid phase was added and mixed for one more min. Finally, water was added and the dough was mixed for 5 more min. to combine the ingredients. The dough was placed in a tightly sealed container and kept at 4 °C for 24 h to let the starches hydrate. The dough was sheeted on a noodle machine (Pastalinda, Pastalinda S.A., Argentina, rollers diameter: 35 mm) at the minimum setting to smooth and firm it, and fed another four times between the rollers, decreasing the gap between rollers each time, until reaching the maximum setting to give the pasta a good shape and texture (Alamprese et al., 2009). This procedure is similar to the lamination process employed by commercial noodle manufacturers. Finally, the pasta thus obtained was rolled into sheets approximately 2 mm thick. Representative subsamples were cut from these sheets of pasta with an adequate cork borer and kept in airtight polystyrene containers to avoid moisture loss. Ambient temperature was maintained at 20 °C during dough preparation and analysis.

Wheat pasta was prepared following the procedure described above.

2.3. Experimental design

In a mixture experiment, the measured response is assumed to depend only on the relative proportion of ingredients or components present in the mixture, which usually sum to 100%. The present work employed a mixture experiment with seven components: corn starch, corn flour, water, mixture of XG/LBG, and egg proteins (dry egg/dry egg-white mixture), NaCl and sunflower oil. However, corn starch, corn flour, NaCl, and sunflower oil contents were fixed at the relative amounts explained in Section 2.2. The mixture of xanthan and locust bean gums was used in a synergistic ratio of 2:1 (Maier et al., 1993).

According to Alamprese et al. (2009), ovalbumin plays an important role in the development of the pasta protein network, both during the dough mixing phase and the cooking process. Increasing the albumin/yolk ratio is advantageous for the structure of the final product thus, in this work, a 10:1 ratio for dry egg and dry egg-white mixture was selected.

In this work, the sum of water, proteins, and gums was 42.7%, but from experience gained in previous works (Larrosa et al., 2011; Lorenzo et al., 2008, 2009), the authors knew that it was not advisable for water, gums, and protein content to take extreme values like 0 and 42.7% (e.g. water = 42.7% without the addition of ligands or water = 0% will not form a dough at all). Consequently a mixture design with constrains was chosen. This type of design is suggested when the proportions of some or all of the components are restricted by upper and lower bounds; the experimental region is just a sub-region of the entire mixture simplex (Cornell, 2002). Combinations of gums (0.5–2.5%), proteins (0.7–6.7%), and water (35.5–39.5%) were used in a simplex-centroid augmented design where the sum of gums and proteins was maintained between 3.2 and 7.2%. Preliminary experiments showed that outside this water content range (35.5–39.5%) it was impossible to laminate the dough. Higher water contents produced a sticky dough, and when lower water contents were used the dough tended to crumble and it was not possible to obtain a homogeneous sheet.

The design consisted of twelve runs: four points at the extreme vertices of the feasible quadrangular region (1, 2, 3, 4), four points at the edge centroids, (5, 6, 7, 8) one point at the overall centroid (9), and three added points (10, 11, 12) to evenly cover the experimental region (Cornell, 2002). Centroid point formulation was prepared twice and both replicates were analyzed. The feasible mixture space is shown in Fig. 1 with the actual design points. As an example, formulation 2 corresponds to 39.5% water, 0.5% gums, and 2.7% proteins. Table 1 shows all the gluten-free tested formulations.

2.4. Oscillatory shear tests

Small amplitude oscillatory shear tests were performed in a Controlled Stress Rheometer RS600 (Haake, Germany) using a

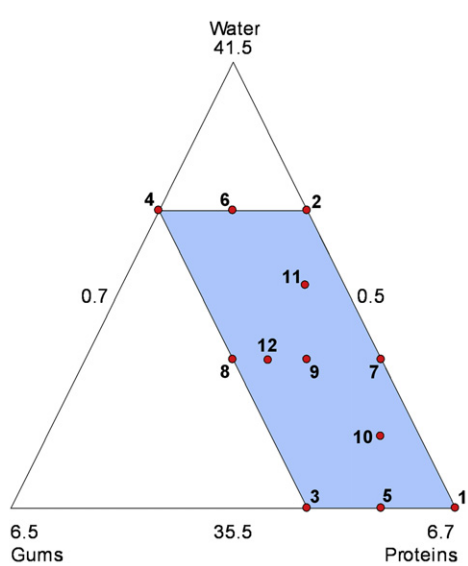

Fig. 1. Design runs for the simplex-centroid augmented design chosen; proportions of components are given as percentual values. Water axis ranges from 35.5% to 41.5%; proteins axis from 0.7% to 6.7%; gums axis from 0.5% to 6.5%.

serrated plate-and-plate geometry (35 mm diameter, 1.6 mm gap). After positioning the sample on the sensor system, excess dough protruding from the edge of the plate was carefully trimmed off. The exposed surface was covered with a thin layer of mineral oil to prevent moisture loss during testing. Samples were rested for an additional 10 min after loading prior to testing so that the residual stresses would relax. A stress sweep test from 0.5 Pa to 100 Pa at a fixed frequency (6.28 rad/s) was used to identify the linear viscoelastic region. A frequency sweep test, ranging from 0.02 to 215 rad/s, was used to study the dough storage modulus (G′) and loss modulus (G″) vs. frequency, (ω). Temperature was maintained at 20 °C throughout the experiment. At least two replicates of each test were performed on each formulation. Wheat control samples were also tested in duplicate.

2.5. Extensibility tests

Extensibility tests on fresh dough samples were performed on squared specimens (80 × 80 × 2) mm with a Texture Analyzer TA-XT2i (Stable Micro System, UK), using a round compression probe (2.5 cm diameter) and a pastry burst rig (TA 108). Breaking force (N) and deformation at break (extension at the moment of rupture, mm) were obtained from force vs. deformation curves. For every formulation (including wheat control samples), ten repeated measurements (five specimens for each batch) were done and mean values were reported.

2.6. Modeling relaxation spectrum from dynamic data

During evaluation of mechanical properties, the relaxation spectrum of the system is a fundamental quantity in the linear theory of viscoelastic materials and its shape is often correlated with specific molecular architectures (Winter, 1997).

The linear viscoelastic behavior of rheologically complex materials, like pasta dough, can be described using the parallel association of N Maxwell elements. Each of them is defined by the elastic response of the spring (G_i) and the relaxation time which is the ratio between the viscosity of the dashpot and the rigidity of the spring ($\lambda_i = \eta_i/G_i$). The behavior is entirely characterized by the knowledge of the discrete relaxation spectrum which is represented by the number N and the values of G_i and λ_i. If the number N is increased ($N \to \infty$), the relaxation spectrum becomes continuous ($H(\lambda)$). In that case, each infinitesimal contribution to rigidity is associated with relaxation times lying in the range between λ and $(\lambda + d\lambda)$; in the case of broad molecular distribution, a continuous relaxation spectrum is more suitable (Baumgärtel and Winter, 1992).

Storage and loss moduli could be related to the relaxation spectrum by:

$$G' = G_e + \int_{-\infty}^{+\infty} H(\lambda)\frac{(\omega\lambda)^2}{1+(\omega\lambda)^2} d\ln\lambda \quad (1)$$

$$G' = \int_{-\infty}^{+\infty} H(\lambda)\frac{(\omega\lambda)}{1+(\omega\lambda)^2} d\ln\lambda \quad (2)$$

where, G_e is the equilibrium elasticity modulus.

Major efforts have been undertaken worldwide for developing the best computer algorithm for that purpose (Baumgärtel and Winter, 1992; Tschoegl and Emri, 1993). In this work, we chose the broadened Baumgäertel–Schausberger–Winter spectrum (denoted as “BSW spectrum”) that consists of a superposition of two power laws. This specific form of the relaxation time spectrum

Table 1
Effect of composition on main parameters of the Baumgärtel–Schausberger–Winter model for gluten-free dough. Standard deviations are shown between parentheses.[a]

Formulation number	Water content (%)	Protein content (%)	Gums content (%)	G_N^0 (Pa)	n_0	n_e	log (λ_e/λ_0)
1	35.5	6.7	0.5	1.1×10^5 (5.9×10^4)[b]	0.315 (0.062)[b]	0.256 (0.032)[b]	1.24 (0.32)[d]
2	39.5	2.7	0.5	5.8×10^3 (3.8×10^2)[g]	0.289 (0.031)[ce]	0.185 (0.071)[f]	0.26 (0.11)[ef]
3	35.5	4.7	2.5	3.5×10^5 (4.2×10^4)[a]	0.336 (0.058)[a]	0.239 (0.011)[bc]	7.04 (0.44)a
4	39.5	0.7	2.5	2.9×10^4 (7.2×10^3)[d]	0.355 (0.029)[a]	0.191 (0.024)[ef]	0.06 (0.02)[f]
5	35.5	5.7	1.5	1.1×10^5 (5.2×10^4)[b]	0.267 (0.011)[ef]	0.240 (0.008)[bc]	2.83 (0.15)[b]
6	39.5	1.7	1.5	6.8×10^3 (6.7×10^2)[fg]	0.309 (0.004)[bc]	0.190 (0.010)[f]	0.51 (0.04)[e]
7	37.5	4.7	0.5	6.6×10^3 (7.0×10^2)[fg]	0.253 (0.010)[f]	0.185 (0.007)[f]	0.19 (0.01)[f]
8	37.5	2.7	2.5	8.5×10^3 (4.7×10^2)[ef]	0.302 (0.010)[bcd]	0.220 (0.007)[cd]	1.45 (0.25)[cd]
9	37.5	3.7	1.5	8.9×10^3 (3.1×10^2)[ef]	0.302 (0.008)[bcd]	0.211 (0.006)[de]	1.56 (0.12)[c]
10	36.5	5.2	1.0	3.5×10^4 (3.3×10^3)[c]	0.305 (0.022)[bcd]	0.243 (0.044)[b]	1.25 (0.95)[d]
11	38.5	3.2	1.0	1.0×10^4 (9.8×10^2)[e]	0.247 (0.011)[f]	0.321 (0.015)[a]	0.18 (0.08)[f]
12	37.5	3.2	2.0	9.6×10^3 (9.1×10^2)[e]	0.287 (0.016)[de]	0.236 (0.010)[bc]	1.26 (0.84)[d]

G_N^0 is the plateau modulus, n_0 and n_e are the slopes of the spectrum in the high frequency glass transition and entanglement regimes, respectively, λ_0 is the crossover time to the glass transition, λ_e the relaxation time corresponding to polymer chains with entanglement molar mass.
[a] Different superscripts within the same column indicate significant differences ($P < 0.05$).

(Eq. (3)) was originally proposed for broadly distributed linear flexible polymers (Baumgärtel and Winter, 1992):

$$H(\lambda) = G_N^0\left[H_g\left(\frac{\lambda}{\lambda_0}\right)^{-n_0} + n_e\left(\frac{\lambda}{\lambda_e}\right)^{n_e}\right]\exp\left(-\left(\frac{\lambda}{\lambda_{max}}\right)^{\beta}\right) \quad (3)$$

where G_N^0 is the plateau modulus, H_g is the glass-transition front factor, n_0 and n_e are the slopes of the spectrum in the high frequency glass transition and entanglement regimes respectively, λ_0 is the crossover time to the glass transition, λ_e the relaxation time corresponding to polymer chains with entanglement molar mass, and λ_{max} is the longest relaxation time. The exponent β controls the sharpness of the cut-off of the spectrum.

In the present work, the linear relaxation spectrum, ($H(\lambda)$), was obtained from the linear viscoelasticity functions by inverting Equations (1) and (2) using a non-linear method, proposed by Baumgärtel and Winter (1992), and Winter (1997), the so-called IRIS method (software IRIS Rheo-Hub 2007).

2.7. Surface response analysis

Models for analyzing data from mixture-process variable experiments are usually obtained by combining traditional Scheffé type models for the mixture variables with response surface models for the process variables. The following second order polynomial model was fitted to the data:

$$Y = \sum_{i=1}^{3}\beta_i X_i + \sum_{i=1}^{3}\sum_{j=i+1}^{3}\beta_{ij}X_iX_j + \sum_{i=1}^{3}\beta_{ii}X_i^2 \quad (4)$$

where Y is the response variable, X_i are the proportion of components expressed in percentage (X_1 = proteins, X_2 = gums, X_3 = water) and β_I, β_{ij}, and β_{ii} were the linear, cross product and quadratic coefficients, respectively. A stepwise methodology was followed to determine the significant terms in Eq. (4). Differences in the computed parameters were considered significant when the computed probabilities were less than 0.05 ($P < 0.05$).

Since:

$$X_3 = 42.7\% - X_1 - X_2 \quad (5)$$

Eq. (4) can be rewritten in terms of only two independent variables as:

$$Y = \beta_1^{'}X_1 + \beta_2^{'}X_2 + \beta_1^{''}X_1^2 + \beta_2^{''}X_2^2 + \beta^{'''}X_1X_2 + \beta_0^{'} \quad (6)$$

After model fitting was performed, residual analysis was conducted to validate the assumptions used in the analysis of variance. This analysis included calculating case statistics to identify outliers and examining diagnostic plots such as normal and residual plots. The proportion of variance explained by the polynomial models obtained was given by the multiple coefficient of determination, R^2, and the adequacy of the model was verified using a "lack of fit" test.

2.8. Optimization

The main objective of optimization was to determine the levels of independent variables (components of the formulation) that lead to the best characteristics of a gluten free pasta dough, considering the rheological properties of fresh wheat pasta dough as the target for the optimization. Based on the effects of the ingredients on each characteristic of the product, the overall desirability criterion (Derringer and Suich, 1980) was used. The general approach is to first convert each response (Y) into an individual desirability function (d) that varies from 0 to 1, where, if the response is at its goal or target, then $d = 1$, and if the response is outside an acceptable region, then $d = 0$. Each response is standardized in desired functions d. Eq. (7) expresses the global desirability function, D, defined as the geometric mean of the individual desirability functions that correspond to force (d_1), deformation at break (d_2), and the elastic modulus G′ (d_3). The algorithm should search for response variable values where D tends to 1.

$$D = \sqrt[3]{d_1 * d_2 * d_3} \quad (7)$$

2.9. Statistical analysis

All statistical analysis, mixture design, generation of response surfaces, desirability functional analysis, optimization, and 3D and contour plots were accomplished using the Expert Design (trial version 7.1.6, Stat-Ease Inc., Minneapolis, USA) statistical software.

3. Results and discussion

3.1. Dynamic rheology

Results of the dynamic oscillatory tests are presented in Fig. 2a for three formulations with different water contents and 1.5% gums. A gel-like viscoelastic behavior, characteristic of a highly structured material, was observed (i.e. the storage modulus is always higher than the loss modulus in the whole frequency range studied). There

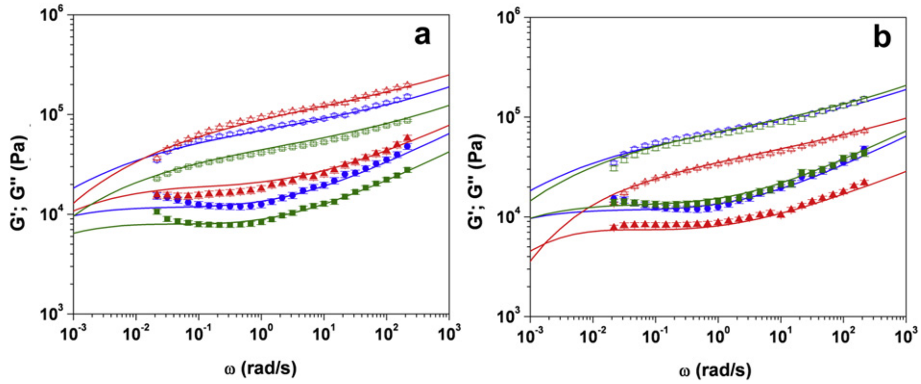

Fig. 2. (a) Effect of water content on dynamic oscillatory data for three formulations of gluten-free dough formulated with mixtures of corn starch and corn flour and 1.5% of XG/LBG gums mixture. Water content: (□ ■) 39.5%; (○ ●) 37.5%; (△ ▲) 35.5%. (b) Effect of gums content on dynamic oscillatory data for three formulations of gluten-free dough formulated with mixtures of corn starch and corn flour, and 37.5% water. Gums content: (□ ■) 2.5%; (○ ●) 1.5%; (△ ▲) 0.5%. Storage (G′, open symbols) and loss moduli (G″, filled symbols) vs. frequency (ω); lines show the predictions using the BSW model.

was a tendency for G″ to exhibit minima which has been related to the formation of physical entanglements among polymeric molecules that form a three-dimensional network of interacting or entangled molecules (Ferry, 1980). Nevertheless, the polymer network formed by protein chains and hydrocolloids is affected by water content. In the dough formulations studied, there exists a three-dimensional network of interacting or entangled carbohydrate and protein molecules that traps the water molecules and starch granules. The structure of the systems is further enhanced when water content decreases. Fig. 2a also shows the predictions of G′ and G″ obtained from the relaxation spectra (continuous lines).

The starch granules probably act as inactive fillers because of their inability to form a cohesive network (Ravindra et al., 2004; Tolstoguzov, 1997), which is mainly formed by the xanthan and locust bean gums. Water plays an important role in determining the viscoelastic properties of dough. Both G′ and G″ decreased as water content increased. The dynamic viscoelastic behavior of the pasta doughs can be understood by taking into account that water molecules acted as a lubricant enhancing the relaxation and mobility of the functional constituents of the dough (Masi et al., 1998).

The BSW model has been successfully employed to represent the linear viscoelastic behavior of several polymeric and emulsified systems (Bengoechea et al., 2008); its parameters could also be used to explain structural characteristics of the systems. In this work the broadened Baumgaertel–Schausberger–Winter model was successfully used to predict the mechanical relaxation spectrum from dynamic oscillatory data (Table 1). The slope of the spectrum in the entanglement regime (n_e), together with the spacing between characteristic times (log (λ_e/λ_0)), tended to decrease when more water was added to the formulation. The higher value of the slope (n_e) in the plateau region may be related to the development of a more entangled network. A significantly higher value of the plateau modulus was also observed in formulations with the lowest water content. This tendency was in agreement with the behavior of the other parameters.

Average curves of the frequency sweep test for gluten-free dough samples (formulated as explained in the preceding section), but containing 37.5% water and increasing XG/LBG gums content, are shown in Fig. 2b. Curves were qualitatively similar, showing a slight dependence of G′ and G″ with frequency. They corresponded to gel-like structural networks, although samples containing 0.5% gums exhibited significantly lower values for both moduli. A plateau region at intermediate frequencies is clearly distinguished in all cases. When doughs between 1.5% and 2.5% gum content are compared, the spectra were quite similar showing statistically equivalent coefficients in the BSW model.

Sivaramakrishnan et al. (2004) studied the inclusion of hydroxy propyl methyl cellulose as gluten substitute in rice bread and their rheological analysis was in agreement with the results obtained in this work.

For doughs with similar water content, both the plateau modulus and the width between characteristic times showed a positive correlation with the increase of hydrocolloid concentration reflecting a decrease in the molecular mobility (Ferry, 1980).

In all the formulations, oscillatory spectra were satisfactorily modeled using the BSW model combined with the Maxwell Generalized model. Fig. 2a and b show, as an example, experimental and predicted values of several formulations.

3.2. Surface response and optimization analysis

With mixtures, it is impossible to vary one factor independently of all the others. When the proportion of one ingredient is changed, the proportion of one or more other ingredients must also change to compensate. This simple fact has a profound effect on every aspect of experimentation with mixtures: the factor space, the design properties, and the interpretation of the results.

Experimental storage modulus G′ (at 6.28 rad/s) was evaluated using response surface methodology to determine its relationship with pasta dough composition. Data were modeled by multiple regression analysis adopting backward stepwise analysis and only the variables significant at $p < 0.05$ levels were selected for the model construction. The regression coefficients of Eq. (6) are given in Table 2.

Fig. 3a shows a contour plot of the predicted response surface. Both additives (gums and proteins) increased the amount of polymers in the system and resulted in increased elasticity (MacGregor and Greenwood, 1980), but gums have a more marked effect than the added proteins as predicted by the regression coefficients in Table 2. Similar results were observed for rice pasta supplemented with guar gum and egg white; increasing biopolymers concentration resulted in a dough that was easy to handle and process (Sozer, 2009) Surface response analysis was also used to determine the relationship between breaking force and dough composition, considering a full quadratic model. The same procedure was applied to deformation at breaking data. The model adequately predicted experimental results, significant probability values ($P < 0.0001$) and non-significant lack of fit ($P > 0.05$) values were found, which indicated that most variations could be well explained by the proposed models (Myers and Montgomery, 2002). Hence, it can be concluded that the proposed models approximate the response surfaces and can be used suitably for prediction at any values of the

Table 2
Regression coefficients for the predictive models of each response variable, statistical significance of the Model and Lack of fit. Standard deviations are shown between parentheses.

	G′ (Pa)[a]	Force (N)	Deformation (mm)
Proteins	33.3×10^2 (9.2×10^2)	-23.2×10^{-2} (9.2×10^{-2})	9.32 (0.097)
Gums	31.2×10^3 (1.4×10^3)	6.75×10^{-2} (1.7×10^{-2})	1.904 (0.114)
Gum *proteins[a]	–	20.5×10^{-2} (9.4×10^{-2})	−0.131 (0.083)
Proteins 2	–	–	−0.131 (0.083)
Constant	23.1×10^3 (7×10^2)	1.56 (0.12)	5.81 (0.94)
Model (p)	0.0357	<0.0001	<0.0001
Lack of fit (p)	0.2795	0.1134	0.6896
Adeq precision	5.89	18.20	11.71

[a] G′ = Storage modulus.

parameters within experimental range (Myers and Montgomery, 2002). Fig. 3b and c show the projection of the breaking force and deformation at break plotted on the 2D composition triangle, respectively.

From the regression coefficients of Eq. (6) shown in Table 2, it can be seen that protein content and the interaction between gums and proteins are the terms that most affect the breaking force. For pasta dough containing low gum content, the breaking force was low and decreasing egg protein content (negative regression coefficient), produced relatively harder dough. Conversely, at high gum fraction, F values increased when protein content rose (Fig. 3b).

Moreover, rising protein or gum contents produced a marked increase of deformation at break, although the interaction protein*gums and the quadratic term on protein were also significant. From Fig. 3c, it is easy to notice that the highest extensibility values (deformation at break) were obtained at lowest water and highest gum contents.

As can be seen in Fig. 3b and c, the overall effect of increasing water content (less proteins and/or gums) was to diminish breaking force and extensibility of the dough, making it more difficult to handle.

Another important parameter in Table 2 is the "*Adeq Precision*" (adequate precision) which compares the range of predicted values at design points to the average prediction error. Ratios over 4 indicate adequate model discrimination. All regressed variables in this work presented an adequate precision more than 4, so the model can be used to navigate the design space.

The low deformation conditions used for some measurements are often inappropriate to practical processing situations because they are carried out at rates and conditions very different from those experienced by the dough during processing or swelling expansion during cooking. However, low strains, which allow measurements but do not disturb or destroy inherent structure, are of great value in studying the influence and action of additives such as hydrocolloids in dough systems because dynamic mechanical parameters are highly sensitive to changes in polymer type and concentration as well as water content (Ferry, 1980).

Data storage and loss moduli (G′, G″) at 6.28 rad/s obtained from small deformation tests were related to the breaking force (F) obtained from extensibility tests. Both moduli were positively correlated with breaking force ($P < 0.001$) as can be seen in Fig. 4. These relationships demonstrate how the combined responses from large and small deformation rheological testing can be related to dough handling or other textural properties of these gluten-free formulations, and how this can be translated into optimization of dough composition and processing conditions (Lorenzo et al., 2008).

A dough formulation suitable to industrial handling must resist high tensions with a good extensibility. The control wheat samples exhibited average G′ = $(8.80 \pm 0.17) \times 10^4$ Pa and higher values of breaking force (2.93 ± 0.09 N) and deformation at breaking point (32.3 ± 1.8 mm) than the gluten-free dough. Therefore the aim of the current work was to determine the optimum combination of water, gum, and protein that lead to maximum breaking force, maximum deformation in the extensibility tests and a similar value of G′.

Based on the effects of the ingredients on each characteristic of the product, and considering that the proposed model approximates the response surfaces and can be used suitably for prediction at any values of the parameters within the experimental range, the composition was optimized according to the overall desirability criteria (Eq. (7)).

According to the fitting performed, the obtained desirability value was 0.676, which is acceptable taking into account the large number of responses being simultaneously optimized. The individual desirability values for each optimized response (G′, deformation and breaking force) were 0.736, 0.672 and 0.624, respectively. The coordinates corresponding to the cited desirability value are 35.5%, 2.5% and 4.7% for water, gums and proteins, respectively.

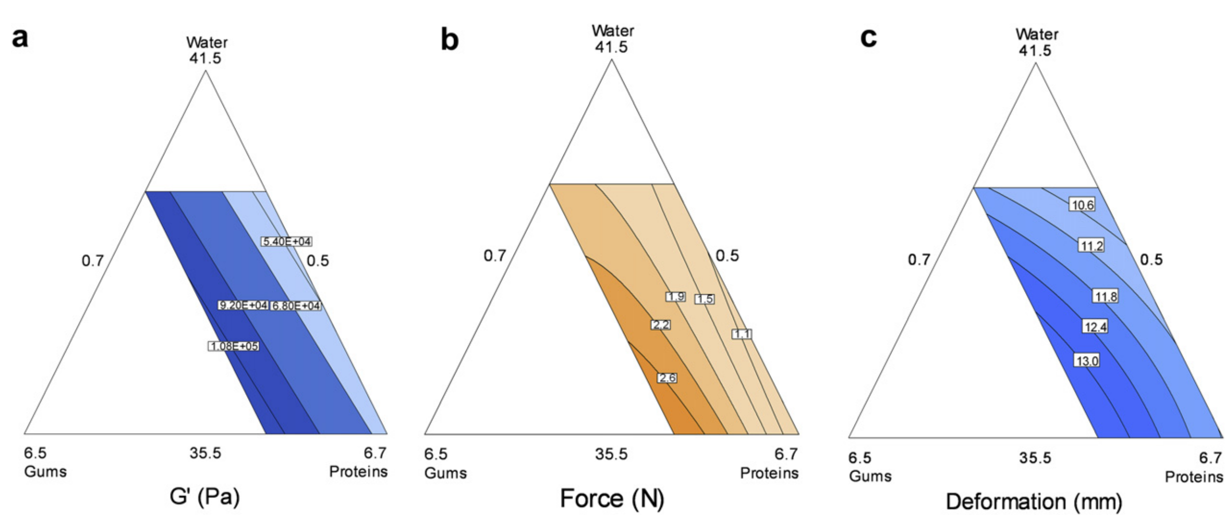

Fig. 3. Contour plots of (a) storage modulus (G′) measured at 6.28 rad/s (b) breaking force, (c) deformation at breaking showing the significant ($P < 0.05$) effects of dough composition. The darkest shade indicates highest value and lines correspond to isoparametric values.

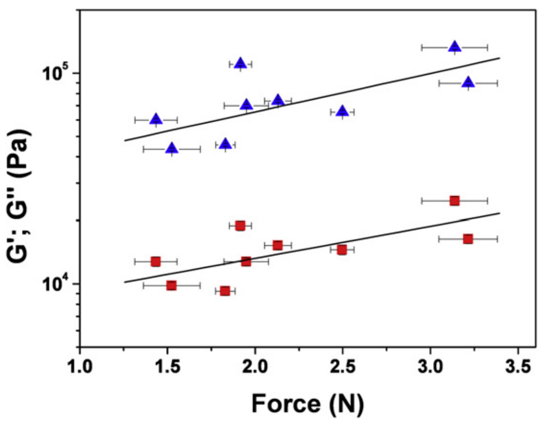

Fig. 4. Relationship between large deformation texture properties and viscoelastic measurements. Storage modulus (G′, ▲) and loss modulus (G″, ■) at 1 Hz (6.28 rad/s) vs. breaking force.

4. Conclusions

Application of a mixture design allowed finding the optimal gluten-free dough composition to achieve the desirable textural properties, making the dough easy to handle under industrial conditions. The best formulation corresponds to a composition of 35.5% water, 2.5% gums, 4.7% proteins, 42.8% corn starch, 10.7% corn flour, 1% NaCl, and 2.8% sunflower oil, that led to the highest values of breaking force, and extensibility and a G′ similar to that of a wheat pasta dough.

The mathematical modeling of the rheological spectra of gluten-free pasta dough allowed to interpret the effect of water and the biopolymers on the viscoelastic behavior of the dough. For doughs with similar water content, both the plateau modulus and the width between characteristic relaxation times showed a positive correlation with the increase of hydrocolloid concentration, reflecting a decrease in the molecular mobility of the matrix.

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