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Rheological characterization of refrigerated and frozen non-fermented gluten-free dough: Effect of hydrocolloids and lipid phase

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ABSTRACT

This work intended to study the rheological and textural behavior of gluten-free dough for "empanadas" and pie-crusts production. Traditionally, these products are made with non-fermented wheat-based dough. They are highly consumed in Latin America, but unsuitable for celiac people. Gluten matrix is a major determinant of the properties of dough, thus it must be replaced with other network forming components, such as hydrocolloids. Different hydocolloids were tested: hydroxypropylmethylcellulose (HPMC) and mixtures of xanthan/guar, and xathan/HPMC gums. Three different kinds of lipid phase were also studied; i.e. sunflower oil and low and high solid content margarine at two different levels (20–30%). Changes in rheological and textural properties during refrigerated storage were evaluated by dynamic oscillatory measurements and puncture and elongation tests on the unbaked dough. Best results were obtained using either of the hydrocolloid mixtures. Besides, the textural characteristics of cooked empanadas were also studied. Freezing before baking did not alter the quality of the crust in the products. ESEM micrographs revealed a continuous matrix formed by hydrocolloid entanglements. Starch granules were homogenously distributed in the dough and acted as inactive fillers. An untrained panel accepted the xanthan/HPMC dough with a 74/90 score and it was significantly preferred over a commercial gluten-free dough.

1. Introduction

Theoretical and experimental progress in polymer and biomaterial science has contributed to increase the knowledge of the processing – structure – rheology relationships of starch and other carbohydrates in food. Many authors have studied the effect of hydrocolloid and protein addition to several bakery products studying their influence for different food processing conditions (Bárcenas and Rosell, 2005; Collar et al., 1999; Conde-Petitt, 2003). Development of gluten-free bakery products involves the application of hydrocolloids to produce a high quality gluten-free food considering the important fact that they must replace the gluten matrix network. Population-based studies, using serological screening, have indicated that the true prevalence of celiac disease is higher than previously thought, at up to 1 in 150 individuals (Dewar et al., 2004).

Celiac disease is an autoimmune enteropathy triggered by the ingestion of gluten-containing grains in susceptible individuals. The gliadin fraction of wheat gluten and similar alcohol-soluble proteins in other grains (mainly barley, rye and oat) are the environmental factors responsible for the development of the intestinal damage (Fasano and Catassi, 2001). The pathological changes and symptoms generally resolve with withdrawal of gluten from the diet and a strict adherence to a gluten-free diet throughout the patient's lifetime.

There is a traditional meal in Latin America called "empanadas", which is quite similar to Cornish pasties. The non-fermented dough used for "empanadas" normally includes wheat flour, fat, and water (Lupano, 2003). Small circles (11 cm diam.) of pastry dough are topped with different fillings and folded over into a half-moon. The pastry edges are firmly pressed together to seal the filling and fluted. Empanadas are baked or fried before eating. This product is commercialized in two distinct ways, either as refrigerated small disks of dough or "ready-to-bake" frozen "empanadas". Low quality of the gluten-free products currently in the market has led to important research in order to improve their poor structure,

Abbreviations: D, deformation at break in elongation test (mm); FE, maximum breaking force in elongation test (mN); FP, maximum breaking force in puncture test (mN); XG, xanthan and guar gum mixture; XH, xanthan and hidroxipropylmethyl cellulose mixture; SO, Sunflower Oil; RM, Low solid fat content margarine (retail margarine); IM, High solid fat content margarine (margarine for industrial uses); G′, storage modulus (Pa); G″, loss modulus (Pa); η*, complex dynamic viscosity (Pa.s).

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mouthfeel and flavor (Arendt et al., 2002; Gallagher et al., 2002, 2004; Lazaridou et al., 2007; Toufeili et al., 1994). Production of gluten-free pastries involves research to find an adequate combination of the key components to produce a dough with a good elasticity, resistance to puncture, and stretching. Type of hydrocolloid and lipid phase are two of the most important components, which affect the handling characteristics of the uncooked dough as well as the overall quality of the baked product.

Storage of bakery products often leads to deterioration of the overall quality of the product. Upon freezing, moisture in the food transforms into ice, often resulting in physical stress to the food matrix. When a frozen food is thawed for consumption, the moisture is readily separated from the matrix causing a softening of the texture. Hydrocolloids were found to be able to give stability to food products during freezing-thawing cycles, and help to minimize negative effects of the freezing and frozen storage of starch based products (Bárcenas et al., 2004; Sanderson, 1996; Selomulyo and Zhou, 2007).

Textural properties of the baked dough and sensorial perception of the consumers are crucial aspects to be considered to assess the quality of the final product. The evaluation of gluten-free dough for "empanada" production was analyzed in a previous work (Lorenzo et al., 2008) and the contribution of gum, proteins, and water content to the rheological properties of the dough were described. It was found that those formulations containing higher percentages of gums (3%) and lower water content (51%) led to an adequate composition for industrial production. However, higher protein contents (whey protein concentrate and dry egg) interfered with the formation of the three-dimensional gum network making the doughs more fragile.

The aim of the present work was to examine changes in the rheological attributes of non-fermented gluten-free dough as affected by composition: i) type of hydrocolloid (hydroxy propylmethylcellulose (HPMC), xanthan/guar, and xathan/HPMC gums), ii) lipid phase (sunflower oil, low and high solid content margarines); and to consider the influence of iii) the storage time (refrigerated and frozen storage), and iv) the baking process on the final product.

2. Experimental

2.1. Materials

Corn starch, (12.5% moisture, 0.3% protein) was obtained from Droguería Saporiti (Argentina); cassava starch (14% moisture and 0.2% protein) from Santa María (Argentina). Retail margarine (Flora-Danica S.A., Argentina) and 100% sunflower oil (Molinos Río de La Plata SACIFI, Buenos Aires) were purchased from a local supermarket and used without further treatment. High solid fat content margarine (for industrial uses) was from CALSA, Argentina. Whey protein concentrate (WPC) containing 80% protein (Arla Food Ingredients S.A., Argentina), food-grade commercial xanthan and guar gums (Sigma Chemical Co., St. Louis, MO), hydroxypropylmethylcellulose (HPMC), Methocell E4M (The Dow Chemical Company, Michigan), dry egg (6% moisture, 38% lipids, Tecnovo S.A., Argentina), and analytical grade NaCl were used. Distilled water was used in all formulations and ethyl alcohol was added as a preserving agent.

2.2. Dough sample preparation

Basic dough formula consisted in a mixture of starches, hydrocolloids (3%), dry egg (3.5%), whey protein concentrate (WPC, 6.5%), NaCl (2%), water, and a lipid phase. Percentage concentrations of the formula are given on a g/100 g total starch basis. Concentration of total hydrocolloids, dry egg, WPC, and NaCl were maintained constant in all the formulations. 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 briefly kneaded by hand, wrapped in a film, put in a tightly sealed container, and kept refrigerated (4 °C) for 24 h to let the starches hydrate and to let the dough consistency stabilize (Manley, 2001). Dough was divided in three pieces, and each piece was rolled out with a rolling pin (20–25 passes) over a flat board. A spacer was placed on each side of the dough to maintain a consistent level while the dough was rolled until a final thickness of 2 mm.

Each dough formulation was prepared twice and both replicates were analyzed. In the description of each assay the number of subsamples taken from each dough batch is recorded.

2.2.1. Effect of hydrocolloids

Different hydrocolloids were tested in dough preparation: HPMC (H), a mixture of xanthan/guar gums (XG, ratio 2:1), and xathan/HPMC (XH, ratio 3:2). In all cases 3% total hydrocolloids content, 20% sunflower oil and 51% distilled water were used.

2.2.2. Effect of lipid phase

Sunflower oil, margarine with high solid fat content (for industrial uses), and retail margarine (with low solid fat content) were studied in dough preparation at two different levels (20% and 30%; g/100 g total starch) for the two hydrocolloid mixtures that presented the best textural results in 2.2.1. Studied formulations are shown in Table 1. The fatty acid compositions of the three lipid phases were provided by the producers: *Sunflower oil*: Lauric (0.5), Myristic (0.20), Palmitic (6.80), Palmitoleic (0.10), Stearic (4.70), Oleic (18.60), Linoleic (68.20), Linolenic (0.50), Arachidic (0.40), Gadoleic (1.00); *Retail Margarine*: Myristic (0.12), Palmitic (11.05), Palmitoleic (0.70), Margaric (0.13), Margaroleic (0.03), Stearic (8.87), Elaidic (36.27), Oleic (24.59), Linoleic (15.85), Linolenic (2.05), Arachidic (0.40), Gadoleic (0.09), Behenic (0.38), Lignoceric (0.11); *Industrial Margarine*: Myristic (3.20), Myristoleic (0.90), Pentadecanoic (0.80), Pentadecenoic (0.30), Palmitic (26.50), Palmitoleic (3.30), Margaric (1.60), Margaroleic (0.50), Stearic (26.20), Elaidic (4.10), Oleic (29.30), Linoleic (2.20), Linolenic (0.50), Arachidic (0.20), Behenic (0.40). The concentration of water was modified according to the lipid content in order to keep constant the sum of these two ingredients; otherwise consistency of the dough was not adequate to allow its manipulation.

2.3. Solid fat content determination

Solid fat content of the margarines (SFC) was measured by pulsed nuclear magnetic resonance (p-NMR) in a Minispec PC/120 series NMR analyzer (Bruker, Karlsruhe, Germany), following the AOCS 16b-93. Prior to NMR analysis, samples were melted at 80 °C for 30 min, the NMR tubes were then filled at this temperature and finally, maintained for 30 min at 20 °C (temperature test) and 0 °C (Martini and Herrera, 2000; Puppo et al., 2002).

2.4. Storage

2.4.1. Refrigerated storage of the dough

Disks of dough were packaged under vacuum conditions in bags CN510 (PO_2: 35 $cm^3/(m^2 day.bar)$ at 23 °C, Sealed Air, Argentina) and kept refrigerated at 4 °C for 20 days to perform textural and dynamic rheological analysis approximately every four days.

Table 1
Compositions of the tested formulations with different type and concentration of lipids; results obtained by textural analyses: deformation at breaking (D), puncture (FP) and elongation forces (FE), and average values of material strength parameter (Aα) as a function of dough composition.

Formulation	Gums	Lipid phase		FP(mN)	FE(mN)	D(mm)	Aα (kPas)
		Type	% (wt.)				
XGSO20	Xanthan gum/guar gum	Oil	20	357[agh]	294[aef]	14.13[aef]	81.5[a]
XGSO30			30	104[b]	77[b]	7.30[bc]	45.5[b]
XGRM20		Retail Margarine	20	285[cde]	211[cd]	9.49[bcd]	107.7[c]
XGRM30			30	315[cdh]	227[cde]	7.72[bc]	136.6[d]
XGIM20		Industrial Margarine	20	262[ce]	284[aef]	10.82[cdf]	202.4[e]
XGIM30			30	413[fg]	255[ade]	16.33[ae]	212.8[e]
XHSO20	Xanthan gum/HPMC	Oil	20	376[afgh]	301[af]	14.62[aef]	55.6[ab]
XHSO30			30	117[b]	80[b]	7.82[bc]	36.1[b]
XHRM20		Retail Margarine	20	275[cde]	212[cde]	7.87[bc]	126.4[cd]
XHRM30			30	343[adgh]	202[cd]	9.21[bcd]	125.9[cd]
XHIM20		Industrial Margarine	20	279[cde]	278[adef]	12.9[adf]	165.1[f]
XHIM30			30	399[fg]	280[aef]	16.69[ae]	174.9[f]

Different superscripts within the same column indicate significant differences ($P < 0.05$).

2.4.2. Frozen storage of "empanadas"

"Empanadas" were prepared using a traditional ground beef filling (Lupano, 2003), frozen, stored at −20°C during 15 days, and then baked (200 °C, 20 min) without previously thawing them. Freshly prepared pastries with the same dough formulations were baked and used as controls.

2.5. Texture analyses

Textural analyses were performed in a TAXT2i Texture Analyzer (Stable Micro Systems,UK), using the Texture Expert Exceed software supplied by Texture Technologies Corp. For every formulation six repeated measurements (three specimens for each batch) were done and mean values were reported.

2.5.1. Puncture tests

On raw specimens, a cylindrical probe 2 mm in diameter at a constant rate of 1 mm/s was used. Tests were performed on disks of 40 mm diameter and 2 mm thick from each dough formulation (Lorenzo et al., 2008).

The Volodkevich bite jaws (HDP/VB) probe, which simulates the action of an incisor tooth (Wen-Ching et al., 2007), was used in measuring the texture of the baked final product, because it has been observed that the first bite of the product is done with the fore teeth.

Maximum breaking force (FP, mN) was determined in both procedures.

2.5.2. Elongation tests

Elongation tests were performed on dog-bone shaped specimens of unbaked dough (Lorenzo et al., 2008). Maximum breaking force (FE, mN) and deformation at break (extension at the moment of rupture, D) were obtained from force vs. deformation curves.

2.6. Oscillatory shear tests

Small amplitude oscillatory shear tests (storage modulus (G'), loss modulus (G'') vs. frequency, (ω)) were performed in a Controlled Stress Rheometer RS600 (Haake, Germany) using a serrated plate-and-plate geometry (35 mm diameter, 1.6 mm gap). Frequency was swept from 0.01 to 22 Hz. To determine the limit of the linear viscoelastic region, dynamics tests were performed at a fixed frequency (1 Hz) and amplitude of the stress was stepwise increased from 0.5 Pa to 100 Pa. Temperature was maintained at 20 °C throughout the experiment. Two replicates of each test were performed on the unbaked samples.

2.7. Environmental scanning electron microscopy (ESEM)

An environmental scanning electron microscope (Phillip-Electroscan 2010, Netherland) was used to examine the dough surface of different samples. Micrographs of raw and baked doughs were taken without any previous treatment of the samples.

2.8. Sensory assessment

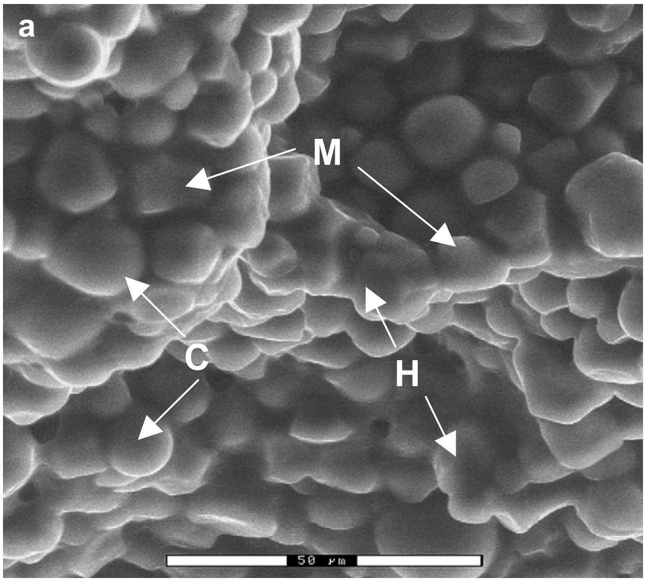
Sensory analyses were conducted by forty panellists from graduate students and faculty members in our Institute who were experienced in sensory evaluation of foods, but received no specific training relevant to these products. Panellists evaluated ground beef filled "empanadas" prepared with two dough formulations, one of the formulations developed in our laboratory and a gluten-free dough purchased from a local market. The samples were simultaneously baked at 200 °C during 20 min. Panellists were asked to indicate how much they liked or disliked each product on a 9-point hedonic scale (9 = like extremely; 1 = dislike extremely) according to flavor and texture characteristics. They were also asked to mark which formulation they preferred according to global evaluation. Warm specimens were distributed in white polystyrene plates and presented to the panellist with three-digit codes and in random order for evaluation. Tap water was supplied to the panellist for rinsing between samples. Experiments were conducted in an appropriately designed and lighted room.

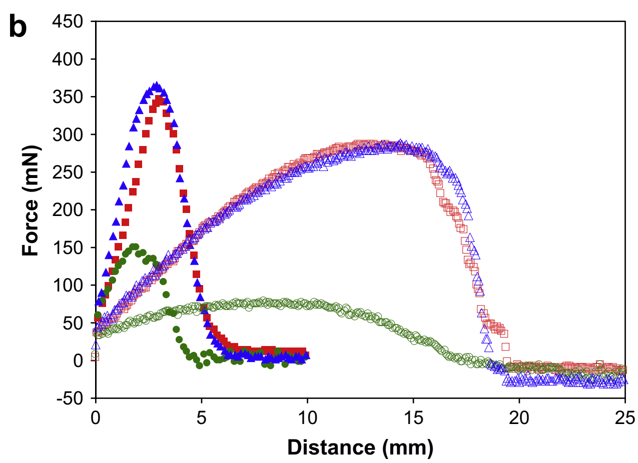
2.9. Statistical analysis

All statistical analyses were accomplished using the SYSTAT software (SYSTAT, Inc., Evanston, IL). Analyses of Variance (ANOVA) were performed separately for the puncture, elongation, and oscillatory shear tests measurements. Type of hydrocolloid or type and content of lipids were the factors analyzed. Bonferroni's test was chosen for simultaneous pairwise comparisons. Differences in means and F-tests were considered significant when $P < 0.05$ (95% of confidence). The standard error of the mean (SEM) was calculated as the standard deviation divided by the square root of the number of observations. Each mean value was reported as mean ± standard error of the mean.

3. Results and discussion

The basic formulation of the dough was taken from previous work where percentages of dry egg, WPC, water, and gums were optimized (Lorenzo et al., 2008). Initial formulation contained 3%





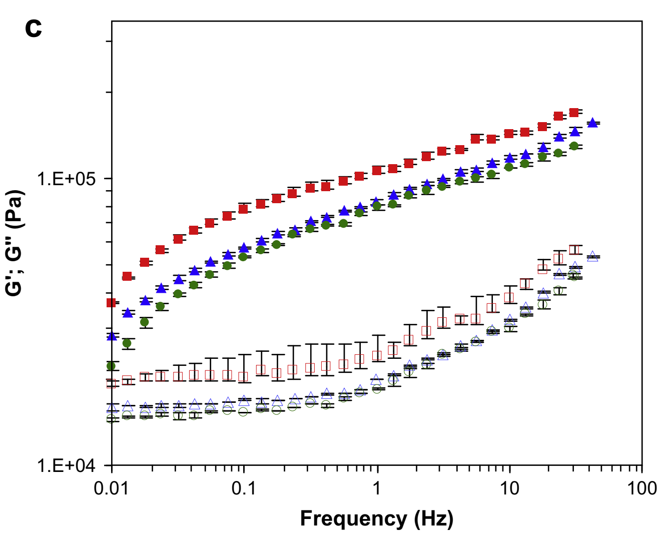


Fig. 1. (a) Environmental scanning electron micrograph of a dough containing 20% sunflower oil and xanthan/HPMC gums (bars = 50 µm) C = cassava starch; M = corn starch; H = hydrocolloid network. (b) Effect of hydrocolloids on dough texture: puncture (P, filled symbols) and elongation (E, open symbols). Xanthan/guar mixture (■; □); HPMC (●; ○), and xanthan/HPMC mixture (▲; △). (c) Effect of hydrocolloids on dough rheology: storage, (G′, filled symbols) and loss moduli (G″, open symbols) vs. frequency (ω). Xanthan/guar mixture (■; □); HPMC (●; ○), and xanthan/HPMC mixture (▲; △). The values are expressed as mean ± standard error of the mean.

gums, 3.5% dry egg, 6.5% WPC, and 51% water. Percentages are given in g/100 g total starch basis.

3.1. Effect of hydrocolloids on dough rheology

Fig. 1a presents the dough microstructure for a formulation containing a mixture of xanthan and HPMC gums as an example. All the tested formulations presented qualitatively the same appearance. The ESEM micrograph shows a continuous hydrocolloid network and a random organization of both starch granules, where clusters of either corn or cassava starches cannot be distinguished.

Fig. 1b shows the results of textural analyses (puncture and elongation) for the formulations containing different hydrocolloids (HPMC and combinations of xanthan/guar, xanthan/HPMC). Each curve corresponds to the mean of six replicates.

It could be observed that those formulations containing a mixture of xanthan/guar gums exhibited the same mean values of FP (366 mN) and FE (297 mN) as those formulated with xanthan/HPMC (Fig. 1b). When the hydrocolloid matrix was only formed by HPMC the samples presented extremely low values for FP, FE, and D (104 mN, 77 mN, 7 mm, respectively). This fragile behavior turns the formulation into an unsuitable dough for industrial handling since it would not resist the large stretching forces leading to cracks and tears in the dough disks. Moreover, this lack of resistance in the structure would cause spills during baking, producing an important quality loss in the final product. Commercial dough disks formulated with wheat flour were measured for comparison. They presented FE = 344 mN (SEM: 9.9) and FP = 325 mN (SEM: 16.6), which were similar to those formulated with the tested hydrocolloid mixtures and much larger than the HPMC formulation.

The results of dynamic rheological measurements in the linear viscoelastic range were expressed in terms of the storage modulus (G′) and loss modulus (G″). Results of the dynamic oscillatory tests are presented in Fig. 1c for the three formulations; the curves were qualitatively similar for all the formulations assayed. G′ was always greater than G″ in the frequency range measured and the increase of the two moduli with frequency was small. Two characteristic regions may be distinguished: a pseudo-terminal region at low frequencies that shows a tendency to a crossover of both viscoelastic functions, and the plateau region. The "plateau region" is an intermediate zone between the "terminal" and the "transition" zones (Ferry, 1980). It is characterized by a decrease in the slope of both moduli (lower than 1) and a possible minimum in the loss modulus (G″). In the present work the frequency range in Fig. 1b entirely corresponds to what is known as the "plateau" zone. The power law exponent of the storage modulus is lower than 0.2 in the whole range, indicating a slight dependence with frequency. The plateau region in G′ is related to the formation of physical entanglements among polymeric chains that form a three-dimensional network of interacting molecules (Ferry, 1980). Several authors have reported a similar trend for flour dough with G′ and G″ increasing with frequency (Agyare et al., 2004; Dreese et al., 1988; Kenny et al., 2001; Lefebvre et al., 2003; Lorenzo et al., 2008; Ribotta et al., 2004).

Doughs formulated with xanthan/guar gums presented the highest values of elastic modulus, while the lowest values corresponded to the HPMC doughs (with or without xanthan gum) in the whole frequency range analyzed ($P < 0.05$). Guarda et al. (2004) detected higher water absorption on wheat bread when adding HPMC instead of xanthan gum. This effect has been attributed to the hydroxyl groups in the hydrocolloid structure which allow more water interactions through hydrogen bonding (Rosell et al., 2001). The lower G′ and G″ curves for both formulations containing HPMC ($P < 0.05$), as well as the observed FP and FE values, could be attributed to this softening phenomenon.

3.2. Effect of lipid phase on dough rheology

The effect of type and content of the lipid phase was evaluated in those formulations that presented the best textural behavior in Section 3.1, i.e. those with xanthan/guar and xanthan/HPMC mixtures.

Table 1 shows the maximum forces in puncture (FP) and elongation (FE) tests for all the assayed formulations and also the extensibility or deformation at the breaking point (D). Textural analyses did not detected any significant differences ($P < 0.05$) between both hydrocolloid combinations used, regardless of the lipid type and concentration.

When margarine was used, the increase in fat content produced doughs with higher resistance to puncture, while the opposite effect was found using sunflower oil. Both type and lipid content also affected FE and D significantly ($P < 0.05$). Margarine provided ductility to the dough; more markedly in the case of the industrial margarine which contained higher solid fat content (46.8%) than the retail ("all purpose") one (24.7%). The formulation with high sunflower oil content showed the lowest FP FE, and D, values, making it the least suitable for industrial handling (Fig. 2 and Table 1).

The effect of lipid phase on the viscoelastic characteristics of the doughs was analyzed using the Friedrich and Heymann theory (Friedrich and Heymann, 1988; Lorenzo et al., 2008). According to this theory, complex viscosity (η^*) could be expressed as

$$\eta^* = \frac{G^*}{\omega} = \frac{\sqrt{G'^2 + G''^2}}{\omega} \approx A_\alpha \omega^{(\alpha-1)} \quad (1)$$

where α is the order of the relaxation function and $A\alpha$ the material strength parameter, related to the rigidity of the network.

Equation (1) was fitted to the frequency sweep curves and average values of the material strength parameter obtained for each formulation are listed in the last column of Table 1. A marked increment of $A\alpha$ with the solid fat content of the lipid phase is observed. When the matrix contained higher solid content (industrial margarine) it showed more elastic behavior, which was reflected in an increase in $A\alpha$ ($A\alpha_{(IM)} > A\alpha_{(RM)}$). Additionally, type of hydrocolloids significantly affected the material strength of the dough ($P < 0.05$). When HPMC replaced guar gum in the hydrocolloid mixture, the decrease in $A\alpha$ value was more noticeable in the doughs containing industrial margarine. The order of the relaxation function (α) was lower than 0.2 for all formulations, indicating the pronounced elastic character of the doughs, typically observed in gel-like samples (Doublier et al., 1992; Steffe, 1996). However, α was significantly higher for those formulations containing oil ($\alpha = 0.19$) than those values corresponding to doughs made with margarine, either retail or industrial ($\alpha = 0.15$), since a liquid lipid phase decreased the solid characteristics of the matrix.

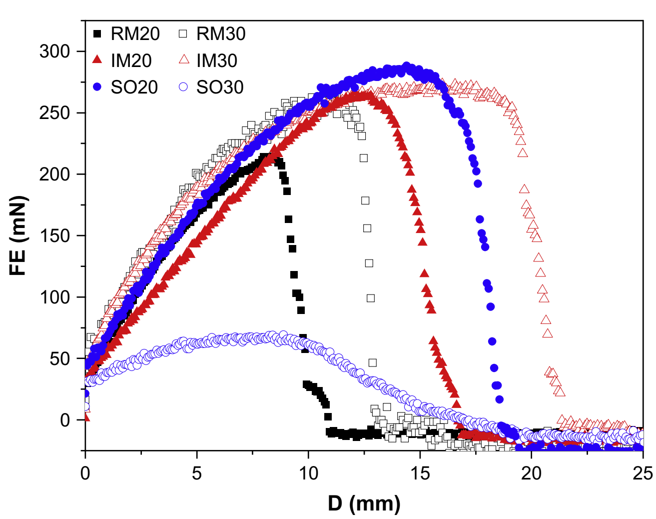


Fig. 2. Effect of lipid phase on dough elongation tests (E). Results obtained for the formulations with xanthan/HPMC mixture. Sunflower oil (●; ○), industrial margarine (high solid fat content) (▲; △), and retail margarine (low solid fat content) (■; □). Filled symbols correspond to 20% and open symbols to 30% lipid content.

3.3. Storage

3.3.1. Refrigerated storage of dough disks

The 20% sunflower oil or 30% industrial margarine showed the highest values for maximum breaking forces (FP and FE) as well as the highest deformation at break but did not differ significantly among themselves; thus, formulations with the lower lipid content (healthier formulations), i.e. XGSO20 and XHSO20 (Table 1) , were chosen to analyze the effect of refrigerated storage (4 °C). Their rheological and textural behavior was evaluated in dough disks at 1, 5, 8, 12, 16, and 20 days.

FP (364 mN), FE (290 mN), remained constant during refrigerated storage for both formulations and significant differences were not detected between them ($P < 0.05$). G′, and G″ did not change either during the storage time. However, the mixture of xanthan/guar ($G' = 1.41 \cdot 10^5$ Pa, SEM $= 7.0 \cdot 10^3$ Pa; $G'' = 2.30 \cdot 10^4$ Pa, SEM $= 7.7 \cdot 10^2$ Pa at 1 Hz) produced a more elastic dough than the xanthan/HPMC formulation ($G' = 9.88 \cdot 10^4$ Pa, SEM $= 3.1 \cdot 10^3$ Pa; $G'' = 1.92 \cdot 10^4$ Pa, SEM $= 7.7 \cdot 10^2$ Pa at 1 Hz).

The deformation at breaking point in the elongation tests (D) remained constant for the formulation containing HPMC. On the other hand, XGSO20 presented a decrease of the extensibility as is shown in Fig. 3.

The capability to retain water of hydroxyl groups present in HPMC could probably be responsible for the longer keepability of the dough. A similar trend was observed in wheat bread when HPMC was added (Collar et al., 1998).

3.3.2. Frozen storage of ready-to-bake "empanadas"

The effect of frozen storage of ready-to-bake "empanadas" on the microstructure and textural behavior of the baked final product was evaluated. Three formulations: XGSO20, XHSO20, and XHIM30

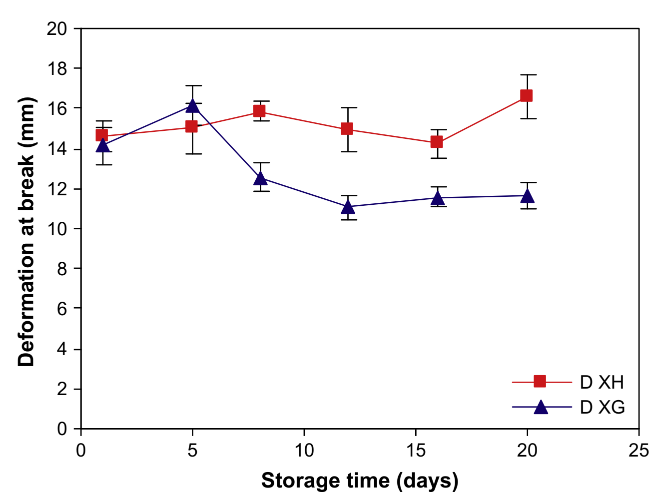


Fig. 3. Effect of refrigerated storage on deformation at breaking point (D) for formulations containing 20% sunflower oil with: xanthan/guar (▲) and xanthan/HPMC (■). The values are expressed as mean ± standard error of the mean.

(Table 1) were tested. The formulation with industrial margarine was included to examine whether a significant difference would be detected after the baking process.

Baking irreversibly alters the structural nature of dough constituents through a series of physical, chemical and biochemical reactions (Pyler, 1988). Temperature, humidity, and duration of baking influence the final product. Oven heat is responsible for the formation of an enveloping crust, coagulation of proteins, gelatinization of starch, and the stabilization of the colloidal dough system (Freeman and Shelton, 1991). Microscopic observations revealed that the crust appeared as a continuous sheet of proteins and hydrocolloids with embedded starch granules, which were not gelatinized because of the rapid dehydration of the surface at the oven temperature (Fig. 4a). The inner structure of the dough showed both intact and gelatinized granules (Fig. 4b and c). When going from the crust to the interior of the dough, less intact starch granules were observed (Fig. 4b). Near the filling, gelatinization is more complete and a distinction cannot be made between starch and the hydrocolloid matrix (Fig. 4c), while in the middle region of the dough (between crust and filling), starch granules are still recognizable. The limited water content of the dough may account for these differences. Fig. 4d presents a photograph of the final baked product.

The maximum puncture force of the baked specimens did not present significant differences ($P < 0.05$) between the control (unfrozen) and frozen samples. Besides, FP was not affected by the storage time in any of the three tested compositions. This effect is in agreement with Sanderson (1981) who has stated that xanthan gum induced cooking and cooling stability of wheat flour-based products and improved the freeze–thaw stability of starch-thickened frozen foods. This result implies an important technological advantage since the product could be frozen without changing its textural quality.

3.4. Sensory assessment

The forty experienced panelists evaluated the appearance, texture, flavor and overall acceptability of the formulations that have been stored for ten days at 4 °C. A formulation developed with xanthan gum/HPMC mixture and 20% sunflower oil (XHSO20) was compared with a commercial gluten-free dough.

There were no significant differences in flavor, texture and overall acceptability between both formulations ($P < 0.05$). The appearance of the commercial dough was perceived as significantly worse by the panel, which was related with the notorious cracks that appeared in these products during baking.

The observations were classified into three perception sensorial groups, the first one corresponded to those that disliked the product (scores 1 to 4, dislike extremely to slightly), the second one was indifferent (scores 5), and the third group expressed that they liked the samples (scores 6 to 9, like slightly to like extremely). More than 70% of the panelists liked all the attributes of the

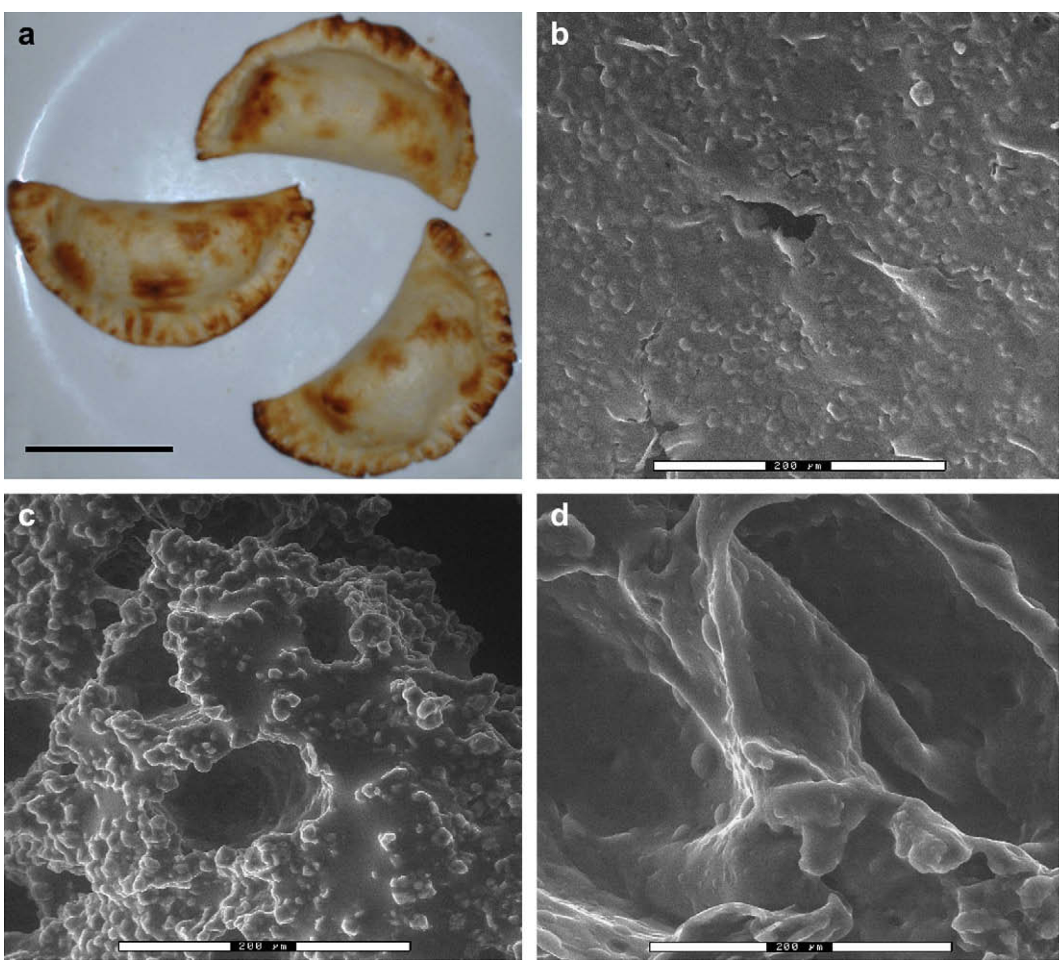


Fig. 4. (a) Photograph of the final baked product (bars = 5 cm); (b–d) Environmental scanning electron micrograph of a dough containing 20% sunflower oil and xanthan/HPMC gums (b) baked dough, external surface, crust (bars = 200 μm); (c) baked dough, middle region between the crust and the internal surface (bars = 200 μm); (d) baked dough, internal surface (bars = 200 μm).

Table 2
Sensory scores of gluten-free empanada's dough. Percentage of panelists that scored each tested property between 6 and 9 is given between parentheses.

	Appearance	Texture	Flavor	Global Acceptability	Preferences
XHSO20	7.4^a (88.9%)	6.8^a (70.1%)	7.1^a (80.6%)	7.5^a (94.4%)	$67.5\%^a$
Commercial dough	6.5^b (75%)	6.9^a (83.1%)	7.0^a (83.3%)	7.0^a (80.6%)	$32.5\%^b$

Different superscripts within the same column indicate significant differences ($P < 0.05$).

products. In particular, over 94% of the panelists liked the formulation containing xanthan/HPMC mixture and sunflower oil. Two thirds of the panelists preferred formulation XHSO20 over the commercial dough (Table 2) ($P < 0.05$). It is important to remark that none of the formulations developed in the present work showed signs of rupture during baking. Meanwhile, more than 90% of the commercial gluten-free disks presented this problem, which is an important parameter to consider since crust rupture produces a low quality product.

4. Conclusion

Textural and rheological behavior of non-fermented gluten-free doughs, a product intended for celiac people, was studied. The study of different hydrocolloid mixtures revealed that formulations containing xanthan gum exhibited the best elasticity and resistance to puncture regardless of the other hydrocolloids present in the dough (guar or HPMC). Formulations containing only HPMC were the least suitable for industrial production of "empanadas" or pie-crusts.

When margarine was used, the increase in fat content produced doughs with higher resistance to puncture, while the opposite effect was found using sunflower oil. Margarine for industrial uses (with higher solids content) provided greater elasticity to the dough than the retail margarine rendering it more ductile.

Doughs were stored at 4 °C for twenty days without any significant changes in rheological properties. Frozen storage did not affect textural characteristics of baked dough either. The panel accepted the xanthan/HPMC dough with a 75/90 score and it was significantly preferred over a commercial gluten-free dough.

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