Journal of Food Engineering 160 (2015) 11–18

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Dynamic rheological analysis of gluten-free pasta as affected by composition and cooking time

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ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form 11 February 2015
Accepted 19 March 2015
Available online 27 March 2015

Keywords:
Gluten-free pasta
Cooking times
Rheology
Relaxation time spectrum
Microstructure

ABSTRACT

The present work analyzes the effect of cooking times and dough composition on the rheological properties of gluten-free pasta. Gluten-free pasta dough was prepared with corn starch, corn flour, NaCl, dry egg and dry egg-white powders, sunflower oil, xanthan and locust bean gums. Small amplitude oscillatory data was used to obtain the relaxation spectrum. For all the formulations assayed G' was always greater than G'' in the frequency range measured and the increase of both moduli with frequency was small. Oscillatory spectra were satisfactorily predicted using the Maxwell Generalized model. Cooking time had a stronger effect on the mechanical spectra than protein and water contents. Hydrothermal treatment produced a significant microstructural change within the network entanglements. The analysis of the rheological behavior showed that water uptake by the matrix, partial gelatinization of the starch, and aggregation of denatured egg proteins led to chemical and morphological changes of the cooked pasta.

1. Introduction

Celiac disease is characterized by immune-mediated damage to the gut mucosa which is caused by intolerance to gluten, a protein found in wheat, rye and barley (Duggan, 2004). Lifelong gluten withdrawal from diet is now considered as the sole main effective therapy. In recent years, significant studies have been carried out on gluten-free products involving diverse approaches which have included the use of additives such as starches, hydrocolloids, dairy products, gums and other non-gluten proteins, prebiotics and combinations, as alternatives to gluten, to improve the structure, texture, acceptability and shelf-life of gluten-free products (Cureton and Fasano, 2009). However, most studies focus on gluten-free breads and there are only a few works related with other type of gluten-free doughs like pasta (Cappa et al., 2013; Gallagher et al., 2004; Lazaridou et al., 2007; Mahmoud et al., 2013; Sozer, 2009; Sozer et al., 2007).

Pasta cooking is an important step in pasta processing. Pasta is traditionally cooked in an excess of water (recommended pasta:water ratio is 1:10) at 100 °C for different immersion times depending on the desired texture of the final product. Hydration of the product occurs by a diffusion-controlled process, and the temperature – moisture conditions induce the gelatinization of starch. Gelatinization is accompanied by an increase in viscoelasticity and starch solubilization. Regarding the changes at the macroscopic level, starch gelatinization proceeds toward the center of the pasta strand as the cooking time increases (Cunin et al., 1995). Thus, starch morphological changes range from strong swelling and partial disintegration in the outer layer of the strand to slight swelling in the center. Additionally, water uptake by the matrix, promotes a significant softening of the pasta (Cafieri et al., 2008; Sozer et al., 2007). The hydrothermal treatment also affects the proteins present in the dough. Particularly, when egg proteins are included in a gluten-free pasta formulation, their rheological properties change considerably. When albumen is heated to about 65 °C, a weak gel is formed and the strength of the gel increases at higher temperatures. In the case of yolk, the viscosity begins to increase appreciably at about 65 °C, and at 70 °C, fluidity is lost completely with the formation of a semisolid crumbly mass (Powrie and Nakai, 1985).

During cooking pasta, structure changes from elastic to a more plastic state. Textural attributes are usually correlated to rheological parameters obtained by mechanical measurements, which are very important in understanding the structure of food and biological materials (Nouviaire et al., 2008).

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http://dx.doi.org/10.1016/j.jfoodeng.2015.03.019

Many rheological methods have been used to predict the quality of cereal food products. Edwards et al. (1996) investigated the rheological properties of noodle dough prepared from three types of Canadian wheat flour and its relationship to water absorption, formulation and work input during dough sheeting. Hatcher et al. (1999) showed the influence of water absorption on the processing characteristics such as raw thickness, sheet length, cooking time and cooked thickness and total work required, color and textural properties (recovery, resistance to compression, maximum cutting stress and surface firmness) of alkaline and white salted noodles prepared from three types of Canadian wheat flour. Furthermore, Yeh and Shiau (1999) and Shiau and Yeh (2001) studied the effects of oxidoreductants and alkali-acids on rheological properties of wheat flour dough; results showed that dough rheology significantly correlated with the quality characteristics of extruded noodles.

In previous works, Larrosa et al. (2013) optimized a formulation for gluten-free pasta containing a mixture of corn flour and corn starch based on rheological parameters of uncooked dough. However, little is known about changes in rheological properties that occur during the cooking stage of gluten-free pasta. Therefore, the aim of the present work was to analyze the microstructural and viscoelastic changes of gluten-free pasta as affected by dough composition and cooking time.

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, Argentina), and cold distilled water were used.

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

2.2. Pasta dough sample preparation

The protocol of Larrosa et al. (2013) and Lorenzo et al. (2008, 2009) was followed to prepare the gluten-free dough. Dry ingredients were premixed and then the sunflower oil and water were added with the processor still running. The dough was sheeted on a noodle machine (Pastalinda, Pastalinda S.A., Argentina, rollers diameter: 35 mm) until a pasta of approximately 2 mm thick was obtained. Subsamples were cut from these sheets and kept in air-tight polystyrene containers to avoid moisture loss. Ambient temperature was kept at 20 °C throughout dough preparation.

2.3. Experimental design

To analyze the effect of composition on cooked gluten free pasta, the formulation previously optimized by Larrosa et al. (2013) was chosen as the basic initial formula. All composition was given as percentage of the total pasta dough (g/100 g of dough). Samples consisted in a mixture of corn starch and corn flour in a 4:1 ratio, water, egg proteins, and fixed amounts of NaCl (1%), sunflower oil (2.8%), and a mixture of xanthan and locust bean gums in a 2:1 ratio (2.5%). The content of water plus egg proteins (dry whole-egg + dry egg-white) ranged between 37.5% and 44.1%, thus the corn starch and corn flour mixture varied from 56.2% to 49.6%, accordingly, to complete 100 g of dough.

To determine the levels of water and proteins analyzed, preliminary experiments were carried out. Results showed that outside the water content range 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. Therefore, three levels for moisture content (34.8%, 36.13%, and 37.5%) and two for egg proteins (2.7% and 6.6%) were adopted to analyze the effect of water and protein content on the quality of cooked pasta (Table 1). Additional central point was included (formulation W2EP2, Table 1) to better evaluate curvature in the mathematical models. This central formulation was replicated three times.

Table 1
Composition of the tested formulations and coded levels for water and protein contents.

Formulation	Composition (%)			Coded levels	
	Dry egg	Dry egg-white	Water	Egg-protein (EP)	Water (W)
W1EP1	2.45	0.25	34.8	−1	−1
W2EP1	2.45	0.25	36.13	−1	0
W3EP1	2.45	0.25	37.5	−1	1
W2EP2	4.23	0.42	36.13	0	0
W1EP3	6	0.6	34.8	1	−1
W2EP3	6	0.6	36.13	1	0
W3EP3	6	0.6	37.5	1	1

2.4. Cooking procedure

Cooking procedure was carried out for dough disk samples (40 mm diameter, 1.6 mm thick), which were cooked in 250 mL boiling deionized water. Boiling was kept at this level for the entire cooking period. Cooking properties of samples were measured at different cooking times, i.e. 0, 5, 10 and 15 min for all formulations. Previously, pasta optimum cooking time for each sample was determined according to the method 66-50 (AACC, 2000); noodles were deemed to be optimally cooked when the noodle strands did not display a clear visible opaque core (Edwards et al., 1995; Khouryieh et al., 2006). In all formulations the optimum cooking time was 10 min, thus, 5 and 15 min were included to evaluate the undercooking and overcooking effect on the rheological characteristics of gluten-free (GF) pasta. After cooking, samples were cooled by soaking in cold water for 60 s and excess water was removed by lightly patting between paper towels. The samples were immediately used for analytical and instrumental measurements.

2.5. Water absorption

For each gluten-free (GF) formulation pasta strands were immersed into test tubes, one for each tube, containing about 9 mL of distilled water and equilibrated at 100 ± 0.5 °C in a thermostatic bath (Haake L, Haake Buchler Instruments, Karlsruhe, Germany). Each subsample was weighed using an electrobalance (AB204, Mettler Toledo, Switzerland) before the sorption tests were conducted. All pasta samples were 40 mm long, had a width of 6 mm and 2 mm thickness. At given times, the samples were removed from the tube and rapidly blotted. Subsequently, the weight of the samples was determined. The weight of water absorbed at each hydration time has been obtained by subtracting the weight of the dry sample from that of the hydrated sample (Cafieri et al., 2008). For each sorption time, two replicates of each sample have been performed.

Water absorption (WA, g/g initial weight) at 100 °C, expressed as the relative weight gained, was modeled as a function of cooking time (t, min) using a power law equation (Cunningham et al., 2007) as:

$$\mathrm{WA} = K \cdot t^{n} \tag{1}$$

where K ($\mathrm{g} * \mathrm{min}^{-n}$/g initial weight) is a pre-exponential factor and n (dimensionless) is the exponent.

2.6. Environmental scanning electron microscopy (ESEM)

An environmental scanning electron microscope (FEI Quanta 200, Hillsboro, Oregon, USA) was used to examine the surface of the samples. Micrographs of raw and cooked GF pasta were taken without any previous treatment of samples cooked for 0, 5, 10, and 15 min.

2.7. Rheological characterization

Dynamic rheological measurements (storage (G') and loss (G'') moduli vs. frequency, (ω)) were performed in a Controlled Stress Rheometer RS 600 (Haake, Germany) using serrated parallel plates geometry (35 mm diameter, 1.6 mm gap) at a small stress magnitude in the linear viscoelastic region (LVR) and maintaining 20 °C for all the experiments. The excess of dough outside the sensor edge was trimmed and the exposed surface was covered with mineral oil to prevent moisture loss during the experimental test. After positioning the sensor samples rested for 10 min to relax from the residual stresses. Frequency sweep tests, ranging from de 0.01 to 300 rad/s were performed in duplicate. Previously, oscillatory tests were conducted at a constant frequency of 6.28 rad/s (1 Hz), varying the amplitude of the stress applied on the samples in order to search for the LVR. The criterion followed to its determination was the linear relationship between strain and stress. When materials are tested in the linear range, material functions such as G' and G'' do not depend on the magnitude of the applied stress.

2.8. Modeling the discrete relaxation spectrum

One of the simplest ways of understanding the linear viscoelasticity of structured materials is to make use of simple mechanical models. These consist of combinations of linear elastic and viscous elements, i.e. springs and dashpots. Thus, if a spring and a dashpot are connected in series the simplest representation of a viscoelastic material is obtained, i.e. the so called Maxwell model. However, experimental data show that the Maxwell model does not account for the stress relaxation behavior of many viscoelastic materials because of their rheological complexity. This problem may be addressed for numerous foods by constructing a model which has several Maxwell elements connected in parallel with a spring (Barnes, 2000; Ferry, 1980; Steffe, 1996).

Each of the N Maxwell elements 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 of the viscoelastic material is entirely characterized by the knowledge of discrete relaxation spectrum which is represented by the number N and different values of G_i (Pa) and λ_i (s) (Ferry, 1980). The following equations are obtained for the storage and loss modulus when the generalized Maxwell model is used to represent the relaxation modulus:

$$G'(\omega) = G_e + \sum_{i=1}^{N} G_i \frac{(\omega\lambda_i)^2}{1 + (\omega\lambda_i)^2} \tag{2}$$

$$G''(\omega) = \sum_{i=1}^{N} G_i \frac{(\omega\lambda_i)}{1 + (\omega\lambda_i)^2} \tag{3}$$

2.9. Statistical analysis

Analysis of variance was performed using SYSTAT software (SYSTAT Inc., Evenston, IL). Tukey's test was chosen for simultaneous pairwise comparisons. Differences in means and F-tests were considered statistically significant when $P \leqslant 0.05$. Surface response analysis was computed using Expert v.7 (Stat-Ease, Minneapolis, USA). In figures and tables SEM indicates standard error of the mean.

3. Results and discussion

3.1. Water absorption during cooking GF noodles

Water sorption tests have been run in order to evaluate the variation in pasta sample weight during cooking and overcooking and the obtained results are shown in Fig. 1. Typical hydration curves show an increase in weight of absorbed water with time where the rapid initial water absorption period is followed by a slower rate in the latter stages. As it was expected water absorption at 100 °C was strongly affected by cooking time. According to Dexter et al. (1983) and Grant et al. (1993) water uptake kinetics during cooking depends on the ability of water to diffuse through the matrix, and the melting kinetics of the crystalline domains. These two phenomena are mainly responsible for the time at which the unpenetrated central core disappears and all the starch crystals melt.

Water absorption experimental data for each formulation were successfully modeled with a power-law equation (Eq. (1)). Individual fitting showed that the pre-exponential factor (K) for all samples varied from 0.20 to 0.33 $\mathrm{g} * \mathrm{min}^{-n}$/g initial weight and exponent "n" ranged between 0.34 and 0.51. Although all determination coefficients R^2 showed the adequacy of the models to experimental data, a test for coincident curves was conducted to determine if the amount of water absorbed depends on the dough composition. This test was useful to evaluate whether or not our sets of experimental data were associated with the same error-free curve or with different curves (Green and Margerison,

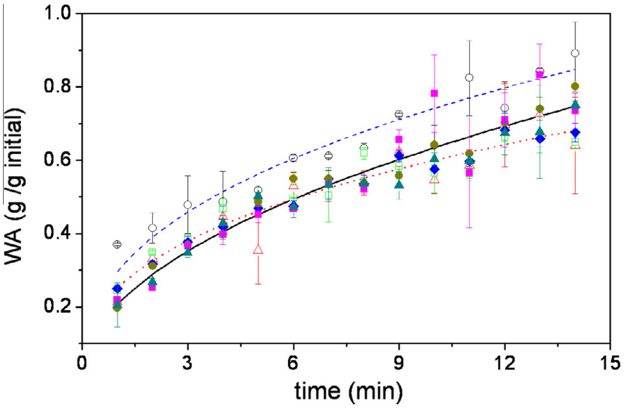

Fig. 1. Water absorption curves (WA) for the assayed formulations (○ W1EP1, △ W2EP1, □ W3EP1, ◆ W2EP2, ● W1EP3, ■ W2EP3, ▲ W3EP3), mean values ± SEM ($n = 2$); mathematical models correspond to formulations: ——— W1EP3, W2EP3, W3EP3; ······ W2EP2, W2EP1, W3EP1; and — — — W1EP1.

1978). Once the statistical analysis was performed, it was observed that the results of several formulations must be grouped and fitted with a same unique curve. Thus, according to water absorption kinetics, formulations were grouped in three sets; one set corresponded to pasta containing the largest amount of egg-proteins (6.6%, W1EP3, W2EP3, and W3EP3), a second group was composed of W2EP2, W2EP1, and W3EP1, which absorbed the smallest amount of water, and finally, W1EP1 showed the highest weight gained. The effect of protein content on water absorption seemed to be mainly detected when the initial water content of the dough was the lowest, i.e. when the absorption rate is expected to be the highest. Since egg proteins gels at temperatures below starch gelatinization temperature, a high amount of proteins appear to hinder water diffusion inside the noodle by forming a barrier and reducing the water absorbed as it could be in Fig. 1.

3.2. Microstructural changes of GF pasta during cooking

Microstructure of samples cooked during different processing times was observed by environmental scanning electronic microscopy. At the same heating time, all the tested formulations presented qualitatively the same appearance. Fig. 2 shows, as an example, micrographs of formulation W2EP2 (36.13% water and 4.65% egg-proteins). Initially the ESEM micrographs showed a continuous hydrocolloid network and a random organization of both starch granules, where clusters of corn starch cannot be distinguished (Fig. 2a). The hydrothermal treatment irreversibly altered the structural nature of dough constituents through a series of physical and chemical reactions. As cooking progressed starch gelatinization and protein coagulation caused the major structural changes. The gelatinized starch was held in place by a diffuse coagulated protein matrix and probably also by amylose that had leached out of the disrupted swollen granules during cooking (BeMiller and Whistler, 1996; Cunin et al., 1995).

After 5 min of processing time, samples showed both intact and gelatinized granules (Fig. 2b); as time progressed the intact granules tended to disappear (Fig. 2c) and after 15 min gelatinization was completed and a distinction could not be made between starch and the hydrocolloid matrix (Fig. 2d).

3.3. Rheological analysis

3.3.1. Amplitude and frequency sweep tests

The limit of linear viscoelasticity, at which rheological properties are independent of stress or strain, can be observed in Fig. 3 for formulation W2EP3 (36.13% and 6.65% proteins) at different cooking times as an example. Gels and starch doughs usually show a dependence of moduli on oscillatory stress in which G' and G'' remain independent up to the critical strain value, and then they deviate when the sample starts to flow (Khatkar and Schofield, 2002; Manoj et al., 1996; Zimeri and Kokini, 2003). For all gluten free pasta analyzed, a similar trend was observed regardless dough composition. When pasta was submitted to the hydrothermal process, similar values of critical strains were observed for all the studied cooking times (Fig. 3). However, for uncooked dough, samples start to flow at lower strain values and both moduli remain constant up to $\gamma = 1 \times 10^{-3}$, approximately. Hyun et al. (2002) observed that the behavior of storage and loss moduli with strain variation could be classified by at least four types of strain-amplitude dependence for complex fluids, i.e., strain thinning (type I: G'

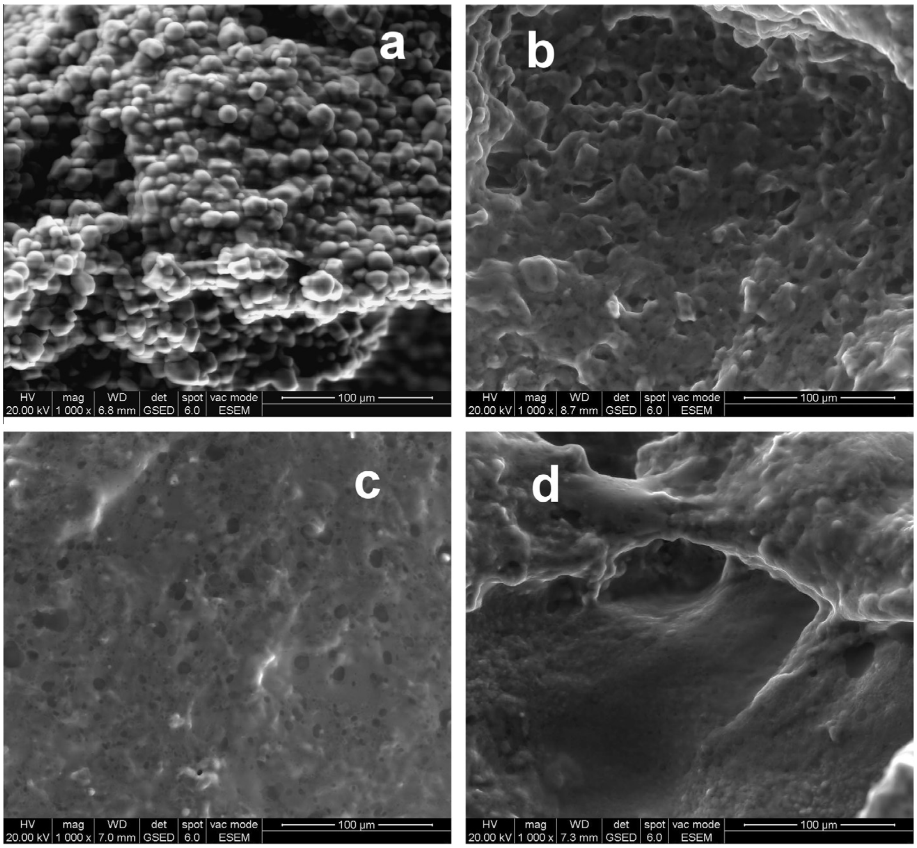

Fig. 2. Environmental scanning microscopy gluten-free pasta cooked matrices for formulation W2EP2 (36.13% water and 4.65% egg-proteins): (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min. White bars indicate 100 µm.

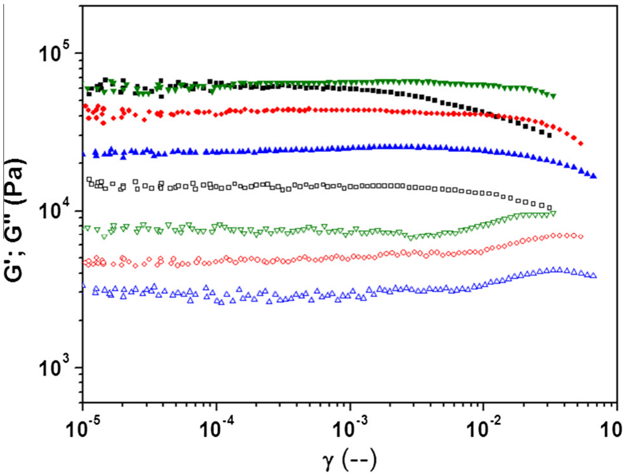

Fig. 3. Strain sweeps for a pasta dough containing 36.13% water and 6.6% proteins (formulation W2EP3) at different cooking times. G' (fill symbols), G'' (open symbols). (■, □) 0 min, (●, ○) 5 min, (▲, △) 10 min, and (▼, ▽) 15 min.

and G'' decreasing); strain hardening (type II: G' and G'' increasing); weak strain overshoot (type III: G' decreasing, G'' increasing followed by decreasing); strong strain overshoot (type IV: G' and G'' increasing followed by decreasing). Cooked pasta of this study could be classified as type III regardless cooking time, since they presented a monotonic decay in the elastic modulus and a non-monotonic change in the loss modulus. G'' increased from its low strain value and then decreased with further increase in the strain amplitude. For the network model, type III is found when the creation rate of network junctions is smaller than their loss rate. Thus, the overshoot (i.e. local maximum of G'') may be regarded as arising from the balance between the formation and the destruction of the network junctions (Lorenzo et al., 2015). Specifically, the maximum of G'' depends more on the creation rate than on the loss rate (Hyun et al., 2011). Fig. 3 shows as an example the strain dependence of both moduli for the formulation W2EP3 at different cooking times.

On the other hand, uncooked dough (cooking time $t = 0$) exhibited a strain thinning behavior (Type I). This type of behavior is most easily observed in polymer solutions and melts (Hyun et al., 2002). The origin of strain thinning is believed to be similar to that of shear thinning. Polymer chains are in a state of entanglement in the small strain region, where G' and G'' are constant. As the strain is increased, polymer chains disentangle, and then align with the flow field. This effect becomes more significant in anisotropic systems which flow more readily, and the moduli subsequently decrease further (Fig. 3).

The mechanical spectra showed a markedly difference between the uncooked pasta and the cooked specimens for all formulations (Fig. 4). Particularly, for the formulations described in Table 1, uncooked dough showed stronger frequency dependence of both moduli with higher values of the loss moduli than cooked pasta samples. This behavior corresponds to a more viscous contribution with a matrix more easily deformed under applied stress. At the studied frequencies, G' values were higher than G”, meaning that gluten-free dough had a behavior more elastic than viscous. Similar behavior was identified by other authors on gluten-free formulations made with rice flour (Gujral and Rosell, 2004; Marco and Rosell, 2008; Sivaramakrishnan et al., 2004). In all cases, dough behaved like viscoelastic materials in the *rubbery* or *plateau* region, that is, where elastic characteristics dominate. While in many cases the region appears to be a flat plateau, there is always a slight increase of G' with frequency, but it can be as small as a few

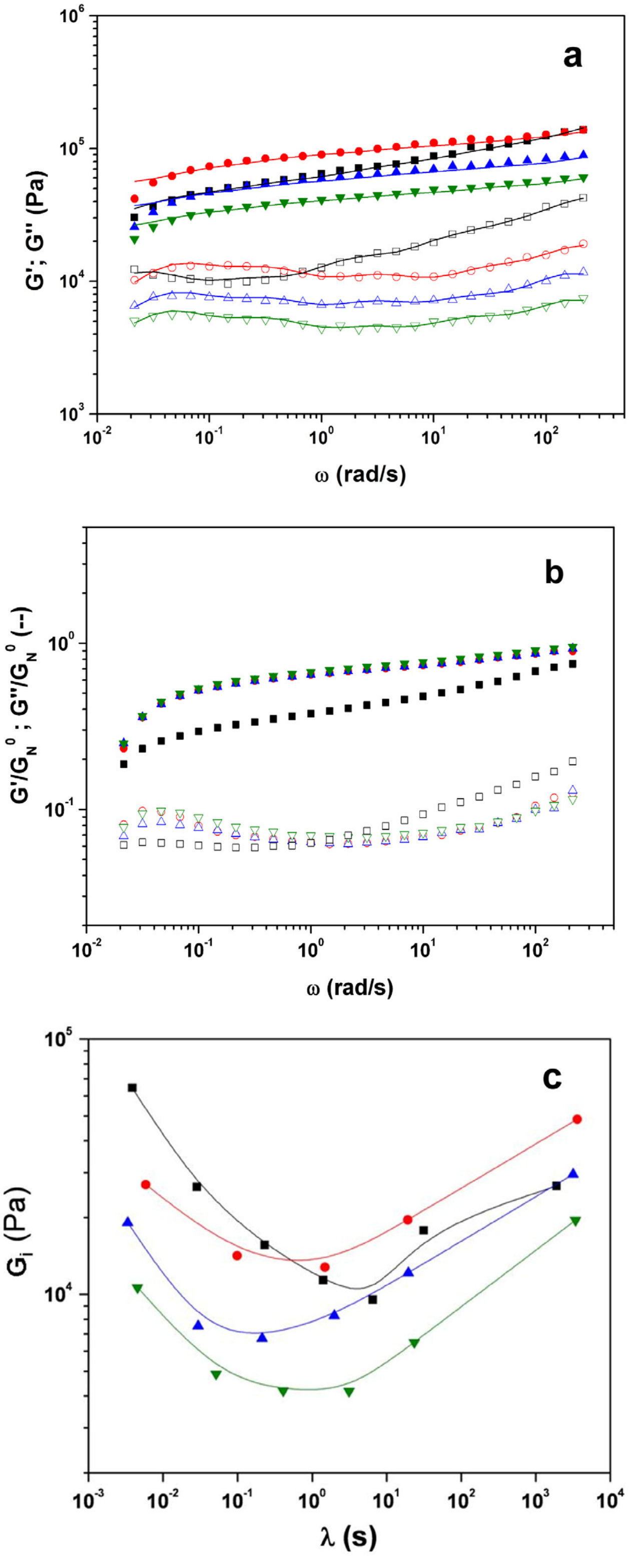

Fig. 4. Dynamic frequency sweep data for a pasta dough containing 36.13% water and 6.6% proteins at different cooking times (W2EP3). (a) Symbols correspond to original data (G', G''): (■, □) 0 min, (●, ○) 5 min, (▲, △) 10 min, and (▼, ▽) 15 min; continuous lines correspond to Maxwell model; (b) normalized dynamic master curves of the elastic ($G'/G_N{}^0$) and viscous ($G''/G_N{}^0$) moduli: (■, □) 0 min, (●, ○) 5 min, (▲, △) 10 min, and (▼, ▽) 15 min. (c) Relaxation moduli G_i as a function of the relaxation times λ_i for formulation W3EP1 containing 37.5% water and 2.7% egg-protein subjected to different cooking times. (■) 0 min, (●) 5 min, (▲) 10 min, and (▼) 15 min.

percent increase in modulus per each ten increase in frequency (Barnes, 2000).

Fig. 4 shows, as an example, the mechanical spectra for a gluten-free pasta formulation containing 36.13 g/100 g water and 6.6 g/100 g proteins at different cooking times (0, 5, 10, and 15 min). Again for cooked pasta the value of G'' was always lower than of G', but the gap between both moduli was wider than in the case of raw specimen spectra. The slope of the storage modulus versus frequency curve (G', ω) was particularly low for all cooked pasta; the value of G'' decreased with increasing frequencies, toward a minimum before rising again, being at the minimum point, $G'/G'' > 10$. Additionally, both moduli showed the same behavior decreasing significantly as cooking time increased.

3.3.2. Discrete relaxation spectrum

In the present work, a non-linear numerical method, proposed by Baumgaertel and Winter (1989, 1992) and Winter (1997) (IRIS method, using the software IRIS Rheo-hub 2007) was used to determine the parameters N, G_i and λ_i of the generalized Maxwell model described in Section 2.8. An iterative process using simultaneously Eqs. (2) and (3) was employed to minimize the sum of the square differences. The computed G_i and λ_i values were used to predict the storage and loss moduli. As can be observed in Fig. 4a, there is an excellent agreement between the experimental and predicted values, confirming the accuracy of the calculations.

Once the relaxation time spectrum was known other material functions such as the plateau modulus $G_N{}^0$ were evaluated from the discrete relaxation spectra of each frequency sweep curve as the sum of the relaxation moduli (Mead, 1994). The plateau modulus ($G_N{}^0$) is a viscoelastic parameter defined for polymers as the extrapolation of the entanglement contribution to the viscoelastic functions at high frequencies. This parameter can be considered as a characteristic parameter of this region and may also be estimated from the minimum in the loss tangent ($\tan \delta = G''/G'$) (Baurngaertel et al., 1992; Lorenzo et al., 2011).

For each formulation frequency sweep curves were superimposed using the inverse of the corresponding plateau modulus ($G_N{}^0$) as a normalization factor to obtain the master curves (Fig. 4b). As it can be seen the superposition is excellent for the different cooking times; conversely, normalized spectra of raw specimens exhibited a markedly different behavior from the cooked samples. In raw dough exists a three-dimensional network of interacting or entangled carbohydrate and protein molecules that traps the starch granules. Corn starch and corn flour particles probably acted as inactive fillers because of their inability to form a cohesive network, which was mainly formed by the xanthan/locust bean gums (Aguilera and Rojas, 1996; Ravindra et al., 2004). After 5 min of hydrothermal treatment the partially gelatinized starch had swollen and formed continuous phase of solubilized amylose and/or amylopectin. Egg proteins were completely denaturized and gelled. Once the raw matrix was transformed by the water uptake and chemical reactions, the microstructure of the specimens was similar within each formulation. Thus, it was possible to obtain a common master curve regardless of cooking time.

Fig. 4c shows relaxation time spectra (G_i vs. λ_i) for the different cooking times corresponding to formulation W3EP1. The relaxation spectrum passes through a minimum in the region were the storage modulus is flat, separating the two sets of relaxation times corresponding to the motions within entanglements strands and motions across entanglements loci (Ferry, 1980). There was a noticeable difference between the shape of raw and cooked pasta relaxation spectra. The G_i, which is an index of the concentration of the relaxation process at a particular time, indicated different

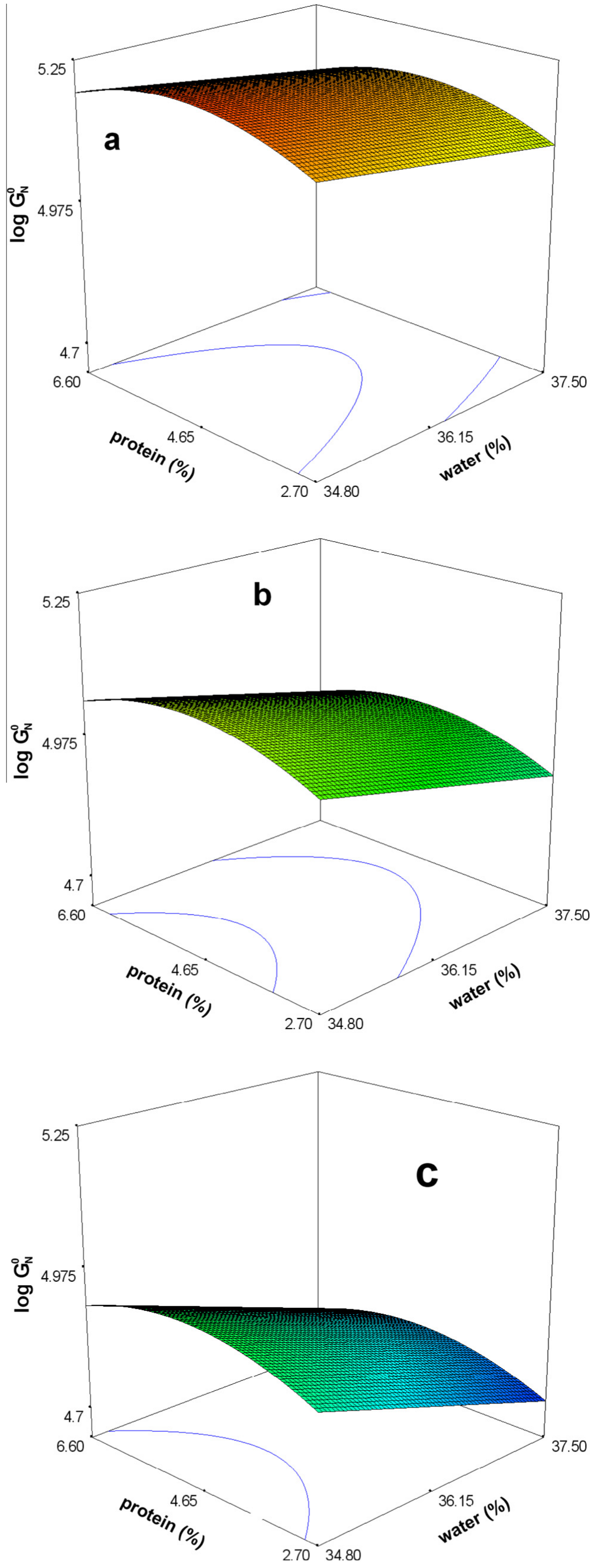

Fig. 5. Effect of cooking time and formulation on the plateau modulus ($G_N{}^0$) of gluten-free pasta: (a) 5 min, (b) 10 min, and (c) 15 min.

macromolecular structures in the dough; the longest relaxation times are associated with the largest molecules. The relaxation process in the assayed gluten-free dough can be separated into two phases, one occurring at short time periods (10^{-3}–10^{-1} s) and the other at longer time periods (1–10^4 s). Raw dough exhibited a sharper spectrum than the cooked samples. On the other hand, the shape of the relaxation time spectra became broadened, with an overall decrease in G_i as cooking time increased between 5 and 15 min and more water diffused into the system.

All the previous analysis showed that hydrothermal treatment produced a significant microstructural change within the entanglements network of the gluten-free pasta dough. For all the formulations studied, water uptake by the matrix, partial gelatinization of the starch and the aggregation of denatured egg proteins led to chemical and morphological changes, which could be observed through the rheological behavior.

The surface response of the plateau modulus as a function of initial water and egg-protein contents was regressed at the different cooking times assayed (Fig. 5). It could be observed a marked decrease of $G_N{}^0$ when cooking time was increased regardless the initial composition of the dough; as cooking time proceeded it became easier to deform dough samples. When pasta is cooked water diffuses into the matrix, leading to a decrease in the melting temperature of the starch crystallites below that of the boiling water. This process leads to a decrease in the number of physical crosslinks between macromolecules caused by the melting of the order domains in the starch. Water keeps penetrating in the matrix of the dough and this promotes the marked softening of the pasta (Cunin et al., 1995; Del Nobile et al., 2003). These physical changes led to a reduction of the elasticity of the pasta and the consequent reduction of the plateau modulus (Fig. 5). Particularly, formulation W3EP1 (W = 37.5%, EP = 2.7%) exhibited the lowest values of $G_N{}^0$ for all cooking times. Increasing initial water content in the dough produced less elastic products ($<G_N{}^0$), although the effect was smaller at long processing times, in which the absorbed water tended to the equilibrium.

4. Conclusions

All cooked GF pasta showed a gel-like behavior, with the storage modulus always higher than the loss modulus, and with a slight dependence on frequency.

Oscillatory spectra were satisfactorily modeled using the Maxwell Generalized model. For each formulation frequency sweep master curves were obtained by using the inverse of the plateau modulus ($G_N{}^0$) as a normalization factor. All cooked formulations were satisfactorily superimposed for the different cooking times, whereas the characteristics of the normalized spectra of raw specimens were markedly different from the cooked samples.

Hydrothermal treatment produced a significant microstructural change within the network entanglements of the gluten-free pasta dough. During the first 5 min of aqueous heating egg proteins gelled and starch was swollen and partially gelatinized, forming a continuous phase of solubilized amylose and/or amylopectin. Afterward, the raw matrix was so transformed by the water uptake and chemical reactions that the microstructure was similar within each formulation, but with lower plateau modulus when cooking time increased.

Acknowledgements

The authors are grateful to Tecnovo, S.A., Argentina, who provided the dried egg and the ovoalbumin protein for this study. The financial support of the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET), Agencia Nacional de Promoción Científica y Tecnológica and Universidad Nacional de La Plata are also acknowledged.

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