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Thermorheological Characteristics of Chestnut flour doughs at High Consistency: Effect of kappa/iota-Hybrid carrageenan

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Abstract

Rheology of commercial chestnut flour (CCF) doughs supplemented with kappa/iota-hybrid carrageenan (KI) was determined at different mixing peaks (C1, target consistency and C5, end consistency) using a controlled stress rheometer. The KI was extracted from *Mastocarpus stellatus,* and mixed with CCF dough at different concentrations (0.5, 1.0, 2.0%, flour basis, f.b.) in the presence of sodium chloride (2.5%, f.b.). Tests conducted in the rheometer were creep-recovery (loading of 50 Pa for 60 s, 30°C) and temperature sweep (30-180°C) measurements. Results showed that mixing properties of doughs were improved at the proposed consistency, mainly in terms of stability at the mixing stage and starch heat resistance during dough processing. Rheology of chestnut flour doughs tested at C5 was improved by the addition of 1% KI. On the contrary, no significant differences were observed for those analysed at C1. Creep-recovery data (fitted by using Burgers Model) showed that the elasticity of doughs analysed at C5 improved with the addition of KI. Thermo-mechanical tests showed that the starch transitions were significantly promoted in the presence of KI. A supplementation of 2% KI has decreased the initial gelatinization temperature significantly (i.e. from 68°C to 60.4°C).

Keywords: Gluten-free; Gelatinization; Creep-recovery; DMTA; *Mastocarpus stellatus* red seaweed; Starch transitions.

Abbreviations: CCF: Commercial chestnut flour; CFF: Chestnut flour fraction; DMTA: Dynamic mechanical thermal analysis; DSC: Differential scanning calorimetry;HPMC: Hydroxypropylmethyl cellulose; KI: kappa/iota-Hybrid carrageenan; RVA: Rapid visco analyser; WA: Water absorption

Introduction

The demands for gluten-free bakery products were raised with an increasing trend in the number of celiac patients (intolerance to the gliadin protein in wheat). Chestnut flours, i.e. free of the toxic prolamins for celiac people, could be a suitable alternative to satisfy their demands for bakery products. Besides, chestnut flour is a good source of sucrose and essential fatty acids [1]. Nevertheless, chestnut flour doughs are low in proteins with viscoelastic properties like gluten, which leads to weak interactions between the components of the dough that are typical to the gluten-free flours [2].

Gluten-free doughs must exhibit appropriate viscoelastic characteristics to maximise the chances of acceptance by the final product consumer. Assorted common ingredients (sugars, salt, fibre, fat or different types of hydrocolloids, among others) are usually used at different ratios in bakery products [3]. These additives show an important role in gluten-free doughs in order to help in mimicking the gluten properties. The specific impact of each additive on commercial chestnut flour dough have been already reported in previous papers (see as *e.g.*) [2,4,5]. Those studies pointed out the fact that chestnut flour dough are very viscous. The supplementation with other gluten-free flours (as chia flour) or classical gelling agents (as HPMC) is necessary in order to improve the technological aptitude of these doughs. Chestnut flour doughs supplemented with these promising additives exhibited high stability at the mixing stage, starch stability and heat resistance to dough processing and improved elasticity. Even though, the rheological characteristics are not fully suitable for further processing. Therefore, the effect of new natural gelling additives as hybrid carrageenans should be assessed, which can be helpful to agglutinate the dough for optimal bakery formulations. The handling of processing conditions [mixing target consistency (proportional to the measured torque) or mixing temperature] could be another possibility in order to improve the rheological behaviour of chestnut flour doughs.

Carrageenans are natural biopolymers contained in specific species of red seaweeds belonging to the *Gigartinales* order. These biopolymers exhibit many uses as a gelling, thickening and stabilising food additive [6]. Carrageenans are polysaccharides that show variety of chemical structures, resulting from a complex interplay between the seaweeds species, the seaweed life stage, and the extraction process used to recover the polysaccharide [7]. Among the various types of carrageenans with different gelling or viscosity enhancement properties, hybrid carrageenans have recently received increased interest. These biopolymers play an important and valued role in modern-day formulations providing texture, structure and physical stability in food products [8]. Namely, KI could be applied in a wide range of water-based products, puddings, pastas or frozen doughs [9]. Some of the traditional uses of these biopolymers are water dessert gels and cake glazes [6]. These products are based on the firm, brittle gel properties of kappa carrageenan with the texture modified as necessary for elasticity, cohesiveness and syneresis control using iota carrageenan [10].

Rheological behaviour of the flour dough is important in bakery processes and also useful to produce better quality products, mainly in gluten-free flours [11]. Viscoelastic characteristics of gluten-free doughs can be studied using rheological testing to determine fundamental dynamic properties that are recording during well-characterised deformations [2]. The study of the thermo mechanical properties of doughs is critically relevant in optimising product development, manufacture methodology or final product quality as well as is useful to determine the stability of foodstuff during and after processing [12].

In this context, this paper aims to contribute to the current knowledge in this field by addressing (i) the mixing properties of doughs from a fractioned chestnut flour (CFF) by particle size supplemented with KI at different concentrations (0.5, 1.0, 2.0%, flour basis, f.b.) in the presence of sodium chloride (2.5%, f.b.) at proposed consistency (2.5 Nm) and (ii) the rheological behaviour at different mixing consistencies (C1, target consistency and C5, end consistency) by analysis of the corresponding parameters from creep-recovery and temperature sweep tests.

Experimental

Raw materials

Commercial chestnut (*Castanea sativa Mill.*) flour (CCF) (moisture content: 9.5 ± 0.4%, f.b.) was supplied by a local food company (Castañas Naiciña, Lugo, Spain). Chemical composition (g/100 g) of the main CCF components (7.0 of protein, 74.9 of carbohydrates, 5.7 of fat and 0.1 of salt) was provided by the supplier.

Fresh *Mastocarpus stellatus* seaweeds (moisture content of 66.6 ± 2.2%, wet basis) were kindly provided by Conservas Mar de Ardora company (A Coruña, Spain). Samples were carefully washed with fresh water and selected according to their size (around 20 cm) and colour (reddish) and KI gum as a hydrocolloid was extracted out of them. The seaweed processing consisted in four steps: i) drying at 35°C (end moisture content: 9.1 ± 0.5% dry basis, d.b.), ii) milling (average particle size: 77.5 µm), iii) seaweed powder equilibration (moisture content: 9.9 ± 0.3% d.b.) in an environment with a constant relative humidity (54% at 20°C) generated with a saturated solution of $Mg(NO_3)_2$, and iv) storage at 4°C in vacuum sealed bags to ensure preservation until the extraction of KI. This biopolymer was extracted using a set of optimized parameters as described earlier in detail [13]. An analytical grade sodium chloride from Sigma-Aldrich, Inc., St. Louis, MO was used to ensure the complete dissolution of the carrageenan.

Physical and chemical properties

The average particle size of the CCF was determined by sieving, employing standard sieves of 40, 63, 80, 125, 200, 250 and 500 µm (Standard ISO-3310.1, Cisa Cedacería Industrial, Spain). The highest fractions (> 200 µm) of CCF were milled using an ultra-centrifugal mill (ZM 200, Retsch GMBH, Germany) with an internal sieve of 200 µm in order to mimic the common particle size in commercial flours. The resultant chestnut flour was mixed with the lowest fractions (< 200 µm). The mixture was labelled as CFF and used as a control sample. The average particle diameter by mass (D_w) was calculated considering the average particle size, D_{pi} (µm), of each mass fraction, w_i (%). Moisture content of the studied chestnut flour was evaluated (after milling) according to ICC Method No. 110/1 [14]. The amylose content, total and damaged starch content of CCF and CFF samples were determined using three different enzymatic test kits (Megazyme, Wicklow, Ireland). All chemicals used for pH solutions and other reagents for different tests were of analytical grade. All analyses were performed at least in triplicate.

Dough processing

Two different tests were conducted at least in triplicate on Mixolab® apparatus (Chopin, France) to prepare and characterize CFF doughs following standard methods described for wheat flours [14]. Briefly, the first one, a mixing test; consisted in the dough mixing at constant mixing rate (80 rpm) and temperature (30°C) during 30 min until the torque produced by dough achieved the target consistency (C1: 1.10 ± 0.07 N m), which corresponds with the same consistency reached by wheat flours in industrial dough. A modification of the standard protocol (new target consistency, C1: 2.50 ± 0.07 N m) was performed in order to improve the mixing dough properties. At fixed consistency, the dough mixing properties as WA level, development time (*i.e.* time for achieve C1) and stability time (*i.e.* torque stability) were determined. The second one, a complete test; after a shorter (8 min) mixing step, involves a heating-cooling cycle (37 min) and provided similar information on dough behaviour that the assays performed with RVA.

In both tests, CFF with several KI content (0.5, 1.0, 2.0%, f.b.) and common bakery sodium chloride content (2.5 % f.b.), labelled as CFF0.5, CFF1.0 and CFF2.0, respectively, was placed into the Mixolab® bowl. The contents of the bowl was mixed and heated by keeping same conditions before mixing test for sample homogenization. At this moment, the apparatus adds distilled water to achieve pre-fixed hydration, taking into account that Mixolab® was programmed to adjust the initial moisture content of samples to 14 % (f.b.) in order to establish a comparison between all assayed CFF. The total mass of flour, biopolymer, salt and distilled water placed into bowl was 75 g. Several preliminary mixing tests were necessary to determine the hydration level to reach the target consistency of dough (C1). Complete test has been carried out after determination of the optimum hydration level to characterize the dough properties as function of mixing and temperature. Namely, several peak torques (C2, C3, C4, C5) as well as the initial (T_0) and final (T_1) gelatinization temperatures has been evaluated (see Figure 1). Additional information about parameters obtained from Mixolab® tests were previously reported [5].

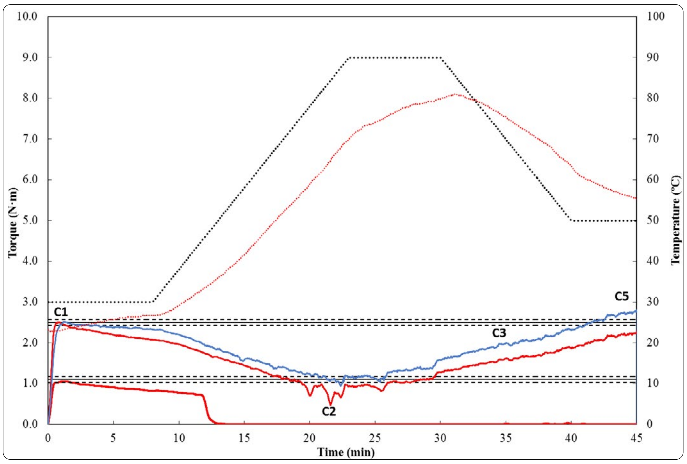

Figure 1. Mixolab® curves for selected CFF doughs prepared at studied target torques. Symbols: CFF (WA, 40.3%, Torque 1.1 Nm) (red line), CFF (WA, 29.4%, Torque 2.5 Nm) (red line), CFF1.0 (WA, 30%, Torque 2.5 Nm) (blue line), bowl temperature (black dotted line), CFF dough temperature (red dotted line) target torque (dashed lines). Curve corresponding to the dough temperature is presented as representative example for CFF dough prepared at proposed consistency (2.5 Nm).

Rheological measurements

Rheological tests were conducted on a controlled stress rheometer (MCR 301, Anton Paar Physica, Austria) equipped with a chamber (CTD 450, Anton Paar Physica, Austria) using sand-blasted parallel plates (50 mm diameter and 2 mm gap) to prevent wall slippage. Samples (*i.e.* doughs previously prepared using Mixolab® up to reach C1 and C5) were loaded carefully to ensure minimal structural damage, and held at rest for 5 min before testing to allow stress relaxation and temperature equilibration. A thin film of Paraffin (Panreac Química S.A.) was applied to the exposed sample edges to prevent evaporation. Initial testing on a series of samples showed little difference between measurements made within 2h of sample preparation so all tests were conducted within this time frame. All measurements were done in duplicate. Error bars were plotted where the measurement uncertainty was greater than the symbol size.

Viscoelastic behaviour was studied under isothermal conditions (30°C) using creep-recovery tests. Initially, a series of creep curves were obtained by sequentially increasing the applied stress (from 10 to 200 Pa). Curves from resulting data, plotted in terms of compliance *vs.* time, overlapped for stresses <150 (Pa), indicating the linear viscoelastic region. Afterwards, creep phase was performed at constant stress, σ = 50 Pa, during 60 s within linear viscoelastic region, while recovery phase was maintained at σ = 0 Pa during 180 s. Creep data was described in terms of creep compliance, $J(t)$ (Pa^{-1}) = γ/σ, where σ represents the constant stress during creep test [15]. Compliance curve data of assayed CFF doughs for creep (Eq. 1) and recovery (Eq. 2) phase were fitted to the Burgers model [16]:

$$J(t) = J_0 + J_m (1-\exp(-t/\lambda)) + t/\eta_0 \tag{1}$$

$$J(t) = J_{max} - J_0 - J_m (1-\exp(-t/\lambda)) \tag{2}$$

where J_0 (Pa^{-1}) is the instantaneous compliance, J_m (Pa^{-1}) is the viscoelastic compliance, λ (s) is mean retardation time, t (s) is the phase time, η_o (Pa s) is the zero shear viscosity and J_{max} (Pa^{-1}) is the maximum creep compliance. The recovery compliance, J_r (Pa^{-1}), evaluated at equilibrium of dough recovery, is evaluated by the sum of J_0 and J_m. The J_r/J_{max} ratio gives information on relative elastic part of the maximum creep compliance.

DMTA was employed to monitor the elastic modulus, G′, and viscous modulus, G″, with temperature in order to determine the temperatures associated with thermal transitions. Heating temperature sweeps (from 30 to 180°C with a constant heating rate of 4°C/min) were performed at a strain amplitude of 0.1% and 1Hz, below the limit of the linear viscoelastic region (<1.0%). Previously, strain sweeps (0.01–10%) were performed over the range 30 to 180°C at an angular frequency of 1Hz.

Statistical analysis

Experimental data were analysed using one-factor analysis of variance (ANOVA). A Scheffé test was performed to differentiate means with 95% confidence ($p < 0.05$) when the analysis of variance indicated differences among means. All statistical treatments were done using PASW Statistics (v.18, IBM SPSS Statistics, New York, USA).

Results and Discussion

Raw characterization

Average particle sizes in mass and mass fractions of studied commercial chestnut flour (*i.e.* CCF and CFF) are shown in table 1. Both flours exhibited significantly different average particle size with values of 186.6 μm and 96.6 μm, respectively. CCF exhibited an important population (34.9%) of coarser particles (> 200 μm). In both tested flours, a large mass fraction (between 53.2 and 56.3%) of particles was found from 80 to 200 μm. CFF also displayed a large population (33.8%) ranged from 63 to 40 μm. Particles with sizes between 80 and 63 μm were the third most important fraction (9.1%) for CFF, followed by factions below 40 μm (3.9%). The population of fractions below 80 μm strongly increased for flour samples with shorter average particle size. These values are consistent with those previously reported for other gluten-free flours [17].

Table 1. Average particle size in mass, D_w, particle size distribution and starch characteristics of studied chestnut flours.*

	D_{pi} (μm)	w_i, mass fraction (%)	
		CCF[2]	CFF[3]
Particle size properties			
$250<x^1<500$	375.0	17.9±0.2	-
$200<x^1<250$	225.0	17.0±0.1	-
$125<x^1<200$	162.5	34.8 ± 0.3^a	28.3 ± 0.1^b
$80<x^1<125$	102.5	21.5 ± 0.1^b	24.9 ± 0.3^a
$63<x^1<80$	71.5	1.9 ± 0.1^b	9.1 ± 0.2^a
$40<x^1<63$	51.5	6.3 ± 0.2^b	33.8 ± 0.1^a
$x^1<40$	20.0	0.7 ± 0.1^b	3.9 ± 0.2^a
Average particle size, D_w (μm)		186.6 ± 11.5^a	96.6 ± 2.4^b
Starch properties			
Total starch (% w/w, d.b.)		41.7 ± 2.2^a	40.8 ± 1.2^a
Amylose content (% w/w, d.b.)		24.1 ± 0.3^a	23.9 ± 0.4^a
Damaged starch (% w/w, d.b.)		3.2 ± 0.1^a	3.5 ± 0.2^a

*Data are presented as mean ± standard deviation. Data values in a row with different superscript letters are significantly different at the $p \leq 0.05$ level.

[1] The chestnut flour fraction is represented by x (μm).

[2] Commercial chestnut flour has been labelled as CCF.

[3] Commercial chestnut flour after milling the highest factions (x>200 μm) has been labelled as CFF and used for all tests in this work.

Chemical composition (% w/w, d.b.) of the chestnut flour starch, as main component of this flour, is also given in Table 1. No significant differences were observed between CCF and CFF samples. Total starch (*i.e.* starch amount without gelatinize before the analysis) presented average values between 41.7 and 40.8%. These starch values are notably lower than those previously reported for commercial chestnut flour (64.4%) [5], even though are in the range of those previously reported for several chestnut varieties [18]. Average amylose content ranged from 23.9 to 24.1%. These values agreed with those previously reported elsewhere for chestnut starch [19] and other gluten-free starches [20]. Damaged starch (*i.e.* starch fraction that is thermal or mechanically modified during processing) exhibited low average values (<3.5%), independently of the chestnut flour average particle size. Similar values to those previously obtained for chestnut flour [5] and notably lower than those (<10.5%) reported for other gluten-free flours [21]. Overall, above results point out that it is possible to reduce the CCF average particle size, without variations in starch composition, in order to obtain softer flours with particle sizes commonly used in the industry. Consequently, CFF sample has been selected in this work to assess the technological aptitude of its doughs using empirical and fundamental rheological measurements.

Empirical rheology

Table 2. Values of parameters from Mixolab® curves for selected CFF doughs prepared at studied target torques.

Additives	-		Kappa/iota-hybrid carrageenan (w/w, % f.b.)		
Parameters	CFF		CFF0.5	CFF1.0	CFF2.0
Target torque, C1 (Nm)	1.1 ± 0.07^b	2.5 ± 0.07^a	2.5 ± 0.07^a	2.5 ± 0.07^a	2.5 ± 0.07^a
Water absorption (%)	40.3 ± 0.3^a	29.4 ± 0.5^b	29.7 ± 0.3^b	30.0 ± 0.4^b	30.4 ± 0.4^b
Development time (min)	1.5 ± 0.1^a	0.7 ± 0.3^b	1.0 ± 0.1^b	1.1 ± 0.1^b	1.2 ± 0.2^b
Stability time (min)	2.1 ± 0.2^c	2.0 ± 0.1^c	3.4 ± 0.2^b	5.5 ± 0.1^a	5.7 ± 0.1^a
Minimum torque, C2 (Nm)	-	0.7 ± 0.1^b	1.0 ± 0.1^b	1.3 ± 0.1^a	1.4 ± 0.1^a
Peak torque, C3 (Nm)	-	1.2 ± 0.1^c	1.5 ± 0.1^b	1.8 ± 0.1^a	1.9 ± 0.1^a
Peak torque, C4 (Nm)	-	-	-	-	-
Peak torque, C5 (Nm)	-	2.2 ± 0.1^c	2.5 ± 0.1^b	2.8 ± 0.1^a	2.9 ± 0.2^a

Data are presented as means ± standard deviation. Data value with different superscript letters in columns are significantly different, $p \leq 0.05$.

The experimental curves obtained by Mixolab® complete tests for representative CFF doughs prepared at standard (C1, 1.1 Nm) and proposed consistency (C1, 2.5 Nm) are shown in figure 1. It was observed that chestnut flour doughs at standard consistency were not able to complete the mixing curve, even in the presence of KI, and thus, no further fundamental rheological evaluation was conducted. The proposed consistency (C1) represents the minimum necessary torque (2.5 Nm) in order to obtain complete curves for CFF doughs in the absence of additives with the selected average particle size (96.6 μm). Likewise, the rise in the target consistency led to changes at the mixing parameters (Table 2). Namely, the WA level significantly dropped (from 40.7 to 29.4%) for CFF doughs prepared at 2.5 Nm, which is consistent with previous results [4]. Likewise, a positive reduction in development time (from 1.5 to 0.7 min) up to reach the target consistency was found for CFF doughs prepared at 2.5 Nm, whereas no statistical differences were observed in the stability time (about 2 min). Concerning the stability, it should be mentioned that obtained values are in well harmony with those reported for other gluten-free flour doughs [22,23], nevertheless are low when compared with those achieved for other flours commonly used in bakery industry such as wheat (5-8 min) or oat (4-5 min) flours [24,25]. This stability lack could be overcame for CFF doughs prepared at proposed consistency in the presence of KI and sodium chloride, since this parameter was significantly increased with increasing KI, remaining practically constant above 1% KI (*i.e.* CFF1.0 doughs) (see Figure 1 and Table 2). The stability value is an indication of flour strength, suggesting softer doughs with lower stability values [26]. No significant differences were noticed in other mixing parameters by the addition of KI in the presence of salt to CFF doughs. This behavior is consistent with the results previously found for doughs prepared with commercial chestnut flour showing larger average particle sizes (168.6 ± 6.6 μm) and supplemented with several gelling agents (not require electrolytes to gel) such as agar or HPMC at standard target consistency 1.1 Nm, although the expected significant increase of WA by the biopolymer and salt addition was not observed. This can be explained by the low WA values used in these tests, which allow working at constant torque with invariant WA even in the presence of additives [4].

Figure 1 also shows that the torque began to decrease when the period of dough stability finishes, which is attributed to the weakening of the protein network by the combined effect of the mechanical shear stress and the temperature [17]. The consistency C2 (minimum torque), one of the protein weakening parameters, was affected positively (from 0.8 to 1.3 Nm, Table 1) by the KI addition, whereas no notable differences were observed in the protein network weakening rate (-0.094 Nm/min). Some noise can be noticed in C2 for CFF doughs in the absence of additives, which is consistent with the fact that CFF doughs were prepared at the minimum target torque which allow achieving complete curves. The minimum torque was detected in the range from 67.5°C to 60.5°C, where further protein changes during heating can be masked by the modification of the physicochemical properties of the starch. Above temperatures correspond with the initial gelatinization temperatures for CFF and CFF1.0 doughs, respectively. It can be clearly observed as the beginning of the gelatinization is enhanced in the presence of KI below 1%, whereas no notable variations were observed in the gelatinization rate (slope between C2 and C3, 0.089 Nm/min). No significant changes were observed by the addition of KI above 1%. As the temperature increases the changes in the starch granules are the main responsible of further torque variations. An increase in C3 in the presence of KI was found, which indicates higher starch stability and heat resistance to dough processing [27]. It was not possible to determine C4, peak torque related with the amylase activity, due to the low WA of tested doughs. Afterwards, a temperature decrease resulted in an increase of the torque due to the augmentation in the dough resistance for the starch gelling. The gelation process was again significantly affected by the addition of KI below 1% to the dough, remaining practically constant above this value with increasing KI content (Table 2). Concerning the consistency C5, it was negatively affected by the KI addition. Even though, the values of this parameter are in the range of those achieved for chestnut [4] and other gluten-free [28] flour doughs prepared at standard torque in the presence of other gelling agents as agar. Results indicated that the best effects on CFF doughs at proposed torque were achieved with KI at 1.0% and sodium chloride. This formulation could be adequate to obtain cookies, following the considerations previously reported for wheat flours [29]. These authors stated that wheat flours with high C3 and C5 values (around 2 and 3 Nm, respectively) can be considered as typical cookie flours with higher cookies diameter and spread ratio.

Fundamental rheology

The viscoelastic properties of tested doughs at two different consistencies (C1 and C5) obtained previously by Mixolab®, were determined at 30°C using creep-recovery tests. The creep-recovery curves, Figure 2, for CFF doughs indicated similar viscoelastic behaviour to those previously reported for other gluten-free formulations [22]. The maximum values of compliance, J(t), were much lower (below 0.0003 Pa^{-1}) than those given for wheat, rice and hydrocolloids blends (below 0.02 Pa^{-1}) [30] and wheat flour (below 0.01 Pa^{-1}) [31], but in the same order range of aforementioned gluten-free doughs obtained from rice flour in the presence of hydrocolloids as agarose (below 0.0009 Pa^{-1}) [22]. No significant differences were noticed in creep-recovery curves for CFF doughs tested at C1 by KI and salt addition. In contrast, these curves were significantly modified in the presence of the same additive for CFF doughs tested at C5. This result can be explained taken into account the KI gelling mechanism. Namely, this biopolymer needs high temperatures to be completely dissolved (about 90°C) in salt solutions, forming afterwards gels by cooling at different temperatures depending on the KI and salt content [7,32].

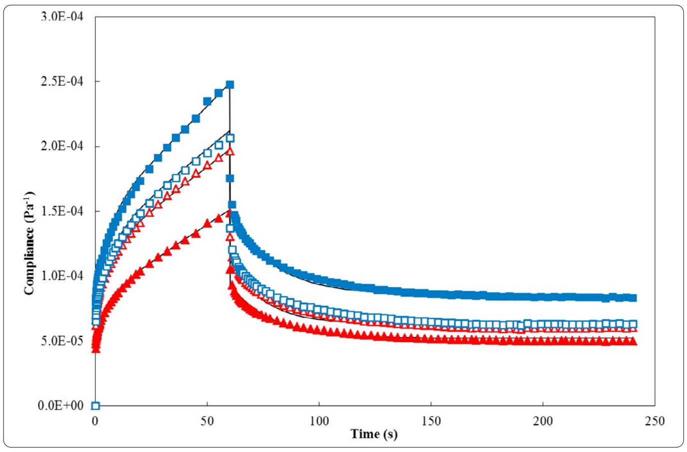

Figure 2. Creep (50 Pa, 30°C) and recovery data of selected CFF doughs prepared at target torque (2.5 Nm). Symbols: CFF (WA, 29.4%, C1) (red open triangles), CFF (WA, 29.4%, C5) (red closed triangles), CFF1.0 (WA, 30%, C1) (blue open squares), CFF1.0 (WA, 30%, C5) (blue closed squares). Lines correspond to Eqs.(1 and 2).

The experimental compliance curve data of all assayed doughs were successfully fitted (R^2>0.989 and 0.960 for creep and recovery, respectively) using the Burgers model, Eqs. (1) and (2), and the corresponding parameters are summarized in table 3. The analysis of creep phase, Eq. (1), indicated that all calculated creep parameters for CFF doughs tested at C5 varied significantly when compared with those tested at C1, where no significant differences were observed by the KI presence. Particularly, the instantaneous (J_0) and viscoelastic (J_m) compliances, the mean retardation time (λ) and the zero shear viscosity (η_0) for CFF doughs in the absence of additive tested at C5 decreased significantly with respect to those tested at C1. The reverse trend was observed for CFF doughs in the presence of additives, where all creep parameters increased significantly when compared with those tested at C1, excepting the retardation time. This parameter followed the same behaviour that CFF doughs without KI tested at C5.

The increasing of KI content in the presence of salt for CFF doughs tested at C5 also led to a significant increase of J_0, J_m and η_0, but without statistical differences between 1.0 and 2.0% KI. Concerning the viscosity at the steady-state, $\eta_{0,}$ (the terminal region of the creep phase), it should be pointed out that the behaviour (*i.e.* values and trends in the presence of additives) of this parameter for CFF doughs tested at C1 and C5 was in well harmony with the behaviour of complex viscosity (ranged from 7.2 10^6 to 9.0 10^6 Pa s) determined at low angular frequency (0.1 rad/s) from mechanical spectra (data not shown). Furthermore, previous studies for durum wheat dough found that the h_0 increased with strength [33]. The authors are not aware that the fundamental rheological studies for CFF or other gluten-free flour doughs tested at C5 were previously reported (even at standard torque).

The analysis of recovery phase, Eq. (2), nicely matched with the results obtained from the creep phase (Table 3). As expected within the linear viscoelastic region, J_0 and J_m for all tested doughs showed the same values as those obtained in the creep phase. The maximum compliance, J_{max}, exhibited the same trends as those aforementioned for creep compliances. Note here that an increase, by 2 orders of magnitude, in the recovery retardation time was observed in all cases when compared with those obtained in the creep phase. J_r/J_{max} ratio was positively modified for CFF doughs tested at C5 in the presence of tested additives, achieving the most enhanced elastic properties for CFF1.0 doughs (about 69%). The magnitude of this parameter was notably larger than the values obtained for chestnut flour doughs with larger particle size (168.6 μm) [4] and other gluten-free formulations [22], prepared and analysed at standard consistency in the presence of different gelling agents as agar or HPMC with similar concentrations (reported J_r/J_{max} varying from 20 to 59% depending on biopolymer nature and its content). In the case of chestnut flour doughs with different particle sizes, these differences can be also related with the larger specific surface of CFF doughs prepared here (*i.e.* lower particles sizes) and, hence the interactions between flour and additives are promoted. The obtained J_r/J_{max} ratio for CFF1.0 doughs prepared with KI in the presence of salt at proposed consistency and tested at C5 are close to those ratios reported for several types of wheat flour (around 65-70%) made at standard consistency and considerably larger WA levels (around 60%) [34].

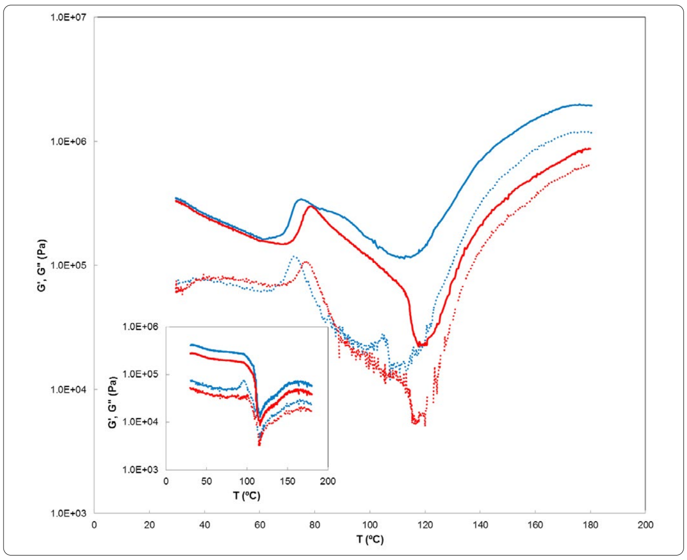

Figure 3. Temperature sweeps (from 30 to 180ºC) for selected CFF doughs prepared at target torque (2.5 Nm). Symbols: CFF (WA, 29.4%, C1) (red lines), CFF (WA, 29.4%, C5) (red lines, inset), CFF1.0 (WA, 30%, C1) (blue lines), CFF1.0 (WA, 30%, C5) (blue lines, inset). Symbols: G´ - continuous lines, G´´ - dotted lines.

Figure 3 displays the evolution of G´ and G´´ moduli during heating step in DMTA tests for representative CFF doughs (*i.e.* CFF and CFF1.0) analysed at C1 and C5 consistencies. The analysis at C1 showed that, at low temperatures, G´ values decreased slightly with increasing temperature up to achieve a minimum, which determines the beginning of the physical phenomena that take place during starch gelatinization (*i.e.* the swelling of the starch granules), and corresponds with the initial gelatinization temperature, T_0 (Table 4). It can be clearly observed that T_0 was positively promoted by the addition of KI (from 68 to 60.4ºC), in well harmony with the results found in Mixolab®. As expected, the values of T_0 identified for CFF doughs in the absence of additives were higher than those (56.9ºC) previously reported for CFF doughs with similar particle size and larger WA (50.9%) [23]. Moreover, with restricted water accessible the peaks are shifted at larger temperatures. In this first region (before T_0), no notable differences were found in the magnitude of the elastic modulus in the presence of tested

Table 3. Values of parameters from creep and recovery modelling, Burgers model, Eqs. (1 and 2), for studied CFF doughs prepared at target torque (2.5 Nm) and taken from Mixolab® in C1 and C5 in order to assess in the rheometer.

Tests	Parameters	C1				C5			
		CFF	CFF0.5	CFF1.0	CFF2.0	CFF	CFF0.5	CFF1.0	CFF2.0
Creep	J_0 10^5 (1/Pa)	6.9 ± 0.3^c	7.1 ± 0.3^c	7.3 ± 0.2^c	7.4 ± 0.3^c	5.1 ± 0.3^d	7.9 ± 0.1^b	8.3 ± 0.2^a	8.8 ± 0.3^a
	J_m 10^5 (1/Pa)	5.0 ± 0.3^c	5.2 ± 0.2^c	5.3 ± 0.2^c	5.5 ± 0.4^c	3.2 ± 0.1^d	6.2 ± 0.1^b	6.8 ± 0.2^a	7.2 ± 0.2^a
	λ (s)	6.8 ± 0.2^a	7.0 ± 0.3^a	7.1 ± 0.3^a	7.2 ± 0.4^a	6.0 ± 0.2^b	6.0 ± 0.2^b	6.1 ± 0.2^b	6.3 ± 0.2^b
	η_0 10^{-5} (Pa s)	7.6 ± 0.3^c	7.3 ± 0.3^c	7.2 ± 0.2^c	7.4 ± 0.3^c	6.8 ± 0.3^d	8.2 ± 0.1^b	8.7 ± 0.1^a	8.6 ± 0.2^a
	R^2	0.990	0.997	0.991	0.995	0.990	0.995	0.997	0.989
Recovery	J_{max} 10^5 (1/Pa)	18 ± 0.5^c	18.5 ± 0.5^c	19 ± 0.5^c	19.2 ± 0.6^c	14 ± 0.5^d	21.2 ± 0.2^b	23.4 ± 0.2^a	23.9 ± 0.3^a
	J_0 10^5 (1/Pa)	6.9 ± 0.3^c	7.1 ± 0.3^c	7.3 ± 0.2^c	7.4 ± 0.3^c	5.1 ± 0.3^d	7.9 ± 0.1^b	8.3 ± 0.2^a	8.8 ± 0.3^a
	J_m 10^5 (1/Pa)	5.0 ± 0.3^c	5.2 ± 0.2^c	5.3 ± 0.2^c	5.5 ± 0.4^c	3.2 ± 0.1^d	6.2 ± 0.1^b	6.8 ± 0.2^a	7.2 ± 0.2^a
	λ (s)	14.8 ± 0.3^a	14.9 ± 0.2^a	15.1 ± 0.1^a	15.3 ± 0.3^a	12.1 ± 0.3^b	12.8 ± 0.4^b	12.1 ± 0.4^b	12.3 ± 0.3^a
	J_r/J_{max} (%)	65.3 ± 0.6^c	66.1 ± 0.5^c	66.3 ± 0.4^c	66.4 ± 0.5^c	64.1 ± 0.2^d	68.1 ± 0.1^b	69.0 ± 0.1^a	69.2 ± 0.2^a
	R^2	0.961	0.963	0.965	0.976	0.960	0.965	0.971	0.965

Data are presented as means ± standard deviation. Data value with different superscript letters in rows are significantly different, $p \leq 0.05$.

additives. Subsequently, G´ sharply rose up to reach the peak gelatinization temperature, T_p, which also decreased (around 4°C) in the presence of studied additives (Table 4). Final gelatinization temperature, T_1, which can be evaluated through the point in which the slope of G´ changes after T_p, is not clearly identified. However, it has been well-stablished for different gluten-free flours using DSC and DMTA [23] that this first peak for CFF doughs corresponds to the addition of two transitions (*i.e.* gelatinization and amylopectin melting, M1). Therefore, although both peaks were not observed in DMTA, a broad temperature interval with G´ constant slop is obtained, and consequently, T_1 corresponding to M1 can be determined (Table 4). Similar trends and temperature values were observed for the G´´ modulus, although, in all cases, the value of this parameter was reduced about one decade when compared with those obtained for the G´ modulus. Above results agrees with those previously reported for CFF doughs in the presence of other gelling agents as agar [4].

Table 4. Values of onset (T0), peak (Tp) and final (T1) temperatures of thermal starch transitions determined by DMTA following the elastic modulus for tested CFF doughs tested at C1.

Peaks	Temperatures (°C)	C1			
		CFF	CFF0.5	CFF1.0	CFF2.0
Gelatinization	T_0	68.0±0.5^a	64.1±0.4^b	61.0±0.5^c	60.4±0.4^c
	T_p	79.7±0.2^a	77.1±0.2^b	76.1±0.3^c	75.8±0.4^c
	T_1	-	-	-	-
M1	T_0	-	-	-	-
	T_p	-	-	-	-
	T_1	108.6±0.5	-	-	-
M2	T_0	113.9±0.5^a	-	-	-
	T_p	119.8±0.3^a	117.6±0.3^b	115.5±0.3^c	115.3±0.4^c
	T_1	125.2±0.4^a	124.0±0.4^b	122.6±0.3^c	122.8±0.5^c

Data are presented as means ± standard deviation. Data value with different superscript letters in rows are significantly different, $p \leq 0.05$.

Concerning the impact of KI, a notably variation in G´ modulus was observed after T_p (Figure 3). This is consistent with the results reported for carrageenan/starch mixed systems analysed by RVA [35]. Latter authors found that the apparent viscosity peak was higher in the presence of carrageenan and the subsequent drop reduced, suggesting that starch/carrageenan interactions could modify starch granule rigidity or surface characteristics. This hypothesis could be in well harmony with our results, since the limitation of the softening of starch granules in presence of carrageenan could limit the drop in viscosity observed on the profiles (Figure 3). This behaviour also nicely matches with the results previously reported for rice flour doughs supplemented with a different gelling biopolymer [24]. Latter authors finding a two-step gelatinization process for rice flour doughs in the presence of HPMC up to 2.0%, where the first step involves the formation of a pre-gel at lower temperature and subsequent gelatinization produces a stable gel. Note here that for CFF doughs supplemented with KI and salt, an additional peak above 90°C (which seems to correspond with the KI solubilisation temperature,) [7] can be clearly observed in G´´. The area of this peak increased with increasing KI content (about 2 orders of magnitude), which corroborates that this transition is related to the KI presence.

In all cases, CFF doughs tested at C1 exhibited other starch transition around 120°C, which can be followed by the evolution of G´ and G´´ moduli with temperature. Both moduli passed through a minimum value. This transition (M2), corresponding to amylose–lipid complexes melting, is shifted to lower temperatures in the presence of additives (see Figure 3). T_0 and T_1 temperatures were determined by means of slope changes of G´ before and after T_p, respectively, with increasing temperature (Table 4), except for T_0 in the presence of KI which was not clearly observed. The M2 peaks took place in a narrow interval of temperatures (around 13.5±1.5°C). The values of temperatures corresponding with M2 transition are again consistent with those previously reported for chestnut flour doughs [36], shifted to larger temperature values due to the initial low WA of the doughs studied here. An additional peak (M3), corresponding to the melting of amylose, has been found around 135°C for other gluten and gluten-free flour doughs with similar physicochemical properties (see Table 1). However, this peak has not been reported in doughs with low WA levels [23]. Above M2 transition, both moduli values increase sharply during baking by the complex phenomena related to the crust formation that give as result a more rigid and stiff material. This behaviour is notably enhanced by the addition of studied additives for CFF doughs tested at C1, sign of a synergistic effect between starch and carrageenan [35].

The analysis of CFF doughs in consistency C5 indicated that all starch has been fully gelatinized during Mixolab® tests (see inset Figure 3). It can be clearly seen that G´ and G´´ moduli for CFF doughs without additives remained practically constant during the temperatures corresponding with the gelatinization transition. It should be remarked that the same behaviour was observed for G´ in the presence of tested additives, however G´´ showed a peak around 90°C (as previously observed for doughs with KI tested at C1). Again, this peak seems to be related with the KI solubilisation. In the whole tested temperature range, the magnitude of G´ and G´´ moduli for CFF doughs tested at C5 varied in comparison to those values obtained in C1, decreasing for doughs without and increasing with additives. This variation was about one order of magnitude for doughs in the temperature range below 120°C. The positive viscoelastic increase observed in the presence of KI is consistent with the results previously found for doughs with high sugars content, as chestnut flour, supplemented with agar [12]. Latter authors explained that high sugar concentrations can assist the association of the agar network, with the consequent gel strength increase. By these properties, gelling agents as tested KI could be used in specific bakery products, such as cakes and doughnuts, where heat stability and good moisture stabilization are required [37]. Overall, these results are consistent with those previously obtained for creep-recovery tests. It should be highlighted that, in all cases (doughs tested at C1 and C5), no significant differences were found between CFF1.0 and CFF2.0. This agrees with the results obtained from empirical rheology, and suggest that CFF1.0 dough is the most promising formulation.

Conclusion

The improvement of the doughs technological aptitude by preparing doughs at high consistency as well as adding of natural gelling additives, as KI, (both relevant steps in the development of gluten-free bakery products) was measured by empirical and fundamental rheology of chestnut flour doughs. CFF doughs made at high consistency leading to an enhancement of stability at the mixing stage and starch heat resistance to dough processing. The increase of the viscoelastic properties of CFF doughs with KI addition in the presence of salt, tested at C5, promotes the doughs strength. The supplementation with 1% KI seems to be the most promising formulation to develop bakery goods based on chestnut flour doughs. Even so, low WA levels used in this work constitute an additional challenge in the chestnut flour doughs industrial processing. Future work is needed to be focused on the handling of other processing conditions as mixing temperature, in order to optimising gluten-free product development. Overall, this study delivered chestnut flour doughs showing promising rheological properties for a wide range of bakery applications, resulting from increasing the consistency during mixing step.

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