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ORIGINAL PAPER

# Influence of quinoa and zein content on the structural, rheological, and textural properties of gluten-free pasta

**Meli Sosa**[1] · **Alicia Califano**[1] · **Gabriel Lorenzo**[1,2]

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## Abstract

This work analyzed the effect of quinoa flour and zein protein on the rheological, structural, and physicochemical characteristics of gluten-free pasta throughout the production process. Supplementing corn flour with quinoa increased dough protein content and greatly decreased the elastic behavior of the dough. Water diffusivity in the dough matrix during the drying process decreased in the presence of quinoa and was related to the smooth homogeneous surface of the dough. Cooking quality of the final product was explained in terms of the rheological and microstructural characteristics using mathematical models that related dough composition with structural parameters. The presence of zein seemed to weaken the protein network; microstructure was more crumbly with starch granules not completely embedded in the carbohydrate–protein matrix. These structural features explained the lower cooking time, higher breakability, and low cohesiveness of cooked zein-containing pasta. The addition of zein negatively altered the structure of pasta, whereas quinoa flour resulted in a cooked product with good textural properties and higher protein content.

**Keywords** Quinoa · Zein · Rheology · Drying process · Microstructure

## Introduction

Celiac disease (CD) is an immune-mediated inflammatory disease of the upper small intestine in genetically predisposed persons triggered by the ingestion of the storage proteins (gluten) from wheat, rye, barley, and possibly oats [1]. Moreover, a new gluten-related syndrome, known as non-celiac gluten sensitivity (NCGS), has been recently identified and confirmed, through double-blind placebo-controlled trials [2]. The only treatment for celiac disease at present is a strict lifelong gluten-free diet, as even trace amounts of gluten are sufficient to cause an immune response [3] and, thus, the need for high-quality gluten-free foods. Gluten-free (GF) products have been around for years for people suffering from celiac disease. However, demand has now widened beyond medical needs.

Gluten corresponds to a protein fraction from cereals like wheat, barley, rye, oats, or their crossbred varieties and derivatives thereof, mainly composed of prolamins and glutelins. In wheat, these protein fractions are called gliadins and glutenins, and form a viscoelastic mass upon addition of water and mixing, which has traditionally been called gluten. Formulation of gluten-free breads or pasta usually requires additives such as hydrocolloids to counterbalance the absence of gluten [4, 5]. The degree of difficulty in producing gluten-free food is due to the technological/functional role of gluten in the food system. Today, most gluten-free products available on the market present low textural quality related to more crumbly structure when compared to products based on wheat flour [6].

GF pasta may be formulated with different flours and starches with the addition of proteins, gums, and emulsifiers that may partially act as substitutes of gluten [7–10]. Xanthan gum and locust bean gum are some of the hydrocolloids that may be added to GF doughs and interact with starches present in the dough [11]. Interactions between xanthan gum and galactomannans (like guar gum, locust bean gum,

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✉ Gabriel Lorenzo
lorenzogabriel@gmail.com

[1] Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA), CICPBA, CONICET, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), 47 y 116, 1900 La Plata, Buenos Aires, Argentina

[2] Departamento Ingeniería Química, Facultad de Ingeniería, UNLP, La Plata, Argentina

tara gum, among others) have synergistic effects, such as enhanced viscosity that can improve dough handling [5, 12].

Amaranth, quinoa, and buckwheat were used by Schoenlechner et al. [13] to produce gluten-free noodles including the three pseudocereal flours, albumen, emulsifiers, and enzymes. They reported that quinoa noodles were better agglutinated but caused higher cooking loss and decreased the taste of the noodles, and concluded that a combination of all three pseudocereal flours seemed most advantageous compared to the pasta obtained with each pseudocereal individually. Quinoa (*Chenopodium quinoa* Willd.) is a pseudocereal; the percentage of bran fraction (seed coat and embryo) in quinoa seeds is higher in comparison with common cereals, such as maize and wheat, which explains the higher levels of protein and fat present in these seeds [14, 15]. Amino acid composition of quinoa proteins is well balanced, with a high content of essential amino acids, superior to that of common cereals [16]. Quinoa also represents a good source of dietary fiber, which is considered to be inadequate in a gluten-free diet [17]. It is an important source of minerals and vitamins, and has also been found to contain compounds like polyphenols, phytosterols, and flavonoids with possible nutraceutical benefits. It has some functional (technological) properties like solubility, water-holding capacity (WHC), gelation, emulsifying, and foaming that allow diversified uses. Besides, it has been considered an oil crop, with an interesting proportion of omega-6 and a notable vitamin E content. Quinoa starch has physicochemical properties (such as viscosity and freeze stability) which give it functional properties with novel uses [18].

Even though maize supplies many micro- and macronutrients necessary for human metabolism, the amounts of some essential nutrients are inadequate [19]. Recently, Giménez et al. [20] have studied the use of composite flours of maize and alternative crops like quinoa and broad bean regarding the nutritional attributes of gluten-free pasta. These authors reported an improvement in the protein quality of the pasta when mixture flours were used.

Besides, quinoa has shown some hypoglycemic effects in vivo and has been recommended as an alternative to the traditional ingredients in the production of cereal-based gluten-free products with a low glycemic index [9].

Zein is the alcohol soluble protein of corn, classified as a prolamin. It is water insoluble due to its amino acid composition, and it is suitable for use in the food industry due to its natural ability to form films and fibers [21]. Several reports have found that, in the mixing of zein–starch doughs, zein is known to form β sheets, which are believed to contribute substantially to the elastic behavior of gluten in wheat dough [22]. However, in the development of GF products, they found that pure zein–starch mixtures presented undesirable texture of gluten-free breads. Conversely, when zein was used in combination with hydrocolloids, it served as a structural enhancer of the crumb that showed its potential as a source of cereal proteins in the production of gluten-free foods.

Considering the viscoelastic behavior of starch–zein mixtures, which is similar to those of gluten and wheat flour doughs, and the high protein content of quinoa flours, a combination of these two ingredients appeared to be suitable to reinforce the matrix of gluten-free pasta. Thus, the aim of the present work was to analyze the ability of zein protein and quinoa flour to produce GF pasta of good textural quality. Therefore, we evaluated the effect of the addition of mixtures of zein and quinoa flour on the linear viscoelastic and textural properties of gluten-free dough used for pasta production using corn starch and corn flour as the main ingredients, and determined the influence of composition both on pasta drying kinetics and final quality of the product.

## Materials and methods

### Materials

Corn flour (moisture 6.98 g/100 g, protein 3.16 g/100 g, ash 1.04 g/100 g) was obtained from Herboeste (Buenos Aires, Argentina), quinoa flour (moisture 12.39 g/100 g, protein 14.52 g/100 g, ash 3.18 g/100 g) was purchased from Sturla (Buenos Aires, Argentina), corn starch from Droguería Saporiti (Buenos Aires, Argentina), and dry egg (moisture 20.3 g/100 g, protein 47.50 g/100 g, ash 3.26 g/100 g) and dry egg-white (moisture 3.32 g/100 g, protein 73.32 g/100 g, ash 4.54 g/100 g) from Ovobrand SA (Brandsen, Argentina). Xanthan (XG), locust bean gum (LBG), and zein protein were food-grade obtained from Sigma Chemical Co. (St. Louis, MO). Analytical grade NaCl, sunflower oil (AGD, Buenos Aires, Argentina), and distilled water were also used.

Moisture content of flour (corn and quinoa), starch, and proteins (dry egg, dry egg-white, and zein) was measured following the standardized protocol AACC 44-40 (AACC, 2000). Total nitrogen content was determined according to 920.87 AOAC method; conversion factors 5.83 for quinoa flour and 6.25 for the rest of proteins was used (Table 1).

### Pasta dough sample preparation

Gluten-free pasta dough was prepared using the protocol of Larrosa et al. [5]. Flours, starches, proteins, and hydrocolloids were premixed, and then, the required oil and water were added in a food processor (Universo, Rowenta, Germany) at 400 rpm until a homogeneous dough was obtained. Then, a noodle machine (Pastalinda S.A., Argentina) was used to laminate the dough obtaining a pasta sheet of approximately 2 mm thick.

**Table 1** Average protein, moisture, ash content, and water absorption index (WAI) of the different components

| Component | Proteins (g/100 g)** | Moisture (g/100 g) | Ash (g/100 g) | WAI (g $H_2O$/g solids) |
|---|---|---|---|---|
| Corn flour | 3.16 ($4.6\times10^{-3}$) | 6.98 (0.33) | 1.04 ($6.0\times10^{-4}$) | 1.43 ($2.4\times10^{-2}$) |
| Quinoa flour | 14.52 ($2.9\times10^{-2}$) | 12.39 ($3.7\times10^{-2}$) | 3.18 ($2.0\times10^{-2}$) | 1.78 ($5.2\times10^{-2}$) |
| Dry egg | 47.50 ($6.8\times10^{-1}$) | 2.03 (0.04) | 3.26 ($5.0\times10^{-4}$) | 1.51 ($7.9\times10^{-2}$)[a] |
| Dry egg-white | 73.32 ($7.1\times10^{-2}$) | 3.32 (0.8) | 4.54 ($4.0\times10^{-2}$) | |
| Zein | 77.18 ($7.2\times10^{-4}$) | 3.18 (0.14) | 0.67 ($5.0\times10^{-4}$) | 1.83 ($7.4\times10^{-2}$) |

**SEM values between parenthesis

[a] WAI value for the egg protein mixture in a 10:1 ratio for egg: egg-white

**Table 2** Gluten-free dough formulation (g/100 g total solids)

| Formulation | Corn flour | Quinoa flour | Egg + egg-white | Zein |
|---|---|---|---|---|
| Q0Z0 | 16.70 | 0.00 | 10.80 | 0.00 |
| Q0Z1 | 16.70 | 0.00 | 7.20 | 3.60 |
| Q0Z2 | 16.70 | 0.00 | 3.60 | 7.20 |
| Q1Z0 | 8.35 | 8.35 | 10.80 | 0.00 |
| Q1Z1 | 8.35 | 8.35 | 7.20 | 3.60 |
| Q1Z2 | 8.35 | 8.35 | 3.60 | 7.20 |
| Q2Z0 | 0.00 | 16.70 | 10.80 | 0.00 |
| Q2Z1 | 0.00 | 16.70 | 7.20 | 3.60 |
| Q2Z2 | 0.00 | 16.70 | 3.60 | 7.20 |

Representative subsamples were cut from these sheets with a geometry according to the test that was going to be performed (tagliatelle, squares, rectangles, etc.) and kept in airtight polystyrene containers to avoid moisture loss. Temperature was maintained at 20 °C during dough preparation and analysis.

## Experimental design

Effect of quinoa flour (Q) and zein (Z) content on gluten-free pasta was studied using a 3 × 3 factorial design were corn flour was partially replaced with Q and egg proteins (EP) by corn zein. Type of flour and protein used in each formulation is shown in Table 2. Basic formulation (in 100 g solids) was fixed and consisted in: 66.8 g corn starch, 16.7 g flour (corn + quinoa), 10.8 g protein (egg + zein), 2.8 g XG, 1.4 g LBG, 1.5 g of NaCl, and 4.1 g of sunflower oil. Dry whole egg/dry egg-white ratio (10:1) and XG/LBG ratio (2:1) were obtained from the previous assays [23]. Basic pasta dough (Q0Z0, Table 2) corresponded to a previously optimized formulation [24] (Table 2).

Water content was determined from preliminary experiments based on dough consistency, which was determined using the electric current consumption of the food processor. With the assessment of a current clamp, the more the water added, the higher the current consumption until a sharp drop was detected, which concurred with the dough formation. The water content was selected immediately after this drop in the current consumption occurred. For the lowest zein content optimum water was 58.4 g/100 g solids, for the intermediate level, 61.0 g/100 g solids, and for the highest zein concentration, 63.5 g/100 g solids. The nine doughs of the design were prepared at least twice to perform all the experiments.

## Dough rheology

Freshly prepared dough samples were studied using dynamic rheological tests in a controlled stress rheometer (Haake-RS600, ThermoFisher Scientific, Germany). Stress sweeps were carried out at 1 Hz ranging from 0.5 to $1.10^4$ Pa to determine the linear viscoelastic range (LVR) for each formulation. 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 assay. After positioning, the sensor samples rested for 10 min to relax from the residual stresses.

In addition, frequency sweeps were performed within the LVR to measure the frequency dependence of the storage ($G''$) and loss ($G''$) moduli in the range 0.09–200 rad/s. All measurements were done in duplicates, using serrated parallel plates (1.6 mm gap, 35 mm diam.).

## Pasta drying process

A lab-scale forced convective oven designed and built "ad hoc" was used for pasta drying at constant air velocity (0.5 m/s). Initially, subsamples of 300 g tagliatelle (8 × 2 × 150 mm) were cut from the laminated dough and put on a perforated rack attached to a balance with a continuous weight data acquisition system to follow the drying kinetic "in situ". The drying cabinet was conditioned at least 12 h before every run.

The initial dough moisture was determined for each sample prior to the drying process and it was used to establish the final point of the process. Operative conditions were 60 °C and 60% relative humidity of the air. On dry pasta samples, water activity (aw) was verified on an Aqualab 3TE water activity meter (Decagon Devices Inc., USA), to ensure that aw < 0.65 was achieved.

### Quality attributes of the cooked pasta

Dried pasta was cooked and the quality of the final product was evaluated. Standardized protocols described in AACC 66-50 were used to determine the optimum cooking time (OCT), water absorption (WAI), and cooking loss (CL) at least in triplicate [25]. In addition, color of both dried and cooked tagliatelle was measured (six replicates) using a Minolta Chroma Meter (CR- 400, Minolta Co., USA), determining CIE color parameters lightness ($L^*$), redness ($a^*$), and yellowness ($b^*$).

### Texture analyses

Texture analyses were performed in a TAXT2i Texture Analyzer (Stable Micro Systems, UK), at least ten replicates for each formulation.

On dry tagliatelle, the three point bending test (bend rig HDP/3 PB) was performed to determine the fragility of pasta. From the maximum force ($F$) and the distance at break ($d$), the fracture stress ($\sigma_{\mathrm{frac}}$) and apparent deformation ($\varepsilon$) were calculated as follows:

$$\sigma\_\mathrm{frac} = 3\ FL/\left(2\ bh^2\right) \tag{1}$$

$$\varepsilon = 6\ \mathrm{hd}/L^2, \tag{2}$$

where $L$ is the distance between support points (50 mm), $b$ is the sample width, and $h$ is the sample thickness, determined for each specimen before measurement.

Texture of cooked pasta was determined with two compression cycles test using a 25 mm diameter probe (P/25). Lasagna-type specimens of 20 mm width were used for this study, the test speed was set on 0.5 mm/s, and the compression distance was 30% of the original size. From the force–time curve, firmness, cohesiveness, springiness, and adhesiveness were calculated [26].

### Environmental scanning electron microscopy (ESEM)

An environmental scanning electron microscope (FEI Quanta 200, USA) was used to examine the surface of the samples. Micrographs of dry and cooked gluten-free pasta were taken without any previous treatment. Two replicates of each formulation were observed and at least five representative fields were obtained from each replicate.

### Statistical analysis

Analysis of variance was performed (SYSTAT Inc., Evenston, IL). Tukey's test was chosen for simultaneous pairwise comparisons. Differences in means and $F$ tests were considered statistically significant when $P < 0.05$.

Surface response methodology (Expert-v.7, Stat-Ease, USA) was used to determine the relationship between dough composition and different properties, considering a complete second order polynomial model using a stepwise methodology [24]. The adequacy of the model was verified using a "lack of fit" test, $R^2$, and "Adequate Precision". SEM indicates standard error of the mean in figures and tables.

## Results and discussion

### Dough rheology

Figure 1 shows the results of the oscillatory shear test. All the studied pasta dough exhibited qualitatively the same stress-thinning behavior, regardless the type of flour or protein used (Fig. 1a). At rest, biopolymer chains are in a state of entanglement, where $G'$ and $G''$ remained constant. As the stress is increased, biopolymer chains disentangle, and then align with the flow field; i.e., the moduli subsequently decreased [27]. A similar behavior was observed for gluten-free pasta dough in a previous work [23]. Stress sweep were modeled using the following equations:

$$G' = G'_0\ (1 + a'\sigma)/\left(1 + \left(b'\sigma\right)^{n'}\right) \tag{3}$$

$$G'' = G''_0\ (1 + a''\sigma)/\left(1 + (b''\sigma)^{n''}\right), \tag{4}$$

where $G'_0$ and $G''_0$ represent the limiting values of both moduli in the linear viscoelastic region and $a'$, $a''$, $b''$, $b''$, $n'$, and $n''$ are regressed parameters. Experimental data of each formulation was satisfactorily fitted using Eqs. 3 and 4 (Fig. 1a).

The critical stress ($\sigma_{\mathrm{cr}}$) was determined as the point where both moduli differ more than 5% from their corresponding linear values. Figure 1b represents the response surface of $\sigma_{\mathrm{cr}}$ as a function of dough composition; response surface coefficients are shown in Table 3. Below $\sigma_{\mathrm{cr}}$, the structure remains intact, the dough behaves solid-like, and $G' > G''$, indicating that the material is highly structured. Increasing the stress above the critical stress the network structure is disrupted and the doughs become progressively more fluid-like. Figure 1b reveals a clear trend that increasing zein content significantly decreased $\sigma_{\mathrm{cr}}$ value. Partial replacement of egg proteins with zein could lead to a less interconnected matrix that required lower values of shear stress to disturb the structure.

Zein is made of different peptide chains linked by disulfide bonds. Based on the difference in molecular size, solubility, and charge of the peptide chains, the protein is

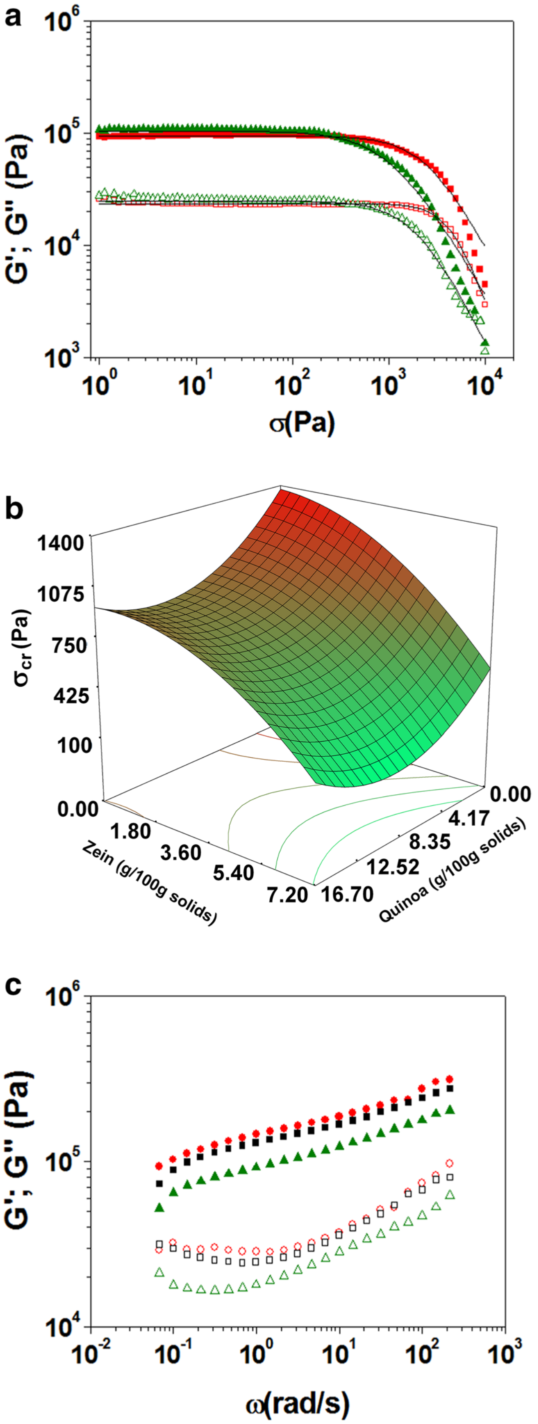

**Fig. 1** **a** Stress sweeps for pasta dough-containing 16.7 g quinoa flour/100 g solids and different zein contents: Q2Z0, no zein (red filled square, red open square); Q2Z2 7.6 g zein/100 g (green filled triangle, green open triangle). *G′* (filled symbols), *G″* (open symbols). Full lines indicated predictions using Eqs. 1 and 2. **b** Effect of zein and quinoa flour content on the critical stress $\sigma_{cr}$. Zein and quinoa contents are expressed in g/100 g solids. **c** Dynamic frequency sweep data for three different pasta dough formulations: Q0Z2 (red open diamond, red filled diamond), Q1Z1 (black open square, black filled square), and Q2Z0 (green filled triangle, green open triangle). *G′* (filled symbols), *G″* (open symbols). Formulations are coded according to Table 2

classified into *α, β, γ*, and *δ*. Zein is one of the most hydrophobic proteins among many cereal proteins [28]. The hydrophobicity is due to the presence of high proportion of non-polar amino acid residues. Hydrophobicity is one of the major factors affecting structure, solubility, and mechanical properties of proteins. Unlike the albumins and globulins present in the egg, the high hydrophobicity of zein could explain its inability to form a continuous structure in the mass and make it a weaker network.

Mechanical spectra of three pasta dough formulations are presented as an example in Fig. 1c. Governed by the synergistic interaction between xanthan and locust bean gum, all formulations revealed a similar shape of the spectrum, i.e., *G′* markedly higher than *G″* and slightly dependent on frequency. In all the cases, dough behaved like viscoelastic materials in the rubbery or plateau region, that is, where elastic characteristics dominate; a similar behavior has been reported by other authors working with GF products [23, 29]. However, increasing *Q* or decreasing *Z* contents produced a shift of the entire spectrum to lower moduli values, which represented a decrease in the elastic properties of the dough. The previous results in non-fermented gluten-free doughs have shown that *G′* and *G″* data could be positively correlated with breaking force (*F*) obtained from extensibility tests [5, 30]. Thus, the observed decrease in the elastic properties of the dough could be related to less resistance to laminate the GF dough.

## Drying process

The experimental curves were determined by measuring weight loss during drying (Fig. 2). The end point of the drying process was established using a target level of water activity (aw ≤ 0.65) which corresponded to a water content ≤ 12.5 g/100 g. This should be below the point that will support any microbiological growth [31]. Drying kinetic of different pasta formulations was expressed in terms of dimensionless moisture content $X^*$:

$$X^* = \left(X_t - X_e\right)/\left(X_0 - X_e\right), \tag{6}$$

where $X_t$ corresponds to the pasta moisture (dry basis) at different drying times, $X_0$ to the initial pasta moisture, and $X_e$ is the moisture of the pasta in equilibrium with the air humidity which was obtained from the sorption isotherms of the pasta determined in a previous work [32].

During the first 10 min of the drying process, a slight moisture increment was observed in all formulations; as the initial dough temperature was lower than the wet bubble temperature of the air in the cabinet, the water vapor condensation occurred at the beginning of the drying process until the dough temperature reached the wet bubble temperature of the air.

**Table 3** Regression coefficients for the predictive models for critical stress $\sigma_{cr}$ (Pa), $L^*$ and $b^*$ both of dry and cooked pasta. Statistical significance of the models (P), $R^2$, lack of fit, and "adequate precision" coefficients are also included

| Model terms | $\sigma_{cr}$ (Pa) | $L^*$ dried | $b^*$ dried | $L^*$ cooked | $b^*$ cooked |
|---|---|---|---|---|---|
| Constant | + 1374.10 | + 81.73 | + 23.05 | + 71.27 | + 20.39 |
| Quinoa | − 92.85 | − 0.362 | − 0.323 | − 0.642 | − 0.359 |
| Zein | − 12.51 | – | − 0.256 | + 0.670 | + 0.368 |
| Quinoa* Zein | + 1.95 | – | – | − 0.039 | – |
| Quinoa$^2$ | + 4.06 | – | + 0.021 | + 0.030 | – |
| Zein$^2$ | − 15.41 | – | – | − 0.062 | – |
| Model (P) | $< 0.0001$ | $< 0.0001$ | $< 0.0001$ | $< 0.0001$ | $< 0.0001$ |
| $R^2$ | 0.864 | 0.875 | 0.773 | 0.648 | 0.817 |
| Lack of fit | 0.1130 | 0.1434 | 0.3816 | 0.094 | 0.1553 |
| Adequate precision | 16.12 | 14.45 | 7.127 | 7.93 | 28.80 |

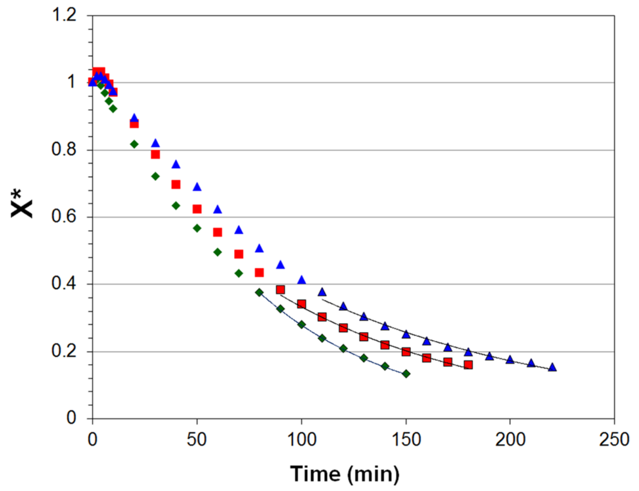

**Fig. 2** Drying kinetics of different pasta formulations (green filled diamond Q0Z1, red filled square Q1Z1, and blue filled triangle Q2Z1) expressed in terms of dimensionless moisture content $X^*$. Full lines correspond to long-time predictions of a diffusional analytical model for moisture transport. Formulations are coded according to Table 2

**Table 4** Average fracture stress ($\sigma_{frac}$), and apparent deformation ($\varepsilon$) of dried tagliatelle and water absorption index (WAI) of cooked pasta prepared with the different gluten-free formulations

| Formulation | $\sigma_{frac} \times 10^{-6}$ (Pa)* | $\varepsilon \times 10^3$ (%) | WAI (g/100 g) |
|---|---|---|---|
| Q0Z0 | 1.762 (0.21)$^{b,c**}$ | 6.085 (0.40)$^{b}$ | 108.28$^{bc}$ |
| Q0Z1 | 1.190 (0.12)$^{a,b}$ | 4.967 (0.43)$^{a,b}$ | 122.20$^{ab}$ |
| Q0Z2 | 1.211 (0.18)$^{a,b}$ | 5.826 (0.55)$^{b}$ | 122.63$^{ab}$ |
| Q1Z0 | 0.935 (0.06)$^{a}$ | 3.403 (0.49)$^{a}$ | 130.29$^{a}$ |
| Q1Z1 | 1.360 (0.10)$^{a,b,c}$ | 4.097 (0.34)$^{a,b}$ | 115.29$^{abc}$ |
| Q1Z2 | 1.455 (0.11)$^{a,b,c}$ | 5.636 (0.56)$^{b}$ | 101.55$^{c}$ |
| Q2Z0 | 1.970 (0.14)$^{c}$ | 5.935 (0.47)$^{b}$ | 102.20$^{c}$ |
| Q2Z1 | 0.803 (0.07)$^{a}$ | 3.452 (0.29)$^{a}$ | 122.53$^{ab}$ |
| Q2Z2 | 1.094 (0.20)$^{a}$ | 4.360 (0.55)$^{a,b}$ | 107.54$^{bc}$ |

Formulations are coded according to Table 2

*SEM values between parentheses

**Different letters within the same column indicate significant differences ($P < 0.05$)

Effective diffusion coefficients ($D_{eff}$) were determined considering a unidirectional mass transport through the thickness of a pasta strand. A diffusional model for water transfer through pasta was assumed and the well-known analytical solution was applied [33]. All the formulations presented values of $D_{eff}$ between $2.5 \times 10^{-11}$ and $8.5 \times 10^{-11}$ m$^2$/s, in agreement with those found in the literature for the traditional pasta [34]. A significant effect ($P < 0.05$) of quinoa on water diffusivity was observed, as $Q$ level increased $D_{eff}$ decreased, a fact that is easily appreciated in Fig. 2. The effect of zein on drying kinetics was only noticeable at high $Q$, showing the opposite effect, increasing zein increased water diffusivity.

Introduction of quinoa proteins has shown a similar effect in the drying process of chitosan edible films [35]. A significant decrease of water diffusivity could be related to the type of protein present in the matrix. The main protein fractions in quinoa flour are albumins and globulins [36, 37], which present more water affinity than corn proteins (mainly prolamins). Thus, replacement of corn flour with quinoa flour could contribute to form a more dense protein structure, with lower porosity and the consequent decrease in water diffusion. The opposite effect could explain the increase in $D_{eff}$ when egg proteins were partially replaced with zein.

## Quality characteristics of dried tagliatelle

All gluten-free dried tagliatelle presented $a_w < 0.65$ as recommended to avoid any microbiological growth [31]. No significant differences were observed between formulations and an average value of 0.595 was obtained.

Good-quality dry pasta should be strong and flexible enough to withstand tensions, especially during packaging and transport [38]. Quinoa flour did not significantly affected fracture stress of dried tagliatelle, while zein showed a tendency to make the pasta more easily breakable

(Table 4). Regarding apparent deformation before breaking, *Q* and *Z* contents as well as their interaction were significant ($P < 0.05$). On those formulations that contained zein, increasing *Q* reduced the maximum deformation on fracture, which contributed to a weakening of dry pasta.

Regression coefficients obtained for the predictive models for $L^*$ and $b^*$ color parameters are shown in Table 3; in all cases, lack of fit and precision adequacy values revealed that the models were convenient. In pasta products made from semolina, the higher the $L^*$ and $b^*$ values, the more desirable the product [39]. All assayed formulations presented high lightness ($L^* > 75$); however, increasing *Q* produced a less luminous product (decreased $L^*$, Table 3; Fig. 3a), regardless of the zein content ($P < 0.05$). Yellowness ($b^*$) ranged from 20 to 23 units. Zein has a negative influence on this parameter (Table 3; Fig. 3b), increasing Z diminished $b^*$, which could be explained by the fact that dry egg has greater yellowness than zein protein. Parameter $a^*$ was small compared with $b^*$ (ranging from $-0.12$ to $+2.98$); yet, increasing *Q* or diminishing *Z* increased redness of the dry product. The previous results of dried traditional tagliatelle prepared with wheat flour and whole eggs gave the following results: $L^* = 86.36$, $a^* = 0.275$, and $b^* = 20.05$, which is in the range of the gluten-free pasta studied [24].

## Quality attributes of cooked pasta

In this work, optimum cooking times ranged from 12 to 17 min showing a marked trend to longer processing times as *Z* concentration was reduced. These results agree with those reported by Yalcin and Basman [40] for GF rice starch spaghetti prepared with different proportions of gelatinized starch and with Palavecino et al. [26] who worked with GF sorghum spaghetti.

Cooking loss is widely used as an indicator of the overall cooking performance of pasta considering it as an index

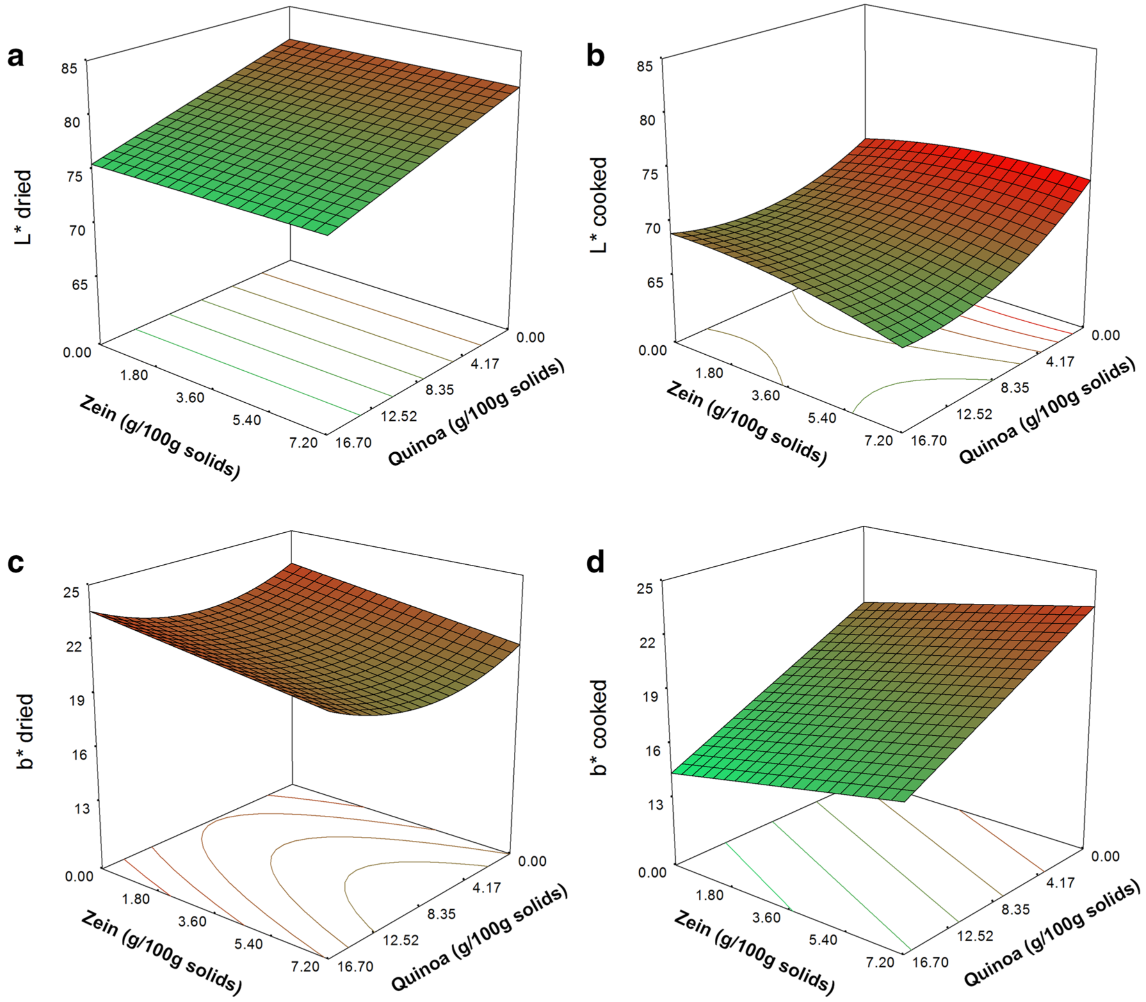

**Fig. 3** Color parameters as a function of quinoa flour and zein contents expressed as g/100 g solids. **a** luminosity ($L^*$) and **c** yellowness ($b^*$) of dried pasta; **b** $L^*$ and **d** $b^*$ of cooked pasta

of resistance to disintegration during cooking [41]. In GF pasta the lack of gluten debilitates the matrix where starch is normally entrapped, giving a final product with high losses during cooking [9]. Our results did not show a significant effect of composition on CL. An average value of 8.72 (1.94) g solids/100 g pasta could be classified as an acceptable value even for wheat pasta [42].

Water uptake during cooking was only affected by the quinoa content (Table 4). As *Q* increased, a significant decrease in WAI values was observed ($P<0.05$), in agreement to the decrease in the effective diffusion coefficient described above in the drying process. A similar trend was reported by Palavecino et al. [26] for egg albumen; apparently, the presence of certain proteins may form a more compact network that prevents water uptake of the other components [24].

Texture of cooked pasta plays an essential role on final acceptance by consumers. Pasta quality was evaluated also in terms of firmness, adhesiveness, and cohesiveness [42]. Both Q and Z contents significantly affected firmness; increasing *Q* produced softer, less firm pasta, while zein addition had the opposite effect (Fig. 5a). These results are consistent with the rheological behavior observed in the uncooked dough. Even when the hydrothermal treatment irreversibly alters most of dough constituents, dough composition modifies in the same way viscoelasticity of the dough and firmness of the cooked product. GF pasta tends to be firmer than the wheat flour product; then, the substitution of corn flour by *Q* was beneficial, since less force would be required to compress the product between molars or between tongue and palate. Mastromatteo et al. [43] reported that cooked GF spaghetti containing a high corn flour content, without or with a very low *Q* addition increased firmness in agreement with the present work. On the other hand, smaller amounts of *Q* did not affect pasta elasticity which resulted in good deformation capacity [44]. Dissimilarities in firmness of pasta with different flours might be attributed to starch granules characteristics. Mixing starches of different origins may be employed to provide distinctive properties to pasta, such as improved texture or rheological characteristics of the dough [45].

Low adhesiveness is important for consumers [46]. It depends on the production methodology and on the quality of the protein network that holds starch in place. All the assayed formulations showed very low adhesiveness; however, increasing *Z* or *Q* significantly ($P<0.05$) raised this parameter (Fig. 4b).

Cohesiveness of gluten-free cooked pasta is usually interpreted based on the competition between starches, proteins, and hydrocolloids to form a continuous network [24]. This parameter could be used as an indicator of how the sample holds together upon cooking. Figure 4c shows the results for this parameter of the cooked pasta. Replacement of corn flour with *Q* did not affect ($P>0.05$) the cohesiveness of the pasta, whereas the samples resulted less cohesive when the *Z* content was increased. Springiness of cooked pasta was also obtained from the TPA analysis. All of the samples presented the same average springiness (0.894 ± 0.099) and it was not affected by the pasta composition.

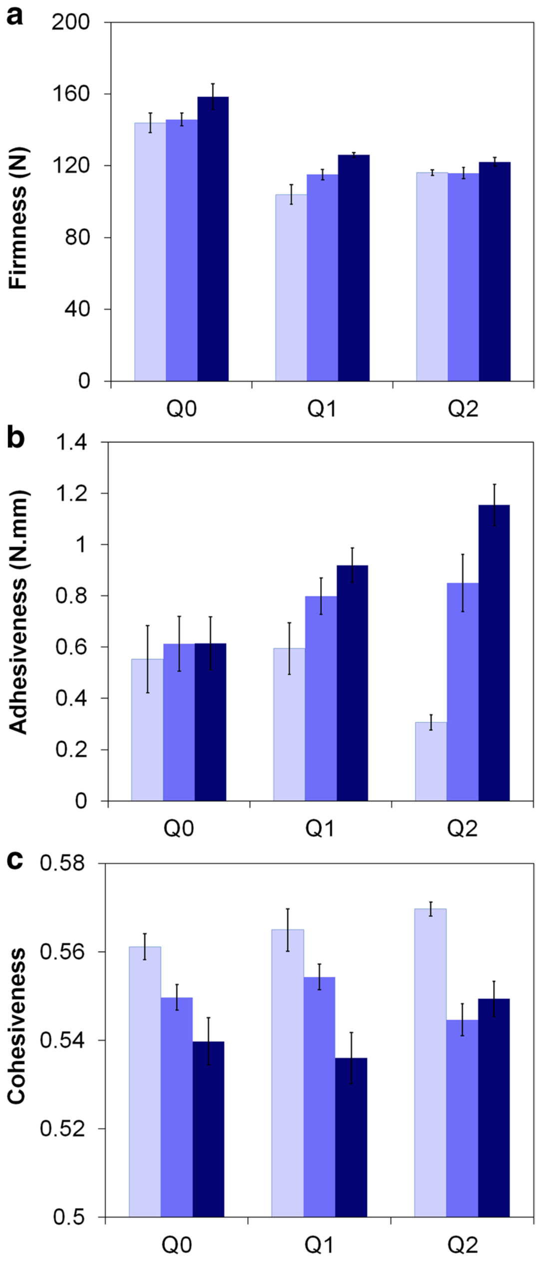

**Fig. 4** Texture behavior of gluten-free cooked pasta at different quinoa content (see Table 2 for codes). **a** Firmness, **b** adhesiveness, and **c** cohesiveness. Zein concentration: 0 (light blue filled square), 3.6 (blue filled square), and 7.2 g/ 100 g solids (dark blue filled square)

Cooking reduced pasta lightness, regardless of the composition. However, as in dried pasta, samples without *Q* presented the highest *L** values (Fig. 3b). Redness (*a**) still

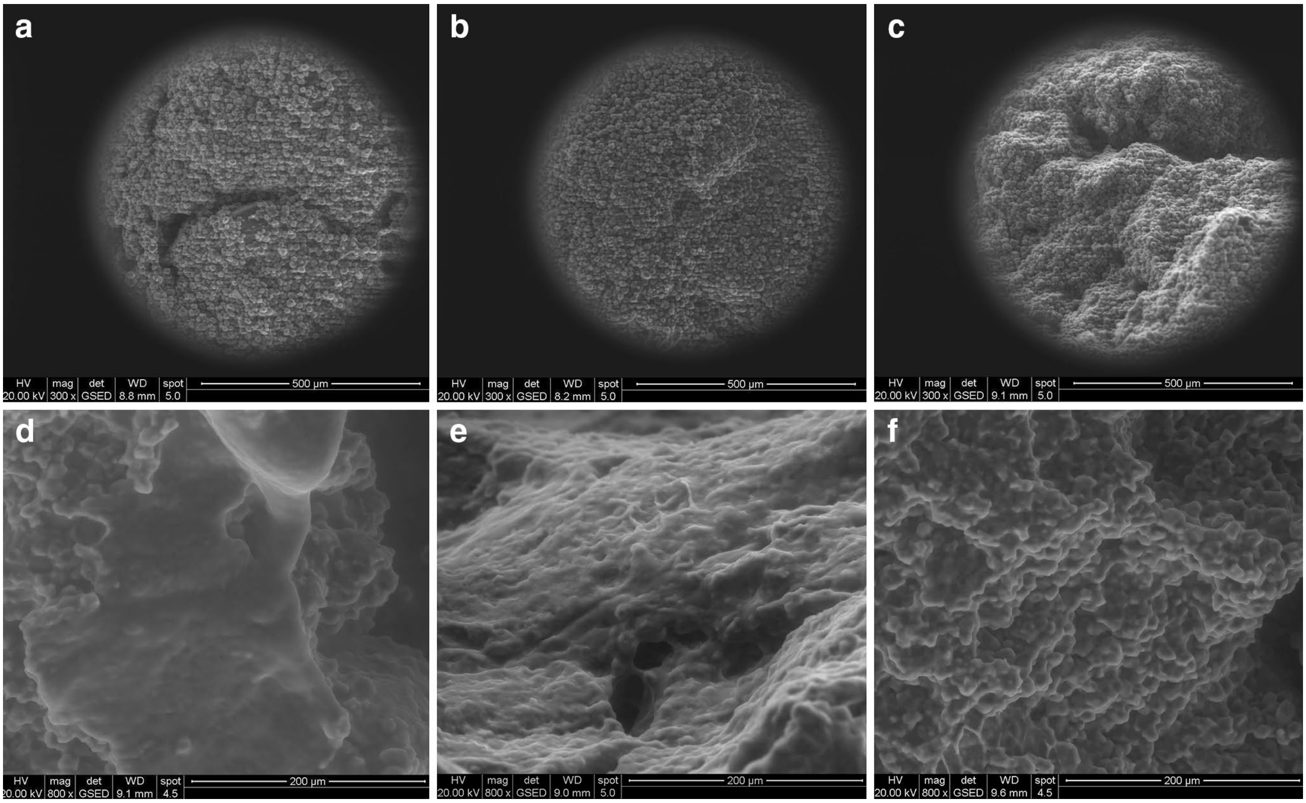

**Fig. 5** Environmental scanning microscopy of dried (**a**–**c**) and cooked (**d**– **f**) gluten-free pasta. Q0Z0 (**a, d**); Q2Z0 (**b, e**); Q0Z2 (**c, f**), formulations coded according to Table 2. Scale bars: 500 µm (**a**– **c**), 200 µm (**d**–**f**)

remained as low as in dried pasta with a slight brownish color when quinoa flour content was high (*Q*2). Stikic et al. [47] found that wheat breads supplemented with different percentages of quinoa presented a yellow-reddish color, but it was well received by a sensory panel.

Yellowness of cooked pasta showed a clear linear dependence on both *Z* and *Q* contents (Table 3). Increasing *Z* increased $b^*$ values, which could be attributed to the differences between the whitish cooked EP and the yellowish cooked zein. A more marked difference was observed with flour replacement. The more the corn flour in the formulation, the higher the yellowness of the gluten-free cooked pasta (Fig. 3d).

When compared with cooked wheat pasta, the traditional tagliatelle exhibited higher $L^*$ values (82.62) than any of the GF formulations, but the redness ($a^* = -2.88$) and yellowness ($b^* = 17.31$) remained in the same region [24].

## Microstructure analysis

To interpret the mechanical behavior of the studied gluten-free pasta, microscopic observations were performed on different formulations. Surface examination of dry pasta showed marked differences depending on composition (Fig. 5a–c). Development of gluten-free pasta using *Q* led to dry tagliatelle with a very smooth and homogeneous surface, where the starch granules are part of a continuous network formed mainly by xanthan and guar gums combined with EP (Fig. 5b). When *Q* was replaced with corn flour, the structure of dry pasta began to show some notorious cracks on the surfaces (Fig. 5a). These structural differences could explain the differences observed in effective diffusion coefficient. The low porosity observed in formulations with high Q decreased the rate of water diffusion through the dough matrix and leads to a decrease in $D_{\mathrm{eff}}$ as mentioned in 3.2. Moreover, when a partial replacement of EP with Z was performed (Fig. 5c), the surface fractures became more evident and deep and could even be observed macroscopically. This could explain the distinctly low OCT values obtained in formulations with high *Z* content. A non-continuous surface and cracks would facilitate water absorption during cooking; in terms, this could lead to faster starch gelatinization, and thus, OCT would be shorter. From this perspective, zein (from the corn flour or added as isolated protein) appeared to interfere the continuous dough formation, leading to an open structure easily dried but with high breakability.

In addition, Fig. 5d–f shows the internal structure of cooked pasta at the optimum cooking time. Q0Z0 and

Q2Z0 presented a similar structure, with swollen and gelatinized starch granules integrated in a developed EP matrix forming a compact structure, with a few starch granules not gelatinized (Fig. 5d, e). Pasta with high level of *Z* seemed to present a weaker protein network, and starch granules were not completely embedded in that film (Fig. 5f). The internal structure of the cooked Q0Z2 presented a crumbly aspect that could be attributed to an incomplete zein-EP association. Although, during cooking, sample was submitted to a temperature above the glass transition temperature of zein ($T_g$ ~ 28 °C), α−zein was not able to form a viscoelastic homogeneous network in the presence of the other components of the dough as it was observed by other authors in starch–zein mixtures [22]. This not uniform structure is in agreement with the significant lower cohesiveness registered in textural analysis (Fig. 5c).

## Conclusions

From the overall results, it could be concluded that the addition of quinoa and/or zein to the gluten-free formulation modifies the quality of pasta.

Quinoa flour addition led to significant improvements in the texture of the final product, while the partial replacement of egg protein with zein increased water absorption and reduced cooking time but caused by cracked microstructure which facilitated water migration in or out of the matrix.

A good-quality pasta is considered that, with high resistance and deformation to the fracture when is dried, low cooking times and high water absorption during cooking, and low firmness, adhesiveness, and high cohesiveness when is cooked. Among the formulations studied, those with high content of quinoa and without zein or in low concentration (Q2Z0 and Q2Z1), fulfill most of these requirements and also significantly improve the nutritional profile of the pasta by increasing the protein content above of 32% respect to the control.

Further work is required to clearly identify the interactions between zein and protein/starch matrix; however, this study confirms that the addition of zein negatively alters the structure of pasta, whereas quinoa flour improves the texture of cooked pasta leading to a product with good technological quality and higher protein content, which contributes to a dietary improvement in the celiac population.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Compliance with ethical requirements** The present article does not contain any studies with human or animal subject.

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