Investigation of the effects of using quinoa flour on gluten-free cake batters and cake properties

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Revised: 5 November 2018 / Accepted: 15 November 2018 / Published online: 29 November 2018
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Abstract This study aimed to determine the influence of substituting rice flour and potato starch with quinoa flour at different levels on the rheological properties of batters and physical, chemical properties and quality parameters of gluten-free cakes. Substituting rice flour and potato starch with quinoa flour resulted in an increase in the batter density. Rheological analysis showed that, Power Law model is the most suitable model to represent the flow behavior of cake batters and the batters exhibited solid-like behavior with the exception of the sample without quinoa flour. Also elastic modulus (G') and viscous modulus (G'') of the batters increased with quinoa flour substitution in the frequency range of 0.01–10 Hz. In addition to this, according to the temperature sweep test results, quinoa flour addition increased the mechanical strength of the batters. Physical, chemical properties and quality parameters of the cakes were significantly improved by quinoa flour substitution. In general, volume of the cakes increased but hardness values of the cake crumbs decreased with the increase in quinoa flour substitution. The cake, produced with 50% quinoa flour, had the highest scores for both taste and overall acceptability.

Keywords Gluten-free cake · Quinoa · Batter rheology · Cake quality

Introduction

Celiac disease (CD) is one of the most prevalent lifelong disorders worldwide, which is an immune-mediated enteropathy triggered by gliadin fraction of wheat and the prolamins of rye (secalins), barley (hordeins) and possibly oats (avidins) (Catassi and Fasano 2008). The consumption of gliadin fraction in CD causes inflammation of the small intestine leading to the malabsorption of several important nutrients including iron, folic acid, calcium and fat soluble vitamins (Gallagher et al. 2004; Kelly et al. 1990). The only available treatment to date for CD is a strict gluten-free diet (GFD) throughout the patient's life time (Gallagher et al. 2004). Since any bread, cereal or other food products made with wheat, rye, barley, triticale, dinkel, kamut and oat flour or ingredients, and by-products made from those grains, processed foods that contain wheat and gluten-derivatives as thickeners and fillers and medications that use gluten as pill or tablet binders are not allowed in a GFD (Gallagher et al. 2004), the dietary changes required for the CD may have a notable impact on daily life.

Refined gluten-free flour or starch, which are generally not enriched or fortified, are used for gluten-free cereal foods (Thompson 1999). This long term habits and food choices of celiac patients on a strict GFD cause unbalanced intake of carbohydrates (Mariani et al. 1998; Öhlund et al. 2010), protein (Mariani et al. 1998), fiber (Mariani et al. 1998; Öhlund et al. 2010; Martin et al. 2013), mineral (Mariani et al. 1998; Öhlund et al. 2010; Martin et al. 2013), vitamin (Öhlund et al. 2010; Martin et al. 2013), and fat (Mariani et al. 1998; Öhlund et al. 2010), in CD patients compared with controls. In addition, gluten removal results in major problems for bakers such as low quality products exhibiting poor mouth feel, texture, and flavor since gluten

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is the main structure-forming protein in many baked product (Gallagher et al. 2004).

Nowadays many gluten-free bakery products have become available in the market prepared using rice, maize, soya, guar and pseudo cereals such as amaranth, quinoa and buckwheat. Pseudo cereals are not only gluten-free grains, they are also rich in nutrients such as protein, dietary fiber, vitamins and minerals, fat, and other bioactive components (Alvarez-Jubete et al. 2010). Quinoa (*Chenopodium quinoa* Willd.) is a grain-like food crop, which is traditionally used to provide high nutrition, and was domesticated by people living in the Andes, particularly in Peru and Bolivia, thousands of years ago (Navruz-Varli and Sanlier 2016). Because of stress-tolerant characteristics of quinoa plants (cold, salt and drought tolerant), its high nutritional value (Abugoch James 2009; Navruz-Varli and Sanlier 2016) and biological properties, quinoa was described as one of the grains of the twenty first century and FAO launched the International Year of Quinoa in 2013. Thus, the use of quinoa flour to enrich gluten-free products and to improve their quality, mouth feel, texture, and flavor provides a promising step towards ensuring consumption of nutritionally balanced products by celiac patients.

The aim of this study was to evaluate the effects of substituting rice flour and potato starch with quinoa flour on the rheological properties of batters, and physicochemical, functional and cake-making properties such as; specific volume, color, texture profile, proximate composition, water retention capacity and sensory properties of gluten-free cupcakes.

Materials and methods

Materials

White quinoa seeds for gluten-free cupcake were purchased from a commercial company (Bora Tar. Ür. Gıda San. ve Tic. Ltd. Şti., Istanbul, Turkey). Milling was performed using laboratory hammer mill (Armfield, UK) and quinoa flour, smaller than 280 µm particle sizes, was used for cake preparation. Commercially available rice flour (Kenton, Ankara, Turkey), potato starch (Başak Gıda Dağıtım Pazarlama San. Tic. A.Ş., Istanbul) sugar (Konya Şeker San. ve Tic. A.Ş., Konya, Ankara), baking powder (Dr-Oetker Gıda San. ve Tic. A.Ş., Izmir), pasteurized whole egg (İpay A.Ş.), shortening (Felda İffco Gıda San. ve Tic. A.Ş., Izmir) and milk (Pınar Süt Mamulleri Sanayi A.Ş., Izmir, Turkey) were purchased from local markets in Izmir. Chemicals that were used for raw material and cake analysis; ethanol (PubChem CID: 702), acetone (PubChem CID: 180) and *n*-hexane (PubChem CID: 8058) were

supplied by Merck (Darmstadt, Germany) and the enzymes that were used for dietary fiber analysis α -amylase, protease and amyloglucosidase were purchased from Sigma-Aldrich (St. Louis, USA).

Preparation of gluten-free cupcakes

Four different batter formulations were prepared using the modified cake batter formulation given by Gularte et al. (2012). Pasteurized whole egg (62.5 g/100 g flour blend) was whisked for 4 min at 10 by using Kitchen-Aid Professional mixer (Kitchen Aid K45 Mixer, St. Joseph, MI, USA). Sugar (57.5 g/100 g flour blend) was added and batter blend was mixed at speed 10 (3 min.). After that, milk (75 g/100 g flour blend) and shortening (36.25 g/100 g flour blend) were added and mixed at speed 4 (4 min). At the final step powder blend was obtained by adding baking powder (3.75 g/100 g flour blend) and flour (100 g) into the blend and mixing the blend for one more minute at speed 2. Flour blends, which are used for sample preparation, were formed by using four different levels of quinoa flour, rice flour and potato starch (0/50/50, 25/37.5/37.5, 50/25/25, 75/12.5/12.5 by quinoa flour/rice flour/potato starch). The batter was placed into silicon cake molds after dividing it into 60 g portions. Baking was performed for 30 min at 170 °C in a convection oven (Vestel, Turkey). The baked cakes were removed from the molds and left for cooling at room temperature for 1 h. The resulting cake formulations were coded as Q₀, Q₂₅, Q₅₀ and Q₇₅ where the sub index refers to quinoa flour content.

Analysis

Physicochemical analysis of flour

Rice flour, quinoa flour and potato starch were analyzed for their moisture (Method 44-19), ash (Method 08-01), lipid (Method 30-20) and protein (Method 46-30) (Nx6.25 for rice and Nx5.96 for quinoa flour) contents according to AACC method 2000. Total dietary fiber contents of the flour were assayed using the AOAC method no 991.43 (AOAC 1998). Water activity of the flour samples were measured using measurement device (Testo AG 400, Lenzkirch, Germany).

Water retention capacity of flour and flour blends

Water retention capacity (WRC) of the flour and flour blends was measured according to the AACC method no 56-11 (AACC 2000).

Density of cake batter

Density of the batters was measured using an Elcometer 1800 (Elcometer, Manchester, UK) which is a cup that consists of a 100 ml cylindrical container. Density was calculated by dividing the weight of the samples by the volume of the cup. Each density was measured at least twice (Gularte et al. 2012).

Rheological characterization of cake batter

Flow and oscillatory measurements of the cake batters were carried out using a controlled stress rheometer (DHR-3, TA Instruments, New Castle, DE, USA) with a Peltier heating system. Parallel plate geometry with a 40 mm diameter was used and 1 mm gap was applied. After loading the sample, the excess batter was trimmed and a thin layer of vaseline oil was applied to the edges of the samples to prevent sample drying. The following tests were performed on each sample: strain sweep test, frequency sweep test, oscillation temperature ramp test and flow ramp test. All measurements except oscillation temperature ramp were conducted at $25\text{ }^{\circ}\text{C} \pm 0.1\text{ }^{\circ}\text{C}$. Strain sweep tests were carried out in the range of 10^{-3} –20%, at 10 rad s^{-1} frequency and the storage modulus (G') and the loss modulus (G'') were recorded in order to determine the linear viscoelastic region of the batters. Frequency sweep tests were performed in the range of 0.01–10 Hz and 0.04% strain to determine the storage modulus (G'), the loss modulus (G''), complex modulus (G^*) and loss tangent ($\tan\delta$) as a function of frequency. Oscillation temperature ramp tests were carried out in the range of 30–120 $^{\circ}\text{C}$, at 0.04% strain and 1 Hz using a gradient equal to 4 $^{\circ}\text{C}/\text{min}$, and storage (G') and loss modulus (G''), complex modulus (G^*) and loss tangent ($\tan\delta$) versus frequency values were recorded. Flow ramp tests were conducted at shear rate between 0.01 and 100 s^{-1} under steady shear conditions. Results were fitted into the Power law Model (1) and Herschel–Bulkley Model (2):

$$\sigma = K \cdot \dot{\gamma}^n \quad (1)$$

$$\sigma = \sigma_0 + K \cdot \dot{\gamma}^n \quad (2)$$

where K is the consistency index (Pa s^n), n is the flow behavior index, σ is the shear stress (Pa) and $\dot{\gamma}$ is the shear rate ($1/\text{s}$). Each test was performed at least two times and averages of the results are reported in this study.

Physicochemical analysis of cakes

Cake samples were analyzed for their moisture (AACC Method 44-15A), ash (AACC Method 08-01), fat (AACC Method 30-25) and protein (AACC Method 46-30)

contents according to AACC (2000). The protein content of the samples was determined using Leco FP-528 Nitrogen/Protein Determinator (Leco, St. Joseph, Mich., U.S.A.) using Nx6.25. Water activity of the samples was evaluated using a water activity meter (Testo AG 400, Lenzkirch, Germany). Percent weight loss of the cakes, which means mass loss during baking, was determined according to Köksel (2009).

Physical characteristics of cakes

The specific volume of the cakes was determined according to AACC Method 72-10 (AACC 2000). The surface and crumb color of cake samples were measured using a Hunter colorimeter model Color Flex (Hunter Associates Inc., Reston, VA, USA). Hunter L^* (lightness/darkness), a^* (red (+)/green (−)), b^* (yellowness (+)/blueness (−)) color scale was used. The total color difference (ΔE) between the control sample (Q_0) and the samples, which were produced using quinoa flour, were calculated by Eq. (3) where subscripts C and Q refer to the control and to the different cake formulations, respectively.

$$\Delta E = \sqrt{(L_c^* - L_Q^*)^2 + (a_c^* - a_Q^*)^2 + (b_c^* - b_Q^*)^2} \quad (3)$$

Texture properties of the cake crumbs were determined 24 h after baking by TA-XT2i texture analyzer (Stable Micro System Co. Ltd., Surrey, England). Texture analyzer was equipped with an aluminum 36 mm diameter cylindrical probe and a load cell of 50 N. *Texture Profile Analysis* double compression test (TPA) was conducted at a speed of 2 mm/s and compression was set to 50% of their original height with a 30 s delay between the first and the second compression. Cake slices with a thickness of 15 mm were used for the analysis and the textural properties (hardness, springiness, cohesiveness and resilience) of the samples were calculated from the TPA curves, which were provided by the equipment software (Gularte et al. 2012). All measurements were conducted in at least eight parallels, and the averaged results are presented.

Sensory analysis

Sensory evaluation of cupcake samples were carried out with 20 semi-trained panelists, all of which were selected among the staff and graduate students of Ege University Food Engineering Department, between the age of 20–60 years. Panelists were asked to assess the samples for flavor, crumb hardness, crumb color and overall acceptability using five-point hedonic scale.

Statistical analysis

One-way ANOVA was used to carry out statistical analysis on the results for comparison ($\alpha = 0.05$). If a significant difference was found, means of the results were compared by using Duncan multiple comparison test ($\alpha = 0.05$) (IBM SPSS Statistics 20; IBM, Chicago, IL).

Results and discussion

Physicochemical analysis of flour

The proximate composition of the flour used in this study is presented in Table 1A. The protein (13.72%), fat (6.84%), ash (2.45%) and total dietary fiber (16.27%) contents of the quinoa flour were significantly higher than the rice flour and the potato starch ($p < 0.05$). Proximate composition analysis results such as protein, fat, ash and total dietary fiber content of the quinoa flour were in an agreement with those found by Föste et al. (2014), Alvarez-Jubete et al. (2009), Rosell et al. (2009) and Collar and Angioloni (2014). Proximate composition of the quinoa flour showed us that quinoa can be considered as a good crop for the production of cereal based gluten-free products such as

bread, pasta and cake for celiac disease patients who suffer from unbalanced intake of carbohydrates, protein, and fat.

Moisture content and water activity are related to the microbial, chemical and physical properties of the flour samples. Moisture of the products has great importance for the safe storage of cereals and their products because of microbial spoilage, particularly certain species of fungi (Hoseney 1994). In addition, water activity of the raw and processed food products cause some specific changes in color, aroma, flavor, texture, stability, and acceptability (Rockland and Nishi 1980). Moisture content of the quinoa flour and rice flour were found as 12.66 ± 0.07 and 13.68 ± 0.07 , respectively. Similar results were reported by Turkut et al. (2016) and Tömösközi et al. (2011). Water activity of the flour samples was found as 0.512 ± 0.00 and 0.635 ± 0.01 for quinoa flour and rice flour as can be seen in Table 1A. In addition, water activity of the potato starch was found as 0.566. All water activity values were lower than the critical limit for microorganism-induced spoilage, which is 0.6 (Barbosa-CÃ et al. 2008).

Water retention capacity

The water holding capacity, which refers to the ability of flour to absorb and retain bound, hydrodynamic, capillary,

Table 1 Flour composition, cake composition and cake properties, A: composition and water absorption capacities of flours; B: physicochemical properties of cake samples; C: baking properties of cake samples

Sample	Moisture content (%)	Fat content (%)	Protein content (%)	Ash content (%)	Total dietary fiber (%)	Water retention capacity (g water/g dry matters)	
A							
Quinoa flour	12.66 ± 0.07 ^a	6.84 ± 0.20 ^c	13.72 ± 0.09 ^b	2.45 ± 0.21 ^b	16.27 ± 0.48 ^c	1.20 ± 0.22 ^a	
Rice flour	13.68 ± 0.07 ^a	1.41 ± 0.03 ^b	6.867 ± 0.10 ^a	0.40 ± 0.06 ^a	7.91 ± 1.50 ^b	1.18 ± 0.21 ^a	
Potato starch	17.24 ± 0.9 ^b	0.29 ± 0.01 ^a	Not determined	0.24 ± 0.00 ^a	0.80 ± 0.01 ^a	0.62 ± 0.22 ^a	
Sample	Moisture content (%)		aw	Fat content (%)		Protein content (%)	Ash content (%)
B							
Q ₀	29.22 ± 0.96 ^{ab}		0.894 ± 0.001 ^a	22.30 ± 5.60 ^a		6.87 ± 0.27 ^a	1.13 ± 0.02 ^a
Q ₂₅	28.20 ± 1.14 ^{ab}		0.891 ± 0.015 ^a	20.91 ± 5.28 ^a		8.10 ± 0.23 ^b	1.35 ± 0.04 ^b
Q ₅₀	27.99 ± 1.62 ^a		0.892 ± 0.003 ^a	21.04 ± 6.87 ^a		9.49 ± 0.08 ^c	1.48 ± 0.02 ^c
Q ₇₅	29.91 ± 0.35 ^b		0.894 ± 0.001 ^a	19.45 ± 4.80 ^a		9.91 ± 0.14 ^d	1.58 ± 0.01 ^d
Sample	Baking loss (%)			Spesific volume (cm ³ /g)			
C							
Q ₀	13.11 ± 1.27 ^a			1.41 ± 0.01 ^a			
Q ₂₅	13.62 ± 0.93 ^a			1.50 ± 0.02 ^b			
Q ₅₀	12.77 ± 0.93 ^a			1.55 ± 0.01 ^c			
Q ₇₅	12.93 ± 1.14 ^a			1.61 ± 0.02 ^d			

Different letters in the same column indicate significant differences between means ($p < 0.05$)

and physically entrapped water against gravity, is an important functional property for processing and finished-product quality of baked quality (Kweon et al. 2011; Shevkani et al. 2014). Flour constituents such as proteins, damaged starch and pentosanes are noted as influencing WRC of the flours (Heywood et al. 2002; Kweon et al. 2011; Shevkani et al. 2014). WRC of flour and flour blends are shown in Tables 1A and 2A. WRC was found as 1.18 ± 0.21 g water/g dry matter for rice flour and 0.62 ± 0.21 g water/g dry matters for potato starch. In addition, WRC of quinoa flour was determined as 1.20 ± 0.22 g water/g dry matters that were higher than potato starch and was agreement in literature (Collar and Angioloni 2014). Water holding capacities of the amaranth, buckwheat, rye, and teff were reported as 1.05 ± 0.05 – 2.43 g water/g flour, 1.13 ± 0.09 – 0.8 ± 0.09 g water/g flour, 1.16 ± 0.12 – 0.91 ± 0.07 g water/g flour, and 1.36 ± 0.11 – 1.00 ± 0.09 g water/g flour, respectively (Shevkani et al. 2014; Collar and Angioloni 2014). WRC values of the flour blends ranged between 0.79 ± 0.25 and 1.01 ± 0.20 g water/g dry matter and although WRC values of the blends were tended to increase with quinoa flour addition, there is no significant difference between them ($p > 0.05$). This trend ascribed to the formation of large clusters of protein molecules or protein aggregates bound by hydrogen bonds and non-covalent forces in quinoa flour (Collar and Angioloni 2014).

Density of cake batters

Density of the cake batters are within 0.79 ± 0.00 and 0.89 ± 0.01 as can be seen in the Table 2A and quinoa flour addition significantly increased the density of the cake

batters ($p < 0.05$). Density of the cake batters usually refer to the air content of the batter. Because of that, an increase in the density of the samples can be associated with a decrease in the air volume incorporated to the batter (Gómez et al. 2007).

Rheological characterization of cake batter

Flow behavior

Flow properties of the gluten-free batters were studied within the 0.01 – 100 s⁻¹ shear rate. Figure 1-I represents the impact of quinoa flour on apparent viscosity and shear stress of the gluten-free batter formulations. The increase in quinoa flour content caused an increase in the viscosity values. As the high viscosity obstruct air incorporation during mixing (Gómez et al. 2007), increase of the batter viscosity explains the reason why batter density increases with the substitution of quinoa flour. High viscosity is a favorable factor for batter stability and quality of the final baked product (Baixauli et al. 2008). The increase in the viscosity of the batter is ascribed to the quantity of water available in the system since amount of the available water in the system is affected with the amount of water absorbed by the flour, which is itself associated to the quantity of proteins (Maache-Rezzoug et al. 1998). Quinoa flour bound more water as compared to the rice flour and potato starch. Hence, there was less free water available to facilitate the movement of particles in quinoa flour added batters giving higher viscosity values (Shevkani et al. 2015). Maache-Rezzoug et al. (1998), Shevkani and Singh (2014) and Shevkani et al. (2015) reported that increase in the protein content of the flour lead to an increase in viscosity.

Table 2 Rheological characterization of cake batters. A: Density of gluten-free batters, WRC of flour blends and statistical results of power law model. B: Minimum and maximum values of the complex modulus G^* and the respective temperatures T during temperature

Sample	Water retention capacity of the flour blends (%)	Density (g/ml)	Consistency index K (Pa s ⁿ)	Flow behavior index n (–)	R ²	RMSE	Adj. R ²
A							
Q ₀	0.79 ± 0.25 ^a	0.79 ± 0.00 ^a	1.756 ± 0.1867 ^a	0.6793 ± 0.0160 ^d	0.9993	0.323	0.9993
Q ₂₅	0.89 ± 0.25 ^a	0.80 ± 0.00 ^a	6.9985 ± 0.6357 ^b	0.4799 ± 0.0196 ^c	0.9928	1.399	0.9928
Q ₅₀	0.91 ± 0.20 ^a	0.84 ± 0.02 ^b	18.0867 ± 0.3669 ^d	0.3502 ± 0.0059 ^a	0.98757	2.277	0.9875
Q ₇₅	1.01 ± 0.20 ^a	0.89 ± 0.01 ^c	16.4750 ± 0.8839 ^c	0.4300 ± 0.0139 ^b	0.9958	1.893	0.9958
Sample	G _{min} [*] (Pa)	T at G _{min} [*] (°C)		G _{min} [*] (kPa)		T at G _{min} [*] (°C)	
B							
Q ₀	12.90 ± 4.7 ^a	56.65 ± 1.70 ^a		1.96 ± 0.4 ^a		92.82 ± 0.3 ^a	
Q ₂₅	44.47 ± 2.1 ^a	51.21 ± 6.6 ^a		3.10 ± 0.3 ^b		97.27 ± 1.4 ^b	
Q ₅₀	87.58 ± 3.9 ^b	52.79 ± 2.6 ^a		6.59 ± 0.6 ^c		99.06 ± 0.0 ^{bc}	
Q ₇₅	162.92 ± 29.5 ^c	50.57 ± 2.9 ^a		8.66 ± 0.1 ^d		99.69 ± 0.4 ^c

Fig. 1 Rheological characterization of cake batters. I: Flow ramp curves of the gluten-free batter samples. II: Strain sweep curves of the gluten-free batter samples (curves are the mean of at least two replicates)

Within the studied shear rate range; shear stress versus shear rate values fitted fairly well to the power-law equation ($r > 0.98$). Table 2A shows the flow index (n) and consistency index (K) of different batter samples for power law. The n which may vary from $n = 1$ (leading to the Newtonian law) to $n < 1$ or $n > 1$ to describe shear-thinning or shear-thickening flow behavior (Fischer et al. 2009) ranged from 0.6793 to 0.3502 for batter samples. So all the batter samples showed shear thinning (pseudoplastic) behavior, which means that the viscosity decreases with the increasing shear rate. In addition, n values significantly

decreased ($p < 0.05$) as the quinoa flour content in the formulations increased indicating the formation of a more complex structure (Baixauli et al. 2008). The consistency index (K) values of the samples ranged from 1.756 to 18.0867 Pa s n and increase in the quinoa flour content caused an increase ($p < 0.05$) in the K values. Hence, the consistency index (K) is an indication of the viscous behavior of food; increase in the consistency index (K) values can be associated with the higher protein contents of the quinoa flour. Similar results were reported by Turkut et al. (2016) such that increasing quinoa level of the

gluten-free bread formulation caused an increase in the viscosity and K values of the dough.

Strain sweep test

Linear viscoelastic regions (LVR) in which characteristics of the samples don't depend on the magnitude of the stress, the magnitude of the deforming strain, or the application rate of the strain (Steffe 1996) of the batter samples were determined using strain sweep test. Storage modulus (G'), loss modulus (G'') and complex modulus (G^*) and damping factor ($\tan\delta$, G''/G') as a function of strain (γ , %) of the batters are shown in Fig. 1-II. It was observed that increasing quinoa level in the formulations caused higher elastic modulus G' than loss modulus G'' (Fig. 1-II, A and B). For all formulations, G' and G'' decreased after a certain limit and also G' was found to decrease more than G'' . As a result of that $\tan\delta$ increased with the strain amplitude. Since the structural properties of the samples are usually best related to elasticity; the long LVR of G' can be used as a measurement of a well-dispersed and stable system (Mariotti et al. 2009). It was determined that increasing quinoa level increases stability and homogeneity of the batters since the higher quinoa level gave longer LVR of G' . Generally, a drop in G' started to occur above 0.04% strain. Therefore, the following frequency and temperature sweep tests were performed at this level of strain.

Frequency sweep test

Storage modulus (G'), loss modulus (G''), complex modulus (G^*) and damping factor curves of the formulations that were obtained from frequency sweep tests are shown in Fig. 2. The low deformation conditions that are used for the oscillatory measurements, do not disturb or destroy the inherent structure. Due to their nondestructive nature, they are of great value in studying the influence and actions of ingredients (Lazaridou et al. 2007). Frequency sweep tests are applied to the gluten-free cake batters to determine how the viscous and elastic behaviors of the batters change with the application of strain rate while the amplitude of the signal is held constant (Steffe 1996). It was determined that the value of moduli increased with an increase in frequency for all batters. In addition, values of the dynamic moduli of the batters were highly influenced by the amount of quinoa in the formulations. Increasing quinoa level of the formulations caused an increase in G' , G'' and G^* and a decrease in $\tan\delta$ of the batters. For all formulations except Q_0 , storage modulus was higher than loss modulus providing values of $\tan\delta$ lower than 1, which indicates a solid elastic-like behavior (Weipert 1990). For the batter without quinoa flour, $\tan\delta$ was higher than 1, which means more liquid like behavior than solid like behavior. High G' and low G''

generally reflect a more rigid and stiff material whose $\tan\delta$ is small (Mariotti et al. 2009), suggesting that increasing quinoa level causes more rigid and stiff gluten-free cake batters evident from higher G' and lower $\tan\delta$ values. Increase in the elasticity of the batters with quinoa flour substitution can be associated with WRC of the quinoa flour, which is affected by the amount of protein content of the flour (Maache-Rezzoug et al. 1998; Shevkani et al. 2015). Maache-Rezzoug et al. (1998) and Shevkani et al. (2015) reported that higher amount of proteins in the batter lead to an increase in its elasticity. Similar results were reported by Föste et al. (2014) showing that gluten-free dough became more elastic with increasing amount of quinoa bran at the 1–10 Hz frequency range.

Temperature sweep test

Temperature sweep tests were conducted in order to understand the structural changes in the batters during heating to get an opinion from the baking stage. The conditions applied in the rheometer are not equal to the real baking process but it is considered a valuable tool to understand the structural events of different samples during baking.

The viscoelastic properties were investigated from 30 to 120 °C and the temperature sweep test curves of the samples are presented in the Fig. 3. The structural changes, which occur during baking stage, are very important since these factors determine the bubble formation, bubble stability and final texture of the product (Shelke et al. 1990). It is determined that G' , G'' and G^* were highly affected from the quinoa flour level and the contribution of the G' to the G^* was higher than that of G'' for the whole temperature range. In addition, the storage modulus were higher for the batters with increased amount of quinoa flour, which denotes the behavior becomes more elastic with increasing quinoa flour. Increase in the elasticity of the batters with quinoa flour substitution may be ascribed to the quantity of protein amount of the quinoa flour is higher than the rice flour and potato starch.

Three stages of change were determined in G' , G'' , and G^* during temperature sweep test. In the first stage, the initial increase in temperature led to a decrease in G' , G'' , and G^* until a critical temperature was reached. Thermal activation of the molecules, absorption of energy by starch molecules, expanding protein network and reducing viscosity resulted in an initial reduction of the stiffness of the batters (Struck et al. 2016) and this reduction of the stiffness occurred between 30 and 60 °C at which G' , G'' , and G^* minimum occurred. Lee et al. (2005) and Baixaui et al. (2008) reported similar reduction of the stiffness in the cake batters. Above the critical temperature at which G' , G'' , and G^* minimum occurs, structure formation was

Fig. 2 Frequency sweep curves of the gluten-free batter samples (curves are the mean of at least two replicates)

Fig. 3 Temperature sweep curves of the gluten-free batter samples (curves are the mean of at least two replicates)

triggered by protein denaturation and starch swelling and as a result G' , G'' , and G^* started to increase. During this stage, viscoelasticity of the batters were increased because of the protein denaturation. In addition, the viscoelasticity of the batters were increased with increasing quinoa flour in batter which ascribed to the higher protein amount of quinoa flour. In the final stage, after reaching a maximum at a specific temperature, G' , G'' , and G^* started to decrease because of the completion of structural modifications. Quinoa flour level significantly increased the maximum G' , G'' , and G^* values and the corresponding temperatures ($p < 0.05$) (Table 2B). The presence of higher protein in the quinoa flour reduces the water mobility hence initiation of the gelatinization was delayed in the quinoa flour added batters. The decrease in the G' , G'' , and G^* with increasing amount of quinoa flour pointed that proteins make the starch granules more resistant to disintegration (Shevkani et al. 2015). Hence, the denatured proteins stabilize the continuous matrix between the dispersed and continuous phases; the quinoa flour addition significantly increased the mechanical strength of the batters (Shevkani et al. 2015). Shevkani et al. (2015) reported that incorporation of protein isolates into rice flour increased the stability of starch granules.

Physicochemical analysis of cakes

Table 1B shows the effects of quinoa flour substitution on the moisture content, fat content, protein content, ash content, and water activity of the gluten-free cakes. Moisture content of the cake samples were found to change between 27.99 ± 1.62 and 29.91 ± 0.35 . Fat content of the cake samples did not show significant difference as a result of quinoa addition ($p > 0.05$). As expected (Föste et al. 2014; Enriquez et al. 2003) quinoa flour caused an increase in the protein and ash content of the cake samples ($p < 0.05$) as a result of quinoa flour's chemical composition.

Water activity of the cake samples are shown in the Table 1B. Water activity (a_w) describes the available or free water in the food products and it is an important factor for the shelf life of the foods. The substitution of rice flour and potato starch with quinoa flour did not cause any difference in a_w values of the cake samples ($p > 0.05$). Rothschild et al. (2015) reported similar water activity results for non-roasted and roasted quinoa gluten-free cakes. Baking loss (%) of the samples are shown in Table 1C. No significant difference was determined in baking loss of the cake samples ($p > 0.05$) which indicates that water retention capacities of the formulations are close to each other (Gómez et al. 2007).

Physical characteristics of cakes

Effects of the quinoa flour addition on the specific volume, crust and crumb color and texture profile of the gluten-free cake samples were analyzed. Specific volume is one of the most important quality parameters for baked products in customer preference. Sample without quinoa flour exhibited the lowest specific volume, whereas the sample Q₇₅ had the highest specific volume (Table 1C). A significant increase was found in the specific volume values of the cake samples with increasing quinoa flour level ($p < 0.05$). The higher protein content of the quinoa flour provide higher specific volume hence proteins increase the volume of cakes by increasing viscoelasticity of the batters and the time the batter gets before becoming semisolid which is related to protein-starch interaction and transition (Shevkani et al. 2015). These results showed us that volume of cakes did not depend on the initial air quantity but on its capacity of retaining it during baking (Gómez et al. 2007). Similar results were also found by Föste et al. (2014), in which the replacement of rice and corn flour by whole grain quinoa flour significantly increased the bread volume.

Color of baked products can be associated with the ingredients present in the product and their interactions to one another. Color characteristics (L^* , a^* , b^* and ΔE) of gluten-free cupcake crusts and crumbs can be seen in Table 3A. The a^* values of crumbs and crusts which indicate redness value showed a tendency to increase with quinoa flour addition. Increase in the redness in the crust of cakes may be ascribed to the caramelisation and Maillard reactions. Increasing of the protein content of the cakes as a result of increasing quinoa flour incorporation was stimulated the Maillard reactions, thus created dark-brown components (Shevkani and Singh 2014). Shevkani and Singh (2014) was reported increase in the redness values of the crusts muffins with protein enrichment. The increasing in the redness values of cake crumb might be associated with the natural color of the quinoa flour. Lightness (L^*) values of crumbs and crusts showed decreasing with increasing quinoa flour ($p < 0.05$). The decreasing may be ascribed to the original color of quinoa flour, which is darker than the rice flour and potato starch. Lorenz and Coulter (1991) reported that increasing levels of quinoa flour caused slightly darker cake crumbs.

The effect of substitution of quinoa flour on the textural characteristics (hardness, springiness, cohesiveness and resilience) of gluten-free cupcakes shown in Table 3B. Textural characteristics were significantly ($p < 0.05$) affected by substitution of quinoa flour. The sample without quinoa flour exhibited the highest hardness value and the addition of quinoa flour caused a significant decrease in the maximum force during fracture, which correlates to hardness. Springiness of the cake crumbs had been related

Table 3 Color, textural characteristics and sensory characteristics of cake samples A: Crust and crumb color of gluten-free cake samples, B: textural characteristics of gluten-free cake samples and C: sensory characteristics of gluten-free cake samples

Sample	Crust color				Crumb color				
	L*	a*	b*	ΔE	L*	a*	b*	ΔE	
A									
Q ₀	53.48 ± 1.20 ^d	17.58 ± 0.78 ^a	35.01 ± 0.48 ^c		78.00 ± 1.10 ^d	6.30 ± 0.78 ^a	31.31 ± 2.04 ^a		
Q ₂₅	50.34 ± 0.06 ^c	18.74 ± 0.03 ^c	36.30 ± 0.28 ^d	3.60 ± 0.14 ^a	71.23 ± 0.49 ^c	8.26 ± 0.10 ^c	34.80 ± 0.14 ^d	7.87 ± 0.38 ^b	
Q ₅₀	47.15 ± 0.43 ^b	18.20 ± 0.99 ^b	34.21 ± 0.58 ^b	6.51 ± 0.33 ^b	71.76 ± 0.87 ^b	6.80 ± 1.56 ^b	33.29 ± 0.75 ^b	6.76 ± 1.03 ^a	
Q ₇₅	44.44 ± 0.61 ^a	18.77 ± 0.24 ^d	33.68 ± 0.91 ^a	9.26 ± 0.70 ^c	68.34 ± 0.95 ^a	8.33 ± 0.27 ^d	33.80 ± 0.59 ^c	10.19 ± 1.10 ^c	
Sample	Textural characteristics								
	Hardness (N)			Springiness		Cohesiveness		Resilience	
B									
Q ₀	59.25 ± 2.91 ^b			0.91 ± 0.02 ^a		0.52 ± 0.02 ^c		0.25 ± 0.01 ^c	
Q ₂₅	33.82 ± 4.16 ^a			0.90 ± 0.04 ^a		0.44 ± 0.02 ^a		0.22 ± 0.01 ^a	
Q ₅₀	31.06 ± 2.24 ^a			0.93 ± 0.01 ^a		0.49 ± 0.02 ^b		0.24 ± 0.01 ^b	
Q ₇₅	30.62 ± 2.28 ^a			0.93 ± 0.03 ^a		0.53 ± 0.02 ^c		0.27 ± 0.01 ^d	
Sample	Sensory characteristics								
	Color		Texture		Appearance		Taste		Overall acceptability
C									
Q ₀	3.68 ± 0.86 ^a		2.85 ± 1.04 ^a		3.20 ± 0.89 ^a		3.60 ± 1.23 ^{ab}		3.43 ± 1.12 ^a
Q ₂₅	4.33 ± 0.65 ^b		3.35 ± 0.88 ^{ab}		4.05 ± 0.76 ^b		3.35 ± 0.88 ^a		3.40 ± 0.77 ^a
Q ₅₀	4.40 ± 0.75 ^b		3.83 ± 0.71 ^{bc}		4.30 ± 0.73 ^b		4.03 ± 0.83 ^b		4.03 ± 0.77 ^b
Q ₇₅	3.20 ± 0.89 ^a		3.95 ± 0.83 ^d		3.78 ± 0.83 ^b		3.85 ± 0.75 ^{ab}		3.75 ± 0.71 ^{ab}

Different letters in the same column indicate significant differences between means ($p < 0.05$)

to the protein aggregation and indicates fresh, aerated and elastic product (Shevkani and Singh 2014). Springiness of the gluten free cakes slightly increased with the increasing quinoa flour which shows that quinoa flour improved the elasticity of the gluten free cakes because of the higher protein content. Cohesiveness quantifies the internal resistance of food structure under some compression and it is an important parameter for manufacturing and packaging because a product with a strong cohesion will be presented to the consumers in its expected state. Quinoa flour addition to the control sample (Q₀) significantly decreased the cohesiveness values of the samples, however increasing of the quinoa flour amount of the samples (Q₂₅, Q₅₀ and Q₇₅) was caused an increase in the cohesiveness values of the Q₂₅ and Q₅₀ and Q₇₅ ($p < 0.05$). Q₂₅ was showed the lowest cohesiveness values and Q₇₅ was showed the highest cohesiveness values. Gularte et al. (2012) reported that replacing rice flour with legume flour resulted an increase in cohesiveness and springiness values. In addition, Shevkani and Singh (2014) showed that enrichment of the gluten free muffins with different protein isolates lead

an increase in cohesiveness and springiness values of the muffins.

Sensory analysis of cake samples

Sensory characteristics; color, texture, appearance, taste and overall acceptability scores of gluten-free cakes are shown in Table 3C. The results showed that quinoa flour significantly improved the sensory characteristics of the gluten-free cakes ($p < 0.05$). In color hedonic evaluation, Q₂₅ and Q₅₀ got higher scores than the Q₀ and Q₇₅ ($p < 0.05$). Texture evaluation gave the highest score to Q₇₅ as can be seen in Fig. 3c in appearance, taste and overall acceptability evaluation; Q₅₀ got the highest scores among all the samples. As can be seen in the scores, an excess quinoa flour amount affected the taste and the overall acceptability scores negatively because of quinoa flours' own bitterness and off-flavor (Föste et al. 2014).

Conclusion

The results obtained in this study showed that substitution of quinoa flour significantly improved the rheological properties of cake batters and the physical, chemical properties and quality parameters of cupcakes obtained from them. Rheological analysis showed that batter stability, homogeneity and mechanical strength were improved with quinoa flour addition. In addition, quinoa flour improved the nutritional and technological properties and sensory attributes. From this study, it may be concluded that 50% quinoa flour formulation can successfully be incorporated into gluten-free cake formulations without creating any negative effect.

Funding Funding was provided by Ege University Scientific Project Commission (Grant No. 14-MUH-50).

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