

College of Traditional Chinese Medicine. Shanghai, China (in English).

14. Zong XF, Liscum G (1996). Chinese medicinal teas. Boulder, CO: Blue Poppy Press (in English).

15. Zhu YP (1998). In: Gou Qi Zi. *Chinese Materia Medica Chemistry, Pharmacology and Applications* (pp. 642–646). Amsterdam, Netherlands: Harwood Academic Publishers (in English).

16. Wang Z. (2006). The Magic Lycium Barbarum from Ningxia Province. China:58–128 (in English).

Поступила в редакцию: 21.05.2023

Адрес для корреспонденции: ivanovap@canri

УДК 664.6

РАЗРАБОТКА БЕЗГЛЮТЕНОВЫХ МАФФИНОВ С УЛУЧШЕННЫМ СОДЕРЖАНИЕМ МИНЕРАЛЬНЫХ ВЕЩЕСТВ

¹Д. Исерлийска: ORCID: <https://orcid.org/0000-0001-9950-082X>,

¹Г. Живанович: ORCID: <https://orcid.org/0000-0003-3278-6119>,

²М. Марудова, ¹А. Илиев

¹Институт сохранения, переработки и качества пищевых продуктов, ²Физический факультет университета Пловдива им. Паисия Хилендарского, г. Пловдив, Болгария

DEVELOPMENT OF GLUTEN-FREE MUFFINS IMPROVED IN MINERAL CONTENT

¹D. Iserliyska: ORCID: <https://orcid.org/0000-0001-9950-082X>,

¹G. Zsivanovits: ORCID: <https://orcid.org/0000-0003-3278-6119>,

²M. Marudova, ¹A. Iliev

¹Institute of Food Preservation and Quality,

²Plovdiv University «Paisii Hilendarski», Faculty of Physics,
Plovdiv, Bulgaria

Реферат.

Пищевая полноценность безглютеновой диеты требуют дополнительного изучения ввиду все более активного исключения из рационов питания разных групп населения

пищевых продуктов, получаемых из пшеницы, являющейся важным источником для получения организмом микроэлементов и клетчатки.

Цель исследования: оценить возможность применения смесей безглютеновой муки, предназначенной для выпечки кексов, в качестве источника, удовлетворяющего потребности организма в основных минеральных элементах у пациентов, страдающих глютеновой болезнью (целиакией).

Материал и методы исследования. Содержание минералов в безглютеновой муке, доступной на болгарском рынке, определяли с помощью атомно-эмиссионной спектроскопии. Тесто для кексов и сами кексы подвергали испытаниям для изучения основных физических свойств, включая вязкость теста, свойства растекания и восстановления, а также определяли его влажность. Анализ профиля текстуры (TPA) проводили с помощью анализатора (StableMicroSystems TA-XT2Plus); термические свойства определяли методом дифференциальной сканирующей калориметрии (DSC), после чего осуществляли органолептический анализ готовой продукции.

Результаты исследования. Безглютеновые мучные смеси содержали магний и железо, близкие к содержанию данных элементов в цельнозерновой муке, содержание кальция превышало исходные значения, а содержание цинка было ниже исходных показателей.

Выводы. На основании проведенных исследований из смесей рисовой муки, кукурузной муки, нута, гречихи и порошка рожкового дерева без добавления яиц была получена безглютеновая мука, сравнимая по минеральному составу с цельнозерновой мукой, пригодная для выпечки маффинов.

Ключевые слова: безглютеновая мука, содержание минеральных веществ, термические свойства, реология теста, текстурный профиль.

Abstract.

The nutritional adequacy of gluten-free diet has been questioned due to the elimination of wheat, an important vehicle for micronutrient fortification and source of fiber.

Objective: the current study was carried out to use blends of gluten-free flours as a good source of essential mineral elements for production of muffins designated to patients with celiac disease.

Material and methods. Initially the mineral content of the gluten-free flours available on the Bulgarian market was determined by means of ICP-AES. Muffin batters and muffins were subjected to basic physical properties tests including batter viscosity, creep and recovery properties and moisture. Texture Profile Analysis (TPA) by TAXT. Plus Texture analyzer, thermal properties, by the method of differential scanning calorimetry (DSC) and sensory analysis was performed to the final products.

Results. The gluten-free flour mixtures contained magnesium and iron close to the content of these elements in the whole grain flour, exceeded calcium and contained less zinc.

Conclusions. Based on the results the gluten-free flours comparable to the whole grain flour mineral composition were mixed and eggless muffins prepared from rice flour/corn flour/chickpeas/buckwheat/carob bean powder blends.

Key words: gluten free flours, mineral content, thermal properties, batters' rheology, texture profile.

Introduction. The only way to control the condition of celiac patients is for them to follow a strict diet excluding gluten-containing foods. Such a drastic change in the diet leads to a high risk of deficiency of certain micronutrients (folic acid, some minerals, especially calcium, magnesium, iron and zinc), as well as excess of some macronutrients, especially saturated fatty acids [6]. A major factor leading to the described deficiency of essential elements is the body's autoimmune response, which reduces the absorption of essential elements due to iron and zinc deficiency [17]. A number of researchers reported the gluten-free diet could be mineral poor [6]. Shepherd et al. (2013) stated out at least one in ten patients on a gluten-free diet suffered deficiency of essential elements, calcium and magnesium, respectively, in both genders, zinc in men and iron in women [17]. Öhlund and co-authors evaluated nutrient intake in children undergoing a gluten-free diet and found out they followed the same trends as healthy children, in particular simple sugars and

saturated fat higher intake but lower intake of fibers, vitamin D and magnesium [10]. There are numerous suggestions in the literature for gluten-free products with increased nutritional value. Yalcin and co-authors offer tarhana based on rice flour combined with chickpea flour to increase the nutritional value [5]. Some researchers used sorghum combined with rice flour and corn starch, others used different mixtures of sorghum, rice and corn with potato starch for the production of pasta [11, 21]. Several authors utilized buckwheat as a source of polyunsaturated fatty acids in bread [4]. Sharoba et al. (2014) also investigated the potential to increase the content of essential elements (Ca, Mg, Fe) using mixtures of corn flour and artichoke flour [16].

The rheological properties of dough have an essential role in processing and quality of baked products [9]. Dough of bakery products could be defined as fluid that contain significant amounts of dissolved high molecular weight compounds (polymers) and/or suspended solids [14]. Hence, they exhibit non-Newtonian behavior, with a high level of elasticity and are very sensitive to the temperature, the water content and, more generally, the composition (starch origin, protein type, presence of lipids) [20]. The gluten, like a structural protein forms a three-dimensional network, controls the flour hydration and determines the dough visco-elastic properties. The gluten-free baked products available on the market often have poor technological quality, exhibiting low volume, poor color, and crumbling texture, besides great variation in the nutrient composition, with low protein and high fat contents [15]. The rheological characteristics of gluten-free doughs are usually described in terms of Herschel–Bulkley's equation, but it could not be applied in all cases, for example it is not suitable for rice flour doughs [13].

The aim of the present work was to test gluten-free flour blends, in order to develop eggless muffins enhanced with essential elements targeting their quality parameters.

Objective: the current study was carried out to use blends of gluten-free flours as a good source of essential mineral elements for production of muffins designated to patients with celiac disease.

Material and methods.

Materials. Based on previous experience and availability the gluten-free flours were selected and purchased from the Bulgarian

market: rice, corn, oat (two conventional and one organic), millet, buckwheat, quinoa, amaranth, chickpea, carob and chestnut (Table 1).

The mineral content of the gluten-free flours, blends and muffins were determined in triplicate by means of ICP-AES (Spectroflame MODULA-FTMOA 81A) in terms of Ca, Mg, Fe and Zn. The content of the studied essential elements was compared to experimental data on their content in white and whole wheat flour (Table 1).

Table 1 – Content of Ca, Mg, Fe и Zn in the selected flours

	Samples	Minerals			
		Ca (mg/kg)	Mg (mg/kg)	Fe (mg/kg)	Zn (mg/kg)
Gluten free flours	Rice	132.0 ±3.0	454.0±20.0	42.0±2.0	9.1±0.5
	Corn	79.0 ±1.3	770.0±10.0	25.0±0.4	13.0 ±0.9
	Oat convent	2100.0 ±20.0	1500.0 ±50.0	73.0±2.0	88.0±2.0
	Oat convent	345.0 ±10.0	310.0±15.0	44.0±2.0	45.0±1.0
	Oat organic	954.0 ±25.0	966.0±15.0	80.0±5.0	63.0±5.0
	Millet	170.0 ±4.5	830.0 ±25.0	45.0±2.0	27.0±1.2
	Buckwheat	520.0 ±10.0	2500.0±70.0	39.0±1.2	35.0±0.9
	Quinoa	175.0 ±4.0	570.0±9.0	18.0±0.5	1.5±0.02
	Amaranth	1580.0±50.0	2150.0±80.0	69.0±1.5	29.0±0.3
	Chickpea	450.0 ±20.0	1750.0±40.0	49.0±2.0	28.0±0.8
	Carob	3200.0 ±150.0	650.0±30.0	35.0±2.0	15.0±0.5
	Chestnut	330.0±5.0	410.0±7.0	13.0±0.2	4.5±0.05
	White flour	179.0 ±7.0	260.0±7.0	49.0±0.5	9.0±0.06
	Whole flour	390.0±5.0	1360.0±25.0	39.0±0.8	29.0±0.5

A mixture was prepared containing 40% chestnut, 30% millet and 30% oat flour. The resulting blend was superior to white flour in terms of the content of all tested elements and inferior to whole wheat flour only in terms of Mg by having 704 mg / kg Ca, 744 mg / kg Mg, 53 mg / kg Fe and 40 mg / kg Zn (data not shown). The test batch of muffins was prepared using the latter blend in order to assess its potential for use in the bakery.

Mineral composition modeling. Due to the large number of variables, it was not possible in the present work to investigate all the available raw materials in all appropriate proportions. The ratio blends in close proportion in terms of the selected essential elements to the whole wheat flour as a control were used. The gluten-free flours study

indicated (Table 1) the largest difference in elemental composition was at the expense of the magnesium shortage and the excess of calcium if compared to the wholegrain flour. An approach was chosen flours with high magnesium content were added to the basic flour available. Rice and corn flours were selected as basic flours for reasons of price and availability. The selected blends and the contents of the investigated essential elements estimated theoretically are presented in Table 2. The proposed blends contained magnesium and iron close to the content of these elements in the wholegrain flour. The calcium content of some mixtures exceeded the control with 50% and zinc was less than the control. Due to the lower zinc content in most of the selected flours, all of the proposed mixtures contained less of this element compared to the reference flour.

Mixtures with high chickpea content were close to the whole flour and contained about 15% less zinc than the control. The replacement of carob with oat flour that would have compensated for this shortage turned to be not a good option for preliminary studies from the previous stage of the project had shown oatmeal impaired the baking properties of the mixtures.

The ten blends were used to produce muffin batters and based on the rheological study four formulations were selected for further experiments designated as F2, F4, F8, F10 and the Control (Table 2).

Muffins preparation. Muffin recipe contained the following ingredients: pure granulated white sugar, double-acting baking powder (Dr. Oetker), sunflower oil, white rice flour, corn, chickpea, buckwheat, carob and whole wheat flour (control) all purchased from the local supermarket. Flour blend 41%, sucrose 16%, baking powder 1%, sunflower oil 13% and water 29% were mixed together in a bowl and blended at speed 3 for 10 seconds. Muffin pans were filled with the batter (55-65 g each) and were baked for 20 minutes or until done at 180°C in a preheated oven. Following the five-minute setting period, muffins were removed from the pans, allowed to cool on wire racks for one hour. Afterwards the analyses were performed.

Table 2 – Mineral composition of gluten-free flour blends

Samples	Whole flour, %	Corn flour, %	Rice flour, %	Chick-pea flour, %	Buck Wheat flour, %	Carob flour, %	Ca, mg/kg	Mg, mg/kg	Fe, mg/kg	Zn, mg/kg
F1	-	45	0	50	0	5	421.00	1254.0	37.50	20.60
F2	-	30	0	65	0	5	476.20	1401.0	41.10	22.85
F3	-	65	0	0	30	5	327.00	1283.0	30.30	18.50
F4	-	55	0	0	40	5	411.45	1456.0	31.10	21.90
F5	-	0	35	60	0	5	476.20	1241.4	45.85	20.73
F6	-	0	10	85	0	5	555.70	1565.4	47.60	25.46
F7	-	0	55	0	40	5	396.60	1282.2	41.25	18.15
F8	-	0	25	70	0	5	508.00	1371.0	46.55	22.62
F9	-	0	40	0	55	5	438.30	1589.1	41.10	21.44
F10	-	0	50	0	45	5	460.00	1384.5	40.30	21.05
Control	100	-	-	-	-	-	340.00	1400.0	39.00	29.00

Physical parameters.

Batters viscosity. The dough viscosity was measured by rotational viscometer HAAKE VT 550 (Germany) in five repetitions. All the measurements were done at 25°C using standard cone-cylinder geometry (10.65 mm diameter and 0.9 mm gap). The flow experiments were conducted under steady-shear conditions with shear rate ranging from 0.0123 to 1000 s⁻¹. The experimental data were evaluated by rheological models such as Herschel–Bulkley, Mizrahi-Berk, Ofoli, Vocadlo and Casson models [5].

Thermal properties. The starch gelatinization and the water state in the batters and muffins were characterized by means of a Differential Scanning Calorimetry Analysis (DSC 204 F1 Phoenix NETZSCH-Gerätebau GmbH, Germany). The samples (15 mg) were closed hermetically in aluminum pans and cooled down from 20°C to -50 °C at cooling rate 5°C min⁻¹ and heated to 150°C at a rate 10°C min⁻¹, in two repetitions. The endothermal transitions of free water melting and starch gelatinization were evaluated with the use of instrument software Proteus Analysis (Netzsch, Germany). The amount of the bound water was calculated as the difference between the total water content and the free water.

Texture analysis. The texture of the gluten-free batters [18] and muffins was examined by texture analyzer (StableMicroSystems TA-XT2Plus) in five repetitions. All experiments were done at 25°C in retardation (stress holding in time) and relaxation (strain holding in time) mode using standard cylinder in cylinder ($d_1 = 30$ mm, $d_2 = 25$ mm, $h = 40$ mm, $m = 30$ g) geometry. 2 kPa compression stress was obtained by 1 mms⁻¹ deformation speed and hold for 180 s and after that caused deformation was hold for 180 s. The retardation and relaxation curves were evaluated by generalized Kelvin and Maxwell models, respectively.

Texture of the final products was evaluated by texture profile analysis method (TPA). A 50 mm diameter cylinder (slightly bigger than the muffins) was used to compress twice the muffins, up to 5 mm deformation (elastic diapason) and 5 s rest between deformations. The Firmness (N), Springiness, Cohesiveness, Gumminess (N) and Chewiness (N) were calculated for statistical analysis.

Sensory evaluation. 9-point hedonic scale was used to evaluate the overall acceptability of the muffin formulations. Analysis of variance (ANOVA) was used for statistical analysis of data.

Statistical analysis. The nonlinear regression in the application of the models was performed using Table Curve 2D software. The statistically significant groups were determined by ANOVA Homogeneous groups for LSD test at $p \leq 0.05$ in Statistica 7.

Acknowledgements. This research was supported by the Agricultural Academy of Bulgaria, grant XTAИ №142: Usage of gluten-free flour mixtures for food production.

Results and discussion

Physical properties. Quality of the muffins depends mainly on the batters physical properties.

Parameters of the viscosity – yield stress, consistency index, flow behavior index of plasticity and elasticity. The coefficients of the viscometric models used are presented in Table 3. The relationship between the yield stress (τ) and the speed gradient $\dot{\gamma}$ at $t = 25^\circ\text{C}$ for all of the batters tested was described the best by the Herschel–Bulkley's model:

The relationship between the yield stress (τ) and the speed gradient $\dot{\gamma}$ at $t = 25^\circ\text{C}$ for all of the batters tested was described the best by the Herschel–Bulkley's model:

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (1)$$

where τ is the yield stress (Pa), τ_0 is the threshold yield stress (Pa), $\dot{\gamma}$ is the speed gradient (s^{-1}), K is the consistency index ($\text{Pa}\cdot\text{s}^n$), and n is the flow behavior index. According to the flow behavior index of this model (n_H), all the batters appeared to be an elastic-plastic body. The buckwheat flour caused higher yield stress according to the other parameters of the model and that way diminished the viscosity. The effect was less apparent in the presence of corn flour and more noticeable if rice flour was concerned. The combo of rice and chickpea flours demonstrated the highest viscosity, hence better performance during baking was expected.

Looking at Table 3 the correlation was at its lowest value in the Casson model and it gave little information using only 2 parameters.

Looking at the Ofoli (4 parameters) and Mizrahi (3 parameters) models, the first parameter of the gluten-free mixtures was almost 0, which could mean the threshold stress was practically 0 and that was not true according to experimental data (see other models). When using the Vocadlo model (3 parameters), the flow index showed anomalies (very large values) losing its physical meaning, as it was according to the literature [12].

Batters creep and recovery: elastic modulus, retardation and relaxation time, viscosity coefficient. The retardation curves were approximated by the generalized Kelvin model [9] (Table 4):

$$\varepsilon(t) = \frac{\sigma_0}{E_0} + \frac{\sigma_0}{E_1} \cdot (1 - e^{-t/\lambda_1}) + \frac{\sigma_0}{E_2} \cdot (1 - e^{-t/\lambda_2}) + \frac{\sigma_0}{E_3} \cdot (1 - e^{-t/\lambda_3}) + \frac{\sigma_0}{\mu_0} \cdot t, \text{ и } \lambda_i = \frac{\mu_i}{E_i} \quad (2)$$

The model is represented by three elements connected in series, where ε is the relative deformation, σ is the retardation stress, E is the elastic modulus (Pa), λ is the retardation time (s), μ is the viscosity coefficient (Pas) and t is the loading time (s). With that model one short, one medium and one long retardation times and three elasticity modules were calculated (Table 4).

The generalized Kelvin model describes the behaviors of the plasticizers like pentosanes and β -glucans as well as other non-protein polymers. The water plasticizing effect is described by μ_0 [3]. As a rule, the higher the amount of free water in the dough the higher plasticity is expected. Poorer dough quality results in lower viscosity values and retardation times. The higher water concentration in whole meal muffin batter was apparent because of the high value of μ_0 . The chickpea containing batters showed higher viscosity and retardation times than the buckwheat mixtures. Also, the corn flour batters showed higher values of viscosity and elasticity than those with rice flour. In some cases the blends used for the end product showed unexpected values, which can be explained by the effect of multi-component mixtures.

Table 3 – Correlations and parameters of models for muffin batters viscosity

Models parameters					
Samples	Yield stress, τ_0 , Pa	Consistency index, K_H , Pa.s ^a	Flow behavior index, n_H		R ²
F2	0.014± 0.002 ^a	104.566±3.296 ^b	0.488±0.002 ^d		0.9971 ^b
F4	8.042± 0.905 ^b	99.428±4.245 ^b	0.417±0.004 ^a		0.9440 ^a
F8	0.012± 0.002 ^a	139.778±2.331 ^c	0.425±0.005 ^a		0.9901 ^b
F10	18.177± 3.878 ^c	18.177± 3.878 ^c	0.452±0.008 ^b		0.9989 ^b
Control	211.672±30.303 ^d	374.734±4.685 ^d	0.470±0.012 ^c		0.9891 ^b
Samples	Yield stress, τ_0 , Pa	Consistency index, K_M , Pa.s ^a	Flow behavior index, n_M		R ²
F2	0.002±0.000 ^b	10.423±0.225 ^a	0.239±0.001 ^b		0.9976 ^d
F4	0.001±0.000 ^a	12.193±0.150 ^c	0.201±0.001 ^a		0.9467 ^b
F8	0.001±0.000 ^a	12.205±0.084 ^c	0.206±0.003 ^a		0.9859 ^c
F10	0.001±0.000 ^a	12.107±0.001 ^c	0.202±0.000 ^a		0.7839 ^a
Control	13.052±1.288 ^c	11.147±0.575 ^b	0.323±0.019 ^c		0.9900 ^c
Samples	Yield stress, τ_0 , Pa	Consistency index, η_{oc} , Pa.s ^{n_H}	Flow behavior index, n_i	Flow behavior index, n_2	R ²
F2	0.005±0.001 ^b	34.116±6.312 ^c	1.448±0.191 ^a	0.327±0.039 ^b	0.9928 ^c
F4	0.005±0.000 ^b	16.829±0.904 ^b	1.784±0.277 ^b	0.224±0.016 ^a	0.9610 ^b
F8	0.002±0.000 ^a	16.858±0.913 ^b	1.785±0.142 ^b	0.225±0.011 ^a	0.9787 ^b
F10	0.005±0.000 ^b	16.830±0.928 ^b	1.784±0.208 ^b	0.224±0.013 ^a	0.7243 ^a
Control	4.156±0.530 ^c	4.184±1.165 ^a	2.456±0.635 ^c	0.303±0.053 ^b	0.9895 ^{bc}
Samples	Yield stress, τ_{ov} , Pa	Consistency index, K_V , Pa.s ^a	Flow behavior index, n_V		R ²
F2	0.155± 0.031 ^b	0.506±0.031 ^a	8245± 1452 ^a		0.9937 ^b
F4	0.436± 0.049 ^c	0.398±0.024 ^a	172262±24512 ^{bc}		0.9918 ^b
F8	0.024± 0.004 ^a	0.408±0.030 ^a	214323± 42315 ^c		0.9874 ^b
F10	0.233± 0.035 ^{bc}	0.413±0.025 ^a	138977± 17476 ^b		0.9901 ^b
Control	314.643±53.284 ^d	0.313±0.024 ^a	3117216±539917 ^d		0.8855 ^a
Samples	Yield stress, K_{oc} , Pa ^{0.3}		Plastic viscosity, K_c , (Pa.s) ^{0.3}		R ²
F2	9.557±0.381 ^a		2.215±0.125 ^{ab}		0.9517 ^b
F4	10.605±0.271 ^a		1.732±0.245 ^{ab}		0.8995 ^a
F8	9.080±0.713 ^a		2.370±0.024 ^b		0.9543 ^b
F10	8.899±0.264 ^a		1.596±0.062 ^a		0.9405 ^b
Control	19.623±4.065 ^b		6.027±0.859 ^c		0.9651 ^b

Means followed by different subscripts in the same column are significantly different at p=0.05

Table 4 – Retardation curves parameters obtained by Kelvin's three-elemental model

Samples	E_0 , Pa	E_{1i} , Pa	λ_{1i} , s	E_{2i} , Pa	λ_{2i} , s	E_{3i} , Pa	λ_{3i} , s	μ_{0i} , Pas	μ_{1i} , Pas	μ_{2i} , Pas	μ_{3i} , Pas	R^2
F1	438.96a	239.33b	13.94c	458.84bc	23.09cd	13236.82d	241.28c	11454.57c	311.17c	11865.39e	3193840.95ef	0.9974b
F2	356.57bc	188.40a	19.71d	398.16b	34.37e	2149.34a	352.84d	12497.72c	356.49cd	23909.53g	758376.41b	0.9941b
F3	344.16c	174.41a	12.76bc	513.78c	26.04d	2086.11a	341.31d	9534.37b	288.85bc	11949.38e	712002.95b	0.9998b
F4	348.31c	260.24bc	11.92bc	695.74d	18.33abc	10744.06cd	245.53c	11015.81c	420.82d	7296.32c	2638010.14e	0.9917ab
F5	394.16ab	263.93bc	11.66bc	330.62ab	15.33ab	9048.31c	197.86b	11325.89c	326.20c	5448.77b	1790276.08d	0.9944ab
F6	243.46e	347.09c	3.72a	424.76bc	25.15d	2916.13a	266.80c	11570.80c	117.17a	9701.89d	778014.33b	0.9714a
F7	252.19e	176.26a	13.42c	913.20e	17.32ab	2326.73a	141.95ab	10071.50c	221.45b	15814.55f	330278.00a	0.9996b
F8	298.83d	212.94ab	15.28cd	355.35b	20.82bcd	3986.49b	175.82b	13868.11cd	277.70bc	6111.15bc	700907.70b	0.9813ab
F9	360.41bc	256.86bc	15.21cd	385.73b	17.50abc	9108.04c	184.02b	11498.27c	366.70cd	5784.43b	1676076.57d	0.9867ab
F10	242.39e	213.42ab	8.13ab	293.57a	16.22ab	3778.36b	121.65a	6206.90a	194.27b	6888.20c	459633.65a	0.9997b
Control	136.36f	227.82b	24.86e	606.51c	58.93f	3853.46b	839.09e	17353.00d	675.66e	35739.99h	3233416.15ef	0.9995b

Means followed by different subscripts in the same column are significantly different at $p=0.05$

Table 5 – Relaxation curves parameters obtained by Maxwell's four-elemental model

Samples	σ_{1i} , Pa	T_{1i} , s	σ_{2i} , Pa	T_{2i} , s	σ_{3i} , Pa	T_{3i} , s	σ_{4i} , Pa	T_{4i} , s	σ_{0i} , Pa	η_{1i} , Pas	η_{2i} , Pas	η_{3i} , Pas	η_{4i} , Pas	R^2
F1	2320.6bc	1.60de	101.1d	2.20a	63.33fg	3.52abc	0.27bcd	40.08efg	8.96cde	3707.3bc	222.09ab	222.88bc	457.17d	0.8964bcd
F2	2284.4abc	1.69ef	93.4cd	3.51def	40.38a	3.83bc	0.25bcd	43.95g	11.67g	3868.6bc	327.59b	154.66b	462.70d	0.85222ab
F3	3143.8d	1.44bcd	73.5abc	3.12cde	53.73d	3.60abc	0.20ab	44.21g	10.34efg	4517.4c	229.59ab	193.33b	359.18c	0.9482e
F4	2154.9ab	1.38abc	85.0bcd	2.71abc	56.01de	4.63c	0.26bcd	43.31g	10.68fg	2982.5ab	230.80ab	259.12c	512.93de	0.8916bcd
F5	2171.5ab	1.25ab	87.1bcd	2.88bcd	52.28cd	6.58d	0.23abc	26.38ab	6.54ab	2710.1a	250.46ab	344.15d	340.26c	0.8893bcd
F6	2312.9abc	1.55cde	68.2ab	3.27def	46.78bc	8.31e	0.17a	32.24bcd	7.36bcd	3575.1b	223.05ab	388.83d	222.64b	0.8678b
F7	2047.7a	1.15a	92.5cd	2.36ab	67.14gh	3.37ab	0.27bcd	42.26fg	8.05bcd	2347.3a	218.61ab	226.18bc	172.46a	0.9166cde
F8	2384.8bc	1.91f	67.0ab	2.50abc	60.24ef	7.71de	0.32cd	34.18cde	6.95abc	4556.1c	167.60a	464.21e	275.59bc	0.8765bc
F9	2390.7bc	1.41bcd	82.6bcd	2.57abc	54.48de	3.43ab	0.26bcd	42.06fg	5.29a	3371.6b	211.95ab	186.62b	237.40b	0.8935bcd
F10	2520.5c	1.24abc	82.6bcd	2.61abc	74.67i	3.10ab	0.34e	35.56def	7.75bcd	3118.6b	215.79ab	231.33bc	237.60b	0.9318de
Control	2426.8bc	1.56de	59.3a	3.81ef	47.28bc	3.55a	0.26bcd	23.56a	10.71fg	3797.4bc	225.67ab	167.91b	252.30b	0.8135a

Means followed by different subscripts in the same column are significantly different at $p=0.05$

The *relaxation curves* were evaluated by generalized Maxwell model (4 parallel Maxwell elements, Hernández-Estrada et al 2014, – Table 5):

$$\sigma(t) = \sigma_1 e^{-t/T_1} + \sigma_2 e^{-t/T_2} + \sigma_3 e^{-t/T_3} + \sigma_4 e^{-t/T_4} + \sigma_0, \text{ and} \quad (3),$$

$$T_i = \frac{\eta_i}{\sigma_i}$$

where σ is the relaxation stress (Pa), T is the relaxation time, η is the viscosity coefficient and t is the deformation holding time (s) [8].

The viscoelasticity and stress relaxation parameters describe mainly the protein-like structures. With that model two very short (the second one is twice bigger than the first one), one medium and one long relaxation time were calculated. Based on the literature the length of the longer relaxation times and higher relaxation stress showed positive correlation with the better bread making quality (Malkin and Isayev, 2006). The received 1st relaxation stress is almost the start stress of the relaxation curves. The last one is the equilibrium relaxation stress. The results obtained demonstrated corn-based batters showing higher values of viscosity and relaxation time, i.e. higher plasticity.

Thermal properties. The changes in moisture content and water activity due to gluten free batters blends used were studied via DSC analysis. The percentage of free and bound water was determined by the enthalpy value of the melting peak provided the 100% free water enthalpy value already known (Table 6).

Table 6 – Free and bound water in gluten free muffin batters

Batters	ΔH , J/g	Free water, %	Bound water, %
F2	23.89	0.242563	0.757437
F4	31.97	0.324601	0.675399
F8	22.74	0.230886	0.769114
F10	22.27	0.226114	0.773886
Control	26.62	0.270281	0.729719

The amount of bound water was relatively high and varies between 67.5% and 77.4%. The F4 batter exhibited the lowest amount of bound water (67.5%) and F10 the highest (77.4%). As a rule the higher water binding capacity the larger the percentages increase due to baking.

During the baking the endothermic phase transition of the starch gelatinization in the dough takes place (Figure 1).

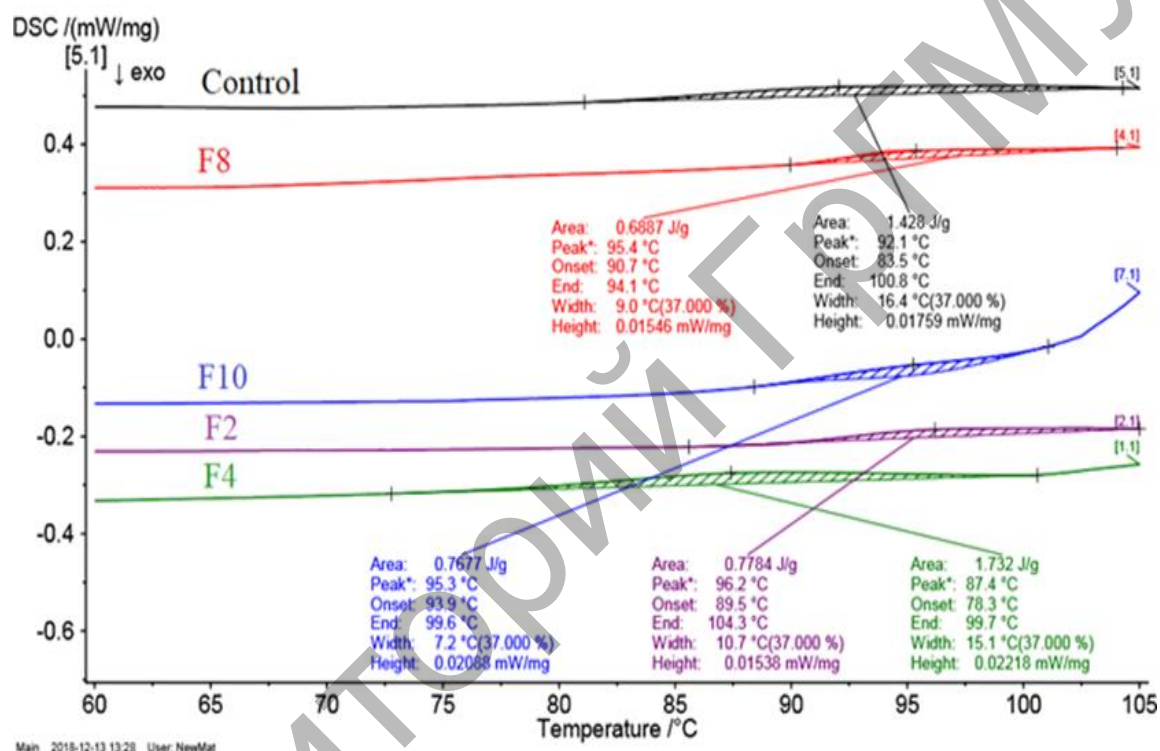


Figure 1 – Muffin batters starch gelatinization by DSC

The lowest value of the initial gelatinization temperature (76 °C) was reported for F4 sample, e.g. the swelling process begun the earliest and at the same time it was the largest characterized by the highest enthalpy value – 1.732 J / g (Table 7).

Table 7 – Starch gelatinization in muffin batters

Batters	Temp. interval, ΔT , °C	Endothermic pick temp., T_p , °C	Enthalpy, (ΔH), J/g
F2	85 - 105	96.2	0.7784
F4	76 - 101	87.4	1.732
F8	90 - 103	95.4	0.6887
F10	87 - 102	95.3	0.7677
Control	82 - 105	92.1	1.428

It happened most likely due to the relatively low proportion of bound water compared to other batters. The situation was similar with the Control where the higher free water content was apparent and the gelatinization process was quite complete. In the F2, F8 and F10 batters, due to the lower free water content, the gelatinization were hindered and the process shifted to higher temperatures. At the same time, the enthalpies of the endothermic transition appeared to be lower meaning the process was not entirely completed [2].

Quality of muffins.

Loss of weight. The loss of weight was due to technological reasons (10% on average). The lowest weight loss was measured for the F2 muffins (7.55%), the other three gluten-free samples showed similar loss, about 10%, and the largest loss was found in muffins made of whole flour (Control), over 17 % (Table 8).

Table 8 – Loss of weight during baking of gluten- free muffins

Samples	Loss of weight, %
F2	7.55%+0.46% ^a
F4	10.19%+0.73% ^b
F8	9.74%+0.59% ^b
F10	10.05%+0.69% ^b
Control	17.31%+0.97% ^c

Most of these losses occur during dough kneading and baking. The ICP-AES test determined the mineral content of the final products showing insignificant differences of about 1.5 % loss if compare to the initial content of the selected flour blends (Table 9).

Table 9 – Mineral content losses in muffin formulations, mg/kg

Samples	Whole grain		Corn	Rice	Chickpeas	Buck wheat	Carob	Mineral content,			
	Gluten free flour							Mg	Ca	Fe	Zn
F2	-	30	0	0	65	0	5	7.28	22.00	0.65	0.35
F4	-	55	0	0	0	40	5	6.46	23.00	0.48	0.34
F8	-	0	25	70	0	0	5	7.92	21.94	0.73	0.34
F10	-	0	50	0	0	45	5	7.08	21.46	0.64	0.33
Control	100	-	-	-	-	-	-	5.89	21.98	0.59	0.43

Table 10 – Texture evaluation of muffins

Formulas	Firmness, N	Springiness	Cohesiveness	Gumminess, N	Chewiness, N
F2	18.44±3.57a	0.93±0.01b	0.80±0.10b	15.00±2.55a	13.93±2.41a
F4	31.38±5.16d	0.90±0.02a	0.76±0.13ab	24.29±4.85c	21.86±3.79c
F8	20.96±2.15ab	0.92±0.02b	0.81±0.10b	17.16±3.23ab	15.90±3.05ab
F10	22.72±2.15b	0.90±0.03a	0.83±0.07b	18.84±2.66b	17.03±2.68ab
Control	27.69±5.02c	0.91±0.02a	0.73±0.10a	20.11±4.02b	18.26±3.63b

Values are mean of duplicate ±SD and means followed by different subscripts in the same column are significantly different at p=0.05

Study on the appearance and structure of muffins. The appearance, volume and structure of the muffins largely depend on the blend ratio used and the composition of the dough. The most difficult to bake were muffins made from whole flour (control). They had a low volume, moist crumb and semi-raw internal structure with large pores because of early formation of the crust during baking. Buckwheat flour (F4 and F10) contributed to a firm structure with small pores and a strongly and deeply cracked surface. The blend of corn and chickpea flour (F2) bound the water, forming a very tight, cracked structure without pores. The best structure was achieved with a combination of rice and chickpea flour (F8), with the highest volume and best porous structure (Figure 2).

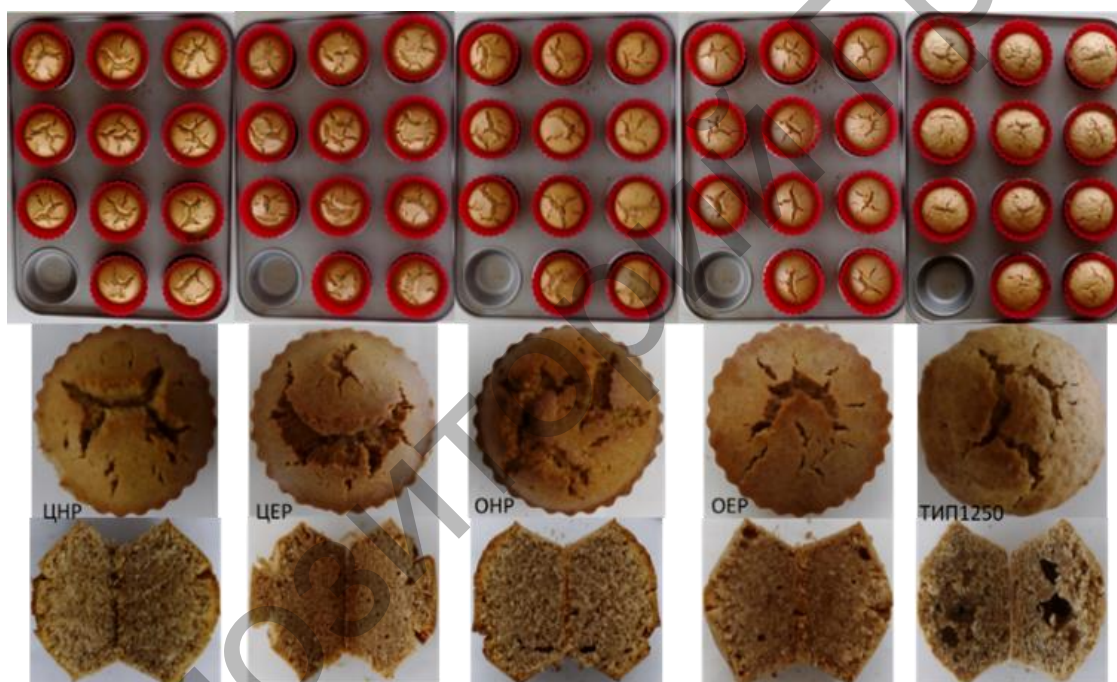


Figure 2 – Appearance, surface and crumb structure of the gluten-free muffins

The batter was characterized by a relatively high value of bound water and the lowest value of the enthalpy of gelatinization. As a result, the elasticity of the sample was lessened and the softness was greater.

Textural properties of muffins. Wholegrain muffins showed relatively high firmness, the lowest cohesiveness (slower relaxation), high gumminess and medium chewiness. The overall texture characteristics of rice flour based muffins were closer to each other if compare to those based on corn flour. The firmness varies between

18.44 N (F2) and 31.38 N (F4). According to the results obtained the buckwheat flour increased the firmness. This effect was more pronounced in corn muffins. These samples exhibited lower springiness and cohesiveness, and the highest gumminess and chewiness. Lower springiness and cohesiveness mean more deformability. The springiness and cohesiveness of muffins varies over a very narrow interval. The gumminess and chewiness were the lowest for the F2 formulation (Table 10).

Sensory analysis of muffins. Consumers rated on overall acceptability of each sample, four in total and the control using a 9-point hedonic scale with 1=dislike extremely and 9=like extremely. All the samples and the control were rated “like slightly” ($x \geq 6$, $p=0.05$) except F8 sample that had the highest rating on overall acceptance “like moderately”, $p=0.05$ (data not presented).

Conclusion. The selected gluten-free flour blends contained Mg and Fe close to the content of these elements in the whole wheat flour, exceeded the Ca content and contained less Zn. The combination of rice and chickpea flours demonstrated the highest viscosity whether the blend based on corn showed higher plasticity. The process of gelatinization was well pronounced in systems containing more free water (F4). Buckwheat flour (F4 and F10) contributed to a tighter structure with small pores and deeply cracked surface. The combination of corn and chickpea flours (F2) bound the free water and very tight, pore less and furrowed structure was formed. The best structure was achieved with the combination of rice and chickpea flours (F8), with the highest volume and porous structure. F8 batter was characterized by a relatively high value of bound water and the lowest enthalpy of gelatinization. As a result, the structure of the crumb was less elastic and softer. The F8 sample had also the highest rating on overall acceptance “like moderately” by the consumers.

Bibliography

1. Appropriate nutrient supplementation in celiac disease / R. Caruso [et al.] // An. Med. – 2013. – Vol. 45 (8). – P. 522–31; URL: <https://www.tandfonline.com/doi/full/10.3109/07853890.2013.849383>.
2. Baeva, M., Effect of sugar on the starch gelatinization in sponge cake batters / M. Baeva, V. Terzievaand, S. Markov // Food Sci. Technol. – 1997. – Vol. 4(6). – P. 16–8.

3. Creep recovery tests to measure the effects of wheat glutenins on doughs and the relationships to rheological and breadmaking properties / Z. Hernández-Estrada [et al.] // J. Food Eng. – 2014. – Vol. 143. – P. 62–8; URL: <https://www.sciencedirect.com/science/article/pii/S0260877414002830>.
4. Development of gluten-free bread using tartary buckwheat and chia flour rich in flavonoids and omega-3 fatty acids as ingredients / L. Costantini [et al.] // Food Chem. – 2014. – Vol. 165. – P. 232–40; URL: <https://www.sciencedirect.com/science/article/pii/S0308814614008115>.
5. Gechev, B. Rheological models of gluten free bread dough / 6Gechev, B., G. Zsivanovits and M. Marudova // AIP Conference Proceedings: AIP Publishing LLC. – 2019. – Vol. 2075(1). – P. 160012; URL: <https://aip.scitation.org/doi/abs/10.1063/1.5091339>.
6. How to improve the gluten-free diet: The state of the art from a food science perspective / M. Gobetti [et al.] // Food Res. Int. – 2018. – Vol. 110. – P. 22–32; URL: <https://www.sciencedirect.com/science/article/pii/S0963996917301606>.
7. Intakes of nutrients in Italian children with celiac disease and the role of commercially available gluten-free products / G. Zuccotti [et al.] // Clin. Nutr. – 2013. – Vol. 26 (5). – P. 436–44; URL: https://onlinelibrary.wiley.com/doi/full/10.1111/jhn.12026?casa_token.
8. Malkin, A. Y. Pressure corrections in Rheology concepts, methods and applications / A. Y. Malkin, A. I. Isayev. – Toronto: ChemTec Publishing, 2006. – P. 253–320.
9. McCann, T. Extensional dough rheology – Impact of flour composition and extension speed / T. McCann, M. Le Galland, L. Day. // J. Cer. Sci. – 2016. – Vol. 69. – P. 228–37; URL: <https://www.sciencedirect.com/science/article/pii/S0733521016300443>.
10. Öhlund, K. Dietary shortcomings in children on a gluten-free diet / K. Öhlund [et al.] // J. Hum. Nutr. Diet. – 2010. – Vol. 23(3). – P. 294–300; URL:

<https://onlinelibrary.wiley.com/doi/full/10.1111/j.1365-277X.2010.01060.x>.

11. Rai, S. Quality characteristics of gluten-free cookies prepared from different flour combinations / S. Rai, A. Kauand, B. Singh // J. Food Sci. Technol. – 2014. – Vol. 51 (4). – P. 785–9; URL: <https://link.springer.com/article/10.1007/s13197-011-0547-1>.

12. Rao, M. A. Applicability of flow models with yield for tomato concentrates / M. A. Rao, H. J. Cooley // J. Food Proc. Eng. – 1983. – Vol. 6 (3). – P. 159–73; URL: <https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1745-4530.1983.tb00289.x>.

13. Rheological properties of gluten free bread formulations / I. Demirkesen [et al.] // J. Food Eng. – 2010. – Vol. 96 (2). – P. 295–303; URL: <https://www.sciencedirect.com/science/article/pii/S0260877409003860>.

14. Ronda, F. Rheological properties of gluten-free bread doughs: relationship with bread quality / F. Ronda, S. Pérez-Quirceand, M. Villanueva / In: J. Ahmed [et al.] // Adv. Food Rheol. Appl. – 2016. – P. 297–334; URL: <https://www.sciencedirect.com/science/article/pii/B9780081004319000127>.

15. Segura, M. E. Chemical composition and starch digestibility of different gluten-free breads / M. E. Segura, C. M. Rosell // Plant Foods Hum. Nutr. – 2011. – Vol. 66 (3). – P. 224–30; URL: <https://link.springer.com/article/10.1007/s11130-011-0244-2>.

16. Sharoba, A., A. Production and evaluation of gluten-free biscuits as functional foods for celiac disease patients / A. Sharoba, A. Abd El-Salamand, H. Hoda // J. Agroaliment. Process. Technol. – 2014. – Vol. 20 (3). – P. 203–14; URL: <https://www.bu.edu.eg/portal/uploads/Agriculture/Food%20Technology/1217/publications>.

17. Shepherd, S. J. Nutritional inadequacies of the gluten-free diet in both recently-diagnosed and long-term patients with coeliac disease / S. J. Shepherd, P. R. Gibson // J. Hum. Nutr. Diet. – 2013. – Vol. 26 (4). – P. 349–58; URL: https://onlinelibrary.wiley.com/doi/full/10.1111/jhn.12018?casa_token

18. Thermal and rheological properties of sponge cake batters and texture and microstructural characteristics of sponge cake made with native corn starch in partial or total replacement of wheat flour / A. Guadarrama-Lezama [et al.] // *LWT - Food Sci. Tech.* –2016. – Vol. 70. – P. 46–54; URL: <https://www.sciencedirect.com/science/article/pii/S0023643816301104>.

19. Utilization of sorghum rice, corn flours with potato starch for the preparation of gluten-free pasta / S. Ferreira [et al.] // *Food Chem.* – 2016. – Vol. 191. – P. 147–51; URL: <https://www.sciencedirect.com/science/article/pii/S0308814615006317>.

20. Vergnes, B. Rheological properties of biopolymers and applications to cereal processing / B. Vergnes, G. Della Valle, P. Colonna / In: G. Kalentuç, K. J. Breslaner (Ed.) // *Characterization of Cereals and Flours. Properties, Analysis and Applications*. New York: Marcel Dekker Inc., 2003. – 222–78; URL: <https://www.taylorfrancis.com/chapters/edit/10.1201/9780203911785-7/rheological-properties-biopolymers-applications-cereal-processing-bruno-vergnes-guy-della-valle-paul-colonna>.

21. Yalcin, E. Chemical and sensory properties of new gluten-free products. Rice and corn tarhana / E. Yalcin, S. Celikand, H. Koksel. // *Food Sci. Biotechnol.* – 2008. – Vol. 17 (4). – P. 728–33; URL: <https://www.koreascience.or.kr/article/JAKO200833338360857.page>.

References

1. Caruso R, Pallone F, Stasi E, Romeoand S, Monteleone G (2013). Appropriate nutrient supplementation in celiac disease. *Annals of Medicine*;45(8):522–531; URL: <https://www.tandfonline.com/doi/full/10.3109/07853890.2013.849383> (in English).

2. Baeva M, Terzievaand V, Markov S (1997). Effect of sugar on the starch gelatinization in sponge cake batters. *Food Sci. Technol.*;4(6):16–18 (in English).

3. Hernández-Estrada Z, Rayas-Duarte P, Figueroaand D, Morales-Sanchez E (2014). Creep recovery tests to measure the effects of wheat glutenins on doughs and the relationships to

rheological and breadmaking properties. *Journal of Food Engineering*;143:62–68; URL: <https://www.sciencedirect.com/science/article/pii/S0260877414002830> (in English).

4. Costantini L, Lukšič L, Molinari R, Kreft I, Bonafaccia G, Manziand L, Merendino N (2014). Development of gluten-free bread using tartary buckwheat and chia flour rich in flavonoids and omega-3 fatty acids as ingredients. *Food Chem.*;165:232–240; URL: <https://www.sciencedirect.com/science/article/pii/S0308814614008115> (in English).

5. Gechev B, Zsivanovitsand G, Marudova M (2019). Rheological models of gluten free bread dough. *In: AIP Conference Proceedings: AIP Publishing LLC.*, 2075(1), 160012; URL: <https://aip.scitation.org/doi/abs/10.1063/1.5091339> (in English).

6. Gobbetti M, Pontonio E, Filannino P, Rizzello GC, De Angelisand M, Di Cagno R (2018). How to improve the gluten-free diet: The state of the art from a food science perspective. *Food Research International*;110:22–32; URL: <https://www.sciencedirect.com/science/article/pii/S0963996917301606> (in English).

7. Zuccotti G, Fabiano V, Dilillo D, Picca M, M.Cravidianand M, Brambilla P (2013). Intakes of nutrients in Italian children with celiac disease and the role of commercially available gluten-free products. *Clinical Nutrition*;26(5):436–444; URL: https://onlinelibrary.wiley.com/doi/full/10.1111/jhn.12026?casa_token (in English).

8. Malkin AY, Isayev AI (2006). Pressure corrections in Rheology concepts, methods and applications. Toronto: ChemTec Publishing:253–320 (in English).

9. McCann T, Le Galland M, Day L (2016). Extensional dough rheology – Impact of flour composition and extension speed. *Journal of Cereal Science*;69:228–237; URL: <https://www.sciencedirect.com/science/article/pii/S0733521016300443> (in English).

10. Öhlund K, Olsson C, Hernelland O, Öhlund I (2010). Dietary shortcomings in children on a gluten-free diet. *Journal of Human Nutrition and Dieteticst*;23(3):294–300; URL:

<https://onlinelibrary.wiley.com/doi/full/10.1111/j.1365-277X.2010.01060.x> (in English).

11. Rai S, Kauand A, Singh B (2014). Quality characteristics of gluten-free cookies prepared from different flour combinations. *Journal of Food Science and Technology*;51(4):785–789; URL: <https://link.springer.com/article/10.1007/s13197-011-0547-1> (in English).

12. Rao MA, Cooley H (1983). Applicability of flow models with yield for tomato concentrates. *Journal of Food Process Engineering*,6(3):159–173; URL: <https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1745-4530.1983.tb00289.x> (in English).

13. Demirkesen I, Mert B, Sumnuand G, Sahin S. (2010). Rheological properties of gluten free bread formulations. *Journal of Food Engineering*;96(2):295–303; URL: <https://www.sciencedirect.com/science/article/pii/S0260877409003860>.

14. Ronda F, Pérez-Quirceand S, Villanueva M (2016). Rheological properties of gluten-free bread doughs: relationship with bread quality. In: Ahmed J., Ptaszek P, Basu S. (Ed.), *In: Advances in Food Rheology and Its Applications*. Woodhead Publishing, 297–334; URL: <https://www.sciencedirect.com/science/article/pii/B97800810043190010127> (in English).

15. Segura ME, Rosell CM (2011). Chemical composition and starch digestibility of different gluten-free breads. *Plant Foods for Human Nutrition*;66(3):224–230; URL: <https://link.springer.com/article/10.1007/s11130-011-0244-2> (in English).

16. Sharoba A, Abd El-Salamand A, Hoda H (2014). Production and evaluation of gluten-free biscuits as functional foods for celiac disease patients. *Journal of Agroalimentary Process and Technologies*;20(3):203–214; URL: <https://www.bu.edu.eg/portal/uploads/Agriculture/Food%20Technology/1217/publications> (in English).

17. Shepherd SJ, Gibson PR (2013). Nutritional inadequacies of the gluten-free diet in both recently-diagnosed and long-term

patients with coeliac disease. *Journal of Human Nutrition and Dietetics*;26(4):349–358; URL: https://onlinelibrary.wiley.com/doi/full/10.1111/jhn.12018?casa_token (in English).

18. Guadarrama-Lezama A, Carrillo-Navas H, Pérez-Alonso C, Vernon-Carter E, Alvarez-Ramirez J (2016). Thermal and rheological properties of sponge cake batters and texture and microstructural characteristics of sponge cake made with native corn starch in partial or total replacement of wheat flour. *LWT - Food Science and Technology*; 70:46–54; URL: <https://www.sciencedirect.com/science/article/pii/S0023643816301104> (in English).

19. Ferreira S, Mello A, Anjos M, Krüger C, Azoubeland P, Alves M (2016). Utilization of sorghum rice, corn flours with potato starch for the preparation of gluten-free pasta. *Food Chemistry*;191:147–151; URL: <https://www.sciencedirect.com/science/article/pii/S0308814615006317> (in English).

20. Vergnes B, Della Valle G, Colonna P (2003). Rheological properties of biopolymers and applications to cereal processing. In: Kalentuç G, Breslaner KJ (Ed.), *In: Characterization of Cereals and Flours. Properties, Analysis and Applications*. New York:Marcel Dekker Inc.:222–278; URL: <https://www.taylorfrancis.com/chapters/edit/10.1201/9780203911785-7/rheological-properties-biopolymers-applications-cereal-processing-bruno-vergnes-guy-della-valle-paul-colonna> (in English).

21. Yalcin E, Celikand S, Koksel H (2008). Chemical and sensory properties of new gluten-free products. Rice and corn tarhana. *Food Science and Biotechnology*;17(4):728–733; URL: <https://www.koreascience.or.kr/article/JAKO200833338360857.page> (in English).

Поступила 14.06.2023

Адрес для корреспонденции: g_zuyvanov@abv.bg