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Microwave-Supported Modulation of Functional Characteristics of Gluten-Free Breads

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Abstract: Currently, the market for gluten-free products is experiencing a significant growth due to, mainly, the increase in the number of gluten-intolerant patients diagnosed and to the merging of a new niche market for consumers who optionally avoid gluten. Native flours are perceived as viable alternatives for industrially used starch and hydrocolloids blends, which lack in the vitamins and minerals that are in abundance in non-refined raw materials. This study delves into the potential of microwave technology in enhancing the functional and nutritional attributes of gluten-free breads. The research was conducted by employing 900 W microwave power for 8 min for buckwheat and teff flours modification with an initial moisture content of 30%. The modified flours were blended with rice flour and baked to verify the potential of microwave high moisture treatment for adjusting the texture and nutritional quality of the bread. The results revealed that microwave treatment of flours helped in retaining a higher level of essential nutrients and bioactive compounds in gluten-free breads.

Keywords: buckwheat; teff; bread; microwave; heat–moisture treatment; polyphenols

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1. Introduction

Gluten-free diets, once a medical necessity for individuals with celiac disease, have become increasingly popular among the general population, leading to a surge in the demand for gluten-free foods, particularly bread [1–5]. However, a common critique of commercial gluten-free breads is their compromised nutritional quality when compared to their gluten-containing counterparts [6]. Many gluten-free bread formulations rely heavily on starch–fiber mixes, which may lack essential nutrients and bioactive compounds that are present in whole grain flours [7]. However, the incorporation of these native flours into bread-making poses several challenges [8]. Their distinct physicochemical properties can affect dough rheology, leading to variations in the texture, volume, and shelf life of the bread [9]. To harness the full nutritional potential of these flours without compromising on the quality of the bread, innovative processing methods are needed.

Heat–moisture treatment (HMT) is one such technique that has been explored for modifying the functional properties of flours. This method exposes flours to controlled heat and moisture conditions, altering the starch granular structure [10]. Recent studies have indicated that HMT can enhance the antioxidant profile of flours, promoting the liberation and availability of bound phenolic compounds [11]. Furthermore, when combined with microwave radiation, a synergistic effect might be observed, offering even greater potential for unlocking the inherent nutritional benefits of the flours.

Microwave-assisted heat–moisture treatment (MW-HMT) of gluten-free flours has been found to have a significant impact on the nutritional and functional characteristics of

resulting breads. The treatment of rice flour with microwave radiation and heat–moisture treatment has been shown to improve the viscoelastic behavior and bread-making performance of gluten-free doughs [12]. Microwave heating of cereal and legume flours has been shown to enhance their functional properties, such as water holding, oil binding, emulsifying, foaming capacities, and protein solubility index [13].

Microwave treatment of maize flour has been found to alter its microstructure, physicochemical characteristics, and pasting properties, affecting its functional properties and thermal behavior [14]. The microwave radiation treatment increases the hydration properties and particle size of the flours, resulting in lower viscosities and higher pasting temperatures [6]. Additionally, the treatment leads to a structuring and stabilizing effect on the flours, resulting in an increase in the viscoelastic moduli and maximum stress that the gels can withstand [15]. These findings suggest that microwave-treated gluten-free flours have the potential to improve the technological, nutritional, and sensory quality of food products.

Microwave-assisted heat–moisture treatment (MW-HMT) has been found to impact the nutritional profile of flours. Studies have shown that microwave heating can enhance the functional properties of flours, such as water holding, oil binding, emulsifying, and foaming capacities, as well as protein solubility [16–21]. Furthermore, microwave-assisted dry-heat and heat–moisture treatments have been shown to modify the techno-functional properties and gel viscoelasticity of rice flour, with effects varying depending on the moisture content of the flour [22,23]. Overall, MW-HMT can lead to changes in the nutritional and functional properties of flours, making it a promising technique for food processing and product development.

The utilization of natively gluten-free flours, such as buckwheat and teff, offers a promising alternative. Not only are these flours inherently gluten-free, but they also bring a rich nutrient profile to the table, including fibers, vitamins, minerals, and antioxidants. Moreover, buckwheat and teff have been recognized for their unique phenolic compounds and antioxidant activities, which can contribute to the overall health benefits of the end products [24–29].

While the specific impact of microwave hydrothermal treatment on the polyphenolic content and antioxidant activity of gluten-free flours was not directly addressed in the provided references, it is worth noting that the antioxidant activity of gluten-free flours can be influenced by various factors, including the presence of polyphenols. Duda et al. (2019) investigated the partial replacement of wheat flour with gluten-free flours in bread and found that the antioxidant activity was more potent in all gluten-free flours tested [30]. Kataria et al. observed that the microwave processing of chia seeds increased the total phenolic content, FRAP, and reducing power, indicating enhanced antioxidant activity [31]. This suggests that gluten-free flours, including those that may have undergone microwave hydrothermal treatment, can potentially exhibit higher antioxidant activity compared to wheat flour.

The aim of the study was to investigate the changes in free, bound, and total polyphenols content, and the percentage of bio-accessible polyphenols in flours after MW-HMT and in bread made with treated flours. The bread quality features like bake loss, specific volume, and color of crust and crumb, as well as texture, on the day of baking and after seven days of storage, were analyzed.

2. Materials and Methods

2.1. Materials and Reagents

Buckwheat flours were purchased at the Polish (PB) (Melvit, Olszewo Borki, Poland) and Spanish (SB) (Farinera La Segarra, Maldà, Spain) markets, respectively. Teff flour of white (WT) and brown (BT) variety cultivated in Spain was bought from the Spanish producer Salutef (San Martín del Valle, Palencia, Spain), and rice flour was purchased in Poland (Melvit, Olszewo Borki, Poland). The chemical content was provided by the flours manufacturers—the PB flour chemical content per dry basis was 72.8 ± 0.5% starch, 5.6 ± 0.1% fiber, 16.1 ± 0.3% protein, 3.3 ± 0.1% fat, and 1.97 ± 0.07% ash, while the SB

flour was 73.9 ± 0.4% starch, 1.65 ± 0.2% fiber, 18.5 ± 0.3% protein, 3.9 ± 0.1% fat, and 1.79 ± 0.08% ash. The WT flour was 79.8 ± 0.4% starch, 6.1 ± 0.2% fiber, 10.3 ± 0.4% protein, 2.1 ± 0.1% fat, and 1.7 ± 0.04% ash, while the BT flour was 79.1 ± 0.6% starch, 7.3 ± 0.2% fiber, 9.1 ± 0.6% protein, 2.4 ± 0.3% fat, and 2.2 ± 0.5% ash. The following standards and reagents were used for the spectrophotometric methods: gallic acid, Folin–Ciocalteu reagent, calcium carbonate $CaCO_3$, sodium nitrate $NaNO_3$ (Pol-Aura, Zabrze, Poland), and distilled water.

2.2. Microwave Treatment

Flours were adjusted to the initial moisture content of ≈30% and then exposed to microwave radiation at the maximum available power (900 W) in a microwave reactor NOVA 10 (Ertec, Wroclaw, Poland). The electromagnetic radiation was applied intermittently in short periods of 20 s with a cooling time of 40 s for the maintenance of temperature homogeneity inside the product and to avoid an excessive pressure increase in the available space of the container. The sample temperature was controlled using temperature strips called Thestoterms (Testo, West Chester, PA, USA). The total treatment time was 8 min with constant mixing. During cooling periods, the oven doors were open and built-in fans were automatically switched on. After treatment, the samples were collected and stored at 4 °C for further analysis.

2.3. Bread Baking

A simple recipe of bread consisting of flour (or flour blends) counting as 100% and water as 110%, with salt 3%, yeast 3%, and oil 2% (calculated per flour weight), was used for all the breads. A total of nine types of bread differing in flour composition were prepared as follows—100% rice flour (control), 50:50 (*w*/*w*) blends of rice flour and native buckwheat flour of Polish and Spanish origin (PBB and SBB), 50:50 (*w*/*w*) blends of rice flour and MW-treated buckwheat flour of Polish and Spanish origin (PBMWB and SBMWB), 50:50 (*w*/*w*) blends of rice flour and native teff flour of white and brown variety (WTB and BTB), and 50:50 (*w*/*w*) blends of rice flour and treated teff flour of white and brown variety (WTMWB and BTMWB). Initially, all ingredients were mixed for 10 min in a planetary mixer FM-201 (Łucznik, Wrocław, Poland) and the doughs were leavened at 30 °C and 80% humidity (around 45 min). The breads were oven cooked in a steam-convection oven (HENDI 227077, Rhenen, The Netherlands) at 170 °C for 20 min and allow to cool down for 1 h. Then, the quality features were measured as described below. Samples of the bread loaves were stored in a fridge (4°) covered in parchment paper for 7 days and the analysis was repeated.

2.4. Quality Features of Breads

2.4.1. Baking Loss and a Specific Volume

The baking loss of bread samples was obtained by weighing the doughs portioned into molds before their baking (wd) and the breads after baking (wb). The weight loss percentage was calculated as follows:

$$\text{Baking loss [\%]} = [(\text{wd} - \text{wb})/\text{wd}] \times 100$$

The volume (v) of bread loaves was determined 1 h after baking using a 3D scanner (Matter and Form v2, Toronto, ON, Canada) with the Quickscan app to take 3D scans with calculated volume. The weight (w) of each sample was also registered, and all the samples were measured in triplicate. The specific volume was calculated according to the following formula:

$$\text{Specific volume [cm}^3\text{/g]} = \text{v/w}$$

2.4.2. Texture Profile Analysis of Bread

The texture of the breads was evaluated through TPA (texture profile analysis) test using an AXIS texture analyzer FC20STAV500/500 (AXIS, Gdansk, Poland) provided with

the software AXIS FM v.2_18, as previously reported in [32]. Hardness (N) was the force at the maximum deformation, whereas cohesiveness, springiness, and chewiness were calculated from the peaks. Analysis was carried out in quadruplicate in RT. The results were reported as mean ± standard deviation.

2.4.3. Color Measurement of the Crust and Crumb of Bread

The color of the flour mixture, dough, and flatbread samples was determined according to CIELAB colors pace parameters using a Konica Minolta CR-310 Chroma Meter (Ramsey, NJ, USA) connected with a data processor (DP-301), launched via RS232 serial port to the personal computer. In more detail, the following parameters were obtained: (i) lightness (L*) ranging from 0 (black) to 100 (white); (ii) greenness or redness (a*) with negative values corresponding to the green axis and positive values corresponding to the red axis; (iii) blueness or yellowness (b*) with negative values corresponding to the blue axis and positive values corresponding to the yellow axis; (iv) chroma (C*) expressing the purity of the color from gray to pure spectral colors; and (v) hue angle (h°) extending from 0° (red), 90° (yellow), 180° (green), or 270° (blue). Analysis was carried out in quadruplicate. The results were reported as mean ± standard deviation.

2.5. Polyphenolic Profile of MW-Treated Bread

The crust and crumb of the baked breads were dried below 50 °C and disintegrated with mortar and pestle. The soluble, insoluble, and total polyphenols content was assessed according to the method in Harasym et al., 2020 [24]. Briefly, two solvents were used: A (HCl/methanol/water concentrate—1:80:10; *v*/*v*/*v*) and B (methanol/sulfuric acid—10:1 *v*/*v*) for the extraction of soluble and insoluble polyphenols, respectively. A total of 0.500 g of each flour sample was weighed into 15 mL centrifuge tubes and 4 mL of solvent A was added. The tubes were agitated in the laboratory on the rotary shaker (06-MX-RD-PRO, Chemland, Stargard, Poland) at 70 rpm for 1 h, then the tubes were centrifuged at 5000 rpm for 15 min at 15 °C (MPW-260, MPW MED. INSTRUMENTS, Warsaw, Poland) and extraction was repeated; the supernatants were combined and used for soluble polyphenol content determination. To extract residuals, 5 mL of solution B was added and the tubes were agitated (Shaking Incubators 3033 with Orbital Motion, GFL, Burgwedel, Germany) at 85 °C for 24 h. After centrifugation at 3500× *g* for 10 min (MPW-350, MPW, Warszawa, Poland), the supernatant containing insoluble polyphenols was collected. For measuring the reaction effect with the Folin–Ciocalteu reagent, 20 µL of a sample, 1.58 mL of distilled water, and 100 µL of Folin–Ciocalteu reagent were mixed. The mixture was left to stand for 4 min and then 300 µL of a saturated solution of Na_2CO_3 was added. The samples were incubated (MLL147, AJL Electronics, Kraków, Poland) at 40 °C for 30 min and the absorbance at 765 nm was measured (UV-Vis Ultrospec 2000, Pharmacia Biotech, Uppsala, Sweden). The results were expressed as gallic acid equivalent (GAE) per 100 g of sample dry matter. The tests were carried out in triplicate. The amount of bio-accessible phenolic compounds was calculated as a ratio of soluble phenolic compounds to total phenolics content.

2.6. Statistical Analyses

The impact of individual parameters on output values was analyzed using analysis of variance (one-way ANOVA). All data were subjected to the Tukey post hoc test. The statistical analysis was performed using Statgraphics Centurion XVI (Statgraphics Technologies, Inc., The Plains, VA, USA).

3. Results

The bread dough consistency and its ability to maintain water inside during the baking process are reflected by the bake loss, while the gas retention ability and elasticity of the dough impact the resulting specific volume (Table 1).

Table 1. Bake loss and specific volume of breads right after baking and after 7 days.

Sample Buckwheat	Time [Days]	Bake Loss [%]	Specific Volume [mL/g]	Sample Teff	Bake Loss [%]	Specific Volume [mL/g]
Control	0	26.3 ± 0.3 ^{c}	3.11 ± 0.05 ^{f}	control	26.3 ± 0.2 ^{c}	3.11 ± 0.05 ^{e}
	7		3.01 ± 0.03 ^{e}			3.01 ± 0.03 ^{e}
PB	0	22.3 ± 0.5 ^{b}	2.78 ± 0.05 ^{d}	WT	23.6 ± 0.2 ^{b}	2.57 ± 0.03 ^{d}
	7		2.21 ± 0.06 ^{a}			2.01 ± 0.02 ^{b}
PBMW	0	19.3 ± 0.7 ^{a}	3.08 ± 0.04 ^{e}	WTMW	20.4 ± 0.2 ^{a}	2.34 ± 0.06 ^{c}
	7		2.61 ± 0.01 ^{c}			2.16 ± 0.07 ^{b}
SB	0	21.4 ± 0.2 ^{b}	2.91 ± 0.03 ^{e}	BT	29.3 ± 0.2 ^{d}	2.03 ± 0.09 ^{b}
	7		2.06 ± 0.01 ^{a}			1.62 ± 0.08 ^{a}
SBMW	0	18.4 ± 0.6 ^{a}	2.68 ± 0.07 ^{c}	BTMW	22.6 ± 0.1 ^{b}	2.23 ± 0.04 ^{b}
	7		2.45 ± 0.06 ^{b}			2.12 ± 0.05 ^{b}

Control—100% rice flour bread, PBB—bread from blend of native Polish buckwheat flour and rice flour, 50:50 (*w*/*w*), PBMWB—bread from blend of Polish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), SBB—bread from blend of Spanish native buckwheat flour and rice flour, 50:50 (*w*/*w*), SBMWB—bread from blend of Spanish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), WTB—bread from blend of native white teff flour and rice flour, 50:50 (*w*/*w*), WTMWB—bread from blend of white teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*), BTB—bread from blend of brown teff flour and rice flour, 50:50 (*w*/*w*), BTMWB—bread from blend of brown teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*). Lowercase letter means significant difference in columns, $p = 0.05$.

The highest bake loss was observed for the rice control bread, showing its poor ability to maintain water inside the matrix. Similar results were observed by Villanueva et al., 2019, for rice bread; however, the authors used HPMC as an additive, which helped to maintain water inside the bread [12]. That behavior shows the importance of specific agent additions in gluten-free bread made from native gluten-free flours. The clean label trend forces the removal of all additives, which challenges the bread baking industry [6]. The addition of buckwheat native flours reduced the bake loss by 15% and 19% for Polish and Spanish samples, respectively. Unexpected characteristics were shown by the brown teff sample where the 50% addition of native flour increased the bake loss by 11% compared to the control rice bread. This behavior is most probably related to fiber content, which was higher in buckwheat flours, while teff flours, being more abundant in starch, exhibited the same characteristics as rice, being prone to fast water loss. Meanwhile, the white teff blends lowered the bake loss by 10%. For each MW-HMT flour, the bake loss of breads was significantly reduced, whereas for buckwheat flour, the values obtained for rice bread were reached with HPMC addition [12]. Also, white teff flour after MW-HMT showed a much improved bake loss of 22.5% compared to 100% in rice bread and 14% in the native flour blend bread. Also, the MW-HMT brown teff-based bread revealed improvement in water maintenance, reaching values similar to the native white teff.

The 100% rice bread revealed the lowest decrease in specific volume, mainly due to the huge initial water loss after baking. Both buckwheat native flour-based breads presented two- or three-times higher specific volume losses of 20% and 28% for Polish and Spanish buckwheat, respectively. MW-HMT buckwheat flours had a stronger capacity to maintain water inside as their specific volume decreases were only 15% and 9% for Polish and Spanish buckwheat, respectively. Both teff native flour-based breads presented two- or three-times higher specific volume losses of 22% and 20% for white and brown teff, respectively. MW-HMT teff flours also showed improved maintenance of water inside the loaf as their specific volume decreases were only 8% and 5% for white and brown teff, respectively.

The volume of the bread was created as a result of leavening; the elasticity of the dough matrix became fixed during baking. The air cells built from mainly starch can better resist the shrinkage and collapse of the foamy, fixed structure compared to the doughs that are richer in fiber, where water loss is slowed down but the air cell walls, being elastic, tend to collapse. The internal structure will also be reflected in texture profile (Tables 2 and 3).

Table 2. Texture profile of buckwheat breads right after baking and after 7 days.

Sample	Time [Days]	Hardness [N]	Cohesiveness	Springiness	Chewiness [N]
Control	0	2.09 ± 0.02 ^{a}	0.008 ± 0.002 ^{a}	0.41 ± 0.02 ^{b}	0.01 ± 0.004 ^{a}
	7	3.64 ± 0.07 ^{b}	0.001 ± 0.0005 ^{a}	0.24 ± 0.06 ^{a}	0.001 ± 0.003 ^{a}
PBB	0	2.96 ± 0.06 ^{c}	0.048 ± 0.006 ^{d}	0.51 ± 0.03 ^{c}	0.072 ± 0.003 ^{b}
	7	7.41 ± 0.09 ^{e}	0.074 ± 0.007 ^{e}	0.63 ± 0.02 ^{d}	0.345 ± 0.003 ^{f}
PBMWB	0	2.39 ± 0.09 ^{b}	0.021 ± 0.006 ^{b}	0.64 ± 0.03 ^{d}	0.032 ± 0.008 ^{b}
	7	5.81 ± 0.10 ^{d}	0.034 ± 0.007 ^{c}	0.60 ± 0.02 ^{d}	0.139 ± 0.01 ^{d}
SBB	0	3.72 ± 0.06 ^{b}	0.036 ± 0.004 ^{c}	0.68 ± 0.08 ^{d}	0.091 ± 0.003 ^{c}
	7	7.23 ± 0.09 ^{e}	0.030 ± 0.005 ^{c}	1.04 ± 0.05 ^{e}	0.225 ± 0.003 ^{e}
SBMWB	0	3.95 ± 0.08 ^{b}	0.015 ± 0.004 ^{b}	0.77 ± 0.04 ^{d}	0.05 ± 0.004 ^{b}
	7	5.97 ± 0.05 ^{d}	0.019 ± 0.005 ^{b}	0.97 ± 0.07 ^{e}	0.11 ± 0.001 ^{c}

Control—100% rice flour bread, PBB—bread from blend of native Polish buckwheat flour and rice flour, 50:50 (*w*/*w*), PBMWB—bread from blend of Polish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), SBB—bread from blend of Spanish native buckwheat flour and rice flour, 50:50 (*w*/*w*), SBMWB—bread from blend of Spanish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*). Lowercase letter means significant difference in columns, $p = 0.05$.

Table 3. Texture profile of teff breads right after baking and after 7 days.

Sample	Time [Days]	Hardness [N]	Cohesiveness	Springiness	Chewiness [N]
Control	0	2.09 ± 0.02 ^{a}	0.008 ± 0.002 ^{a}	0.41 ± 0.02 ^{b}	0.010 ± 0.004 ^{a}
	7	3.64 ± 0.07 ^{b}	0.001 ± 0.0005 ^{a}	0.24 ± 0.06 ^{a}	0.001 ± 0.003 ^{a}
WTB	0	4.16 ± 0.06 ^{c}	0.051 ± 0.006 ^{b}	0.56 ± 0.03 ^{c}	0.119 ± 0.004 ^{d}
	7	8.31 ± 0.09 ^{e}	0.066 ± 0.005 ^{b}	0.91 ± 0.07 ^{e}	0.499 ± 0.006 ^{e}
WTMWB	0	4.92 ± 0.09 ^{c}	0.020 ± 0.006 ^{a}	0.72 ± 0.03 ^{d}	0.070 ± 0.008 ^{c}
	7	7.19 ± 0.10 ^{d}	0.029 ± 0.003 ^{a}	0.90 ± 0.02 ^{e}	0.190 ± 0.010 ^{e}
BTB	0	3.51 ± 0.06 ^{b}	0.046 ± 0.004 ^{b}	0.78 ± 0.06 ^{d}	0.126 ± 0.013 ^{d}
	7	9.28 ± 0.09 ^{f}	0.093 ± 0.005 ^{c}	0.71 ± 0.02 ^{d}	0.613 ± 0.005 ^{f}
BTMWB	0	3.96 ± 0.08 ^{b}	0.013 ± 0.004 ^{a}	0.68 ± 0.08 ^{d}	0.030 ± 0.004 ^{b}
	7	7.04 ± 0.05 ^{d}	0.001 ± 0.005 ^{a}	0.39 ± 0.07 ^{b}	0.000 ± 0.001 ^{a}

Control—100% rice flour bread, WTB—bread from blend of native white teff flour and rice flour, 50:50 (*w*/*w*), WTMWB—bread from blend of white teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*), BTB—bread from blend of brown teff flour and rice flour, 50:50 (*w*/*w*), BTMWB—bread from blend of brown teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*). Lowercase letter means significant difference in columns, $p = 0.05$.

Staling of the control bread—100% rice bread—revealed a hardness increase of almost 74% after 7 days of storage, but for native buckwheat flour blend breads, the increase was even higher, being 2.5 times and 1.9 times for Polish and Spanish samples, respectively. The bread made from blending rice flour with both MW-treated buckwheat flours revealed a 32% and 51% increase in hardness for Polish and Spanish buckwheat, respectively. Compared to native flour blends, the loaf shrinkage was decreased for MW-HMT flours by 22% and 17.5% for Polish and Spanish buckwheat breads, respectively. Those results showed a good correlation with other researchers reporting the loss in quality features of bread after the addition of native buckwheat flours [33,34]. The obtained results are also well correlated with bake loss and loaf shrinkage, showing the highest rise in hardness value for breads that are more rich in starch buckwheat cultivar (Spanish). The highest cohesiveness was noted for the PBMWB sample while the lowest was observed for the 100% rice bread control, both after baking and after 7 days of storage. The lowest springiness value was observed in the 100% rice flour sample after 7 days of storage while the highest value was found in the SBB and SBMWB samples also after 7 days. The chewiness values were the lowest for the 100% rice bread control, both after baking and after 7 days of storage, while the highest values were found for native buckwheat flours after 7 days.

For native teff flour blend breads, the increase in hardness after 7 days of storage was even higher, being 2.0 times and 2.6 times for white and brown samples, respectively. The

bread made from blending rice flour with MW-treated teff flours revealed an increase in hardness of only 1.46 times and 1.77 times for white and brown teff, respectively.

Compared to native flour blends, the loaf shrinkage was decreased in MW-HMT flours by 13.5% and 24% for white and brown teff breads, respectively. The highest cohesiveness was noted for BTB after 7 days of storage. The lowest springiness value was observed for the 100% rice flour sample after 7 days of storage, while the highest was found in WTB and WTMWB samples also after 7 days. The highest chewiness value was noted for the BTB sample after 7 days of storage.

Problems with teff incorporation into the bread matrices were also reported by other researchers [35,36]. The smooth incorporation of teff and buckwheat into bread matrices is highly problematic. This is why a lot of studies have been dedicated to improving the quality of bread making using those two native gluten-free flours and applying different means of treatment [36–42].

The color changes in buckwheat and teff breads are shown in Figures 1 and 2, respectively.

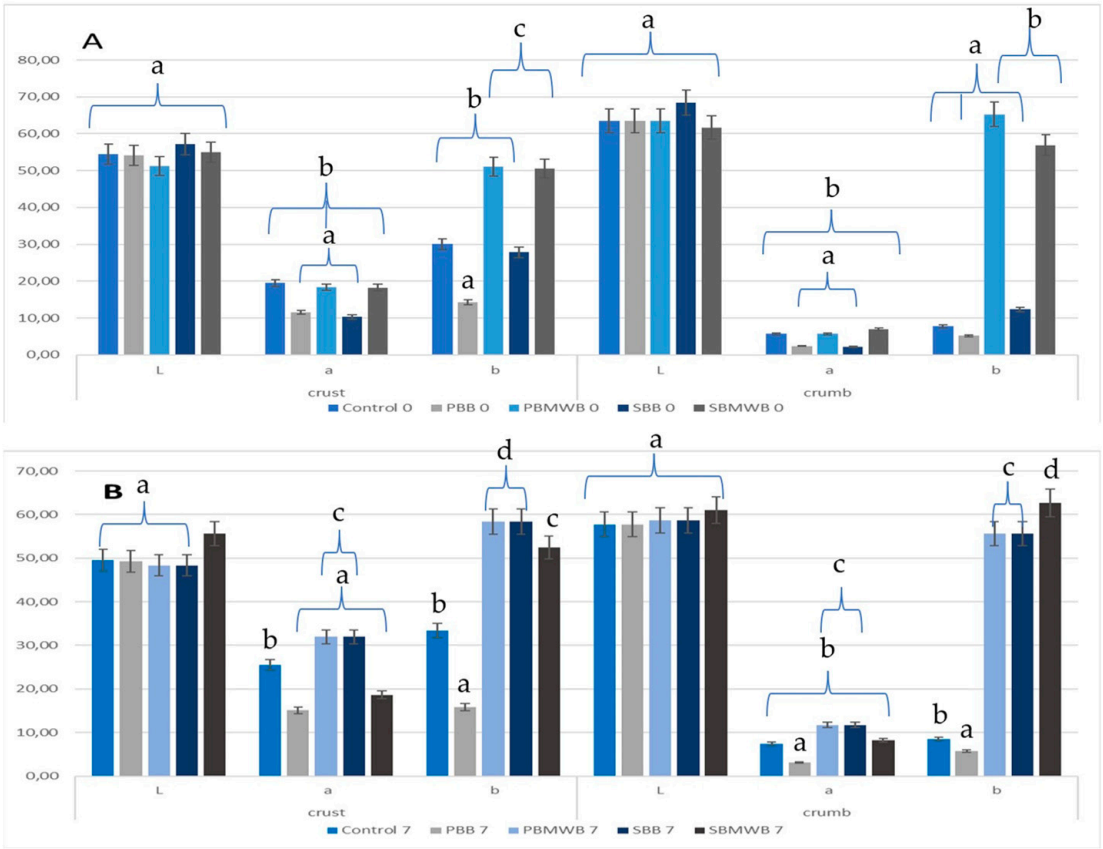


Figure 1. Color of the buckwheat breads the day of baking (**A**) and after 7 days (**B**). Control—100% rice flour bread, PBB—bread from blend of native Polish buckwheat flour and rice flour, 50:50 (*w*/*w*), PBMWB—bread from blend of Polish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), SBB—bread from blend of Spanish native buckwheat flour and rice flour, 50:50 (*w*/*w*), SBMWB—bread from blend of Spanish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*). Lowercase letter means significant difference at $p = 0.05$.

The changes in the L*a*b* components were strongly dependent on the flour; however, most of the samples, except brown teff, had moderate impact on the control bread's L*a*b* parameters. In the crumb, the yellowness-blueness axis was more pronounced and for the crust, the opposite trend was observed for brown teff. After 7 days, the brownish notes were increasing for the Polish buckwheat bread's crust and crumb, probably due to water escaping and the increased visibility of fiber particles.



Figure 2. Color of the teff breads the day of baking (**A**) and after 7 days (**B**). Control—100% rice flour bread, WTB—bread from blend of native white teff flour and rice 5%:50 (*w*/*w*), WTMWB—bread from blend of white teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*), BTB—bread from blend of brown teff flour and rice flour, 50:50 (*w*/*w*), BTMWB—bread from blend of brown teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*). Lowercase letter means significant difference at $p = 0.05$.

The total, soluble, and insoluble polyphenol content in the flours, treated flours, and resulting bread are shown in Figure 3 for buckwheat samples and Figure 4 for teff samples.

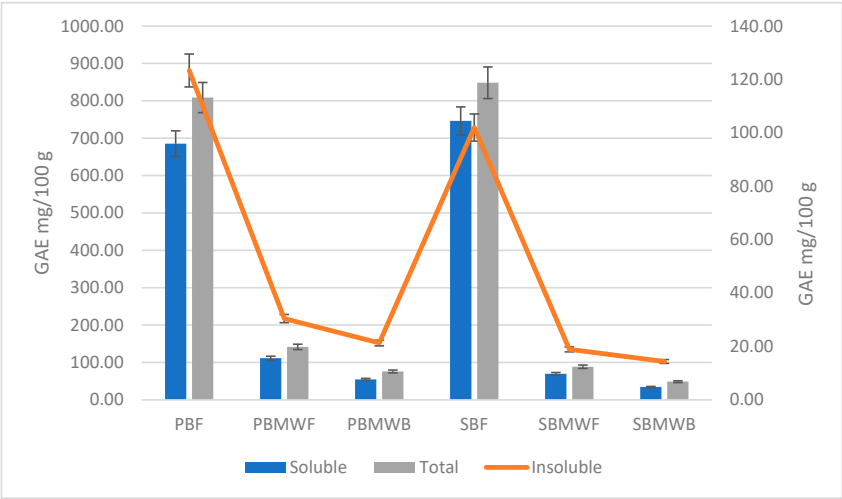


Figure 3. Polyphenols type and content in raw and processed buckwheat flours and breads made. PBF—Polish buckwheat flour, PBMWF—Polish buckwheat flour after microwave treatment, PBMWB—bread made from Polish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), SBF—Spanish buckwheat flour, SBMWF—Spanish buckwheat flour after microwave treatment, SBMWB—bread made from Spanish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), GAE—gallic acid equivalent.

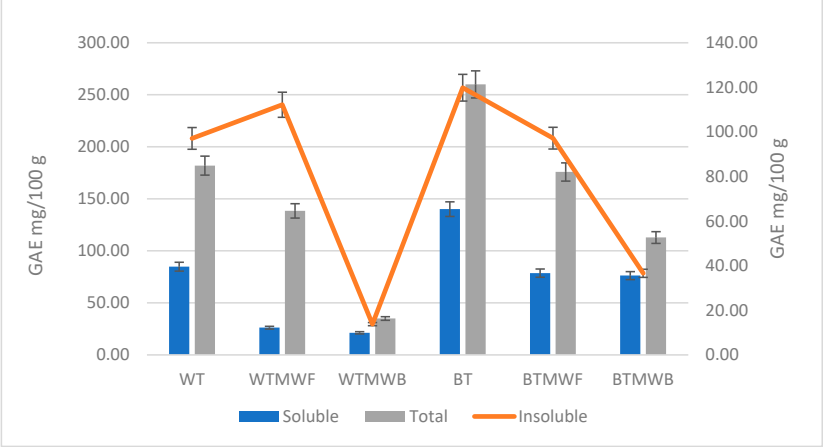


Figure 4. Polyphenols type and content in raw and processed teff flours and breads made. WTF—white teff flour, WTMWF—white teff flour after microwave treatment, WTMWB—bread made from white teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*), BTF—brown teff flour, BTMWF—brown teff flour after microwave treatment, BTMWB—bread made from brown teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*), GAE—gallic acid equivalent.

The changes in flour polyphenol content were strongly dependent on variety. Higher total polyphenols were observed in Spanish buckwheat vs. the Polish sample, and the content subsequently decreased after the MW-HMT of flours. The same trend was observed for teff flours; however, the reduction was not as large as in the buckwheat samples.

The percentage of bio-accessible polyphenols calculated as soluble fraction vs. total content in different matrices changed after the thermal treatment of flour, resulting in a significant decrease in the teff sample. Baking in the bread matrix further changed the characteristics, showing a subsequent decrease in bio-accessible polyphenols for buckwheat flours and contrary behavior for the teff-based breads (Figure 5).

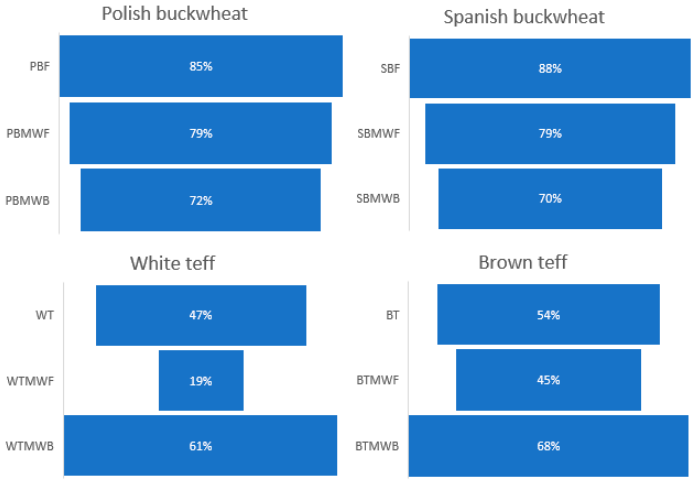


Figure 5. Bio-accessible polyphenols percentage in different matrices. PBF—Polish buckwheat flour; PBMWF—Polish buckwheat flour after microwave treatment, PBMWB—bread made from Polish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), SBF—Spanish buckwheat flour, SBMWF—Spanish buckwheat flour after microwave treatment, SBMWB—bread made from Spanish buckwheat flour after microwave treatment and rice flour, 50:50 (*w*/*w*), WTF—white teff flour, WTMWF—white teff flour after microwave treatment, WTMWB—bread made from white teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*), BTF—brown teff flour, BTMWF—brown teff flour after microwave treatment, BTMWB—bread made from brown teff flour after microwave treatment and rice flour, 50:50 (*w*/*w*).

The bio-accessible polyphenols ratios in different samples are presented in Figure 5.

MW treatment modifies the profile of bio-accessible polyphenols in buckwheat and teff flours. The changes are dependent on variety for both crops and, interestingly, the bread matrix further modifies the bio-accessibility of polyphenols, specifically in teff-based breads.

4. Conclusions

1. While the specific impact of microwave hydrothermal treatment on the polyphenolic content and antioxidant activity of gluten-free flours was not particularly widely addressed in the provided references, other researchers' studies have shown that microwave radiation can modify the physical and rheological properties of rice flour, which is commonly used in gluten-free products. Additionally, gluten-free flours, including those that may have undergone microwave hydrothermal treatment, have been found to exhibit higher antioxidant activity compared to wheat flour [24,42,43]. Further research is needed to specifically investigate the effects of microwave hydrothermal treatment on the polyphenolic content and antioxidant activity of gluten-free flours.
2. The treated buckwheat and teff flours showed an improvement in all crucial functional parameters of bread quality as well as a modified phenolic compound profile, which impacts the resulting nutritional quality of the breads. Doughs made from microwave-treated buckwheat flour resulted in the more pleasant external presence of brown bread, and the greyish notes of both rice and buckwheat disappeared. Teff is a particular minor cereal with low bread-making potential. However, the MW treatment improves the performance of teff flour; for such a particular crop, its success still depends on the starch/protein/fiber ratio, as the better improvement was observed for white teff, which is naturally richer in protein.

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