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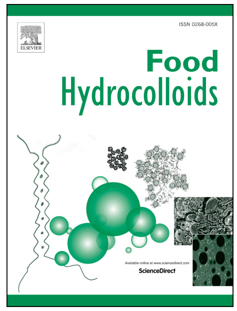

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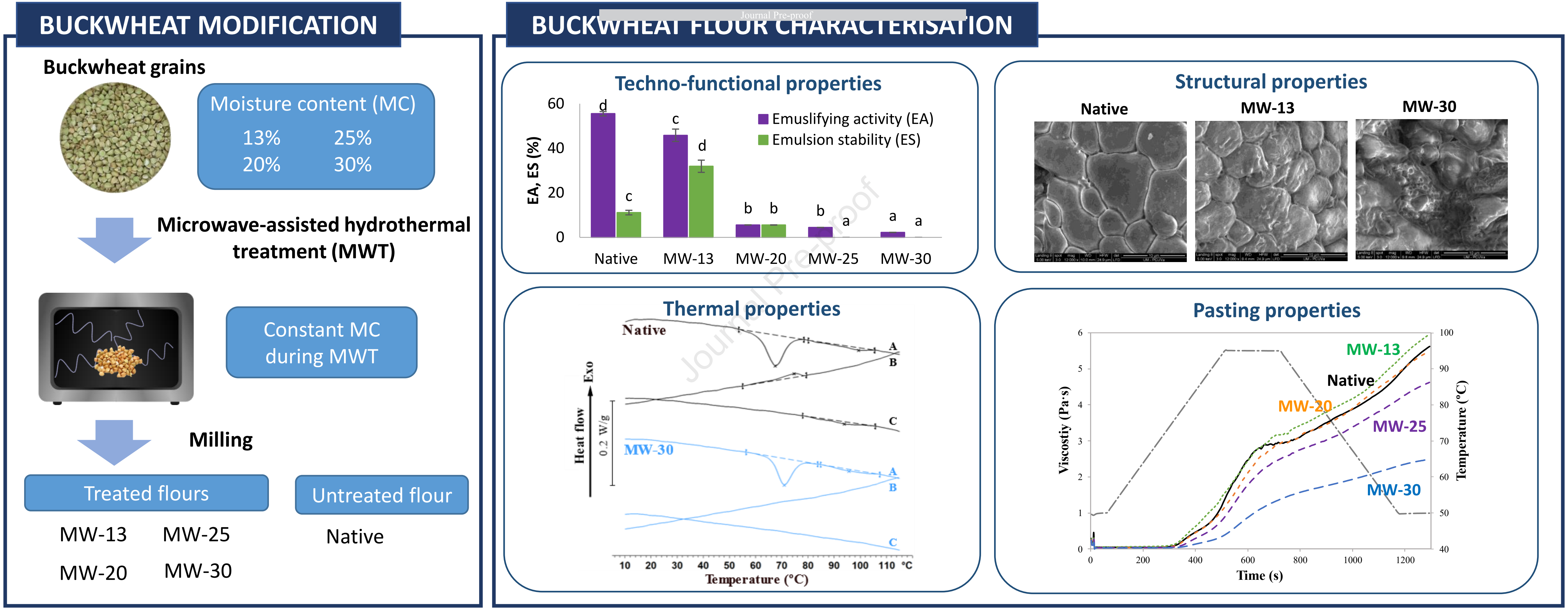

BUCKWHEAT MODIFICATION
Buckwheat grains
Moisture content (MC)
13% 25%
20% 30%
Microwave-assisted hydrothermal treatment (MWT)
Constant MC during MWT
Milling
Treated flours
MW-13 MW-25
MW-20 MW-30
Untreated flour
Native
BUCKWHEAT FLOUR CHARACTERISATION
Techno-functional properties
Emuslifying activity (EA)
Emulsion stability (ES)
EA, ES (%)
Native MW-13 MW-20 MW-25 MW-30
Structural properties
Native MW-13 MW-30
Thermal properties
Native
MW-30
Exo
Heat flow
0.2 W/g
Temperature (°C)
Pasting properties
MW-13
Native
MW-20
MW-25
MW-30
Viscostiy (Pa·s)
Temperature (°C)
Time (s)

Buckwheat grains treated with microwave radiation: impact on the techno-functional, thermal, structural, and rheological properties of flour

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Abstract

The physical modification of buckwheat grain, a pseudocereal with great interest in gluten-free (GF) product development, using microwave-assisted hydrothermal treatment (MWT), was evaluated. Buckwheat grains were microwaved (8 min at 18W/g) at four moisture contents (MC): 13%, 20%, 25%, and 30%, maintained constant throughout the treatment using a hermetic container. The impact of MWT on the techno-functional and rheological properties of flour was significantly affected by the MC of the grains. The flour obtained from grains treated with 30% MC (MW-30) was the most modified, showing the highest water absorption capacity (+43%) and a dramatic reduction in its emulsifying activity to almost zero, indicating the loss of its protein functionality during treatment. Differential scanning calorimetry (DSC) revealed a delay in the gelatinisation temperature (+3.7 °C) with a significant reduction in the gelatinization enthalpy (-27%), which is compatible with a partial pre-gelatinization of the flour. In contrast, the lowest grain MC led to opposite effects on most of the flour properties measured. The most significant difference was its improved ability to form stable emulsions (ES) (+188%) and a significant, albeit moderate, increase in gel structural stability and tolerance to stress. Based on these results, MWT combined with the MC of grain during treatment may be a viable and effective alternative to modulate the techno-functional properties of buckwheat flour and improve its applicability in GF food formulations.

Keywords: Microwave treatment; Rheological properties; Thermal properties; Physical modification; Buckwheat

1 Introduction

The demand for gluten-free (GF) products is steadily increasing due to the rise in diagnoses of related diseases and people choosing to follow GF diets, as they are considered to be healthier by eliminating allergens (Witczak, Ziobro, Juszczak, & Korus, 2016). However, GF products tend to have poorer nutritional qualities than their gluten-containing counterparts (Matos Segura & Rosell, 2011; Miranda, Lasa, Bustamante, Churruca, & Simon, 2014; Villanueva, Abebe, Collar, & Ronda, 2021). Therefore, the inclusion of nutritious ingredients such as buckwheat can improve the variety and quality of GF diets. Buckwheat is a pseudocereal rich in vitamins, minerals (especially manganese, copper, and magnesium), and antioxidants with high levels of flavonoids, particularly rutin. It also contains high amounts of dietary fibre, protein (with a well-balanced amino acid profile), and resistant starch (Bhinder, Kaur, Singh, Yadav, & Singh, 2020).

The main limitation in the development of GF products is the range of utilisation that GF matrices allow because of their natural characteristics. In the food industry, physical modifications have been applied to flours and starches to improve their properties and expand their range of applications. Physical methods are considered safe and effective; among them, heat-moisture treatment (HMT) is one of the most widely used (Liu, Lv, Peng, Shan, & Wang, 2015). During HMT, flour is exposed to a high temperature (above starch gelatinisation) for a variable time (15 min to 16 h) without sufficient water available for gelatinization (10–30%) (Gunaratne, 2018). Traditional HMT is applied to modify buckwheat starch and flour by improving its thermal stability and health benefits, making it more suitable for food products such as noodles, soup, dumplings, and bread (Liu et al., 2015a; Liu et al., 2015b; Xiao, Liu, Wei, Shen, & Wang, 2017). Xiao et al. (2017) treated buckwheat starch and flour at different moisture levels (200, 250, 300, and 350 g/kg) at 110 °C for 16 h. The HMT-modified samples exhibited higher gelatinisation temperatures and were more stable during heating and shearing. However, this treatment led to softer buckwheat gels. HMT decreased rapidly digestible starch while increasing slowly digestible starch and resistant starch, which may have potential applications for reducing the glycaemic index of foods. The authors also demonstrated a more significant effect of the treatment on buckwheat flour than on starch, which is related to the high content of proteins, lipids, and non-starch polysaccharides.

The use of microwave-assisted hydrothermal treatment (MWT) for the physical modification of flour is a promising alternative to the traditional HMT processes, as microwaves generate heat quickly and efficiently by inducing the movement of polar and ionic molecules, causing friction between them that allows heat to be generated from inside the sample. This is in contrast to conventional heating, in which heat is applied externally. Microwaves, therefore, allow for faster treatment and reduce the energy required compared to conventional thermal heating. MWT has been applied to starch from non-gluten cereals, pseudocereals, tubers, and legumes to modify starch structure and physicochemical properties like solubility, swelling power, rheological behaviour, and gelatinization (Brasoveanu & Nemtanu, 2014; Gupta, Gill, & Bawa, 2008). The modifications caused have been demonstrated to depend greatly on the starch type and its moisture content (MC), exposure time to microwave, and temperature (Brasoveanu & Nemtanu, 2014). Recently, studies have been conducted on the application of MWT in rice flour (Solaesa, Villanueva, Muñoz, & Ronda, 2021; Villanueva, Harasym, Muñoz, & Ronda, 2018). These authors modulated the techno-functional properties of the flours by controlling their water content during the treatment. Solaesa et al. (2021) observed the greatest modifications in rice flour samples treated at 8% and 30% constant MC, such as higher swelling power and water solubility, and superior capacity to form more resistant and consistent gels. Villanueva et al. (2018b) reported higher gelatinization temperature and lower gelatinization enthalpy for rice flour samples treated at 20 and 30% initial MC.

However, limited work has been conducted on the treatment of grains by microwaves, although it is an interesting strategy to improve the industrial scale-up of this technology, as it can simplify the treatment process, improve the homogeneity of the treatments, and eliminate the risks associated with the handling of powdery systems, such as potentially explosive atmospheres. In addition, buckwheat kernel has a large grain size and intact plant structures which will affect the kinetics of heat transfer and water mobility during MWT compared to flour treatment. In particular, the water binding capacity of the bran structures located outside of the grains will affect the mobility of water and its availability to produce changes in the molecular structure of the biopolymers (protein and starch), located mainly inside the grain. Most studies on grains have focused on roasting (Jogihalli, Singh, & Sharanagat, 2017; Sharanagat et al., 2019) or pregelatinization (Sun et al., 2018) of the grain but not on its hydrothermal physical modification. Thus, to the best of our knowledge, there are no studies on HMT assisted by microwave radiation applied to buckwheat grain, although it is a matrix of great nutritional interest for use in GF product development.

Therefore, the main objective of this study was to evaluate the ability of microwave-assisted hydrothermal treatment of buckwheat grain to modify the techno-functional and physico-chemical properties of buckwheat flour as a function of grain moisture content (MC) (13%, 20%, 25%, and 30%) held constant during treatment using a hermetic container.

2 Materials and methods

2.1 Samples

Dehulled buckwheat (*Fagopyrum esculentum* Moench) grains of the Kora variety were provided by Grupa Producentów Ekologicznych Dolina Gryki Sp ZOO (Miedzylesie, Poland). The proximal composition was (g/100 g buckwheat): 12.6% protein, 3.0% fat, 4.4% dietary fibre, 1.8% ash, and 13.0% moisture, measured using the 46-19.01, 30-10.01, 32-06.01, 08-01.01, and 44-19.01 AACC official methods (AACC, 2010), respectively. The starch content (65.7 g/100 g buckwheat) was measured using the optional rapid method for total starch described by Englyst, Hudson, & Englyst (2006).

2.2 Microwave treatment

Buckwheat grain MC was set to 13% (the natural MC of the grain), 20%, 25%, and 30%. The batches were obtained by adding distilled water to the grain while stirring the mixture in a rotary mixer MR-2L (Chopin, Tripette et Renaud, France) for 1 h and storing it for 24 h at 4 ± 2 °C to reach equilibration.

Microwave treatments were performed in a customised microwave oven R342INW (SHARP, Sakai, Japan) at 900W and 2450 MHz on 50 ± 0.05 g of buckwheat grains tempered at different MC (13%, 20%, 25%, and 30%) placed into a 1L hermetic Teflon® container, which was continuously rotated by an external device controlled by a power supply unit at speed of 70 rpm to achieve an even distribution of energy and temperature during the treatment. After preliminary studies, the microwave treatment time was set at 8 min for 10s exposure/60s rest cycles (48 cycles). The sample was allowed to cool for 30 min before opening the container. The MC of the samples varied less than 1% during treatment. The maximum temperature reached in each treatment was measured using Testoterm® temperature strips from TESTO (Barcelona, Spain), which were placed in a container in permanent contact with the sample. This temperature averaged 105 ± 5 °C in all samples, with no significant differences between them. Once treated 20%, 25%, and 30% MC samples were dried at 30 °C up to a final MC of approximately 13%. Three batches were obtained for each of the MC samples. The grain was ground in a stone mill Fidibus Medium (Komo, Hopfgarten, Austria) to < 500 µm. The > 500 µm fraction, always < 0.5% w/w, was rejected. The samples were named according to the MC at which they were treated: MW-13, MW-20, MW-25, and MW-30. The samples were maintained at 4 ± 2 °C until analysis. The flour from untreated milled grains was used as a control (native) sample.

2.3 Colour characteristics

Flour colour was determined using a PCE-CSM5 colorimeter and CQCS3 software. The CIELAB coordinates with a D65 standard illuminant and a 10° standard observer were obtained. L* (lightness from 0–black to 100–white) and chromatic coordinates a* (from green (−) to red (+)) and b* (from blue (−) to yellow (+)) were measured. Hue (*h*) and chroma (*C**) were also obtained from the CIELAB coordinates (Solaesa et al., 2021). The colour difference (ΔE) between each treated sample and the native sample was calculated using the equation $\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. Six measurements were taken for each sample.

2.4 Particle size distribution

A laser diffraction particle size analyser (Mastersizer 2000, Malvern Instruments Ltd., UK) was used to study the particle size distribution of the flours. Results were expressed as D_{10}, D_{50}, and D_{90}, (10%, 50%, and 90% of the sample had a smaller particle size than these values, respectively). The particle size distribution was characterised by the median diameter (D_{50}) and dispersion ($(D_{90}-D_{10})/D_{50}$). Three measurements were taken for each sample.

2.5 Scanning electron microscopy (SEM)

A Quanta 200-F microscope (FEI, Oregon, USA) was used to study the morphological changes in the flours obtained after MWT and milling. The microscope was equipped with an X-ray detector, which allowed analysis of the samples without prior metallisation. The samples were observed at an accelerating voltage of 5 keV in the low-vacuum mode using a secondary electron detector. Photomicrographs were obtained at different magnifications to illustrate the modifications.

2.6 Techno-functional properties

The water absorption capacity (WAC), water absorption index (WAI), water solubility index (WSI), and swelling power (SP) of buckwheat flour samples were measured as described by Abebe, Collar & Ronda (2015), with slight modifications. Flour dry matter (dm, 2 g) was mixed with water (20 mL) in centrifuge tubes. For WAC measurements, the mixture was vortexed, kept for 10 min at room temperature, vortexed again, and finally centrifuged for 25 min at 3000 × g. The supernatant was removed, and the remainder was weighed. Results are expressed as grams of water retained per gram of flour dry matter (dm). To determine the WAI, WSI, and SP, the mixtures were heated for 15 min at 95 °C, cooled to room temperature, and centrifuged for 10 min at 3000 × g. The supernatant was poured onto a pre-weighed evaporating dish overnight at 110 °C to determine the soluble solid content. WAI (grams of sediment per gram of flour dry matter (dm)), WSI (grams of soluble solids per 100 g of flour dm), and SP (grams of sediment per gram of insoluble solid flour dm).

Emulsifying activity (EA) and emulsion stability (ES) were determined using the method described by Kaushal, Kumar, & Sharma (2012), with some modifications. Flour dm (7 g) was mixed with distilled water (100 mL). Corn oil (100 mL) was added, and the mixture was mixed for 1 min at 1000 rpm using an Ultra-Turrax T25 homogeniser (IKA, Staufen, Germany). The mixture was distributed into 50 mL centrifuge tubes and centrifuged for 5 min at 1300 × g. EA was calculated as the ratio of the emulsion volume to the total initial volume and was expressed as a percentage. Subsequently, the tubes were heated at 80 °C for 30 min, allowed to cool for an additional 30 min, and centrifuged for 5 min at 1300 × g. The ES was calculated from the ratio of the emulsion volume after heating to the total initial volume and was expressed as a percentage. Techno-functional properties were obtained at least in triplicate.

2.7 Pasting properties

The pasting properties of the buckwheat flour were determined using a Kinexus Pro+ rheometer (Malvern Instruments, UK) equipped with a starch cell. First, the flour (3.5 g) was dispersed in water (25 mL). A temperature of 50 °C was applied for 1 min, followed by heating to 95 °C at a rate of 6 °C/min, holding at 95 °C for 3.5 min, cooling to 50 °C at a rate of 6 °C/min, and holding at 50 °C for 2 min. The paddle speed was set at 160 rpm. Pasting temperature (PT), peak viscosity (PV), peak time (Pt), trough viscosity (TV), breakdown viscosity (BV), final viscosity (FV), and setback viscosity (SV) were calculated from the pasting curve. The determination was performed in duplicate.

2.8 Rheological properties of gels

The gels obtained, as described in the previous section (2.7 Pasting properties) were used for dynamic oscillatory tests on a Kinexus Pro + rheometer (Malvern Instruments, UK) equipped with a parallel plate geometry (40 mm) with a serrated surface and a 1 mm gap. The gels were placed between plates and allowed to rest for 5 min. The temperature was stabilised at 25 °C using a Peltier plate controller. Strain sweeps were performed from 0.1–1000% at 1 Hz frequency. The linear viscoelastic region (LVR) was established, and the maximum stress

(τ_{max}) beyond which the dough structure broke and the stress at the crosspoint (G' = G″) was determined. Frequency sweeps were performed from 10–1 Hz in the LVR at constant deformation of 1%. The frequency sweep data were fitted to the power-law model, as described by Ronda, Villanueva, & Collar (2014). The recorded viscoelastic parameters G'_1, G''_1, and $(\tan \delta)_1$ are the coefficients obtained by fitting the frequency sweep data to the potential model and represent the elastic and viscous moduli and the loss tangent, respectively, at a frequency of 1 Hz. The *a*, *b*, and c are the exponents of the potential equation, and quantify the dependence of the dynamic moduli and loss tangent on the oscillation frequency. The complex modulus G_1^* was calculated from $(G'_1 + G''_1)^{1/2}$. All tests were performed in duplicate.

2.9 X-ray diffraction (XRD)

XRD was performed using a Bruker-D8-Discover-A25 diffractometer (Bruker AXS, Rheinfelden, Germany) equipped with a copper tube operating at 40 kV and 40 mA, with CuKα radiation (λ=0.154 nm). Diffractograms were obtained in flour samples in the range of 5–40º (2θ) at a rate of 1.2°/min, a scan step size of 0.02°, a divergence slit width of 1°, and a scatter slit width of 2.92°.

2.10 Differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC3, STARe-System, Mettler-Toledo, Switzerland) was used to obtain the thermal properties related to the gelatinisation and retrogradation transitions of the flour samples (hydrated to 30 g solids/70 g water) using the method described by Villanueva et al. (2018b). The enthalpy (ΔH), expressed in J/g dm, and the peak temperature (T_p), expressed in °C, were extracted from the thermograms obtained in both the first/gelatinization scan performed on fresh samples (gelatinisation and dissociation of amylose-lipid peaks) and the second/retrogradation scan, performed on 7 d-stored samples (4 ± 2 °C, melting of the recrystallised amylopectin and dissociation of amylose-lipid peaks). Both scans were performed from 0 to 120 °C at 5 °C/min. The temperature range ($R_{gel} = T_{endset}-T_{onset}$) was calculated for the gelatinisation transition. To study the reversibility of the amylose-lipid complex, immediately after the gelatinisation sweep, a cooling sweep was performed from 120 to 0 °C °C at -5 °C/min, followed by a second heating sweep from 0 to 120 °C at 5 °C/min. The samples were analysed in duplicate.

2.11 *Statical analysis*

Statgraphics Centurion 18 (Bitstream, Cambridge, MN, USA) was used for the statistical analysis. The least significant difference (LSD) analysis of variance (ANOVA) was used to assess the significant differences ($p < 0.05$) between samples.

3 Results and discussion

3.1 *Colour characteristics*

The colour values of the treated and native flours are listed in Table 1. The MWT had a significant effect ($p < 0.05$) on all the measured colour characteristics. Luminosity decreased with increasing MC, resulting in darker flours than those in the control. Only the MW-13 sample had the same luminosity as native flour. Hue (h) also decreased for all treatments, always remaining within the first quadrant of the a*–b* diagram, which indicates a more reddish hue in the treated flours than in the native flour. The effect increased with MC. The chroma (C*) did not follow a clear trend, decreasing with treatment for low moisture values (13% and 20%) and increasing again to the value of native flour in the 25–30% MC treatments. This indicates that the vividness of the colour of the treated flours depended on the grain MC during the MWT. Despite the significant changes in the colour parameters ($p < 0.05$), colour differences with respect to the native flour were only visibly differentiated ($\Delta E > 5$) for the MW-30 sample. Darker and reddish flours have also been obtained from microwave-roasted sorghum (Sharanagat et al., 2019) and pregelatinized buckwheat (Sun et al., 2018). The formation of reducing sugars during MWT, favoured by a higher moisture content (Solaesa et al., 2021), enhances the Maillard reaction and, in addition to the thermal oxidation of polyphenols (Sharanagat et al., 2019), may explain the darker and more reddish colours of treated flours and an increase in the effect with higher MC.

3.2 *Morphology and particle size distribution*

Scanning electron micrographs of native and microwave-treated flours are shown in Figure 1. Native buckwheat starch granules, which varied in shape (spherical, ovoid, and polygonal) and exhibited a smooth surface, were packed into clusters of different sizes. These particles have attached or entwined globular or irregular particles of proteins (Sun et al., 2018). Progressively greater differences were observed between the micrographs of native and treated flours as the MC increased. MW-13 and MW-20 had slightly larger and more packed aggregates as well as some roughness on the surface of the starch granules. For MW-25, this behaviour was accentuated, and some deep holes appeared on the granule surface and other exudates gluing the starch granules together. As reported by Villanueva et al. (2018b) for rice flour, these exudates may be amylose being excreted from the starch granules during MWT. This could also be expected in the case of buckwheat flour, considering the high MC of the grain during treatment and the temperature reached in the process, as well as the moderate/high amylose content of common buckwheat (*Fagopyrum Esculentum* Moench) starch, which is in the range of 23.4-29.1% (Ikeda, Kishida, Kreft & Yasumoto, 1997). The MW-30 sample showed the largest particles and the presence of gelatinised granules, which was consistent with the partial pre-gelatinization observed in the DSC scan (see Section 3.7).

The particle size distributions of the flours obtained from the treated and untreated grains are shown in Table 1. An increase in the particle size of the treated samples and a significant reduction in their size dispersion were observed, which were in agreement with the SEM observations. The higher changes were obtained for MW-25 and MW-30, with D_{10} increases of 96% and 107%, D_{50} of 33% and 56%, and D_{90} of 18% and 26%, respectively. This indicates that smaller and intermediate-sized particles were the most affected by the treatment, which indicates a greater difficulty in reducing the treated grains to small particle sizes during the milling process. The changes in the particle structure observed in the SEM micrographs may explain this difference in milling behaviour. Treated starch granules stick together due to amylose leaching, and more compact amorphous regions caused by structural rearrangements of the starch granules (Villanueva et al., 2018b) may be responsible for this behaviour.

3.3 Techno-functional properties

The MC of the grain during the MWT significantly ($p < 0.05$) affected all techno-functional properties of the treated flours (Table 2). The WAC of the flour increased with MC up to 43% over the control flour in sample MW-30. Similar effect was observed in microwaved-pregelatinized buckwheat grains (Sun et al., 2018), even when they were treated under highly different conditions: at their natural moisture content (10.83%), in open containers (variable humidity over time), and under static conditions (non-uniform distribution of heating). The same effect has been observed in roasted sorghum grains (Sharanagat et al., 2019). These authors related the increased water affinity to the development of a porous structure and the increased damaged starch content due to mechanical damage and/or starch gelatinisation during MWT. The enhancement in the hydrophilic tendency of starch molecules may also be explained by the disruption of hydrogen bonds between the amorphous and crystalline regions, with an expansion of the amorphous region (Solaesa et al., 2021). This behaviour was more intense at a higher MC during the MWT. The highest water affinity of MW-30 was also enhanced by partial gelatinisation, as can be concluded from the SEM images.

WAI and SP are affected by factors such as starch molecule conformation; the content, molecular weight distribution, and length and degree of branching of amylopectin and amylose; the interaction between starch chains within the amorphous and crystalline domains; and the presence of phosphate groups (Villanueva, De Lamo, Harasym, & Ronda, 2018a). WAI and SP exhibited a similar tendency and presented a moderate increase for the MW-13 sample (+3% and +4%, respectively), and then a progressive and slight reduction in the MW-25 and MW-30 samples (-6% and -4%, respectively). WSI is related to the amount of soluble solids released from starch granules and is used as an indicator of starch degradation and dextrinization (Jogihalli et al., 2017). WSI only changed significantly in the MW-13 sample (11.5%). The increase in WAI, SP, and WSI for MW-13 may be caused by the weakening of amylose-amylopectin bonds and creation of more amylose-water interactions (Solaesa et al., 2021; Villanueva et al., 2018a). However, the reductions in WAI and SP for treatments at higher MC may be attributed to structural rearrangements and reassociations occurring in starch chains during MWT, leading to stronger intramolecular bonds due to the interactions between amylose and amylopectin molecules, formation of ordered double-helical amylopectin side chain clusters, which are more rigid, and the formation of amylose-lipid complexes (Sun, Han, Wang, & Xiong, 2014; Villanueva et al., 2018a).

The ability of flour protein to form stable emulsions that resist mechanical stress is important for food applications such as cakes and frozen desserts (Bhinder et al., 2020). EA is generally affected by protein characteristics such as solubility, hydrophobicity, molar mass, conformational stability, and psychochemical factors (pH, temperature) (Tang & Ma, 2009). EA decreased significantly during the MWT. The decrease was moderate for sample MW-13, whereas samples treated with MC above 20% nearly lost their emulsifying activity. The ES of most treated samples also decreased and was null for MW-25 and MW-30. However, MW-13 showed a notably higher stable emulsion-forming capacity than native, with an 188% increase in ES. The improvement in emulsifying properties could be a consequence of the thermal unfolding of buckwheat proteins, with an increase in their hydrophobic surface area and flexibility. However, the decrease in emulsifying properties observed in the samples treated under stronger conditions (higher MC) may be due to a decrease in protein solubility by heat-induced aggregation, as well as a decrease in flexibility caused by the rearrangement of unfolded proteins (Tang & Ma, 2009). It is well known that the kinetics of protein denaturation depends on the temperature and treatment time as well as on the MC (Pérez-Quirce, Ronda, Melendre, Lazaridou, & Biliaderis, 2016). Therefore, this factor could have greatly influenced the observed effects, as more intense treatments (higher MC) could have denatured the proteins and aggregated them, thus cancelling their emulsifying functionality, whereas softer treatments (lower MC) could have merely unfolded the proteins, allowing for more bond formation and increasing their emulsifying stability.

3.4 Pasting properties

The pasting curves, plotted in Figure 2, did not present the usual profile of cereal flours, as there was no clear drop after the peak in the plateau area at 95 °C. In the studied buckwheat flours, the breakdown was practically null or negligible. Low breakdown has been reported in several studies for some buckwheat cultivars, indicating high stability during heating and shaking (Bhinder et al., 2020).

Two different behaviours were observed in terms of pasting properties (Table 2). MW-13 presented a slight but significant ($p < 0.05$) decrease in PT, and increase in PV, TV, FV, and SV compared to native flour. However, the rest of the treated samples showed the opposite behaviour, with an increased PT and decreased PV, TV, FV, and SV; with the effect being more pronounced at higher MC. Similar behaviour was observed by Kamble, Singh, Pal Kaur, Rani, & Upadhyay (2020) for microwaved-wheat semolina at 900 W for 1, 1.5, and 2 min, with an increase in pasting parameters (PV, BV, FV, and SV) for 1 min and significant decreases after 1.5 and 2 min of MWT. This different effect on pasting properties depending on the intensity (power and time) of the MWT was also reported by Sharanagat et al. (2019) for microwave-roasted sorghum. These studies did not report the MC of treated semolina or grains during treatment, which leads to the possibility that they were treated at their natural MC, without moistening. In the present study, the MC of the grains, which were always treated at the same power and time, seemed to determine the type and intensity of the changes induced by the treatment. Changes in pasting properties may be the result of structural rearrangements and starch chain association during microwave heating (Kamble et al., 2020). The increased PT and delayed gelatinisation may be due to the increased heat requirement for the structural disintegration of starch granules and paste formation caused by the strengthening of intragranular bonding forces occurring during the treatment (Zavareze & Dias, 2011). The higher MC in flour during treatment facilitates molecular mobility and allows for faster and deeper changes in the starch structure under constant MC treatment conditions. Thermal treatment of the MC-13 sample allows a certain disaggregation of the starch structure, although its low MC likely restricted the aggregation or the establishment of new/more ordered structures. These results show that the effect of MWT on flour properties increased significantly with the MC of the grain during treatment. This can be affirmed given that the temperature reached by buckwheat grains during MWT was the same regardless of the MC, which is not usually the case when MWT is applied directly on flours. A previous work has shown that the temperature reached by rice flour during MWT presented an inverse correlation with moisture content during treatment (Solaesa et al. 2021), making it difficult to analyse the individual effect of each variable. Solaesa et al. (2021) determined that the physical properties of microwaved-rice flour were modified to a greater extent when treatment was performed at a very low MC (8%), associated to the highest temperature reached in said treatment (173°C), much higher than that reached by flour treated at 30% MC (114°C).

The reduction in SV is an indicator of lower amylose retrogradation tendency, which may improve the application of these treated flours as thickening agents for products such as soups or sauces, as they would have a lower tendency for syneresis and more stability toward heating and cooking (Bhinder et al., 2020; Sharanagat et al., 2019). The reduction in retrogradation can be explained by the generation of new interactions between amylose and amylose and/or amylopectin-amylose chains as a result of HMT treatment, leading to a reduction in amylose leaching, and thus a reduction in setback viscosity (Liu et al., 2015b; Villanueva et al., 2018b).

3.5 Rheological properties of gels

Rheological properties of the gel samples were determined using dynamic oscillatory tests. Table 3 shows the parameters obtained from fitting the power law model to the frequency sweep data and the maximum stress (τ_{max}) within the linear viscoelastic region (LVR) and the cross-point (G’=G’’, tan δ=1) obtained from the strain sweeps. All samples exhibited significant differences in their viscoelastic properties with respect to the control, although two opposite trends were observed among the treated samples. The gels obtained from MW-13, MW-20, and MW-25 were stronger than the control gel, whereas those from MW-30 were significantly weaker. The highest increases in the elastic (G_1’), viscous (G_1’’), and complex (G*) moduli, +23%, +16%, and 22%, respectively, were observed for MW-13 sample. This increase was accompanied by a drop in the loss tangent, which denotes reinforcement in the solid-like behaviour of the gels (Villanueva et al., 2018a). All the gels increased their viscous behaviour with frequency, as exponent “a” was always below exponent “b”, which explains why exponent “c” was always positive and thus, the loss tangent increased with the angular frequency. The

τ_{max} and crosspoint (G'=G") values increased up to a maximum of +84% and +30%, respectively, for the MW-13 sample, indicating a more resistant structure of the gel. Similar results have been reported for microwaved-treated rice starch (Villanueva et al., 2018a) and rice flour (Solaesa et al., 2021). This improvement in gel resistance to stress could be caused by cross-linking between starch chains in the amylose portion during HMT, which allowed the formation of more junction zones in the continuous phase of the gel matrix (Gunaratne, 2018). However, MW-30 exhibited the opposite behaviour. The gel made from this sample showed reduced elastic, viscous, and complex moduli (-52%, -41%, and -51%, respectively), as well as τ_{max} (-65%) and stress at the crossover point (-65%), with respect to the control sample. This could be explained by its partial gelatinisation during the MWT, which resulted in a less rigid gel due to the partial collapse of the starch granule structure (Zavareze & Dias, 2011).

3.6 Crystalline structure

X-ray diffraction patterns of the flour samples are shown in Figure 3. Buckwheat flour presented an A-type diffraction pattern with peaks at 15°, 17°, 18°, and 23°, that were maintained after treatment, although a change in the intensity of the peaks was observed in the treated flour. For all samples, the intensity of the 20° peak, associated with V-type crystallinity, increased with respect to the native flour. This behaviour was previously reported by Villanueva et al. (2018) for microwave-treated rice flour and may be associated with an increase in the type II amylose-lipid complex. The MWT may have favoured the formation of type II amylose-lipid complexes, which appear as polycrystalline specimens in the XRD pattern (Biliaderis, 2009). It has previously been reported that when heated to high temperatures, typically above 90 °C, the randomly oriented helices of the amylose-lipid Type I complex may change into the type II form as they become regularly oriented and organised, likely through lamellae thickening (Biliaderis, 2009; Wokadala, Ray, & Emmambux, 2012).

For the other peaks, samples treated at the lowest MC (MW-13 and MW-20) presented a moderate increase in intensity, whereas the intensity of the peaks in the MW-25 and MW-30 samples was slightly lower than that of the control flour. Xiao et al. (2017) found a relative crystallinity increase in buckwheat flour treated with conventional HMT from 19% (untreated flour) to 26% (in the sample treated at 35 g/100 g MC for 16 h at 110°C). However, microwaved buckwheat grains showed no significant difference ($p<0.05$) in relative crystallinity compared to the native sample (64%). The much shorter treatment time (8 min vs. 16 h) and the protective action of the grain's components could be the reasons for this difference. Both increases and decreases in the X-ray diffraction pattern for the MWT of starches have been reported, depending on the source and treatment conditions (Brasoveanu & Nemtanu, 2014). Increases in the diffraction patterns due to hydrothermal treatments have been related to the displacement of the double helical chains within the starch crystals, resulting in a more ordered crystalline matrix (Zavareze & Dias, 2011).

3.7 Thermal properties

The thermal properties obtained from the first (gelatinisation) and second (retrogradation) DSC scans are summarised in Table 4. In the gelatinisation scan, two peaks were observed at 67–71 °C and approximately 98 °C, as is typical in several cereal and pseudocereal flours, such as corn, rice, wheat, and buckwheat. At lower temperatures, the first peak is related to starch gelatinisation (melting of amylopectin crystallites) and the second peak is related to the disruption of the type I amylose-lipid complex (Biliaderis, 2009). The temperature of the gelatinisation peak ($T_{p\text{-}gel}$) was affected differently by the MWT, depending on the grain MC during the treatment, as has also been described for the remaining measured properties. The $T_{p\text{-}gel}$ showed a decrease for the MW-13 sample and then increased progressively with MC, exceeding the value of the control flour by up to +4 °C in the MW-30 sample. The increase in $T_{p\text{-}gel}$ on HMT, that was previously reported for treated buckwheat flour and starch (Liu et al., 2015a; Xiao et al., 2017), may be due to the improvement in amylose-amylose, amylose-amylopectin, and amylose-lipid interactions. These interactions suppress the mobility of the starch chains in the amorphous regions. Consequently, the amorphous regions would require a higher temperature to cause swelling that can contribute to the disruption of the crystalline regions. The extent of these interactions has been shown to be influenced by starch source, amylose chain length, and by the MC prevailing during HMT (Hoover, 2010). The opposite trend observed in the MW-13 sample, also observed by other authors when applying dry heat treatment (DHT), can be attributed to the rupture of hydrogen bonds in or between starch granules during the heating process under a restricted amount of water, which would make it easier for water to enter starch molecules during the gelatinisation process, leading to lower gelatinisation temperatures (Lei et al., 2020). The temperature range, R_{gel}, significantly decreased for MW-25 and MW-30. This behaviour was opposite to that reported for buckwheat flour and starch treated by conventional HMT, where the temperature range increased with increasing MC (Liu et al., 2015a; Xiao et al., 2017). However, Villanueva al. (2018b) also found a reduction in R_{gel} for MWT of rice flour, indicating that MWT promoted the formation of more uniform and perfect amylopectin crystallites. The gelatinisation enthalpy, ΔH_{gel}, was significantly ($p < 0.05$) different only from that of the native flour for the MW-30 sample. This sample showed a lower ΔH_{gel}, which may be related to partial gelatinisation, as well as the dissociation of double helices and disruption of amorphous regions within starch granules during hydrothermal treatment (Xiao et al., 2017). The amylose-lipid dissociation peak obtained in the first scan was not significantly affected by the MWT.

In the second scan, two peaks were observed in both the control (untreated) and treated samples MW-13 and MW-20. However, in the MW-25 and MW-30 samples, only the first peak was observed. The first peak ($T_{p\text{-}ret}$ of approximately 49 °C) corresponded to the melting of recrystallised (retrograded) amylopectin during storage, appeared at a substantially lower temperature, and showed a much wider temperature range than the gelatinisation peak obtained in the first scan, owing to the fewer perfect crystallites formed during the retrogradation process than those present in the original native starch structure. The second peak ($T_{p\text{-}am\text{-}lip}$ of approximately 93 °C) was related to the reversible amylose-lipid dissociation peak, which in this second scan showed a substantially higher enthalpy than that in the first one, particularly in the control sample. Similar results were reported by Liu, Donner, Yin, Huang, & Fan (2006) for native buckwheat flours. The retrogradation peak presented a similar $T_{p\text{-}ret}$ in all samples, whereas the enthalpy, ΔH_{ret}, increased with MWT, from 2.2 J/g dm in the control sample to 2.9–3.2 J/g dm in the treated samples, with no significant differences among them. The increased amylopectin recrystallisation extent, which was also reported by Villanueva et al. (2018) for MWT rice flour, may negatively affect the shelf life of treated flour gels. The enthalpy of dissociation of the amylose-lipid complex obtained after 7 d of storage of the gels, $\Delta H_{am\text{-}lip}$, increased in the control sample with regard to that obtained in the first scan (applied to fresh, non-gelatinised samples) because of the better conditions for complex formation when amylose leaked from the starch granules during gelatinisation (Eliasson, 1994). However, the opposite behaviour was observed for the MWT samples: $\Delta H_{am\text{-}lip}$ decreased progressively with MC to the point of being undetectable for MW-25 and MW-30. Figure 4 shows the results of the reversibility study of the amylose-lipid complex in both flours obtained from treated (MW-30) and untreated (native) grains. For this analysis, a cooling scan from 120 °C to 0 °C at -5 °C/min was performed immediately after gelatinisation one to study the formation of the amylose-lipid complex. Subsequently, a new heating cycle identical to the gelatinisation cycle was applied to check amylose-lipid complex dissociation. As can be seen, an exothermic peak corresponding to the formation of amylose-lipid complex appeared during the cooling sweep applied to the gel formed after the gelatinization scan of the native sample. However, this formation peak was not visible for the MW-30 sample, although the peak of its dissociation during the gelatinisation scan was evident. The same occurred with MW-25, whereas MW-20 and MW-13 led to intermediate situations in which successive formation/dissociation peaks were obtained, albeit with lower enthalpy than in the native sample. The high polyphenol content of buckwheat may be involved in this behaviour. After dissociation of the amylose-lipid complex in the gelatinisation scan, free amylose could be associated with other compounds, such as polyphenols, instead of reforming the amylose-lipid complex. Microwave radiation has been shown to enhance the formation of V-type inclusion complexes and non-inclusive complexes of lotus seed starch and green tea polyphenols (Zhao et al., 2019). Rutin, a flavonoid found at considerable concentrations in buckwheat, has also been shown to form such complexes (Zhu, 2015). Food processing may involve tissue disruption and cellular decompartmentalization, resulting in the release of intracellular and extracellular compounds that are originally confined (Zhu, 2015). In this instance, the released endogenous polyphenols may come into contact and interact with other components such as starch. In our analysis, MWT, especially when applied under the most intense conditions (at the highest MC values), may have promoted the formation of noninclusive amylose-polyphenol complexes through hydrogen bonds and complexes that are not detectable by DSC (Deng et al., 2021). If the formation of these complexes is confirmed, it can have beneficial effects, such as lowering the glycemic index (Zhao et al., 2019; Zhu, 2015). Further studies are needed to confirm this hypothesis.

4 Conclusions

The MWT of buckwheat grains significantly modified the morphology and techno-functional, thermal, and rheological properties of flour. This treatment, of only 8 min of MW radiation, resulted in a promising alternative for physical modification. The observed effects varied as a function of MC, being, in general, more intensive for the treatments performed at higher MC (25% and 30%). Therefore, the selection of grain MC during MWT allowed the modulation of the final flour properties and broadening of the scope of buckwheat food applications. The increased emulsion stability of MW-13 can improve products, such as cakes and frozen desserts, where it is necessary to form stable emulsions that resist mechanical stress. The lower amylose retrogradation tendency of MW-25 and MW-30 in the pasting properties may improve its application as a thickening agent for products such as soups or sauces, as it would be able to generate soft texture gels with lower short term retrogradation. The different gel consistencies obtained with MWT, harder and more resistant to MW-13, MW-20, and MW-25, and softer and weaker for MW-30, offer a range of options to produce sauces and creams with different consistencies. However, increased amylopectin recrystallisation may negatively affect the shelf life of the MW-treated flour gels. The possible formation of polyphenol-starch complexes, proposed as a reasonable hypothesis derived from the thermal measurements of phase transitions, needs further study given the importance it could have on the control of the glycaemic index of products made from microwave-treated buckwheat. Further studies are also needed to verify the suitability of the modified flours to produce food products with improved technological, nutritional, and sensory qualities.

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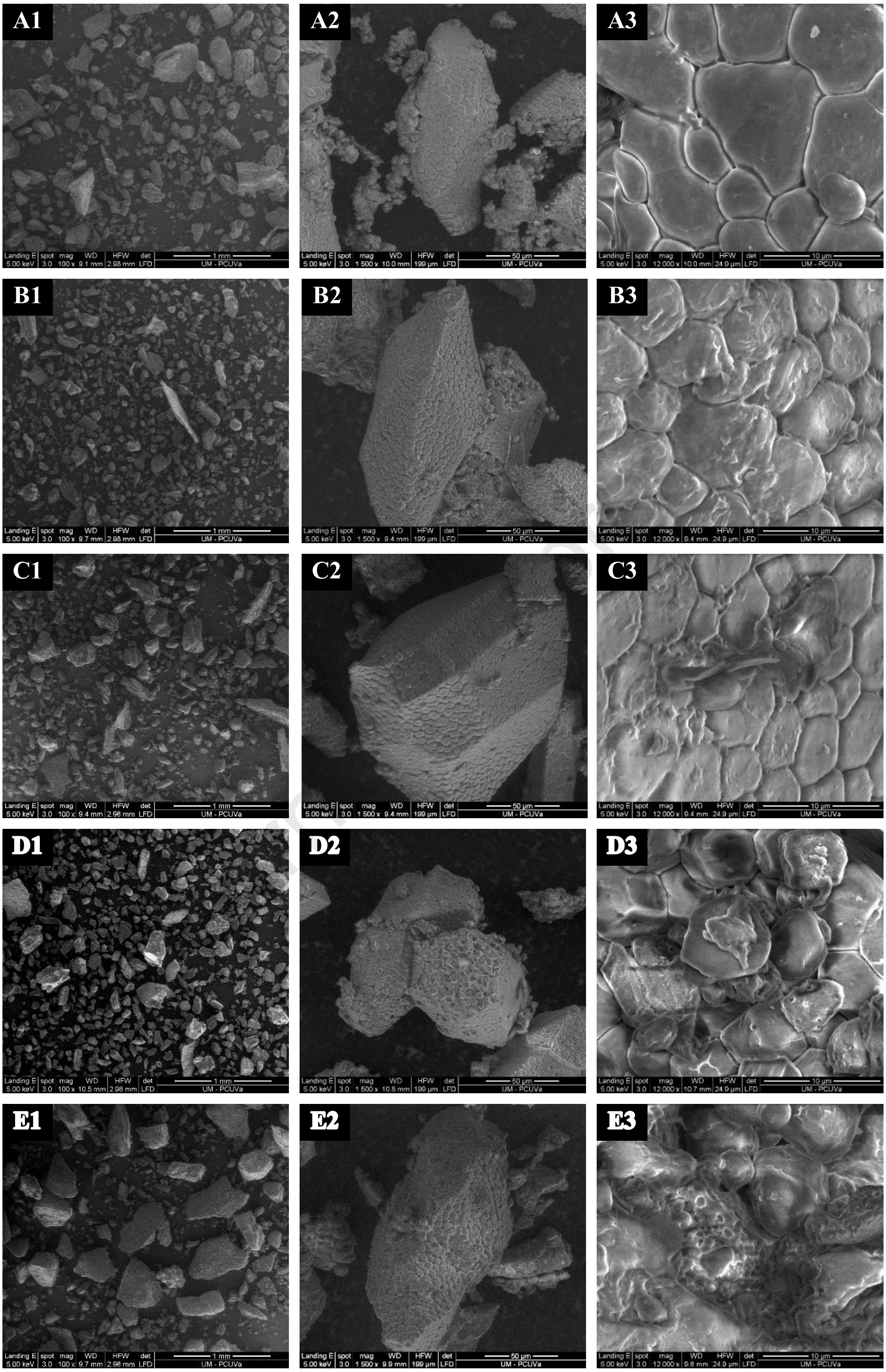

Figure 1. Scanning electron microscopy (SEM) images of buckwheat flours. A: Native, B: MW-13, C: MW-20, D: MW-25, and E: MW-30, at different magnifications 1: × 100, 2: × 1500, and 3: × 12000.

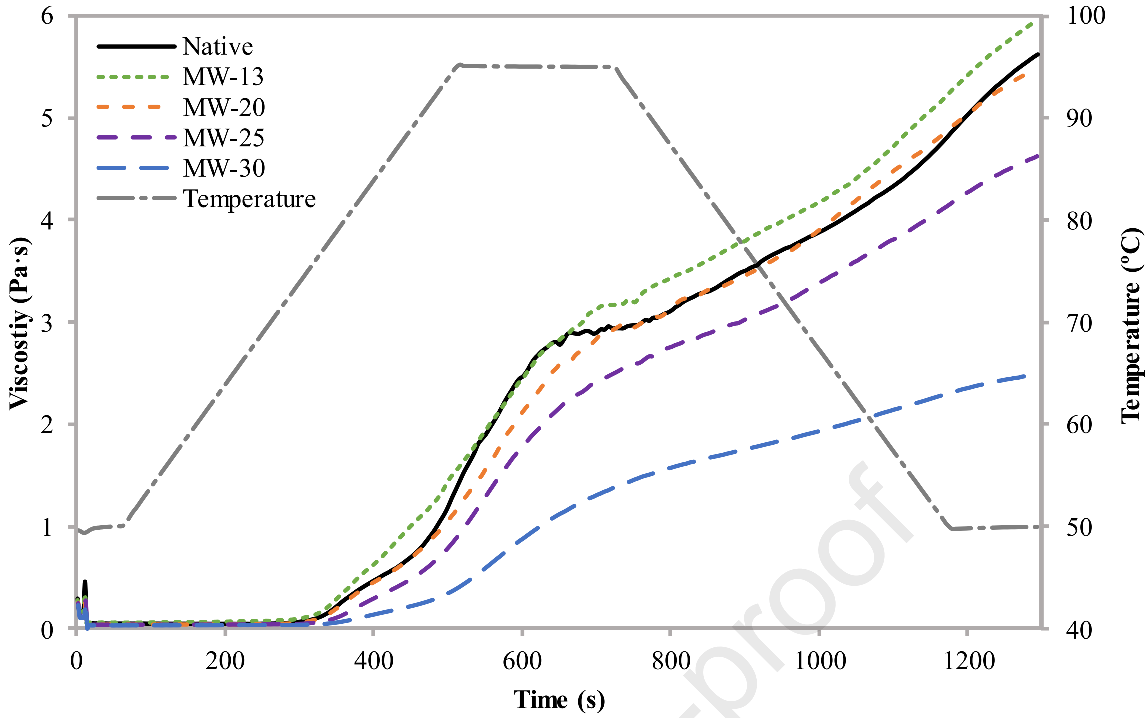

Figure 2. Pasting profiles of flour samples obtained from microwave-treated buckwheat grains at moisture contents of 13%, 20%, 25%, and 30%, and the untreated control flour (native). The temperature profile is plotted on the second axis.

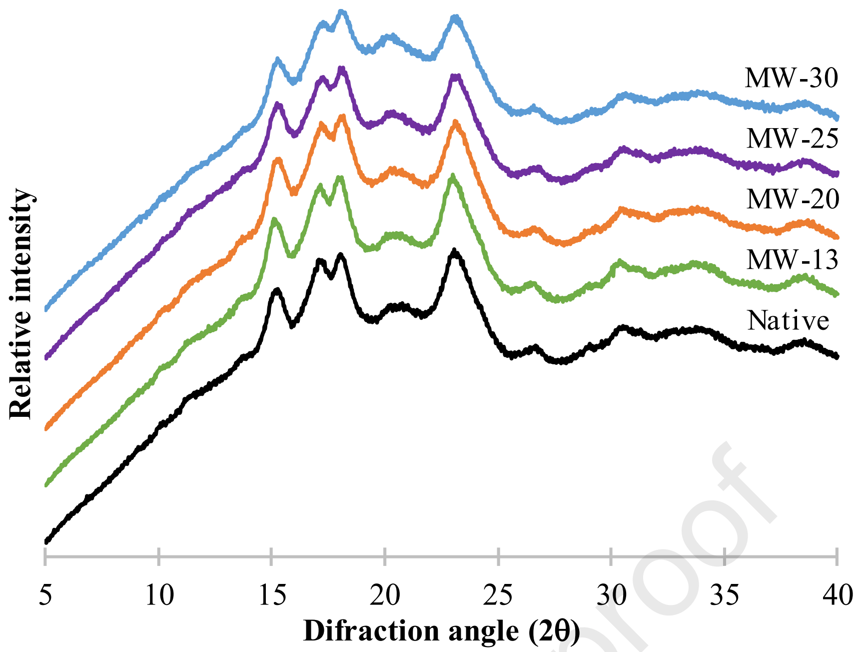

Figure 3. X-ray diffraction (XRD) patterns of untreated control flour (native) and of flours obtained from microwave-treated grains at 13%, 20%, 25%, and 30% moisture content.

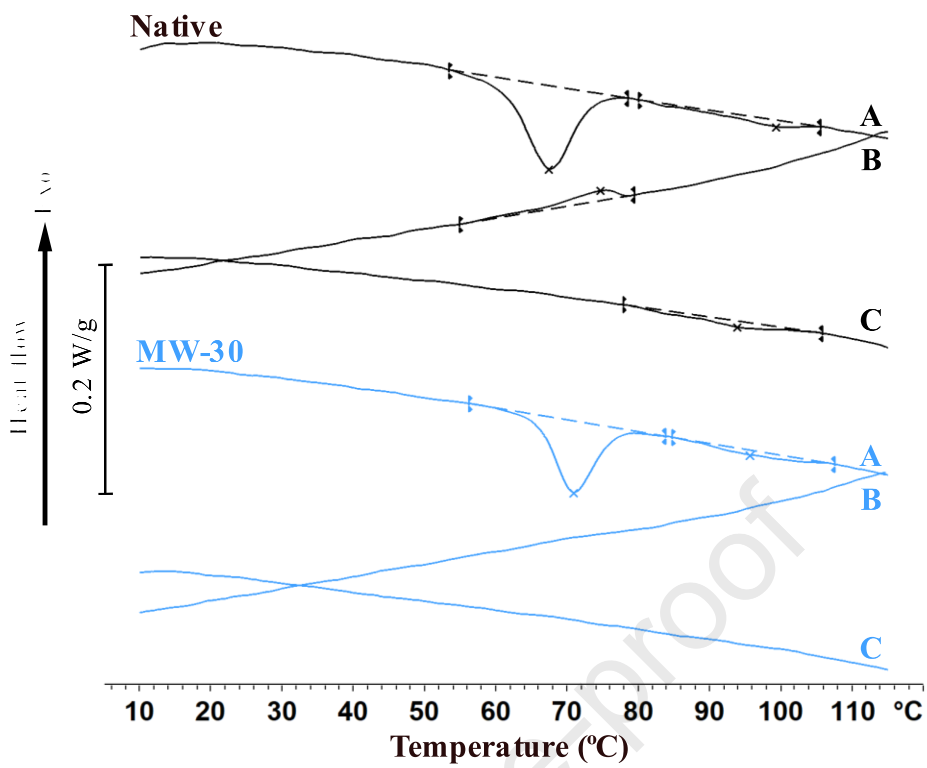

Figure 4. Differential scanning calorimetry (DSC) thermograms successively performed on untreated flour (native, black) and flour obtained from microwave-treated grain at 30% moisture content (MW-30, blue). A: first heating sweep (gelatinization) from 0 to 120 °C, B: cooling sweep from 120 to 0 °C, and C: second heating sweep from 0 to 120 °C.

Table 1. Colour characteristics and particle size distribution of flour samples obtained from native and microwave-treated buckwheat grains.

Sample	Colour characteristics						Particle size distribution			
	L*	**a***	**b***	**C***	**h**	**ΔE**	**D_{10} (μm)**	**D_{50} (μm)**	**D_{90} (μm)**	**$(D_{90}-D_{10})/D_{50}$**
Native	77.3 d	2.21 a	8.84 cd	9.1 c	76.0 e	-	23.3 a	117.6 a	315.5 a	2.48 d
MW-13	77.9 d	2.95 c	9.03 d	9.5 d	71.9 d	1.3 a	28.2 b	124.6 b	324.0 b	2.37 c
MW-20	75.8 c	2.70 b	7.73 a	8.2 a	70.7 c	1.9 b	30.5 b	124.0 b	334.7 c	2.45 d
MW-25	73.8 b	3.02 c	7.94 b	8.5 b	69.2 b	3.7 c	45.5 c	156.0 c	372.3 d	2.09 b
MW-30	71.8 a	3.53 d	8.73 c	9.4 d	68.0 a	5.6 d	48.3 d	183.6 d	396.7 e	1.89 a
SE	0.3	0.05	0.07	0.1	0.3	0.2	0.8	0.9	1.3	0.01
p-value (MC)	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	**<0.001**

MW-13, MW-20, MW-25, and MW-30 samples obtained from microwaved buckwheat grains treated with 13%, 20%, 25%, and 30% moisture content (MC), respectively. L*, a*, and b*: CIELAB colour coordinates; C*: chroma; h: hue; ΔE: colour difference from native flour; D10: diameter where 10% of particles had smaller particle size; D50: median diameter, diameter where 50% of particles had smaller particle size; D90: diameter where 90% of particles had smaller particle size; (D90-D10)/D50: size dispersion; SE: pooled standard error obtained from ANOVA. Mean values with different letters for the same parameter indicate significant differences between means at $p < 0.05$. Bolded p-values ($p < 0.05$) indicate that the effects of MC on microwave treatment are significant at > 95% confidence level.

Table 2. Techno-functional and pasting properties of flour samples obtained from native and microwave-treated buckwheat grains.

Sample	WAC (g/g)	WAI (g/g)	SP (g/g)	WSI (g/100g)	EA (%)	ES (%)	PT (ºC)	PV (mPa·s)	Pt (s)	TV (mPa·s)	BV (mPa·s)	FV (mPa·s)	SV (mPa·s)
Native	1.15 a	9.04 c	9.48 c	4.64 a	56 d	11 c	74.5 b	3007 d	707 a	3001 d	7 a	5723 d	2722 c
MW-13	1.30 b	9.32 d	9.83 d	5.18 b	46 c	32 d	73.4 a	3165 e	716 a	3165 e	0 a	6020 e	2855 d
MW-20	1.32 b	9.01 c	9.47 c	4.86 a	6 b	6 b	74.7 b	2835 c	714 a	2834 c	2 a	5444 c	2610 c
MW-25	1.37 c	8.46 a	8.89 a	4.80 a	4 b	0 a	76.5 c	2505 b	716 a	2505 b	0 a	4662 b	2157 b
MW-30	1.64 d	8.70 b	9.14 b	4.77 a	2 a	0 a	78.4 d	1358 a	716 a	1358 a	0 a	2494 a	1137 a
SE	0.01	0.05	0.06	0.07	1	1	0.1	35	4	34	3	57	36
p-value (MC)	**<0.001**	**<0.001**	**<0.001**	**0.005**	**<0.001**	**<0.001**	**<0.001**	**<0.001**	0.322	**<0.001**	0.372	**<0.001**	**<0.001**

MW-13, MW-20, MW-25, and MW-30 samples obtained from microwaved buckwheat grains treated with 13%, 20%, 25%, and 30% moisture content (MC). WAC: water absorption capacity, WAI: water absorption index, SP: swelling power, WSI: water solubility index, EA: emulsifying activity, ES: emulsion stability. PT: pasting temperature, PV: peak viscosity, Pt: peak time, TV: trough viscosity, BV: breakdown viscosity, FV: final viscosity, SV: setback viscosity, SE: pooled standard error obtained from ANOVA. Mean values with different letters for the same parameter indicate significant differences between means at $p < 0.05$. Bolded p-values ($p < 0.05$) indicate that the effects of MC on microwave treatment are significant at > 95% confidence level.

Table 3. Rheological properties of gels made with flour samples obtained from untreated and microwave-treated buckwheat grains.

Sample	G_1' (Pa)	a	G_1'' (Pa)	b	$(\tan\delta)_1$	c	G_1^* (Pa)	Crosspoint (Pa)	τ_{max} (Pa)
Native	1019 b	0.075 c	174 b	0.231 b	0.171 b	0.156 a	1034 b	334 b	244 b
MW-13	1249 d	0.048 ab	201 d	0.212 a	0.161 a	0.164 a	1265 d	433 c	448 d
MW-20	1141 c	0.045 a	180 bc	0.214 a	0.158 a	0.169 a	1155 c	387 bc	386 c
MW-25	1149 c	0.037 a	184 c	0.205 a	0.160 a	0.169 a	1163 c	391 c	401 c
MW-30	491 a	0.062 bc	103 a	0.254 c	0.209 c	0.192 b	502 a	117 a	85 a
SE	15	0.004	3	0.003	0.002	0.004	15	15	9
p-value (MC)	**<0.001**	0.061	**<0.001**	**0.001**	**<0.001**	**0.042**	**<0.001**	**<0.001**	**<0.001**

MW-13, MW-20, MW-25, and MW-30 samples obtained from microwaved buckwheat grains treated with 13%, 20%, 25%, and 30% moisture content (MC). The power law model was fitted to the frequency sweep experimental data ($G' = G'_1 \cdot \omega^a$; $G'' = G''_1 \cdot \omega^b$; $\tan\delta = (\tan\delta)_1 \cdot \omega^c$), where G_1', G_1'' and $\tan(\delta)_1$ are the coefficients obtained from the fitting and represent the elastic and viscous moduli and loss tangent, respectively, at a frequency of 1 Hz. The *a*, *b*, and *c* exponents quantify the degree of dependence of the dynamic moduli and the loss tangent with the oscillation frequency. G_1^*: complex modulus at a frequency of 1 Hz. τ_{max}: maximum stress that the samples could tolerate in the LVR. SE: pooled standard error obtained from ANOVA. Mean values with different letters for the same parameter indicate significant differences between means at $p < 0.05$. Bolded p-values ($p < 0.05$) indicate that the effects of MC on microwave treatment are significant at > 95% confidence level.

Table 4. Thermal properties of flour samples obtained from untreated and microwave-treated buckwheat grains.

Sample	First scan					Second scan			
	ΔH_{gel} (J/g dm)	$T_{p\text{-}gel}$ (ºC)	R_{gel} (ºC)	$\Delta H_{am\text{-}lip}$ (J/g db)	$T_{p\text{-}am\text{-}lip}$ (ºC)	ΔH_{ret} (J/g dm)	$T_{p\text{-}ret}$ (ºC)	$\Delta H_{am\text{-}lip}$ (J/g dm)	$T_{p\text{-}am\text{-}lip}$ (ºC)
Native	8.8 b	67.4 b	12.8 c	0.7 a	98.0 a	2.2 a	48.6 a	2.3 c	93.7 a
MW-13	9.1 b	66.7 a	12.1 bc	0.5 a	97.8 a	2.9 b	49.4 a	0.9 b	92.5 a
MW-20	8.6 b	67.9 c	12.3 bc	0.7 a	97.5 a	3.0 b	48.7 a	0.6 a	92.9 a
MW-25	8.5 b	69.2 d	11.5 ab	0.7 a	98.6 a	3.0 b	48.8 a	nd	nd
MW-30	6.4 a	71.1 e	10.5 a	0.6 a	98.1 a	3.2 b	48.6 a	nd	nd
SE	0.2	0.1	0.3	0.1	0.8	0.1	0.6	0.0	1.4
p-value (MC)	**0.002**	**<0.001**	0.058	0.804	0.791	0.534	0.707	**<0.001**	0.873

MW-13, MW-20, MW-25, and MW-30 samples obtained from microwaved buckwheat grains treated with 13%, 20%, 25%, and 30% moisture content (MC). Firs scan was performed on fresh samples. Second scan was performed after storage of flour suspensions at 4 °C for 7 d. ΔH_{gel}: starch gelatinisation associated enthalpy; $T_{p\text{-}gel}$: peak temperature for gelatinisation peak; R_{gel}= (T_e-T_o) for the gelatinisation peak, where T_o is the onset temperature and T_e is the endset temperature; $\Delta H_{am\text{-}lip}$: enthalpy associated with dissociation of amylose-lipid complex; $T_{p\text{-}am\text{-}lip}$: peak temperature for amylose-lipid complex dissociation peak; ΔH_{ret}: enthalpy associated with the melting of recrystallised amylopectin; $T_{p\text{-}ret}$: peak temperature of melting of recrystallised amylopectin; nd: non-detectable; dm: dry matter. SE: pooled standard error obtained from ANOVA. Mean values with different letters for the same parameter indicate significant differences between means at $p < 0.05$. Bolded p-values ($p < 0.05$) indicate that the effects of MC on microwave treatment are significant at > 95% confidence level.

HIGHLIGHTS

- Microwaves are a promising alternative for the physical modification of buckwheat.
- Grain moisture content during treatment determined the final properties of the flour.
- Treatment with 13% moisture content improved the ability to form stable emulsions.
- Microwave treatment increased the water absorption capacity of the flour.
- Type I amylose-lipid complex was not re-formed after dissociation in treated flours.
- A range of gel consistencies were obtained under different treatment conditions.

Conflict of Interest

The authors confirm that they have no conflicts of interest with respect to the work described in this manuscript.

Author statement

Ainhoa Vicente: Conceptualisation, methodology, investigation, formal analysis, data curation, writing–original draft, writing–review and editing.

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