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Hydrothermal Treatment via Microwave Radiation Improves Viscoelastic Properties of Native Gluten-Free Flours for Extrusion 3D Printing

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Abstract: The market for gluten-free products is experiencing significant growth due to the increase in the number of gluten/wheat affected patients diagnosed, but largely as a result of the emergence of a new niche market dedicated for consumers who optionally avoid gluten. Native flours are perceived as viable alternative for industrially used starch and hydrocolloids blends, mainly due to their lack of vitamins and minerals, which are abundant in non-refined raw materials. Edible inks for on-demand printing are under significant consideration, while texture building capacity remains an issue. As heat-moisture treatment has proved to be useful for stabilizing the pasting and rheological behavior of various native flours, HMT supported by microwave heating was investigated as printable ink stabilizers. For Spanish and Polish buckwheat flours and two different varieties of teff (white and brown) flour pasting, structural and textural characteristics after the microwave supported heat moisture treatment in 30% of initial moisture content were evaluated. The peak viscosity was reduced by 54% and 60% for Polish and Spanish flour, respectively, while for teff, the reduction was 15% and 43% for the white and brown varieties, respectively. Significant improvement in viscoelastic modulus G' (for Polish and Spanish buckwheat flour, 32% and 16%, respectively; for white and brown teff varieties, 14% and 18%, respectively) was observed for all the treated samples regardless of the species or variety; this resulted in better performance during 3D printing.

Keywords: buckwheat; *Fagopyrum esculentum*; teff; *Eragrostis tef*; microwaves; gels; 3D printing



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1. Introduction

Gluten free flours lack the capacity of building up a sufficiently elastic structure suitable for 3D extrusion printing due to the lack of gluten protein complex [1]. On the other hand, gluten complex, which is capable of creating an exceptional three dimensional protein/starch network, is also a main contributor to several food allergies. Together with other wheat compounds, immunizing or sensitizing characteristics are the main reason for avoiding wheat/gluten-based products and searching for gluten-free alternatives [2,3].

Specialized healthy food products, including gluten-free snacks, are important for people with conditions like non-celiac wheat sensitivity and irritable bowel syndrome. Factors that influence the consumption of gluten-free snacks by people with non-celiac wheat sensitivity and irritable bowel syndrome include beliefs about the health benefits of a gluten-free diet, perceptions that gluten-free products are more nutritious, and the belief that a gluten-free diet can help clear acne [4].

Personal research and recommendations from healthcare professionals are influential sources of information that drive individuals to try a gluten-free diet [5]. In the case of irritable bowel syndrome, self-reported wheat sensitivity is prevalent, and individuals

with this condition often experience symptom improvement on a wheat-free diet [6]. Additionally, individuals with suspected non-celiac gluten/wheat sensitivity who respond to a double-blind placebo-controlled gluten challenge test have a different gut microbiota composition, lower risk of eating disorders, and higher mental health scores when compared to placebo responders [7]. The impact of wheat ingredients, including gluten, fermentable oligo-, di- monosaccharide, and polyols (FODMAPs), and amylase trypsin inhibitors (ATIs), on gut dysbiosis in irritable bowel syndrome and non-celiac gluten sensitivity suggests that these factors play a role in the consumption of gluten-free snacks [8].

Novel technologies like 3D printing present the potential to produce personalized snacks tailored to specific nutritional needs, featuring intricate designs and customized textures [9]. Nonetheless, the field of 3D food printing is not without its unique challenges [10–13]. Numerous research investigations have explored the viability of extrusion printing for enhancing the nutritional value of cereal-based foods by employing different types of wholegrain flours [14–17].

The absence of gluten in native gluten-free flours causes a problem: the lack of gluten related structure/texture forming characteristics in gluten-free products. Physical treatments, contrary to chemical modifications or additives supplementations, have demonstrated the stunning capacity to change the internal structure of native components of cereal flours, which resulted in increased structure-creating capacity [18]. However, the results were heavily dependent on the botanical characteristics of the treated flour, thereby requiring a separate investigation for each type of flour.

The thermal treatments of flours and starches combined with alteration in moisture content cause physical modifications of the starch that results in changing their physical-chemical and functional properties without destroying the granular structure [19]. In these cases, the moisture/starch ratio, temperature, and heating time are critical parameters that must be controlled [18,19]. Depending on the conditions applied, these treatments are classified into two groups. The first is heat-moisture treatment (HMT); this is classified as a hydrothermal process and consists of heating starch granules above the glass-transition temperature (T_g) for a specific length of time. It differs from annealing (excess water ($\geq 40\%$ w/w) at a temperature between T_g and T_o), in that the process occurs under conditions of relatively low moisture ($< 35\%$ w/w) and uses higher processing temperatures (80–140 °C).

Hydrothermal modification techniques like Heat Moisture Treatment (HMT) and Annealing (ANN) can significantly alter the functional attributes of starch and flour. The extent of these alterations is heavily dictated by the inherent composition of amylose-amylopectin in starch and the presence of non-starch constituents in flours such as proteins, phenolic compounds, lipids, and minerals. During treatment, these constituents potentially interact with starch, impacting aspects like solubility and crystallinity. The modification's extent and the resultant functional attributes are influenced by factors such as temperature, moisture content, and the duration of the hydrothermal treatment. Varying these conditions causes diverse effects on starch and flour. Furthermore, hydrothermal modifications can influence molecular arrangements and the dynamics between starch granules, encompassing both intra- and inter-granule interactions, which are crucial in defining the functional properties of the modified starch and flour. The source of the starch or flour, be it potato, rice, mung beans, or sweet potato, also plays a pivotal role in determining the specific impacts of hydrothermal modifications on their functional properties. Each source possesses unique characteristics that interact distinctively with the modification process. Moreover, the number of hydrothermal modification cycles can also have a bearing on the functional attributes of starch and flour, with multiple cycles potentially leading to varied effects compared to a single cycle [20–28].

Electromagnetic fields, especially the microwave spectrum, serve as very efficient energy transmitters [29,30]. The microwave radiation absorption capacity of flour, the moisture change during the treatment, the particle morphological structure, the crystallinity/amorphous region ratio, and flour thermal properties were studied, revealing

a significant gelatinization temperature rise and the amylopectin retrogradation extent in treated-flours [31–33]. The treatment resulted in lower viscometric profiles, amylose retrogradation, and higher pasting temperatures [31–33].

Hydrothermal treatment via microwave radiation has been shown to improve the viscoelastic properties of teff and buckwheat flours and resulted in increased particle size, hydration properties, and stability of starch crystallites [34,35]. These findings suggest that hydrothermal treatment via microwave radiation can enhance the viscoelastic properties of teff and buckwheat flours, making them potential ingredients for improving the technological, nutritional, and sensory quality of food products.

Common buckwheat was chosen as it is one of the most popular gluten-free raw material for Poland and Ukraine; attempts have also been made to try and introduce this buckwheat into other regions, including Spain. Teff is a very nutritious minor crop with low agricultural demands; as a result, there is widespread demand for teff as part of wider biodiversity improvement initiatives.

The rheological characteristic of two different common buckwheat flours and two different varieties of teff flour were studied after undergoing the microwave treatment with different initial moisture contents (30%). The resulting gels were evaluated for pasting, viscoelastic, and textural characteristics after preparation and after 3D extrusion-based printing.

2. Materials

2.1. Raw Materials and Reagents

The raw materials were buckwheat flours purchased at local markets in Poland (Melvit, Olszewo Borki, Poland) and Spain (Farinera La Segarra, Maldà, Spain), and teff flour of the white (TW) and brown (TB) varieties, cultivated in Spain (Salutef, San Martín del Valle, Palencia, Spain). The chemical content was provided by manufacturers. Total starch content was analyzed with a Megazyme kit (K-TSHK, Megazyme, Bray, Ireland). Apparent amylose content was determined by the lectin concanavalin A (Con A) method (K-AMYL, Megazyme, Bray, Ireland) and damaged starch content determined according to AACC methods using an RTU kit (K-SDAM, Megazyme, Bray, Ireland). In all spectroscopic methods, the absorbance was read at 510 nm, and at least three replicates were produced for each sample.

2.2. Microwave (MW) Treatment

Microwave assisted heat moisture treatment was conducted with microwave radiation as a heat source. Flours were previously adjusted to the moisture content of $\approx 30\%$, conditioned for 24 h, and then exposed to microwave radiation at power of 900 W using a NOVA 10 microwave reactor (Ertec, Wrocław, Poland). The electromagnetic radiation was applied intermittently in periods of 20 s exposure and 40 s cooling for the temperature homogeneity inside the product and to avoid an excessive pressure increase in the available space of the HDPE container. The sample temperature was monitored using Testoterm temperature strips (Testo, West Chester, PA USA). The total treatment sample weight was 100 g and the MW total treatment time was 8 min with constant mixing. For cooling periods, the oven doors were opened and built in fans were automatically switched on. After treatment, the samples were collected and stored at 4 °C for further analysis.

2.3. Granulometry Analysis

The LPzE-2e vibratory sieve shaker (Multiserw Morek, Brzeźnica, Poland) was used for granulometry analysis at 0.65 mm vibration amplitude for 10 min with screens of 106, 150, and 200 microns according to the method suggested by Harasym et al. [36]. Each sample was analyzed in triplicate and presented as mean \pm standard deviation.

2.4. Pasting Properties

Pasting properties of flour blends (viscometric profiles) were obtained using ICC Standard method 162 and a Rapid Visco Analyser (RVA-4500, Perkin Elmer, Waltham,

MA, USA). A total of 3.5 g of each sample was transferred to an aluminum container and the amount of distilled water (as solvent) was adjusted to obtain a total weight of 28.5 g. The methods profile started from suspension equilibration at 50 °C for 1 min. Then the temperature was raised to 95 °C at a rate of 5 °C/min, followed by a holding period of 5 min at 95 °C. The suspension was then cooled to 50 °C at a rate of 5 °C/min and finally maintained at 50 °C for the last 4 min. A stirring speed of 960 rpm was applied for the first 10 s and then maintained at 160 rpm for the rest of the analysis. The TCW3 v.3 software (Perkin Elmer, UK) was used to calculate the parameters peak viscosity (PV), trough viscosity (TV), breakdown (BD = PV – TV), final viscosity (FV), and setback (ST = FV – TV) and pasting temperature. Samples were measured in triplicate. The results were reported as mean \pm standard deviation.

2.5. Frequency Sweep

Frequency sweep tests were performed on the flour gels using a rheometer (MCR 102, Anton Paar, Ashland, VA, USA) with a serrated parallel plates geometry (40 mm) to characterize the gel viscoelastic properties. The viscoelastic properties were measured through oscillation tests in the linear viscoelastic region (LVR). Frequency sweep data were fitted to the power law model [37]. Paste samples were prepared the previous day using suitable diameter capsules and were then wire-cut to obtain a ca. 1 mm height, 40 mm diameter cylinder. Then the samples were placed on the plate and left to equilibrate for 5 min before each test. Viscoelastic behavior was determined in terms of storage or elastic modulus (G') and loss or viscous modulus (G'') with a frequency sweep performed from 10 to 1 Hz in the linear viscoelastic region at a constant stress of 1 Pa. Samples were measured in triplicate. The results were reported as mean \pm standard deviation.

2.6. Gel Texture

The gels were prepared using paste prepared with RVA equipment following the method described at Section 2.4. The obtained suspensions were poured into cylindrical molds of 20 mm diameter and stored for 24 h at 4 °C. Then the gels were liberated from molds, cut into 20 mm diameters, and measured with a TPA test. The texture of the gels was evaluated using a TPA (Texture Profile Analysis) test with an AXIS texture analyzer FC200STAV500/300 (AXIS, Gdansk, Poland) provided with the AXIS FM v.2_18 software, as previously reported by [38]. Hardness (N) was the force at the maximum deformation, whereas cohesiveness, springiness, gumminess, and resilience were calculated from the peaks. Analysis was carried out in quadruplicate at 25 °C. The results were reported as mean \pm standard deviation.

2.7. Gels 3D Printing Performance

To prepare the sample gel, each raw material was mixed with distilled water. Each flour suspension was equilibrated at 50 °C for 1 min, then the temperature raised to 95 °C at a rate of 5 °C/min, holding at 95 °C for 5 min, then cooled to 50 °C at a rate of 5 °C/min, and finally maintained at 50 °C for the last 4 min. Stirring speed was set at 960 rpm for the first 10 s and then maintained at 160 rpm for the rest of the analysis. The gels were poured into disposal 100 mL syringes and stored for 24 h at 4 °C. An extrusion-based head for the Zmorph VX printer, operated with Voxelize 3.0.0. software (Zmorph, Wroclaw, Poland), with a 1.2 mm plastic nozzle was used throughout the 3D printing process. The monolayer height and width and moving speed of the nozzles were set to 1 mm, 3 mm, and 10 mm/s, respectively. The 20 mm diameter cylinders of 20 mm height were printed (Figure 1) on the underlying plastic square, then stored for 4 h under cover at 4 °C. Following this, the texture profile was analyzed. The texture of the resulting cylinders was assessed according to 2.7. All measurements were performed on five extruded samples.

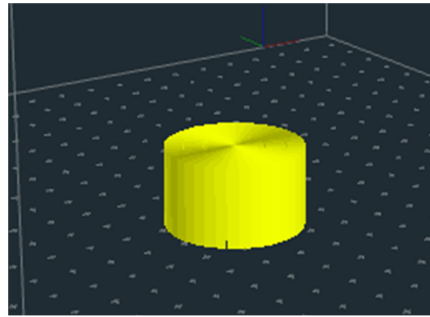


Figure 1. Cylinder design for gel printing.

2.8. Statistical Analyses

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

3. Results and Discussion

3.1. Particle Size and Amylose/Damaged Starch Content

The BP sample chemical content per dry basis was $72.8 \pm 0.5\%$ starch, $5.6 \pm 0.1\%$ fiber, $16.1 \pm 0.3\%$ protein, $3.3 \pm 0.1\%$ fat, and $1.97 \pm 0.07\%$ ash, while the SP sample was $73.9\% \pm 0.4$ starch, $1.65 \pm 0.2\%$ fiber, $18.5 \pm 0.3\%$ protein, $3.9 \pm 0.1\%$ fat, and $1.79 \pm 0.08\%$ ash. The WT sample was $79.8 \pm 0.4\%$ starch, $6.1 \pm 0.2\%$ fiber, $10.3 \pm 0.4\%$ protein, $2.1 \pm 0.1\%$ fat, and $1.7 \pm 0.04\%$ ash, while the BT sample was $79.1 \pm 0.6\%$ starch, $7.3 \pm 0.2\%$ fiber, $9.1 \pm 0.6\%$ protein, $2.4 \pm 0.3\%$ fat, and $2.2 \pm 0.5\%$ ash. The flour granulometry measured by sieving and amylose/damaged starch content are shown in Table 1.

Table 1. Granulometry profile and amylose/damage starch content in native and MW-treated samples.

Sample	>200 μm [%]	200–106 μm [%]	150–106 μm [%]	<106 μm [%]	Amylose [%]	Damaged Starch (% w/w)
BP	25.57 ± 0.62^d	41.67 ± 0.89^b	26.52 ± 1.30^d	6.25 ± 1.58^{bc}	23 ± 2^a	1.60 ± 0.10
BPT	43.70 ± 2.12^g	40.35 ± 1.77^b	12.35 ± 1.20^a	3.60 ± 0.85^{abc}	20 ± 3^a	1.70 ± 0.15
SB	36.55 ± 0.21^f	66.85 ± 1.77^d	10.80 ± 0.57^a	8.75 ± 0.49^c	33 ± 3^b	0.91 ± 0.09
SBT	31.80 ± 1.05^e	78.80 ± 0.85^f	15.95 ± 0.35^b	1.40 ± 1.56^{ab}	29 ± 2^b	0.99 ± 0.04
WT	2.13 ± 1.27^{ab}	71.00 ± 1.13^e	22.00 ± 3.54^c	4.88 ± 5.93^{abc}	32 ± 1^b	1.37 ± 0.01
WTT	0.40 ± 0.28^a	87.85 ± 0.78^g	11.00 ± 0.28^a	0.75 ± 0.21^a	26 ± 5^{ab}	1.01 ± 0.07
BT	13.60 ± 1.70^c	30.95 ± 0.64^a	16.55 ± 0.92^b	15.95 ± 1.77^d	28 ± 3^{ab}	1.72 ± 0.02
BTT	3.85 ± 0.35^b	47.00 ± 1.56^c	18.88 ± 0.20^{bc}	2.32 ± 0.31^{ab}	21 ± 4^a	1.24 ± 0.06

BP—Polish buckwheat, BPT—Polish buckwheat treated, SB—Spanish buckwheat; SBT—Spanish buckwheat treated, WT—white teff, WTT—white teff treated; BT—brown teff; BTT—brown teff treated, lower-case letters mean values are significantly different at $p \leq 0.05$ in the column.

Comparing the particle size distribution of buckwheat flours, the native Polish buckwheat flour was mainly distributed into three fractions (>200 μm , >200–150 μm , and 150–106 μm), while Spanish buckwheat flour showed a greater number of bigger particles, evenly distributed between the >200 μm and 200–150 μm fractions. The microwave treatment significantly reduced the smallest fraction (<106 μm) share, and that phenomenon was observed for all the native flours samples. As the MW-treated flours were not processed after treatment, the granulometry ranges reveal the changes occurring during the processing. Constant mixing and heating led to thermo-mechanical modifications of the granule surfaces, facilitating disruption, agglomeration, and recreation of particles.

A similar behavior was observed by Vincente et al. and Calix-Riviera et al. [34,35] for lower initial moisture content treatments. A 30% initial water content allows amylose

leaching and protein hydration, resulting in a sticky matrix causing smaller particles to adhere to bigger ones. Also, the originally bigger flour particles tend to disrupt smaller particles as result of agitation impact; this explains the disappearance of the >200 μm fraction in almost all samples except BP. The BP sample is the one of more abundant in fiber share and damaged starch, which can promote amylose leaching, particle adhering, and bigger size formation.

3.2. Pasting Characteristics and Viscoelastic Behavior of Gels

Pasting profiles of native and treated samples of Polish and Spanish buckwheat flours are shown in Figure 2A; white and brown Spanish teff samples are shown in Figure 2B.

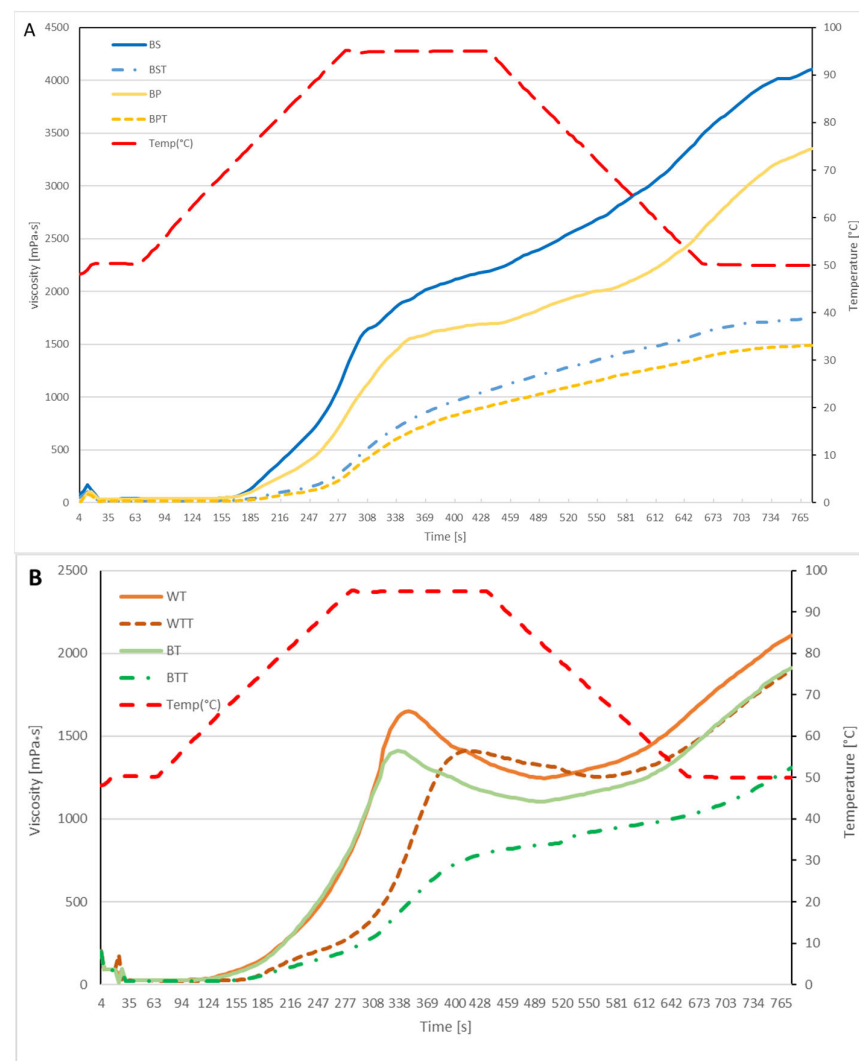


Figure 2. Pasting curves of native and MW-treated samples, (A)—buckwheat: BS—native Spanish buckwheat, BST—Spanish buckwheat treated, BP—native Polish buckwheat, BPT—Polish buckwheat treated; (B)—teff: WT—native white teff, WTT—white teff treated, BT—native brown teff, BTT—brown teff treated.

A particular behavior was observed for buckwheat flours (A) of different origin; the pasting curves were smooth and did not present the separated peak within the 95 °C ramp, while a constant rise after the cooling began without any breakage. The MV treatment resulted in even less pronounced changes, providing almost negligible differences between two buckwheat flours after MV supported heat-moisture treatment. The teff flours were characterized by a significantly (almost twice) lower viscosity compared to buckwheat;

pasting profiles provided the typical peak-drop-rise characteristics. Almost identical native flours with less viscous brown teff after MW thermal treatment smoothen the characteristics. The white teff still presented a differentiated pasting profile, while brown teff was characterized by a huge drop in viscosity and simultaneously slow and constant rise of viscosity when the drop of temperature started.

The pronounced viscosity peak proves the maximum viscosity reached by the paste, followed by disruption of the internal structure, resulting in thinning of the paste and viscosity drop. Buckwheat contains a lot of fiber; this fiber is not so prone to breakage, as starch granules do, thereby creating a dynamic internal environment, exchanging and maintaining water without a loss of viscosity. Compared to buckwheat, teff flour contains more starch, makes it more susceptible to temperature changes. Increases and decreases in viscosity is a characteristic for pastes and gels creations, and not particularly expected for 3D printing inks, as they may result in rapid syneresis of water and disruption of internal structure, resulting in the loss of rigidity and elasticity, which are crucial parameters for 3D printing.

Generally, the MW treatment modified the viscometric parameters of the pastes towards greater stability, as shown in Table 2. The peak viscosity, which occurs while maximum resistance is given by a sample to the rotating paddle under the certain temperature and speed conditions, was negligible in the case of buckwheat, independent of place of origin or treatment. Meanwhile, teff samples, except the brown treated sample, reached certain level of viscosity without further changes. For untreated buckwheat flours, the breakdown values were generally higher (this was the reverse for teff flours) while setback values were very similar for all the treated samples, despite being more pronounced in buckwheat than in teff.

Table 2. Viscometric parameters of native and MW-treated samples.

Sample	PV [mPa × s]	TV [mPa × s]	BV [mPa × s]	FV [mPa × s]	SV [mPa × s]	Pasting temp. [°C]
BP	1563.0 ± 21.2 ^c	1695.0 ± 8.5 ^c	0 ± 0 ^a	3352.0 ± 15.6 ^c	1657.0 ± 24.0 ^b	70.2 ± 0.1 ^a
BPT	725.0 ± 35.4 ^a	925.0 ± 36.8 ^a	0 ± 0 ^a	1491.5 ± 41.7 ^a	566.5 ± 78.5 ^a	78.4 ± 0.4 ^c
SB	1994.0 ± 8.5 ^d	2205.0 ± 32.5 ^d	0 ± 0 ^a	4104.0 ± 28.3 ^d	1899.0 ± 4.2 ^c	71.7 ± 0.1 ^b
SBT	799.0 ± 14.1 ^b	1075.0 ± 17.0 ^b	0 ± 0 ^a	1740.0 ± 84.9 ^b	665.0 ± 101.8 ^a	79.5 ± 0.1 ^d
WT	1651.0 ± 39.6 ^c	1329.0 ± 45.3 ^c	322.0 ± 5.7 ^c	2106.5 ± 54.4 ^c	777.5 ± 99.7 ^b	72.5 ± 0.2 ^b
WTT	1413.0 ± 26.9 ^b	1391.5 ± 10.6 ^c	21.5 ± 16.3 ^a	1894.3 ± 8.6 ^b	502.8 ± 2.0 ^a	79.2 ± 0.4 ^c
BT	1411.5 ± 4.9 ^b	1158.5 ± 14.8 ^b	253.0 ± 9.9 ^b	1911.4 ± 18.1 ^b	752.9 ± 3.3 ^b	71.0 ± 0.1 ^a
BTT	811.6 ± 2.5 ^a	801.2 ± 17.3 ^a	10.4 ± 14.7 ^a	1310.4 ± 16.6 ^a	509.2 ± 0.6 ^a	80.4 ± 0.1 ^d

PV—peak viscosity; TV—through viscosity; BV—breakdown viscosity; FV—final viscosity; SV—setback viscosity; BP—Polish buckwheat, BPT—treated Polish buckwheat; SB—native Spanish buckwheat, SBT—treated Spanish buckwheat, WT—native white teff, WTT—white teff treated, BT—native brown teff, BTT—brown teff treated, lower-case letters mean values are significantly different at $p \leq 0.05$ in the column.

Pasting temperature increased in all cases of treated samples; this resembles the slowed absorption during the heating ramp. Similar results were observed by Vincente et al. and Calix-Riviera et al. [34,35] for buckwheat and teff flours after MV treatment. The generalized slowed water absorption is connected to both the overall particle size distribution change in the samples as well as amylose release and melting characteristics of particle samples; this was proven by several authors for both flour and starch samples [31–33].

The internal structure of set gels was assessed with dynamic oscillatory tests within the viscoelastic region. Table 3 presents the G' and G'' moduli and ($\tan \delta$), as well as the exponents a , b , and c obtained from fitting the power law model to experimental data obtained from frequency sweeps.

Table 3. Viscoelastic moduli of native and treated samples.

Sample	G' [Pa]	a	G'' [Pa]	b	$\tan \delta$	c
BP	2490.3 ± 236.2^a	0.065 ± 0.0056^a	353.69 ± 1.23^a	0.1163 ± 0.0035^b	0.142 ± 0.0021^a	0.0511 ± 0.003^d
BPT	2971.2 ± 125.2^b	0.0879 ± 0.0061^c	607.2 ± 0.96^b	0.0687 ± 0.032^a	0.206 ± 0.0064^b	0.02 ± 0.001^c
SB	2440.0 ± 302.4^a	0.0742 ± 0.0052^b	642.6 ± 2.31^c	0.0751 ± 0.0045^a	0.263 ± 0.0011^c	0.0001 ± 0.0000^a
SBT	2836.0 ± 121.4^b	0.0751 ± 0.0012^b	710.8 ± 1.21^d	0.0677 ± 0.0011^a	0.25 ± 0.0009^c	0.006 ± 0.0001^b
WT	1633.6 ± 93.5^b	0.1196 ± 0.0011^b	201.69 ± 3.14^b	0.1528 ± 0.0009^b	0.1233 ± 0.0003^a	0.0332 ± 0.002^b
WTT	1868.0 ± 101.9^b	0.1106 ± 0.0020^a	279.3 ± 4.65^c	0.1335 ± 0.0004^a	0.1491 ± 0.0074^b	0.0236 ± 0.003^a
BT	1464.4 ± 52.3^a	0.1238 ± 0.0009^c	165.55 ± 3.98^a	0.1578 ± 0.0014^b	0.1127 ± 0.0062^a	0.0352 ± 0.00025^b
BTT	1728.1 ± 39.1^b	0.1113 ± 0.0011^a	325.72 ± 2.11^d	0.1309 ± 0.0007^a	0.1875 ± 0.0027^c	0.0211 ± 0.0010^a

SB—native Spanish buckwheat, SBT—Spanish buckwheat treated, BP—Polish buckwheat, BPT—Polish buckwheat treated; WT—native white teff, WTT—white teff treated, BT—native brown teff, BTT—brown teff treated, lower-case letters mean values are significantly different at $p \leq 0.05$ in the column.

The structural change of the paste is very well demonstrated by the G' and G'' moduli changes in particular samples as a result of MW treatment. Buckwheat flours were both reinforced with MW treatment, resulting in 18% and 16% increase in G' value for PB and SB, respectively. Opposite results were reported by Vincente et al. [34], where 30% moisture content buckwheat was MW radiated and underwent a huge drop in elastic modulus. This difference may stem from the study design, as in [34] the grain was both soaked and MW treated, and then analyses were taken from the gel right after forming. The buckwheat gels increased their viscous behavior with frequency, as their G'' modulus significantly increased for PB and SB. Also, the exponent “a” was always lower than exponent “b”, resulting in positive values of exponent “c”; this means that the loss tangent increased with the angular frequency rise.

In teff flours, the variety had an interesting impact, as the elastic and viscous moduli values of gels made with WT were always higher than BT. Similar results were observed by Calix-Riveira et al. for other Spanish cultivated teff varieties [35] for native flours. Such behavior suggests firmer internal consistency, probably affected by the lower lipid content in the white variety. Lipids restrict access to the starch granules, which can hinder the intramolecular organization by amylose chains during cooling. After MW treatment, the difference disappeared for elastic modulus G' ; oppositely, for BTT, the G'' value was slightly higher, which can be caused by internal firm organization slowing due to higher fat content and fatty acids (FA) release as the effect of microwave exposure [39].

An increase in particle size and modification of natural imbibition and breakdown characteristics for starch granules resulted in an observed rise in the elastic modulus for treated samples. Grain size impacts the characteristics of the resulting flour, which was visible in the viscous modulus change. The buckwheat flour obtained from bigger particles, compared to teff grains, were more prone to an increase of the viscous modulus, probably due to higher amylose leaching and a lower fat content. Teff, being richer in starch compared to buckwheat, is also richer in fat, which is known to restrict the access of water to starch granules. Additionally, the high fiber content and the soluble fiber content of buckwheat also contributed to the rise of viscous modulus.

Higher gel viscosity contributes to higher printing accuracy [40]. As such, observing the change towards more consistent behavior in native flours after MW treatment opens the possibility for dedicated engineering of such complex matrix functional characteristics.

3.3. Texture Characteristics of Gels

The gel cylinders formed with flour-based paste after temperature treatment revealed different texture profile parameters depending on their botanical origin and the type of processing applied (Table 4).

Table 4. Texture parameters of solidified gels from native and MW-treated samples after 24 h.

Sample	Hardness [N]	Cohesiveness	Springiness	Guminess [N]	Resilience
PB	0.73 ± 0.03 ^c	0.219 ± 0.026 ^c	0.659 ± 0.246 ^c	0.160 ± 0.016 ^b	1.220 ± 0.150 ^c
PBT	0.37 ± 0.01 ^a	0.107 ± 0.012 ^b	0.330 ± 0.121 ^{ab}	0.040 ± 0.004 ^a	0.610 ± 0.007 ^b
SB	2.20 ± 0.02 ^d	0.211 ± 0.025 ^c	0.508 ± 0.041 ^{bc}	0.483 ± 0.061 ^c	0.710 ± 0.003 ^b
SBT	0.55 ± 0.01 ^b	0.053 ± 0.006 ^a	0.127 ± 0.006 ^a	0.029 ± 0.004 ^a	0.390 ± 0.008 ^a
WT	1.50 ± 0.02 ^c	0.344 ± 0.044 ^b	0.520 ± 0.008 ^b	0.770 ± 0.09 ^a	0.792 ± 0.004 ^a
WTT	0.90 ± 0.01 ^a	0.165 ± 0.028 ^a	0.410 ± 0.033 ^a	0.150 ± 0.07 ^a	0.697 ± 0.041 ^a
BT	1.80 ± 0.05 ^d	0.420 ± 0.015 ^c	0.620 ± 0.030 ^c	0.730 ± 0.10 ^b	0.719 ± 0.110 ^a
BTT	1.10 ± 0.03 ^b	0.248 ± 0.057 ^a	0.400 ± 0.050 ^a	0.270 ± 0.09 ^b	0.713 ± 0.032 ^a

PB—Polish buckwheat, PBT—treated Polish buckwheat SB—native Spanish buckwheat, SBT—treated Spanish buckwheat; WT—native white teff, WTT—white teff treated, BT—brown teff, BTT—brown teff treated, lower-case letters mean values are significantly different at $p \leq 0.05$ in the column.

The weakest gels were those obtained from buckwheat samples; however, during the analysis, the high stickiness of the gels was noted. The hardest gels were obtained from Spanish buckwheat, which, compared to Polish buckwheat, contained more starch and less fiber. Also, in opposition to the rheological data, brown teff resulted in harder gels than white teff. The cohesiveness reduction as result of MW treatment was observed for all the samples; this was most pronounced for Spanish buckwheat. Springiness, the internal capacity of the sample to go back to its undeformed condition after the deforming force is removed, was more strongly impacted in buckwheat samples, where it was reduced 2 and 4 times for PB and SB samples, respectively. Resilience, being the indicator of how the gel regains its form after the first compression, was negatively impacted in buckwheat gels, but surprisingly not in teff flour made gels. Gumminess, being the result of hardness and cohesiveness interaction in the sample, was negatively impacted in buckwheat but not significantly changed in teff.

These species-specific results may be strongly dependent on the particle sizes of each flour, which was impacted by the botanical sizes of each grain. The stabilization of specific texture parameters can be beneficial for 3D printing edible inks, where changes due to extrusion unintentionally applied while printing can destroy the functional properties of printed forms.

3.4. Texture Profile of Printed Forms

The printed cylinders were covered with plastic cups and stored overnight. The next day, the TPA provided the texture characteristics shown in Table 5.

Table 5. Texture parameters of 3D printed forms from solidified gels made from native and MW-treated samples.

Sample	Hardness [N]	Cohesiveness	Springiness	Guminess [N]	Resilience
PB	0.58 ± 0.03 ^b	0.100 ± 0.016 ^b	0.473 ± 0.139 ^c	0.050 ± 0.006 ^b	1.220 ± 0.150 ^c
PBT	0.39 ± 0.01 ^a	0.089 ± 0.012 ^b	0.231 ± 0.021 ^b	0.034 ± 0.002 ^a	0.610 ± 0.007 ^b
SB	1.89 ± 0.09 ^c	0.105 ± 0.015 ^b	0.401 ± 0.019 ^c	0.197 ± 0.010 ^c	0.710 ± 0.003 ^b
SBT	0.52 ± 0.03 ^b	0.043 ± 0.006 ^a	0.100 ± 0.016 ^a	0.022 ± 0.001 ^a	0.390 ± 0.008 ^a
WT	1.00 ± 0.05 ^a	0.217 ± 0.021 ^b	0.330 ± 0.008 ^b	0.220 ± 0.060 ^b	0.691 ± 0.024 ^b
WTT	0.90 ± 0.07 ^a	0.135 ± 0.012 ^a	0.360 ± 0.043 ^b	0.120 ± 0.030 ^a	0.581 ± 0.031 ^a
BT	1.20 ± 0.02 ^b	0.210 ± 0.025 ^b	0.470 ± 0.050 ^c	0.250 ± 0.060 ^b	0.601 ± 0.010 ^a
BTT	0.90 ± 0.08 ^a	0.151 ± 0.032 ^a	0.300 ± 0.010 ^a	0.140 ± 0.040 ^a	0.603 ± 0.012 ^a

PB—Polish buck-wheat, PBT—treated Polish buckwheat; SB—native Spanish buckwheat, SBT—treated Spanish buckwheat; WT—native white teff, WTT—white teff treated, BT—brown teff, BTT—brown teff treated, lower-case letters mean values are significantly different at $p \leq 0.05$ in the column.

The extrusion impact on the texture characteristics of the buckwheat and teff gels was studied using TPA profile analysis. Hardness seemed to be further affected by extrusion during printing, especially in buckwheat gels, while teff gels seemed to be more uniform in their results. Cohesiveness was not particularly impacted in the Polish buckwheat flour sample, as the result of MW treatment, oppositely to all the rest of the sample, were decreased. Again, the teff gel samples looked to be less affected during the 3D printing process, with a slight decrease after MW treatment. Results suggest that the MW treatment stabilized the viscoelastic characteristics of the native flour, reducing the elasticity changes and increasing the viscosity but enabling the more predictive behavior during external force (extrusion) application.

During the extrusion stage, it is desirable to have ink in a sol-state with low viscosity for proper extrudability [40]. In the formation stage, the speed of sol-gel transition (gelation time) is important to avoid continuous spreading of the ink. An increased elastic modulus (G') helps the printed structures to be self-supporting during the self-supporting stage [41–44].

4. Conclusions

The experiment was meant to investigate the transformative potential of microwave supported heat-moisture treatment at 30% of initial moisture content of gluten-free flours, specifically buckwheat and teff. The aim was to understand whether this low-cost method could effectively modulate the behavior of these native flours in the context of 3D extrusion printing. The research primarily focused on three critical aspects of the extrusion printing process: the sol-state viscosity during extrusion, the speed of sol-gel transition (gelation time) during formation, and the elastic modulus (G') for structural support during the self-supporting stage. These factors collectively determine the printability and integrity of 3D-printed food structures.

The results revealed that microwave heating significantly influences the rheological properties of the flour-based ink. First, it reduces the viscosity of the ink, rendering it more amenable to extrusion. This effect is crucial as it enhances the extrudability of the ink, allowing for precise and consistent deposition of material during printing. Achieving the desired sol-state viscosity is essential for the success of 3D food printing. The increase in elastic modulus (G') observed in the microwave-treated flours is also the crucial result for further investigation using MW supported heat moisture treatment. This elevated G' imparts self-supportability to the printed structures, minimizing the need for external scaffolding or support materials. This not only simplifies the printing process but also opens up possibilities for intricate and delicate designs, expanding the potential of 3D food printing.

The study demonstrates that microwave heating of native gluten-free flours with 30% initial moisture content represents a cost-effective and highly promising method for modulating the rheological properties of edible inks in 3D food printing. The ability to optimize sol-state viscosity and elastic modulus has the potential to make 3D printing more accessible, efficient, and versatile. These findings can start the development of customized and nutritionally tailored edible inks using natural diversity of plant-based starch-rich flours.

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