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Insight into the Gluten-Free Dough and Bread Properties Obtained from Extruded Rice Flour: Physicochemical, Mechanical, and Molecular Studies

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Abstract: The present study aimed to evaluate the effect of the extrusion process and particle size on the properties of rice flour (microstructure, pasting properties), gluten-free dough (rheological properties), and bread (texture, specific volume, water absorption capacity, low-field nuclear magnetic resonance (LF NMR) relaxometry). Rice flours were extruded at 80 and 120 °C with feed moisture (15 and 30%) and with the same particle size (<132 and >132–200 µm). Significant differences were observed between the pasting profiles of the flours before and after extrusion. The pasting profile of extruded flours confirmed that hydrothermal treatment partially gelatinized the starch, decreasing the viscosity during heating. The water binding properties increased with the extrusion temperature and moisture content and also with the particle size of the flour. The most important parameter influencing the mechanical properties of the dough was the moisture content of the flour and significant differences were observed between fine (<132 µm) and coarse flours (>132–200 µm). The molecular dynamics of particles containing protons in the bound and bulk fractions in each sample do not depend on the extruder parameters or granulation of the obtained fraction. LF NMR results confirmed that extrusion of rice flour led to a significant decrease in the T_{21} value compared to the control sample and an increase in the T_{22} value in breads made with flours with particle size <132 µm. A linear relationship was found between the spin-spin relaxation times (T_1) changes and the equilibrium water activity (a_r). The results showed that bread with extruded rice flour at the same die temperature resulted in a significantly higher bread volume (31%) and lower hardness (27%) compared to the control. The highest hardness was observed in the case of samples prepared with extruded flour with the addition of 15% moisture, regardless of temperature and particle size.

Keywords: extrusion; pasting properties; dough rheology; structure; water behavior; LF NMR

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1. Introduction

The production of high-quality gluten-free bread is still a major technological challenge due to the inability of gluten-free flour to form a viscoelastic dough and because there are no raw materials, ingredients, or additives that can fully replace gluten. Nowadays, the improvement of gluten-free bread's rheological properties, specific volume, and texture has attracted more attention. Several additives have been used, such as hydrocolloids (xanthan gum [1], hydroxypropylmethylcellulose (HPMC), carboxymethylcellulose, apple

pectin [2]), enzymes [3], protein isolate [4], and modification of flour properties [5–7] have been employed to counteract these problems. One of them is the extrusion cooking of flour, considered a crucial method of the high-temperature short-time (HTST) process to modify the functional properties of starch-based ingredients [8,9]. The main factors influencing the properties of extrudates include the size of the flour particles, the nature of raw materials, the speed of the screw, the moisture of the feed, and the die temperature [10,11]. The extrusion process led to partial starch gelatinization, increasing the swelling capacity of the starch granule and even causing the break-up of the granules, thus altering dough and bread properties. Starch gelatinization during extrusion allows the formation of numerous hydrogen bonds with water and forms a three-dimensional network that retains gases during the preparation of gluten-free bread [12]. Such changes in the constituent level modify the rheological behavior of flour. So far, the effects of extruded wheat flour [13], sorghum flour [14,15], extruded millet [16], and corn flour [17] on dough rheology and the textural and organoleptic properties of bread have been analyzed. Previous studies demonstrated that wheat bread with extruded black rice had a higher specific volume and lower hardness than bread with non-extruded black rice flour [18]. Jafari et al. [14] found that the incorporation of extruded sorghum flour (10%) could also improve the flavor and overall acceptability of the sorghum-wheat composite bread. Moreover, the milling step and its methods have been reported to affect the properties of rice flour, especially the particle size of rice flour [19], the content of damaged starch [20], and thus the volume of gluten-free bread. Therefore, size fractionation plays an important role in creating the quality of bakery products. Clerici et al. [21] indicated that pregelatinizing rice flour through an extrusion and modifying it with an organic acid considerably improves the color and texture characteristics of the crust of gluten-free bread. Sanchez et al. [22] also found that the addition of extruded waxy rice flour (15 and 30%) improved bread volume and crumb structure, decreased initial hardness, and delayed bread staling.

Due to its thickening properties, pregelatinized rice flour has been widely used [23–25]. The effects of extruded rice flour on dough and bread quality have not been fully understood and more detailed information is needed. Taking into account the mentioned factors, the present study aimed to evaluate the effect of feed moisture (15 and 30%) and die temperature (80 °C and 120 °C) as well as particle size (<132 µm and >132–200 µm) on the properties of rice flour (microstructure) and gluten-free dough (rheological properties) and bread (texture, specific volume, water activity, LF NMR relaxometry).

2. Materials and Methods

2.1. Rice Flour Preparation

Gluten-free rice flour was obtained under laboratory conditions during one-stage milling in the Quadrumat® Junior laboratory mill (Brabender, Duisburg, Germany) of grain rice.

Extrusion cooking was carried out on a single-screw TS-45 extruder (Metalchem, Gliwice, Poland) fitted with a single-flight screw. The length-to-diameter ratio for the extruder is 12:1, the screw diameter is 45 mm, the length is 550 mm, and the nozzle diameter is 8 mm. The screw speed was set at 80 rpm. Rice flour was extruded at a maximum barrel temperature of 80 and 120 °C. Before extrusion, the moisture was adjusted to reach a final moisture content of 15% and 30%. The extruded product was dried by air convection and then ground using a Universal M 20 mill (IKA®-Werke GmbH & CO. KG, Staufen, Germany).

The particle size was determined using an AS200 basic analytical sieve shaker (Retsch GmbH & Co. KG, Haan, Germany). Fine flours were obtained by sieving through a 132 µm screen, and coarse flours were retained between a 132 and 200 µm sieve. The finest particles were obtained by sieving a set of particles of different sizes, instead forcing them to reduce the size of all particles during milling. Non-extruded rice flour was used as the control.

2.2. Flour Characteristics

2.2.1. Basic Chemical Composition

The total nitrogen content was determined using the Kjeldahl method according to ISO 20483 [26] and was used to calculate the protein content by multiplying the result by the conversion factor of 5.75, which is suitable for rice. The ash content was determined according to AACC Method 08-12.01 [27].

2.2.2. Pasting Properties

Pasting properties of gluten-free flours were determined according to the method described by Makowska et al. [28] using a rapid viscosity analyzer (TecMaster RVA-4500, Perten Instruments AB, Hägersten, Sweden). In summary, 3.5 g of flour samples were weighed and then dispersed in 25 mL of distilled water for the RVA measurement (corrected to compensate for a moisture content of 14 wt.). The suspensions were held at 50 °C for 1 min and then raised to 95 °C at a rate of 6 °C/min, held at 95 °C for 5 min and cooled to 50 °C at the same rate, and finally held at 50 °C for 1 min. The stirring rate was 960 rpm for the first 10 s followed by 160 rpm for the remaining test. During the analyses, the peak, the trough, the final viscosity, and the breakdown and setback parameters were recorded.

2.2.3. Microstructure

The microphotographs of the gluten-free flours were taken using a Zeiss EVO 40 scanning electron microscope (Carl Zeiss AG, Oberkochen, Germany).

2.2.4. Oil and Water Binding Capacity

The water binding capacity (WBC) and the oil absorption capacity (OAC) of the native and extruded flours were determined according to the method suggested by Jeżowski et al. [29]. Briefly, 1 g of each flour sample was weighed in a test tube containing 20 mL of distilled water (for WBC) or 20 mL of rapeseed oil (for OAC). The mixture was then shaken for 15 min and allowed to stand for 5 min at 22 °C. After this time, the suspension was centrifuged at 4500× *g* for 15 min (Rotofix 32A from Hettich, Tuttlingen, Germany). WBC is expressed as the weight of water (g) absorbed by 1 g of flour and OAC as the weight of oil (g) absorbed by 1 g of flour.

2.3. Dough and Bread Making

The dough was made using the following formula: rice flour (200 g), rapeseed oil (20 g), sucrose (18 g), salt (3 g), instant dried yeast (3 g), and water (160 g). Dough hydration plays an important role in determining the gluten-free bread quality. The use of extruded flour requires the addition of a larger volume of water to obtain a constant consistency. However, the aim of this study was to evaluate the effect of the extrusion process and particle size on dough and bread properties, as well as water behavior. Thus, the same amount of water was added to the recipe. The test samples replaced the unextruded rice flour with the extruded rice flour at 10%, and the other components were unchanged. All compounds were mixed with the KitchenAid mixer (model 5KPM5EWH, KitchenAid, Benton Harbor, MI, USA) for 7 min at a speed of 70 rpm. The dough was fermented at 35 °C and a relative humidity of 75% (RH) for 60 min. After proofing for 20 min at 35 °C and a RH of 75%, the dough was baked in an oven (MIWE Michael Wenz GmbH, Amstein, Germany) at 230 °C for 35 min. The bread was cooled for 2 h at 20 °C and weighed and packed in polypropylene pouches before further analysis.

2.4. Rheological Properties of Dough

The viscoelastic properties were determined with a RheoStress1 rheometer (Haake Technik GmbH, Vreden, Germany) operating in a controlled deformation mode (CD) of 0.05%. Mechanical spectra were analyzed within the 0.1–100 Hz frequency range using 20 mm diameter parallel plate measurement geometrics (PP20 Ti) and 1.0 mm gap. The complex viscosity (η^*), storage modulus (G'), and the loss modulus (G'') were determined.

The obtained spectra were fitted to the Ostwald de Waele equation for η^* and power law equations for G' and G'' [30].

$$\eta^* = K^* \cdot \omega^{n^*-1}$$

where η^*—complex viscosity (Pa/s), K^*—consistency index (Pa/s^n), ω—angular velocity (rad/s), and n^*—flow behavior index (−).

$$G' = K' \cdot \omega^{n'}$$

where G'—storage modulus (Pa), K'—equation constant (Pa/s^n), ω—angular velocity (rad/s), and n'—equation constant (−).

$$G'' = K'' \cdot \omega^{n''}$$

where G''—loss modulus (Pa), K''—equation constant (Pa/s^n), ω—angular velocity (rad/s), and n''—equation constant (−).

2.5. Bread Properties Analyses

2.5.1. Specific Volume

The specific volume of gluten-free bread was determined by the rapeseed displacement method, according to the AACC 10-05 International Approved Methods [31], and calculated in mL/g of bread.

2.5.2. Texture Analysis

The texture profile analysis of bread was performed with a TA.XTplus texture analyzer (Stable Micro System Co., Ltd., Surrey, UK) equipped with a 5 kg load cell [30]. Each sample was compressed twice with a cylindrical plunger probe with a diameter of 35 mm. The test parameters were as follows: 10.0 mm/s pre-test speed, 5.0 mm/s test speed, 5.0 mm/s post-test speed, and 40% strain. Bread loaves were cut into slices (25 mm thick each and the ends were discarded) and used to evaluate hardness, springiness, cohesiveness, chewiness, and resilience.

2.5.3. Water Activity

Measurements of water activity and transpiration rates were performed with a water diffusion and activity analyzer 'ADA-7' (COBRABID, Poznań, Poland) according to the method described in detail previously [32].

2.5.4. Low Field Nuclear Magnetic Resonance (LF NMR) Relaxometry

Measurements of spin-lattice (T_1) and spin-spin (T_2) relaxation times were performed using a pulse NMR spectrometer PS15T, operating at 15 MHz under a system-controlled temperature (Ellab, Poznań, Poland) in accordance with the method described by Cichocki et al. [33]. The inversion-recovery pulse sequence was applied for measurements of T_1 relaxation times [34]. Distances between RF pulses (t) were changed within the range from 20 to 80 ms and the repetition time was from 10 s. Each time, 32 FID signals and 119 points from each FID signal were collected. Calculations of the spin-lattice relaxation time values were performed with the assistance of the CracSpin program. The program for calculating relaxation parameters from experimental data uses the 'spin grouping' approach. Marquardt's minimization method has been applied for fitting multiexponential decays. Time changes of the current value of the FID signal amplitude in the used frequency of impulses are described by the following formula:

$$M_z(t) = M_0 \left\{ 1 - 2\exp\left(\frac{-t}{T_1}\right) \right\}$$

where $M_z(t)$ is the actual magnetization value and M_0 is the equilibrium magnetization value.

Measurements of spin-spin (T_2) relaxation times were taken using the pulse train of the Carr-Purcell-Meiboom-Gill spin echoes ($90 - \tau/2 - (180)_n$) [34]. The distance (τ) between 180 RF pulses ranged from 0.5 to 0.9 ms. The repetition time was 10 s. The number of spin echoes (n) was 100. Five accumulation signals were used.

To calculate the spin-spin relaxation time values, the authors applied the adjustment of the echo amplitudes to the formula [35]:

$$M_{x,y}(t) = M_0 \sum_{i=1}^{n} p_i \exp\left[\frac{-t}{T_{2i}}\right]$$

where $M_{x,y}(t)$ is the echo amplitude, M_0 is the equilibrium amplitude, and p_i is the fraction of protons relaxing with the spin-spin time T_{2i}.

Mean correlation times (τ_c) were calculated used the method described by Małyszek et al. [36].

The calculations were performed by using the dedicated software using a nonlinear least-squares algorithm. The accuracy of the relaxation parameters has been estimated with the standard deviation. The presence of two proton fractions was determined for all analyzed systems.

2.6. Statistical Analysis

The data was studied with one-way analysis of variance (n = 3) using Tukey's HSD multiple comparison post-hoc test to identify statistically homogeneous subsets at α = 0.05. Furthermore, a three-way analysis of variance was performed that took into account flour particle size (Factor 1), feed moisture (Factor 2), and die temperature (Factor 3) when applicable. The principal component analysis (PCA) was performed on the correlation matrix. Statistical analyses were performed using Statistica 13.3 (TIBCO Software Inc., Palo Alto, CA, USA).

3. Results and Discussion

3.1. Basic Flour Composition

The protein content was approximately 8–9%/100 g DM (Table 1), which is similar to the results of Martínez et al. [11]. In general, proteins are usually concentrated in the finest fraction (<132 μm), which is confirmed by a 7% higher protein content in the case of control samples (non-extruded flour). In extruded flours, those with a larger particle size (>132–200 μm) were characterized by a slightly higher protein content than non-extruded flour. The protein content of extruded flour was increased with increasing particle size ($p < 0.05$). According to Myoung Kim and Shin [37], higher protein content means less free starch granule fractions in particle size distributions.

A similar situation was observed in the case of the determination of ash, where the control sample (non-extruded flour) with particle size <132 μm had a higher mineral content than extruded flours. No significant differences were observed between flour samples extruded at 80 and 120 °C at the same moisture content.

Table 1. Protein and ash content in analyzed gluten-free flours.

Sample	Protein (%)	Ash (%)
<132 µm		
C, <132 µm	9.10 ± 0.18 ^{A,a}	0.613 ± 0.014 ^{A,a}
15%, 80 °C	8.52 ± 0.23 ^{B,b}	0.543 ± 0.043 ^{B,b}
30%, 80 °C	8.54 ± 0.06 ^{B,b}	0.467 ± 0.008 ^{C,cd}
15%, 120 °C	8.09 ± 0.06 ^{C,c}	0.528 ± 0.018 ^{B,b}
30%, 120 °C	8.35 ± 0.01 ^{BC,bc}	0.464 ± 0.009 ^{C,cd}
>132–200 µm		
C, >132 µm	8.46 ± 0.01 ^{C,b}	0.463 ± 0.009 ^{BC,cd}
15%, 80 °C	9.07 ± 0.04 ^{A,a}	0.512 ± 0.002 ^{A,bc}
30%, 80 °C	8.63 ± 0.09 ^{B,b}	0.468 ± 0.01 ^{BC,cd}
15%, 120 °C	9.10 ± 0.09 ^{A,a}	0.491 ± 0.034 ^{AB,bc}
30%, 120 °C	9.16 ± 0.03 ^{A,a}	0.437 ± 0.015 ^{C,d}

Different superscripts (A–C) in columns indicate significant differences between particle sizes, while different lower case (a–d) indicates significant differences within the analyzed parameter ($p < 0.05$).

3.2. Rice Flour Microstructure

The morphology of the rice flour particles from the different extrusion parameters are shown in the scanning electron microscope (SEM) images (Figure S1). Non-extruded native rice starch has a heterogeneous morphology with visible starch granules, as shown in Figure S1A,B. The shear forces and high temperature during extrusion caused gelatinization of the starch, which in turn created a rough and broken structure. A similar phenomenon was observed by Wang et al. [38] in extruded corn starch. It is well known that thermal treatments can modify starch granules and denature proteins, and the extent of starch granule morphological changes depends mainly on the processing conditions, such as temperature and moisture. Extrusion performed below gelatinization temperature, preserving the integrity of the starch granules, and treatments carried out above gelatinization temperature induce structural alterations, destroying the molecular order of the starch granule [7]. Moisture contained in the feed material is the main factor responsible for its vitrification during extrusion [39]. Generally, the higher the humidity, the smaller the cells formed after the extrusion process and the more uniform the structure of the resulting products. These changes were observed regardless of particle size (Figure S1C–J). Importantly, temperature also affected the morphology of the extruded flours. The obtained structure was more homogeneous with increasing temperature (from 80 to 120 °C). As indicated by Wang et al. [40], starch gelatinization begins at about 70 to 80 °C, depending on the botanical origin of the starch. At this temperature, in the presence of water, starch gels form homogeneous gels, which is consistent with the morphological changes we observed.

3.3. Pasting Properties of Flour

The observed changes in the morphology of extruded flours (see Section 3.2) may significantly affect the starch pasting process. The viscosity of starch pastes depends on several factors, among which the most important are the botanical origin of the starch, its starch concentration in the analyzed sample, the volume of solvent used, the pH level, and the presence of minerals and other biopolymers [41,42]. For this reason, constant analysis conditions were used for all flours, and the results are presented in Table 2. The maximum viscosity increases with increasing moisture content of flours prior to extrusion (at the same temperature) and decreases significantly with the increase in temperature (at constant moisture content). Nevertheless, each extruded flour was characterized by a viscosity much lower than the flour before extrusion, which means that this process significantly affected the high degradation of starchy structure. This is confirmed by studies on wheat starch, described by Chiang and Johnson [43], in which they analyzed the influence of extrusion parameters (moisture content of raw material, screw speed as well as operational

temperature) and showed that starch gelatinization increased with increasing temperature and water content; however, as observed also in our research, when these variables act at extreme opposite values, the maximum gelatinization rate occurs.

Table 2. RVA measurement results.

Sample	Peak Viscosity (cP)	Trough (cP)	Breakdown (cP)	Final Viscosity (cP)	Setback (cP)
<132 µm					
C, <132 µm	$3667 \pm 144^{A,a}$	$2099 \pm 63^{A,b}$	$1568 \pm 116^{A,a}$	$4949 \pm 111^{A,a}$	$2850 \pm 56^{A,a}$
15%, 80 °C	$499 \pm 149^{C,c}$	$308 \pm 47^{C,d}$	$241 \pm 52^{C,ef}$	$491 \pm 106^{D,d}$	$183 \pm 58^{D,f}$
30%, 80 °C	$1170 \pm 13^{B,b}$	$606 \pm 27^{B,c}$	$565 \pm 36^{B,c}$	$1413 \pm 28^{B,b}$	$807 \pm 16^{B,c}$
15%, 120 °C	$355 \pm 57^{C,c}$	$248 \pm 25^{C,d}$	$122 \pm 19^{C,f}$	$363 \pm 66^{D,d}$	$115 \pm 42^{D,f}$
30%, 120 °C	$1059 \pm 3^{B,b}$	$619 \pm 3^{B,c}$	$441 \pm 2^{B,cd}$	$1126 \pm 12^{C,c}$	$507 \pm 11^{C,e}$
>132–200 µm					
C, >132 µm	$3585 \pm 93^{A,a}$	$2642 \pm 191^{A,a}$	$943 \pm 111^{A,b}$	$4861 \pm 106^{A,a}$	$2219 \pm 86^{A,b}$
15%, 80 °C	$496 \pm 27^{C,c}$	$295 \pm 8^{C,d}$	$201 \pm 20^{C,ef}$	$463 \pm 21^{C,d}$	$168 \pm 12^{D,f}$
30%, 80 °C	$1065 \pm 20^{B,b}$	$579 \pm 12^{B,c}$	$486 \pm 19^{B,cd}$	$1377 \pm 25^{B,b}$	$797 \pm 17^{B,c}$
15%, 120 °C	$463 \pm 69^{C,c}$	$285 \pm 37^{C,d}$	$178 \pm 38^{C,f}$	$466 \pm 73^{C,d}$	$181 \pm 37^{D,f}$
30%, 120 °C	$1023 \pm 26^{B,b}$	$671 \pm 14^{B,c}$	$351 \pm 17^{B,de}$	$1307 \pm 23^{B,bc}$	$635 \pm 9^{C,d}$

Different superscripts (A–D) in columns indicate significant differences between particle sizes, while different lower case (a–f) indicates significant differences within the analyzed parameter ($p < 0.05$).

During analysis, the sample is thermostated at a high temperature (95 °C) and subjected to a constant mechanical shear stress, which further breaks up the starch structure. At this time, a breakdown of the viscosity of the analyzed gruel is observed. From a technological point of view, the ability of starch to withstand high-temperature heating and shear stress rates affects its suitability and is considered an important quality factor [44]. The higher the peak viscosity, the greater the breakdown, with the largest breakdown observed for flours before the extrusion process (Table 2). The higher water content in extruded flours also caused the values of the breakdown parameters, as in the case of peak viscosity. Low breakdown values occurred in flours where degradation of the starch fraction did not lead to significant viscosity peaks. Similar observations have been reported by Leonel et al. [45], who analyzed the cassava starch. They analyzed changes in the gelatinization process of extruded starch and also showed that the higher the viscosity, the greater the breakdown. In the last stage of the analysis, the sample is cooled, during which the starch molecules, especially amylose, recombine, causing the formation of a gel structure, which is observed in the increase in the final viscosity. This process is associated with the reorganization of starch and the beginning of the retrogradation process [46]. As expected, a higher final viscosity was observed in flours that contained more water (30%) before the extrusion process. Nevertheless, each time, non-extruded flour—both with lower and higher granulation—was characterized by up to 10 times higher final viscosity. Doubler et al. [47] and Mercier and Feillet [48] also noted that the extrusion process affects the decreases in the final viscosity and breakdown. The increase in viscosity depends on the tendency of the starch to reassociate, and the more intensive the treatment, the lower the breakdown and final viscosity values could then be observed. Final and setback viscosities were crucial factors to form a network structure in paste without gluten. The extrusion process also significantly improved the stability of starch pastes. The setback parameter determines the susceptibility of starch to retrogradation, compared to non-extruded flours. The lower the value of this parameter, the lower the retrogradation rate [49]. It was found that the extrusion process using rice flour with a lower moisture content (15%) reduced the value of the setback parameter by about four times compared to extruded flour with a moisture content of 30%, which proves the higher technological suitability of extruded flours.

3.4. Oil and Water Binding Capacity

The particle size of non-extruded flour was shown to have no significant effect on the water binding capacity (WBC) and the oil absorption capacity (OAC). All samples of extruded rice flour showed significantly higher water absorption compared to the control samples (Table 3), which is also the result of a higher degree of starch damage (Table S1). According to the literature, the finest flour with a higher level of damaged starch granules had high water absorption than intact starch granules [50] and absorbed more water probably due to its higher surface-to-volume ratio. On the contrary, flours with a particle size >132–200 µm were characterized by the highest water absorption, especially at higher process temperatures (120 °C), which may be due to the increased amount of gelatinized starch. These results are in line with those of Kadan et al. [51] who found that the water absorption of rice flour increased with increasing extrusion temperature. Furthermore, Lenel et al. [45], in their studies on extruded cassava starch, proved that the higher the extrusion temperature, the higher the water absorption was observed. In addition, the beneficial effect is also the higher water retention capacity of extruded flour, which could also affect the delay of water migration from the crumb to the outer part and thus decrease the staling rate [52].

Table 3. Water binding capacity (WBC) and oil absorption capacity (OAC) of gluten-free flours.

Sample	WBC (g/g)	OAC (g/g)
<132 µm		
C, <132 µm	$1.69 \pm 0.08^{C,e}$	$1.46 \pm 0.06^{AB,ab}$
15%, 80 °C	$4.56 \pm 0.35^{AB,cd}$	$1.38 \pm 0.06^{B,ab}$
30%, 80 °C	$3.99 \pm 0.11^{B,d}$	$1.56 \pm 0.13^{AB,a}$
15%, 120 °C	$4.94 \pm 0.36^{A,c}$	$1.60 \pm 0.08^{A,a}$
30%, 120 °C	$4.61 \pm 0.49^{AB,cd}$	$1.49 \pm 0.02^{AB,ab}$
>132–200 µm		
C, >132 µm	$1.41 \pm 0.05^{C,e}$	$1.39 \pm 0.06^{AB,ab}$
15%, 80 °C	$5.37 \pm 0.22^{AB,abc}$	$1.48 \pm 0.06^{AB,ab}$
30%, 80 °C	$5.10 \pm 0.18^{B,bc}$	$1.40 \pm 0.07^{AB,ab}$
15%, 120 °C	$6.19 \pm 0.63^{A,a}$	$1.52 \pm 0.13^{A,a}$
30%, 120 °C	$5.89 \pm 1.09^{AB,ab}$	$1.26 \pm 0.12^{B,b}$

Different superscripts (A–C) in columns indicate significant differences between particle sizes, while different lower case (a–e) indicates significant differences within the analyzed parameter ($p < 0.05$).

The extrusion process did not significantly change the oil absorption capacity of the flours. In all the samples, OAC remained at a similar level. Tabara et al. [53] showed an increase in the oil binding ability of rice flour after heat treatment at 120 °C for 120 min. The authors suggested that structures of rice glutenin could be changed by heat treatment at 120 °C and that smaller subunits of rice glutenin after heat treatment could cause deterioration in breadmaking properties, e.g., resulting in a smaller specific volume of bread.

3.5. Rheological Properties of Dough

The rheological characteristic of dough is a complex phenomenon that arises from the fact that on the one hand, the dough needs to be solid enough in order to maintain proper structure of the bread and that on the other hand, the dough needs liquid to allow its preparation. These materials exhibit both elastic and viscous properties, so their rheological properties are best described by mechanical spectra consisting of the storage modulus (G′), which represents the elastic behavior, and the loss modulus (G″) that relates to liquid behavior of the sample [30]. The mechanical spectra of the investigated rice flour dough samples are presented in Figure S2. The values of Ostwald de Waele/Power law equations are presented in Table 4. The used models were very well fitted to the experimental data, as indicated by values of R^2 above 0.97. All samples investigated regardless of processing

conditions were characterized by the dominance of solid-like behavior as indicated by the K′ values being greater than K″, with the observed phenomenon being typical for dough samples. The extrusion process has significantly changed all considered rheological parameters, but the course of the changes was dependent on the processing conditions. The moisture content of the flour subjected to extrusion was the most important parameter influencing the mechanical properties of the dough. The increase of the moisture content from 15% to 30% resulted in an increase in mechanical parameters, i.e., complex viscosity, storage, and loss modulus. Significant differences were also observed between fine (<132 µm) and coarse flours (>132–200 µm), which can be attributed to differences in WBC (Table 3). Larger particles were prone to form doughs of higher complex viscosity and with stronger solid-like behavior, which resulted in higher values of WBC. The combination of both of these factors (temperature and particle size) resulted in further synergism that caused an increase of complex viscosity, which was mainly associated with an increase of storage modulus. Surprisingly, no effect of the processing temperature or its interaction with other parameters was observed. Nevertheless, gelatinization temperature of rice starch is highly dependent on the botanical origin [54], so possible exceptions from that observation may be expected. The overall extrusion process is an effective method to obtain preparations that in terms of dough properties, reassemble finely milled rice flour but with less pronounced solid-like characteristics.

Table 4. The viscoelastic properties of dough.

Sample	K* ( )	n* (-)	R^2	K′ ( )	n′ (-)	R^2	K″ ( )	n″ (-)	R^2
<132 µm									
C, <132 µm	$6.6 \pm 0.2^{B,c}$	$0.858 \pm 0.015^{A,ab}$	1.000	$38.6 \pm 1.7^{B,c}$	$0.156 \pm 0.026^{B,b}$	0.963	$6.1 \pm 0.3^{B,c}$	$0.255 \pm 0.011^{C,c}$	0.972
15%, 80 °C	$5.8 \pm 0.1^{B,c}$	$0.762 \pm 0.030^{B,ab}$	1.000	$33.2 \pm 0.8^{B,c}$	$0.260 \pm 0.001^{A,a}$	0.996	$11.3 \pm 0.3^{AB,bc}$	$0.359 \pm 0.007^{A,a}$	0.998
30%, 80 °C	$16.8 \pm 0.1^{A,b}$	$0.873 \pm 0.003^{A,ab}$	1.000	$102.1 \pm 0.4^{A,b}$	$0.130 \pm 0.005^{B,b}$	0.996	$15.8 \pm 0.2^{A,b}$	$0.297 \pm 0.002^{B,b}$	0.996
15%, 120 °C	$6.3 \pm 0.6^{B,c}$	$0.749 \pm 0.010^{B,b}$	0.998	$36.5 \pm 0.3^{B,c}$	$0.256 \pm 0.015^{A,a}$	0.997	$12.1 \pm 0.1^{AB,bc}$	$0.349 \pm 0.009^{A,a}$	0.996
30%, 120 °C	$15.6 \pm 0.1^{A,b}$	$0.872 \pm 0.001^{A,ab}$	1.000	$95.4 \pm 0.7^{A,b}$	$0.144 \pm 0.012^{B,b}$	0.993	$16.4 \pm 0.1^{A,b}$	$0.290 \pm 0.002^{B,bc}$	0.996
>132–200 µm									
C, >132 µm	$84.0 \pm 3.7^{A,a}$	$0.851 \pm 0.038^{A,ab}$	1.000	$494.4 \pm 20.3^{A,a}$	$0.129 \pm 0.002^{B,b}$	0.998	$98.5 \pm 4.3^{A,a}$	$0.127 \pm 0.025^{B,d}$	0.962
15%, 80 °C	$5.7 \pm 0.1^{C,c}$	$0.764 \pm 0.071^{A,ab}$	1.000	$32.1 \pm 0.3^{C,c}$	$0.281 \pm 0.002^{A,a}$	0.992	$11.4 \pm 0.1^{B,bc}$	$0.358 \pm 0.006^{A,a}$	0.998
30%, 80 °C	$19.6 \pm 0.1^{B,b}$	$0.875 \pm 0.010^{A,a}$	1.000	$118.3 \pm 0.7^{B,b}$	$0.130 \pm 0.003^{B,b}$	0.990	$17.2 \pm 0.2^{B,b}$	$0.276 \pm 0.001^{B,bc}$	0.990
15%, 120 °C	$7.3 \pm 0.1^{C,c}$	$0.759 \pm 0.042^{A,ab}$	1.000	$41.7 \pm 0.8^{C,c}$	$0.265 \pm 0.008^{A,a}$	0.996	$14.7 \pm 0.3^{B,bc}$	$0.355 \pm 0.001^{A,a}$	0.998
30%, 120 °C	$20.3 \pm 0.1^{B,b}$	$0.873 \pm 0.013^{A,ab}$	1.000	$123.0 \pm 0.7^{B,b}$	$0.126 \pm 0.007^{B,b}$	0.995	$18.0 \pm 0.1^{B,b}$	$0.274 \pm 0.013^{B,bc}$	0.993
Factor					*p*-value				
Fraction	0.005	0.821		0.005	0.475		0.167	0.032	
Temperature	0.483	0.730		0.407	0.533		0.178	0.127	
Moisture	0.000	0.000		0.000	0.000		0.001	0.000	
Fraction×Temperature	0.215	0.913		0.191	0.105		0.497	0.369	
Fraction×Moisture	0.017	0.883		0.013	0.017		0.924	0.011	
Temperature×Moisture	0.271	0.806		0.265	0.095		0.498	0.706	
Fraction×Temperature×Moisture	0.732	0.887		0.686	0.711		0.575	0.844	

Different superscripts (A–C) in columns indicate significant differences between particle sizes, while different lower case (a–d) indicates significant differences within the analyzed parameter ($p < 0.05$). Power equation constants *K* (exponent) and *n* (scaling factor) denoted with *, ′, and ″ are related to complex viscosity, storage, and loss modus, respectively.

3.6. Water Behavior

The molecular properties of protons in the gluten-free bread crumbs showed the presence of a free induction decay proton population (T_1) and two Carr-Purcell-Meiboom-Gill proton populations (T_{21} and T_{22}). The presence of three fractions of protons is typical for bread crumbs [32,55] and other bakery products with a relatively low moisture content [56]. The T_1 relaxation time represents water molecules belonging to the bulk fraction, i.e., those that interact with other water molecules. The T_{21} represents the fraction of bound protons that can be linked with water molecules directly bound to the solid-body components of the crumb by ionic or hydrogen bonds, while the T_{22} can be mainly linked with the presence of starch protons in the system.

The speed of relaxation processes in a biological system is significantly influenced by the speed of molecular movements. Depending on the compounds present in the vicinity of water molecules, water can be bound by hydrogen or ionic bonds. Hydrogen bonding, however, allows water molecules to rotate freely around the bond, while ionic bonding of water molecules significantly limits its dynamics [57].

The relaxation times indicate that the spin-lattice relaxation times (T_1) range from 85 to 110 ms (Table 5). The values of the control samples of the crumbs obtained from <132 µm and >132–200 µm granulation differ significantly. This means that the size of the granulation determines the quantitative relationship of both fractions of protons in the control systems. The changes in T_1 values within the extruded samples were less pronounced, which corresponds to the changes in the rheological properties of the dough. The coarse control sample was characterized by a much shorter relaxation time among all samples, indicating an increase in the amount of bound to bulk water in that system. This phenomenon was accompanied by the increase of consistency parameters in power law equations. Similar but less pronounced changes could be observed for fine flour extruded and different moisture contents, as samples with higher K values had lower T_1 relaxation time. Significant changes in the value of this parameter were found in most analyzed samples, so it can be concluded that the different quantitative relationships between the protons of the bound and bulk fractions in each sample do not depend on the extrusion parameters or granulation of the obtained fraction.

Table 5. LF NMR relaxometry results.

Sample	T_1 (ms)	T_{21} (ms)	T_{22} (ms)	$(\tau_c)_U$	$(\tau_c)_D$
<132 µm					
C, <132 µm	$102.8 \pm 0.5^{D,e}$	$2.7 \pm 0.2^{A,c}$	$10.9 \pm 0.2^{D,f}$	5.78×10^{-8}	2.59×10^{-8}
15%, 80 °C	$109.5 \pm 0.4^{A,a}$	$0.42 \pm 0.06^{D,g}$	$16.5 \pm 0.4^{B,b}$	1.56×10^{-7}	2.04×10^{-8}
30%, 80 °C	$108.1 \pm 0.3^{A,b}$	$0.48 \pm 0.05^{D,g}$	$16.4 \pm 0.4^{BC,b}$	1.45×10^{-7}	2.03×10^{-8}
15%, 120 °C	$106.1 \pm 0.8^{B,c}$	$0.81 \pm 0.09^{B,e}$	$18.1 \pm 0.6^{A,a}$	1.10×10^{-7}	1.87×10^{-8}
30%, 120 °C	$105.1 \pm 0.6^{C,d}$	$0.65 \pm 0.10^{C,f}$	$16.2 \pm 0.5^{C,b}$	1.22×10^{-7}	2.01×10^{-8}
>132–200 µm					
C, >132 µm	$84.4 \pm 1.1^{D,f}$	$0.39 \pm 0.06^{D,g}$	$14.7 \pm 0.5^{A,c}$	1.42×10^{-7}	1.84×10^{-8}
15%, 80 °C	$106.8 \pm 0.5^{B,c}$	$3.0 \pm 0.2^{B,b}$	$10.8 \pm 0.3^{D,f}$	5.58×10^{-8}	2.67×10^{-8}
30%, 80 °C	$107.2 \pm 0.4^{A,bc}$	$2.54 \pm 0.06^{C,d}$	$12.6 \pm 0.4^{B,d}$	1.36×10^{-7}	2.01×10^{-8}
15%, 120 °C	$106.2 \pm 0.5^{C,c}$	$2.6 \pm 0.2^{C,cd}$	$12.0 \pm 0.3^{C,e}$	6.00×10^{-8}	2.48×10^{-8}
30%, 120 °C	$106.3 \pm 0.4^{C,c}$	$3.4 \pm 0.2^{A,a}$	$12.1 \pm 0.3^{C,e}$	5.20×10^{-8}	2.47×10^{-8}

Different superscripts (A–D) in columns indicate significant differences between particle sizes, while different lower case (a–g) indicates significant differences within the analyzed parameter ($p < 0.05$).

Analysis of spin-spin relaxation times (T_2) allowed the observation of the molecular dynamics of particles containing protons in the studied systems. The bound water fraction (T_{21}) relaxes with a time of 0.5–3 ms, while the fraction of the starch protons (T_{22}) relaxes with times of 10–20 ms (Table 5). The effect of granulation on changes in proton dynamics resulting from different extrusion parameters was observed. For small granulation (<132 µm), extrusion results in a significant decrease in the T_{21} value compared to the control sample and an increase in the T_{22} value in breads using these flours. Inverse relationships were noted for samples with larger granulation (>132–200 µm). This indicates that the size of the granulation influences water binding. An increase in the value of T_{21} and a simultaneous decrease in the value of T_{22} means inhibition of rotational movements of water molecules as a result of binding water to the matrix. On the other hand, the reverse relationship means that most of the bonds between the matrix and water are broken. This is manifested by an increase in the dynamics of rotational movements of bulk fraction molecules.

The translational motion of the water molecules was also analyzed by determining the rate of water translation inside the sample (V_D) and the rate of the evacuation of water molecules from the surface (Figure 1). It was observed that, as in the case of spin-spin relaxation times (T_{21} and T_{22}), changes in the values of the crumbs with the addition of extruded flours compared to the control samples were significantly different (Table 5). For granulation <132 µm, the extruded flour limits the water translation rate, while for samples >132–200 µm, the translation rate increases. The rate of water evacuation from the surface V_P increases compared to the control for samples with granulation >132 µm (Figure 1). In the case of samples >132–200 µm, no significant changes were observed. Analysis of the equilibrium value of water activity showed an increase in the value of this parameter in the tests with the addition of flour after extrusion.

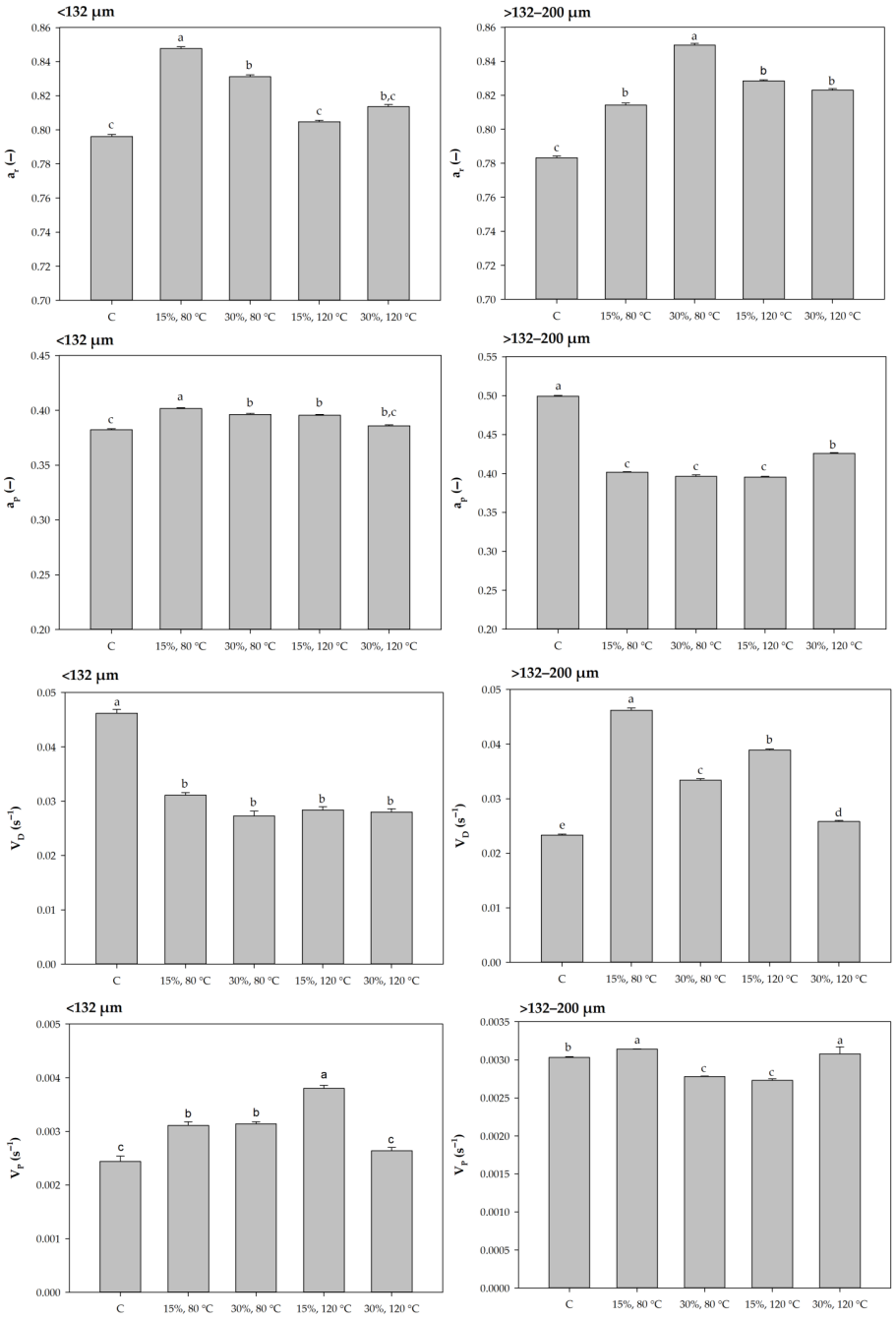

Figure 1. Results of equilibrium value (a_r) and limit water activity (a_P), as well as transport rate (V_D) and rate of the surface conduction (V_P) of water.

A linear relationship was found between the changes in the spin-lattice relaxation times (T_1) and the equilibrium water activity (a_r) (Figure 2). The increase in the value of a_r is due to the increase in the amount of bulk water fraction in relation to the amount of bound water fraction, which is manifested by an increase in the value of the T_1 relaxation time.

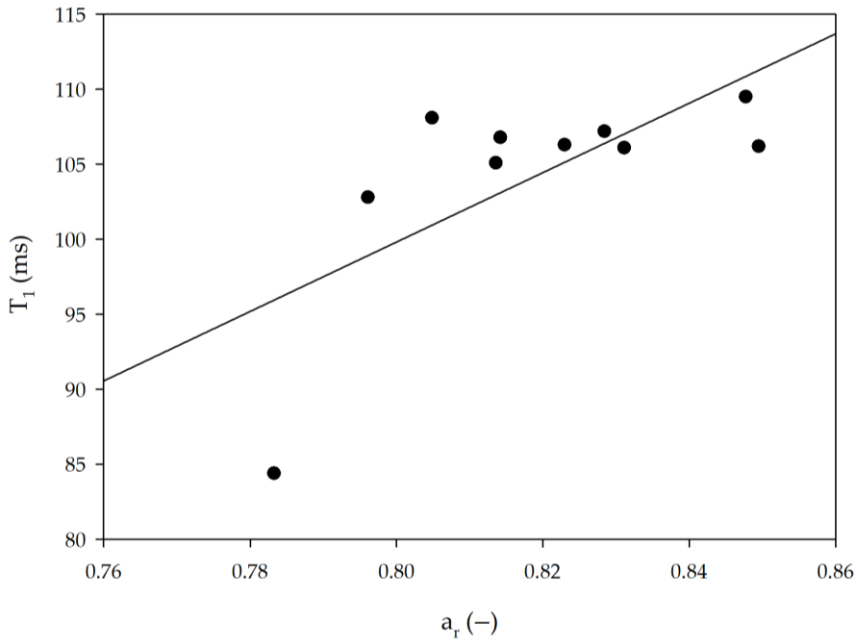

Figure 2. The dependence between rate of equilibrium value of water activity (a_r) and spin-lattice relaxation times (T_1) in analyzed crumb samples.

Relaxation times spin-lattice T_1 and spin-spin T_2 as the macroscopic parameters reflected mutual relations between bulk and bound water in the system (T_1) and its mobility (T_2). On the basis of the values of the relaxation times T_1 and T_2, the mean values of the correlation times (τ_c) were calculated. For this purpose, the system of BPP (Bloembergen-Purcell-Pond) equations [58] describing the relationship between the macroscopic relaxation times T_1 and T_2 and the microscopic average correlation time τ_c was analytically solved due to the parameter τ_c. Mean correlation time τ_c allows for the determination of the possibility of free rotation of water molecules or their very limited dynamics in polymer networks [59]. The values of the spin-lattice T_1 and spin-spin T_2 relaxation times allowed the calculation of the mean correlation time (τ_c). It is a parameter that characterizes the rotational motion of water molecules. Since two fractions of protons were observed, the mean correlation time values for both fractions were determined (Table 5). Relationships between mean correlation time and intermediate water activity (a_p) were found, which is the result of a two-exponential increase in water activity over time [60]. The higher the value of a_p is greater, the greater the mean correlation time describing the bound fraction is. It means that the value of a_p increases with the increase in the order of the bound water fraction. The directly proportional relationship between the mean correlation time of the bulk water fraction and the translation rate (V_D) indicates the competitiveness of water molecular movements in the crumb. The longer the mean correlation time, the more ordered the arrangement of the water molecules. Thus, in the analyzed crumbs, the translational movement of water molecules is slower the greater the disorder of water molecules.

3.7. Texture and Volume of Gluten-Free Breads

The addition of extruded rice flour increased the hardness and chewiness compared to non-extruded rice flour (Table 6). It is well known that the higher the water content, the lower the gelatinization temperatures [61]. In the case of lower moisture content (e.g., 15%), a higher starch gelatinization temperature is needed; thus, it is possible that a longer time

is required for the formation of starch gel. Moreover, the formation of the continuous gel phase (network) depresses the expansion of air bubbles, which leads to a denser and chewy crumb structure.

Table 6. Texture parameters and specific volumes of breads analyzed.

Sample	Hardness (N)	Springiness (%)	Cohesiveness (−)	Chewiness (−)	Resilience (−)	Specific Volume (mL/100 g)
<132 µm						
C, <132 µm	$85.1 \pm 9.9^{C,d}$	$0.847 \pm 0.005^{A,a}$	$0.425 \pm 0.016^{A,a}$	$3128 \pm 488^{B,c}$	$0.197 \pm 0.008^{A,a}$	$201 \pm 14^{A,a}$
15%, 80 °C	$166.6 \pm 9.7^{A,a}$	$0.870 \pm 0.065^{A,a}$	$0.467 \pm 0.043^{A,a}$	$6918 \pm 1072^{A,a}$	$0.246 \pm 0.006^{A,a}$	$127 \pm 6^{B,d}$
30%, 80 °C	$94.0 \pm 4.2^{C,cd}$	$0.782 \pm 0.034^{A,a}$	$0.378 \pm 0.020^{A,a}$	$2835 \pm 241^{B,c}$	$0.195 \pm 0.009^{A,a}$	$140 \pm 1^{B,cd}$
15%, 120 °C	$124.5 \pm 10.8^{B,b}$	$0.854 \pm 0.024^{A,a}$	$0.407 \pm 0.050^{A,a}$	$4431 \pm 858^{AB,abc}$	$0.216 \pm 0.031^{A,a}$	$137 \pm 3^{B,cd}$
30%, 120 °C	$105.8 \pm 14.3^{BC,bcd}$	$0.801 \pm 0.100^{A,a}$	$0.456 \pm 0.120^{A,a}$	$4019 \pm 1554^{B,bc}$	$0.246 \pm 0.074^{A,a}$	$137 \pm 4^{B,cd}$
>132–200 µm						
C, >132 µm	$116.6 \pm 2.8^{B,bc}$	$0.796 \pm 0.0437^{A,a}$	$0.356 \pm 0.045^{B,a}$	$3361 \pm 497^{B,c}$	$0.186 \pm 0.024^{A,a}$	$153 \pm 2^{B,bc}$
15%, 80 °C	$153.5 \pm 0.8^{A,a}$	$0.912 \pm 0.098^{A,a}$	$0.443 \pm 0.062^{AB,a}$	$6358 \pm 1421^{A,ab}$	$0.226 \pm 0.017^{A,a}$	$167 \pm 4^{A,b}$
30%, 80 °C	$116.9 \pm 9.1^{B,bc}$	$0.864 \pm 0.038^{A,a}$	$0.382 \pm 0.054^{AB,a}$	$3920 \pm 576^{B,c}$	$0.194 \pm 0.031^{A,a}$	$131 \pm 6^{C,d}$
15%, 120 °C	$155.0 \pm 3.5^{A,a}$	$0.835 \pm 0.033^{A,a}$	$0.488 \pm 0.034^{A,a}$	$6436 \pm 431^{A,ab}$	$0.243 \pm 0.021^{A,a}$	$128 \pm 3^{C,d}$
30%, 120 °C	$107.6 \pm 13.6^{B,bcd}$	$0.790 \pm 0.072^{A,a}$	$0.39 \pm 0.034^{AB,a}$	$3374 \pm 516^{B,c}$	$0.197 \pm 0.019^{A,a}$	$135 \pm 5^{C,d}$

Different superscripts (A–C) in columns indicate significant differences between particle sizes, while different lower case (a–d) indicates significant differences within the analyzed parameter ($p < 0.05$).

A tendency to increase hardness and chewiness was observed especially when the moisture content was 15%, regardless of the temperature and the size of the particles. Martinez et al. [11] also found that the hardness of gluten-free bread formulated with 10% substituted extruded with the addition of 2%, 10%, and 15% moisture flour (at 110 and 140 °C) increased significantly. On the contrary, Jaffari et al. [14] observed that increasing die temperature and decreasing the feed moisture led to decreased hardness, cohesiveness, springiness, chewiness, and gumminess of extruded sorghum–wheat composite bread. As mentioned by Jafari [15], increasing the hardness of extruded rice bread could be related to the reduction of the integrity of the starch granules after the extrusion process. Higher feed moisture (30%) at the same die temperature (80 °C) and with the same particle size (<132 µm) resulted in bread with a 44% decrease in hardness. Low springiness and cohesiveness values are associated with an increased susceptibility of bread to crumbling [62]. No significant differences were found in the springiness and cohesiveness of gluten-free bread made with extruded flours compared to the control. Our results are consistent with previous findings by Martinez et al. [11], who analyzed gluten-free bread with extruded rice flour with the addition of HPMC (2%) and a different volume of water to obtain a constant consistency.

Specific volume values range from 127.41 to 201.34 mL/100 g and these results are similar to other research bases on rice flour [21] and lower than their wheat counterparts [63]. A decrease in the specific volume was observed when extruded flours were incorporated into the bread formula, except sample 15%, 80 °C, >132–200 µm, which gave a similar specific volume to that of the control (>132–200 µm). These results are consistent with Martinez [11], who analyzed specific volume of gluten-free bread with extruded rice flour with constant consistency. It could also be related to the fact that bread formulated with extruded flour decreases the fraction of pore [14]. The lower specific volumes of gluten-free bread were obtained using extruded flours characterized with a higher damaged starch (Table S1) and a higher water absorption capacity than intact starch granules. Thus, the specific loaf volume might decrease in bread made from extruded flour due to an insufficient amount of water. Interestingly, gluten-free bread formulated with non-extruded flour (<132 µm) has a significantly higher volume (31%) and lower hardness (27%) compared to the variant of gluten-free bread prepared with flour with a larger particle size (>132–200 µm). A possible explanation could be that finer flours (with increased surface area) exhibited a higher susceptibility to enzymatic hydrolysis and monosaccharides and their availability as

an energy source for yeast during fermentation [64]. Thus, the possible greater yeast activity led to a better ability to generate CO_2 and higher specific volume. De la Hera et al. [65] found that the coarser maize flours provided breads with more volume and less firmness than the finer flour breads. As a cause, authors suggested that the higher tendency of dough to retain the gas produced (stronger dough structure) during fermentation increased its specific volume.

On the other hand, in previous studies, it has been found that the lower specific volume of the composite bread containing extruded rice flour could be the result of the poor air retention capacity of the extruded sorghum-wheat composite dough matrix [14]. Lower dough viscosity formulated with extruded flour (see Section 3.3) prevents air bubbles entrapment in the dough, which results in lower specific volume. The differences in hardness are related to differences in the specific volume ($r = -0.4$, $p < 0.05$). Other authors also found that gluten-free bread with lower specific volumes had denser and more tightly packed crumb structures [66]. Furthermore, Araki et al. [64] highlighted a high negative correlation between damaged starch content and the specific volume of bread made from rice flour even with addition of wheat vital gluten. Interestingly, decreasing feed moisture and decreasing die temperature (15%, 80 °C, >132–200 µm) significantly increased the specific volume (167 mL/100 g). This relationship has been demonstrated only for the particle size >132–200 µm. According to the literature, the water absorption capacity of flours cannot fully explain the effect of particle size on bread volume. This sample of gluten-free bread made with extruded flour with the highest volume was those (15%, 80 °C, >132–200 µm) of the larger particle size and also with high water absorption capacity (5.37 g/g).

3.8. Statistical Consideration of the Extrusion Effect of Rice Flour on Analyzed Parameters of Dough and Final Products

In order to systematize the relationships between different parameters describing the physicochemical properties of bread with flour extrusion parameters, principal component analysis was employed. The two first components explain over 2/3 of the variance between samples (Figure 3). Both plain rice flour samples were distinguished, with a position on the PCA plot vastly different from any other sample. This observation confirms the significant influence of the extrusion process on the instigated properties of dough and bread. The parameters that had the largest influence on that matter were the pasting properties and WBC. Flour preparations subjected to extrusion could be classified into two subsets: the first consisting of observations with positive values of PC2 that include flours with higher moisture content and those with negative values of PC2 that include lower moisture samples. This differentiation cannot be directly related to any specific parameter that was determined during this study, but rather it is a complex effect of changes in bread texture and rheological properties of the dough.

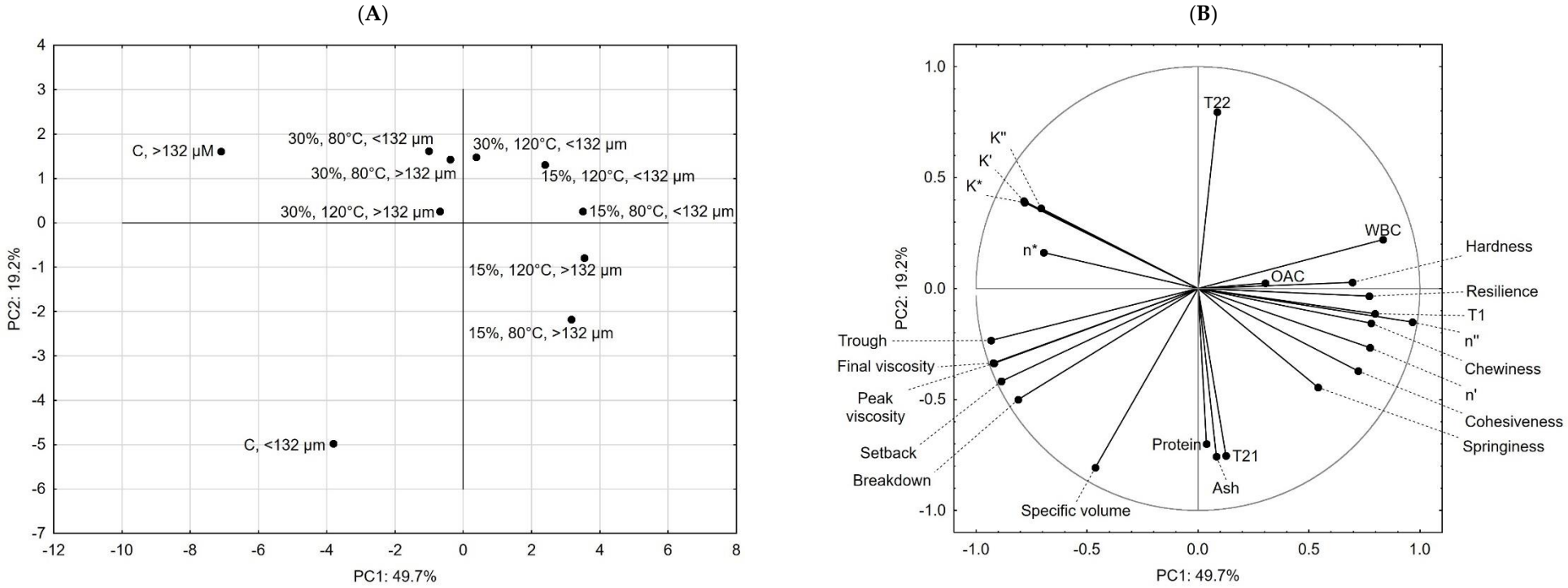

Figure 3. PCA of score plot (**A**) and loading plot (**B**) of physicochemical, mechanical, and molecular properties of analyzed rice flours.

4. Conclusions

Rice flour extrusion cooking altered the flour and model gluten-free bread properties, and the extent of these changes depends on the extrusion conditions. The addition of extruded flours subjected to high-intensity extrusion treatments produced doughs with a higher elastic modulus and consistency index. It was proved that the particle size of flour had a strong effect on the properties of gluten-free bread. The analysis of molecular properties and water activity showed that the extrusion process significantly affected the behavior of water in the crumb samples of the analyzed breads. The observed changes depended on the particle size of the flour used in the bread recipe. A significant reduction in the rotational motion of water molecules in flour samples with lower granulation was observed, which resulted in a decrease in the rate of water translation inside the sample. Reducing feed moisture (15%) at the same die temperature and particle size increased gluten-free bread hardness and chewiness. In comparison to the control sample, no significant differences in the springiness and cohesiveness of gluten-free bread made with extruded flours were observed.

In conclusion, extrusion and fractionation can be a promising approach to produce flours with different functional properties, without any chemical modification, useful in gluten-free breadmaking. With increasing awareness of health, future studies will be conducted to evaluate the effects of these flours on health risks resulting from the formation of potentially harmful compounds during baking process.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app13064033/s1, Figure S1: Scanning electron microscopic images of flours: (A) C, <132 µm; (B) C, >132–200 µm; (C) 15%, 80 °C, <132 µm; (D) 15%, 80 °C, >132–200 µm; (E) 30%, 80 °C, <132 µm; (F) 30%, 80 °C, >132–200 µm; (G) 15%, 120 °C, <132 µm; (H) 15%, 120 °C, >132–200 µm; (I) 30%, 120 °C, <132 µm; (J) 30%, 120 °C, >132–200 µm. Mag. 20 K; Figure S2: The mechanical spectra of the rice flour dough samples. Table S1. Starch damage results, determined according to AACC Methods 76–31.

Author Contributions: Conceptualization, M.B.R.; methodology, H.M.B., Ł.M., J.L. and P.Ł.K.; formal analysis, M.B.R. and P.Ł.K.; investigation, M.B.R., H.M.B., Ł.M., J.L., P.K., J.K., P.J., A.O., M.R. and Ł.S.; data curation, M.B.R.; writing—original draft preparation, M.B.R., P.Ł.K., H.M.B. and J.L.; writing—review & editing, S.M.-S.; supervision, M.B.R. and S.M.-S.; project administration, M.B.R.; funding acquisition, M.B.R. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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