

Article

# Influence of Rice Variety and Freezing on Flour Properties

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**Abstract:** Two rice varieties were used to study the effect of freezing and grinding processes on rice flour properties. The freezing and grinding processes followed by sieving mainly affected the particle size distribution, starch damage, and amylose content of flours. In case of both rice varieties, the percentage of fine particles increased in the flours obtained from frozen rice. Freezing caused the increase of the flour yields from 45.5–50.9% to 54.6–56.5% and the decrease of the flour fineness modules. Moreover, the amylose content and starch damage registered changes when grinding frozen rice, but in case of those parameters, the values are influenced additionally by the native starch properties of variety and most probably by the texture of the endosperm. The swelling power, water solubility index, and gelatinization temperature were higher in flour from frozen rice compared to the flour from non-frozen rice. The modifications generated by rice freezing prior to grinding resulted in increased mechanical properties and decreased thermo-mechanical weakening of proteins. The hardness of the gel was directly correlated with the amylose content, while the freezing process led to the increase of the dough breakdown and starch retrogradation.

**Keywords:** rice; freezing; grinding; damaged starch; hydration properties; gel texture; thermo-mechanical properties; Mixolab



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## 1. Introduction

Rice flour is an important raw material used in many foods due to the functional properties. Thus, it is considered to be the most suitable cereal flour for the production of gluten-free breads, but it is also used for obtaining breakfast cereals, different snack foods, noodles, puddings, and salad dressings [1,2]. The quality of these food products highly depends on the physicochemical and thermo-mechanical properties of the rice flour.

The rice cultivar [3–7] and freezing treatment [8–10] have an important impact on physicochemical properties, due to their influence on starch behavior during processing. Considering the amylose content, rice can be categorized as low, medium, and high amylose content cultivars [6]. Different behavior is expected for different rice cultivars, because the amylose content has a high influence on gelatinization, retrogradation, and pasting properties of flour, and further on end use products [11,12]. Previous studies performed on cooked rice or polysaccharides gels subjected to freezing treatment, regardless of temperature (freezing at low or ultra-low temperature) and time of storage at freezing temperature, revealed important changes in the mechanical properties of the gel and starch retrogradation [8–10].

The type of grinder used for rice milling might also exert a high influence on the technological functionality of the flour. Different grinding methods are available to be used for producing rice flour, such as wet grinding, semidry grinding, and dry grinding. The most used grinding machines are roller mills, hammer mills, disc mills, and pin mills [2]. Due to the differences in the mechanical action on the rice kernels, the methods and type of grinding machines influence the particle size distribution and starch damage, which are nominated in the literature to be the essential parameters that influence the physicochemical properties and end use of the rice flour for different categories of foods [1,2,13]. The

flours with high amounts of damaged starch are susceptible to rapid water absorption and hydrolysis by amylase. In addition, the swelling power of the flours increases with the increase of the amount of fine particles. The tests performed by Ngamnikom and Songsermpong [2] on three types of mills revealed that freezing the rice samples prior to grinding ensures obtaining flour with fine particle size and lower amounts of damaged starch compared to the conventional dry grinding processes. To the best of our knowledge, there is no study available in the literature on the influence of freezing the grains prior to grinding on the technological functionality of the resulting flours and rheological properties of the dough.

The objectives of this study were to evaluate the impact of freezing at low temperature on the milling properties of two rice varieties, and on the functional and thermo-mechanical properties of the rice flours. In addition, the impact of freezing at low temperature on the starch properties and gel texture properties were examined.

## 2. Materials and Methods

### 2.1. Materials and Samples Preparations

The Basmati and Arborio commercial rice varieties (Riso Scotti Danubio, Romania) were acquired from the local market (Galati, Romania).

The half of quantities of commercial rice varieties were frozen by low temperature,  $-18\text{ }^{\circ}\text{C}$ , in a refrigerator (Hotpoint Ariston, Indesit, Netherland) fitted with a quick-freezing unit and electronic system for temperature measurement. The rice samples were stored in the freezer at  $-18\text{ }^{\circ}\text{C}$  for 3 months.

The raw and frozen samples of commercial rice varieties were ground in a first round with the laboratory disc mill (type WZ-2, Sadkiewicz Instruments, Poland), followed by a second round of grinding with a blade mill grinder (Bosch MKM6003, Germany) for 1 min. The resulting flour samples were stored at ambient temperature until further analyses.

### 2.2. Assessment of Milling Performance

The particle size distributions and fineness module of the raw and frozen grinding samples were determined using the Godon and Willm [14] method, the samples being sieved through 630, 400, 315, 160, and  $125\text{ }\mu\text{m}$  mesh.

The yield of rice flours was calculated as flour obtained by sieving through 400 mesh size divided by the weight of rice samples subjected to grinding.

### 2.3. Proximate Analyses of Raw Samples

The proximate composition of the commercial rice varieties samples was determined as follows: moisture using SR ISO 712:2005 method [15], protein (nitrogen-to-protein conversion factor of 5.95) using semimicro-Kjeldahl method (Raypa Trade, R Espinar, SL, Barcelona, Spain), fat through the Soxhlet extraction method with ether (SER-148; VELP Scientifica, Usmate Velate (MB), Italy), crude fiber through Fibretherm Analyser (Gerhardt GmbH & Co. KG, Königswinter, Germany), and ash using SR ISO 2171/2002 method [15]. The starch content was estimated by subtracting the components determined experimentally from one-hundred.

### 2.4. Functional Properties of Raw and Frozen Rice Flour Samples

The method described by Abebe et al. [16] and slight modified by Villanueva et al. [17] was used to estimate the water absorption index (WAI), water solubility index (WSI), and swelling power (SP). Flour (2.5 g) ( $w_0$ ) was mixed with 30 mL distilled water and further heated for 10 min at  $90\text{ }^{\circ}\text{C}$  in a water bath. The samples cooled to room temperature were further centrifuged at  $4000\times g$  for 10 min and the sediments ( $w_s$ ) were collected. The soluble solid of the supernatants ( $w_{ds}$ ) was determined after evaporation overnight at  $110\text{ }^{\circ}\text{C}$ . The WAI, WSI, and SP were determined as follows:

$$\text{WAI} = \frac{w_s}{w_0}, \text{ g/g} \quad (1)$$

$$\text{WSI} = \frac{w_{\text{ds}}}{w_0} \times 100, \text{ g/100 g} \quad (2)$$

$$\text{SP} = \frac{w_s}{w_0 - w_{\text{ds}}}, \text{ g/g} \quad (3)$$

Solvent retention capacity (SRC) profile of the flour samples was determined, according to the AACC Method 56-11.02 [18], using for the following solvents: water (W-SRC), 5% sodium carbonate (SC-SRC), 50% sucrose (S-SRC), and 5% lactic acid (LA-SRC). The SRC values were calculated as the percentage of solvents retained by the flour samples after centrifugation for 15 min at  $1000 \times g$  and were reported at moisture basis (14%).

### 2.5. Starch Properties of Raw and Frozen Flour Samples

Amylose content was assayed by the method of Gibson et al. [19] using the Amylose/Amylopectin Assay Kit (Megazyme International Ireland Ltd., Wicklow, Ireland). The starch damage was determined using the AACC Method 76-31.01 [18] and the dedicated Assay Kit (Megazyme International Ireland Ltd., Wicklow, Ireland).

### 2.6. Gel Texture Properties of Raw and Frozen Flour Samples

The gels were prepared by thermally treating at  $100^\circ\text{C}$  for 10 min the 15% rice flour suspensions prepared in deionized water. After cooling to room temperature, the texture properties of the gels were measured using the CT3 1000 texture analyzer (Brookfield, MA, USA) equipped with a circular probe (TA41) with 30 mm length and 43 mm depth. Three independent measurements were performed on each sample. The following setup was used for texture measurements: distance 10 mm, test and return speed of 1 mm/s, and load cell (force) of 10 kg. The TexturePro CT V1.5 software was used for real-time collection of results, namely hardness, adhesiveness, resilience, cohesiveness, springiness, gumminess, and chewiness characteristics.

### 2.7. The Thermo-Mechanical Properties of Raw and Frozen Flour Samples

The thermo-mechanical properties of flours were determined using the Mixolab device (Chopin Technology, Villeneuve La Garenne, France). In order to impose thermal and mixing constraints to the samples, the following protocol was employed: total dough weight of 90 g, mixing rate of 120 rpm, first plateau at  $30^\circ\text{C}$  of 8 min, followed by temperature increase by  $4^\circ\text{C}/\text{min}$  up to  $90^\circ\text{C}$ , second plateau at  $90^\circ\text{C}$  of 7 min, followed by temperature decrease by  $4^\circ\text{C}/\text{min}$  to  $50^\circ\text{C}$ , and finally the third plateau at  $50^\circ\text{C}$  of 10 min [20]. The following torque values were extracted from the Mixolab curves: C1 maximum torque, C5 torque after 8 min of mixing, C2 related to protein weakening while heating the dough, C3 indicating starch gelatinization, C4 associated to hot gel stability and C5 related to starch retrogradation during the cooling phase [21,22]. These Mixolab parameters were used to calculate mechanical weakening of proteins ( $\text{MPW} = (C1 - C5)/C1$ ), thermo-mechanical weakening of proteins ( $\text{TMPW} = (C5 - C2)/C1$ ), cooking stability ( $C4/C3$ ), breakdown ( $C3 - C4$ ), starch retrogradation ( $C5 - C4$ ), and percent of retrogradation ( $\text{SR} = (C5 - C4)/C5$ ) [21–23].

### 2.8. Statistical Analysis

The experiment was performed in triplicate, and the results are reported as average values together with standard deviation. Statistical analysis of the results was performed using Minitab software. Experimental data were analyzed using the one-way ANOVA and Tukey test with a 95% confidence interval, after assessing the normality and variance equality conditions.

## 3. Results and Discussion

### 3.1. Effect of Rice Freezing on the Grinding Process

The proximate composition of Basmati and Arborio rice varieties is presented in Table 1. It can be observed that the Basmati variety had significantly higher protein content

and significantly lower crude fiber and starch contents compared to the Arborio variety, while the results obtained for fat and ash contents of the two varieties are very close.

**Table 1.** Proximate compositions (% d.w.) of Basmati and Arborio commercial rice varieties.

Components	Basmati	Arborio
Protein, %	8.72 ± 0.07 <sup>a</sup>	6.74 ± 0.05 <sup>b</sup>
Fat, %	1.23 ± 0.04 <sup>a</sup>	1.26 ± 0.04 <sup>a</sup>
Crude fiber, %	1.26 ± 0.06 <sup>b</sup>	1.83 ± 0.06 <sup>a</sup>
Ash, %	0.41 ± 0.02 <sup>a</sup>	0.38 ± 0.02 <sup>a</sup>
Starch, %	76.19 ± 0.17 <sup>b</sup>	77.60 ± 0.09 <sup>a</sup>

Data expressed as mean ± standard deviation ( $n = 3$ ). Mean values on the same row which do not share a superscript letter are significantly different at  $p < 0.05$ .

The performance indicators of the grinding process of Basmati and Arborio commercial rice varieties are presented in Table 2.

**Table 2.** Influence of rice freezing on the performance of grinding process.

Parameters	Basmati		Arborio	
	Raw	Frozen	Raw	Frozen
Product after grinding				
Particle size distribution				
>630 µm, %	21.1 ± 0.10 aB*	3 ± 0.17 bB	21.4 ± 0.10 aA	13.6 ± 0.10 bA
>400 µm, %	33.3 ± 0.17 bA	42.4 ± 0.10 aA	27.8 ± 0.10 bB	29.9 ± 0.10 aB
>315 µm, %	12.1 ± 0.17 aB	9.9 ± 0.10 bB	14.6 ± 0.17 aA	13.1 ± 0.17 bA
>160 µm, %	21.9 ± 0.17 bB	24.9 ± 0.17 aA	29.7 ± 0.26 aA	18.2 ± 0.20 bB
>125 µm, %	6.2 ± 0.17 bA	12.4 ± 0.10 aA	4.4 ± 0.17 bB	10.9 ± 0.17 aB
<125 µm, %	5.4 ± 0.44 bA	7.3 ± 0.20 aB	2.2 ± 0.10 bB	14.3 ± 0.17 aA
Fineness modules	3.25 ± 0.01 <sup>aA</sup>	2.77 ± 0.01 <sup>bA</sup>	3.26 ± 0.01 <sup>aA</sup>	2.74 ± 0.01 <sup>bB</sup>
Product after grinding and sieving through 315 mesh size				
Flour yield, %	45.5 ± 0.17 <sup>bB</sup>	54.6 ± 0.17 <sup>aB</sup>	50.9 ± 0.10 <sup>bA</sup>	56.5 ± 0.17 <sup>aA</sup>
Flour fineness modules	1.89 ± 0.01 <sup>aB</sup>	1.36 ± 0.02 <sup>bB</sup>	2.11 ± 0.02 <sup>aA</sup>	1.53 ± 0.02 <sup>bA</sup>

Data expressed as mean ± standard deviation ( $n = 3$ ). \* Within a row, mean values corresponding to the same rice variety which do not share a superscript lowercase letter are significantly different ( $p < 0.05$ ). Within a row, mean values corresponding to the same type of treatment (raw or frozen) which do not share a superscript uppercase letter are significantly different ( $p < 0.05$ ).

Analyzing the particle size distribution results (Table 2), it can be seen that milling the two varieties of raw rice resulted in similar percentages of particles that exceed 630 µm, while for the particles of 400–630 µm, 160–315 µm, and less than 160 µm the differences are significant. Thus, higher percentages of particles with size ranging from 400 to 630 µm (33.3%), and lower than 160 µm (11.6%) were obtained by grinding the Basmati variety, while when grinding the Arborio variety, most of the particles (29.7%) were in the 160 to 315 µm range. Moreover, in case of the Arborio variety, the amounts of particles between 400 and 630 µm and those between 315 and 160 µm are close: 27.9% and 29.7%, respectively. Even in these conditions, the whole products resulted by milling the two commercial rice varieties have close fineness modules: 3.25 and 3.26 in case Basmati and Arborio rice varieties, respectively. The flours samples resulted after sieving process were composed of the particles with sizes that do not exceed 315 µm, and the fineness modules were 1.89 and 2.11 for flours from Basmati and Arborio varieties, respectively. It can be noticed that the difference between fineness modules of the two flours samples (about 12%) is lower compared to the whole grinding products, ~29%. These results highlight the influence of the variety on the grinding behavior; the Arborio variety is an Italian short-grain rice while Basmati is an Italian long-grain rice. In particular, the structure of the endosperm, which varies with rice variety [24], greatly influences the grinding behavior of the rice.

Because of the high shearing, grinding might cause an increase in temperature, making the product rubbery and therefore more difficult to be broken into small particles [25]. Grinding the grain sample with low temperature allows overcoming these inconveniences. At freezing, the rice samples become more brittle and can be more easily broken with less mechanical action [2]. The impact of rice freezing on the performance of the grinding process is presented in Table 2. It can be observed that the freezing significantly affected the particle size distribution of both whole grinding products ( $p < 0.05$ ) and of flours ( $p < 0.05$ ) of the two commercial rice varieties. Thus, in the case of freezing the Basmati variety, the whole grinding product had the percentage of particles exceeding 630  $\mu\text{m}$  considerably reduced ( $p < 0.05$ ) compared to the corresponding raw sample (from 21.1% to 3%), while the percentage of particles of 400–630  $\mu\text{m}$  increased from 33.3% to 42.4% ( $p < 0.05$ ), and the percentage of particle smaller than 160  $\mu\text{m}$  increases from 11.6% to 19.7% ( $p < 0.05$ ). In a first grinding step, the coarse reduction of the grain occurs under compression, further shearing and friction yielding larger volumes of fine particles [26]. It appears that in the case of grinding the frozen samples by means of the disc mill, the shearing and friction forces play a major role in shaping the particle size distribution of the final product. Further, cutting forces acting in the last stage of grinding are known for giving a definite particle size with few or no fines [26]. As a result of the increase of the volume of fine fractions when grinding the frozen samples, the flour extraction significantly increased from 45.5% to 54.6% ( $p < 0.05$ ), and the fineness module significantly decreased from 1.89 to 1.36 ( $p < 0.05$ ).

On the other hand, freezing the Arborio rice variety allowed obtaining whole grinding products with higher amounts of particles smaller than 160  $\mu\text{m}$  and lower amounts of particles with size in the 160 to 400  $\mu\text{m}$  range, compared to the corresponding raw rice sample (Table 2). For the Basmati variety, the flour yield significantly increased from 50.9% to 56.5% ( $p < 0.05$ ), and the fineness module significantly decreased from 2.11 to 1.53 ( $p < 0.05$ ). Our observation regarding the decrease of the particle size when grinding the frozen samples compared to the raw sample agrees with the findings of Ngamnikom and Songsermpong [2].

The results from Table 2 revealed the different grinding behavior of the two varieties after freezing. Moreover, it can be observed that the flour yield significantly increased ( $p < 0.05$ ) with different percentages when subjecting the rice grains to freezing treatment prior to grinding: the flour yield increased by 20% and 11% for Basmati and Arborio flours, respectively. On the other hand, a similar decrease of about 28% of the fineness module was registered for both flours.

### 3.2. Functional Properties of Flour Samples Obtained from Raw and Frozen Rice

The functional properties of the flours obtained from raw and frozen Basmati and Arborio commercial rice varieties are shown in Table 3. The SP and WSI of Basmati raw flour were lower, and WAI was higher compared to Arborio raw flour. According to Yu et al. [7], Singh et al. [27], and Chung et al. [28], SP and WSI depend on the content and structure of amylopectin. Thus, the high content of amylopectin, and the presence of high proportion of long chains in the amylopectin structure, increase starch crystallinity and the temperature of starch gelatinization [28]. Likewise, the structure of starch granules, and especially the distribution of amylose and amylopectin, can influence the SP and WSI values [7]. Thus, the higher content of amylose, and its distribution in central region of starch granules contribute to maintaining the compactness of the granules, providing a lower solubility [7]. According to our results, the low values of SP and WSI obtained for Basmati flour can be explained by the significantly higher amylose content ( $p < 0.05$ ), 17.96%, compared to the Arborio flour, 4.32% (Table 4), and by the higher gelatinization temperature of 84.4 °C, in case of Basmati flour, compared to the 77.8 °C registered for Arborio flour, respectively, as indicated by the Mixolab curves.

**Table 3.** Functional properties of flours obtained from raw and frozen Basmati and Arborio rice.

Parameters	Basmati		Arborio	
	Raw	Frozen	Raw	Frozen
Hydration properties				
Water absorption index, g/g	5.37 ± 0.11 <sup>bA*</sup>	5.72 ± 0.08 <sup>aA</sup>	5.23 ± 0.08 <sup>bA</sup>	5.41 ± 0.08 <sup>aB</sup>
Water solubility index, %	2.01 ± 0.20 <sup>aB</sup>	2.18 ± 0.04 <sup>aB</sup>	2.59 ± 0.08 <sup>bA</sup>	3.11 ± 0.08 <sup>aA</sup>
Swelling power, %	2.05 ± 0.13 <sup>aB</sup>	2.22 ± 0.09 <sup>aB</sup>	2.64 ± 0.05 <sup>bA</sup>	3.71 ± 0.10 <sup>aA</sup>
Solvent retention capacity				
Water, %	135.37 ± 0.55 <sup>aA</sup>	132.72 ± 0.63 <sup>bA</sup>	130.89 ± 0.79 <sup>aB</sup>	121.90 ± 0.79 <sup>bB</sup>
Sucrose, %	170.20 ± 0.72 <sup>bB</sup>	174.15 ± 0.79 <sup>aB</sup>	176.47 ± 0.50 <sup>bA</sup>	177.92 ± 0.47 <sup>aA</sup>
Sodium carbonate, %	166.98 ± 0.07 <sup>aA</sup>	161.75 ± 0.66 <sup>bA</sup>	157.91 ± 0.37 <sup>aB</sup>	155.92 ± 0.45 <sup>bB</sup>
Lactic acid, %	178.09 ± 0.73 <sup>aA</sup>	176.24 ± 0.67 <sup>bA</sup>	177.18 ± 0.65 <sup>aA</sup>	174.93 ± 0.55 <sup>bA</sup>

Data expressed as mean ± standard deviation ( $n = 3$ ). \* Within a row, mean values corresponding to the same rice variety which do not share a superscript lowercase letter are significantly different ( $p < 0.05$ ). Within a row, mean values corresponding to the same type of treatment (raw or frozen) which do not share a superscript uppercase letter are significantly different ( $p < 0.05$ ).

**Table 4.** Starch properties of flours obtained from raw and frozen Basmati and Arborio commercial rice varieties.

Parameters	Basmati		Arborio	
	Raw	Frozen	Raw	Frozen
Amylose, %	17.96 ± 0.40 <sup>aA</sup>	13.2 ± 0.26 <sup>bA</sup>	4.32 ± 0.11 <sup>bB</sup>	6.65 ± 0.13 <sup>aB</sup>
Damaged starch, %	5.16 ± 0.14 <sup>aA</sup>	5.09 ± 0.16 <sup>aA</sup>	4.92 ± 0.11 <sup>aA</sup>	4.48 ± 0.11 <sup>bB</sup>

Data expressed as mean ± standard deviation ( $n = 3$ ). \* Within a row, mean values corresponding to the same rice variety, which do not share a superscript lowercase letter are significantly different ( $p < 0.05$ ). Within a row, mean values corresponding to the same type of treatment (raw or frozen), which do not share a superscript uppercase letter are significantly different ( $p < 0.05$ ).

Initially proposed for predicting wheat flour functionality, the SRC was additionally used in the last years for investigating the hydration properties of the gluten free flours. The SRC profiles of the flour samples obtained raw and frozen Basmati and Arborio are presented in Table 3. The Basmati flour presented significantly higher values of W-SRC and SC-SRC ( $p < 0.05$ ) and significantly lower value of Su-SRC ( $p < 0.05$ ), compared to Arborio flour. SC-SRC is associated with starch damage, LA-SRC with protein characteristics, and Su-SRC is associated with pentosans characteristics, while W-SRC is influenced by all of flour constituents [18]. The differences between the SRC profiles of Basmati and Arborio rice flours might be explained by the differences observed in terms of proximate composition (Table 1), the damaged starch content (Table 4).

Regarding the hydration properties of flours obtained from frozen Arborio rice, the results indicated in Table 3 revealed the significant increase of WSI and SP values compared to the flours obtained from the corresponding raw rice samples ( $p < 0.05$ ). These results can be explained by the changes registered in the particle size distribution, and particularly by the increase of the percentage of fine particles. Ngamnikom and Songsermpong [2] noted that usually the presence of fine particles results in increased SP values.

Compared to the flours obtained from raw Basmati and Arborio rice samples, the flours obtained from the corresponding frozen samples presented significantly lower SC-SRC values ( $p < 0.05$ ), probably due to the differences in the starch damage of these flour samples. The decreases of starch damage in flours resulted from frozen rice grains agree with the observation of Ngamnikom and Songsermpong [2]. On the other hand, the LA-SRC values of the flours from frozen rice varieties decreased very little for both rice varieties compared to the flour from raw rice, and these results could be explained by the differences in terms of particle size distribution. Higher percentages of fine particles were obtained in case of the flours from frozen rice, and they might be formed by starch granules detaching from the protein matrix. Some of the proteins could have been separated into

fractions larger than 315  $\mu\text{m}$ . This phenomenon could also explain the decrease of W-SRC in the flours obtained from frozen rice.

### 3.3. Texture Properties of Flour Gels

The texture properties of the gels obtained by thermally treating the suspension prepared with flours from raw and frozen Basmati and Arborio rice samples are presented in Table 5.

**Table 5.** Texture properties of flours gels obtained from raw and frozen Basmati and Arborio rice samples.

Parameters	Basmati		Arborio	
	Raw	Frozen	Raw	Frozen
Hardness, N	0.32 $\pm$ 0.03 <sup>aA</sup>	0.19 $\pm$ 0.03 <sup>bA</sup>	0.16 $\pm$ 0.03 <sup>bB</sup>	0.23 $\pm$ 0.03 <sup>aA</sup>
Springiness, mm	8.38 $\pm$ 0.11 <sup>aA</sup>	7.70 $\pm$ 0.11 <sup>bA</sup>	6.97 $\pm$ 0.15 <sup>bB</sup>	7.35 $\pm$ 0.13 <sup>aB</sup>
Adhesiveness, mJ	0.51 $\pm$ 0.04 <sup>bB</sup>	0.84 $\pm$ 0.05 <sup>aA</sup>	0.90 $\pm$ 0.03 <sup>aA</sup>	0.34 $\pm$ 0.03 <sup>bB</sup>
Cohesiveness	0.71 $\pm$ 0.03 <sup>aB</sup>	0.74 $\pm$ 0.05 <sup>aA</sup>	0.81 $\pm$ 0.04 <sup>aA</sup>	0.79 $\pm$ 0.03 <sup>aA</sup>
Gumminess, N	0.23 $\pm$ 0.04 <sup>aA</sup>	0.14 $\pm$ 0.04 <sup>aA</sup>	0.13 $\pm$ 0.03 <sup>bB</sup>	0.19 $\pm$ 0.02 <sup>aA</sup>
Chewiness, mJ	1.59 $\pm$ 0.03 <sup>aA</sup>	1.08 $\pm$ 0.07 <sup>bB</sup>	0.85 $\pm$ 0.05 <sup>bB</sup>	1.32 $\pm$ 0.03 <sup>aA</sup>
Resilience	0.08 $\pm$ 0.01 <sup>aA</sup>	0.07 $\pm$ 0.01 <sup>aA</sup>	0.08 $\pm$ 0.01 <sup>aA</sup>	0.08 $\pm$ 0.01 <sup>aA</sup>

Data expressed as mean  $\pm$  standard deviation ( $n = 3$ ). \* Within a row, mean values corresponding to the same rice variety, which do not share a superscript lowercase letter are significantly different ( $p < 0.05$ ). Within a row, mean values corresponding to the same type of treatment (raw or frozen), which do not share a superscript uppercase letter are significantly different ( $p < 0.05$ ).

The gels obtained from Basmati rice flour presented significantly higher value of hardness compared to the one from Arborio ( $p < 0.05$ ), indicating a more advanced retrogradation starch of Basmati flour. According to Yu et al. [7], this hardness can be related to the amylose crystallization in a shorter time. Moreover, the high content of amylose and the presence of long amylopectin chains lead a harder gel. Additionally, springiness, gumminess, and chewiness were also significantly higher in case of the gel obtained from Basmati rice flour compared to the one from Arborio ( $p < 0.05$ ), indicating that the gel network was more rigid. The results from Table 5 revealed that the gel prepared with frozen Basmati rice flour had significantly lower hardness values compared to the corresponding raw sample ( $p < 0.05$ ). On the other hand, in case of samples from Arborio variety, freezing the rice sample prior to grinding resulted in gels with significantly higher hardness value ( $p < 0.05$ ) (Table 5). This diversity regarding the mechanical behavior of the gels could be explained by the differences of starch properties, more specifically by amylose content and amylose retrogradation. Otherwise, the two rice varieties have different behavior after freezing and grinding: the flour from Arborio variety had higher amylose content compared to raw Arborio sample, while the flour from frozen Basmati rice had lower amylose content compared to the raw Basmati sample. The texture properties of the grains and behavior during grinding [2], but also the starch properties, defined mainly by amylose content, gelatinization temperature, gel texture, and pasting viscosity [3], could justify the differences in the results registered for the two rice varieties (Table 5).

### 3.4. The Thermo-Mechanical Properties of Flour Samples from Raw and Frozen Rice

The influence of rice freezing prior to grinding process on the thermo-mechanical properties of the flour samples from Basmati and Arborio rice varieties was studied by means of Mixolab, and the results are summarized in Table 6.

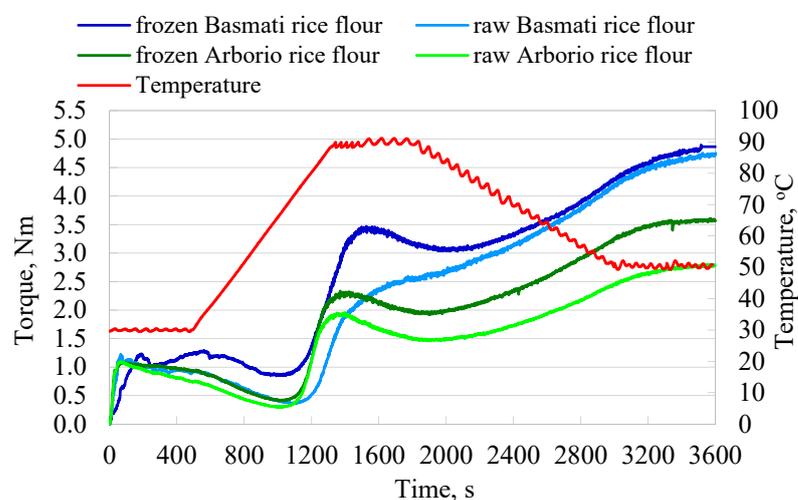
The behavior of the dough during kneading at constant temperature of 30  $^{\circ}\text{C}$  is revealed by MPW. Arborio flour exhibited significantly higher MPW (30.56%) compared to Basmati flour (5.13%) ( $p < 0.05$ ), for which the dough was much more stable, having a higher resistance to kneading at constant temperature of 30  $^{\circ}\text{C}$ . This resistance was also maintained when kneading the sample during heating, from 30 to temperatures over 50  $^{\circ}\text{C}$ . Thus, C2 was significantly higher and TMPW was significantly lower in the case of Basmati

flour dough, compared to the Arborio flour dough ( $p < 0.05$ ) and the temperature at which C2 was obtained was higher (Table 6). However, when comparing the frozen samples, the dough prepared with flour from frozen Arborio rice appeared to be more stable during kneading at constant temperature. On the other hand, when comparing the raw and frozen rice samples, lower differences were registered for the TMPW values corresponding to Arborio rice, compared to the Basmati rice. Nevertheless, according to the results from Figure 1, doughs prepared with flour from frozen rice had lower stability during kneading and while heating from 30 to temperatures over 50 °C.

**Table 6.** Thermo-mechanical properties of rice flours obtained from raw and frozen Basmati and Arborio rice.

Parameters	Basmati		Arborio	
	Raw	Frozen	Raw	Frozen
Proteins functionality				
WA, %	59.50 ± 0.10 <sup>aB</sup>	57.90 ± 0.10 <sup>bB</sup>	64.60 ± 0.06 <sup>aA</sup>	62.00 ± 0.06 <sup>bA</sup>
C1, Nm	1.17 ± 0.01 <sup>aA</sup>	1.16 ± 0.01 <sup>aA</sup>	1.08 ± 0.01 <sup>aB</sup>	1.07 ± 0.01 <sup>aB</sup>
CS, Nm	1.23 ± 0.01 <sup>aA</sup>	0.90 ± 0.01 <sup>bB</sup>	0.75 ± 0.01 <sup>bB</sup>	0.94 ± 0.01 <sup>aA</sup>
C2, Nm	0.86 ± 0.01 <sup>aA</sup>	0.37 ± 0.01 <sup>bB</sup>	0.30 ± 0.02 <sup>bB</sup>	0.42 ± 0.01 <sup>aA</sup>
TC2, °C	54.40 ± 0.10 <sup>bA</sup>	58.70 ± 0.10 <sup>aA</sup>	52.50 ± 0.10 <sup>aB</sup>	50.80 ± 0.10 <sup>bB</sup>
Starch behavior				
C3, Nm	3.42 ± 0.01 <sup>aA</sup>	2.21 ± 0.01 <sup>bB</sup>	1.93 ± 0.01 <sup>bB</sup>	2.29 ± 0.02 <sup>aA</sup>
TC3, °C	84.40 ± 0.10 <sup>aA</sup>	82.40 ± 0.10 <sup>bA</sup>	77.80 ± 0.10 <sup>aB</sup>	76.80 ± 0.10 <sup>bB</sup>
C4, Nm	3.06 ± 0.01 <sup>aA</sup>	2.57 ± 0.01 <sup>bA</sup>	1.47 ± 0.01 <sup>bB</sup>	1.95 ± 0.01 <sup>aB</sup>
TC4, °C	89.40 ± 0.10 <sup>aA</sup>	88.60 ± 0.10 <sup>bA</sup>	86.20 ± 0.10 <sup>aB</sup>	86.10 ± 0.10 <sup>aB</sup>
C5, Nm	4.90 ± 0.02 <sup>aA</sup>	4.74 ± 0.01 <sup>bA</sup>	2.79 ± 0.01 <sup>bB</sup>	3.58 ± 0.01 <sup>aB</sup>
Dough performance indicators				
C3 – C4, Nm	0.36 ± 0.01 <sup>aB</sup>	−0.36 ± 0.01 <sup>bB</sup>	0.46 ± 0.02 <sup>aA</sup>	0.34 ± 0.02 <sup>bA</sup>
C4/C3	0.90 ± 0.01 <sup>bA</sup>	1.17 ± 0.02 <sup>aA</sup>	0.76 ± 0.01 <sup>bB</sup>	0.85 ± 0.01 <sup>aB</sup>
C5 – C4, Nm	1.84 ± 0.01 <sup>bA</sup>	2.17 ± 0.01 <sup>aA</sup>	1.32 ± 0.02 <sup>bB</sup>	1.64 ± 0.03 <sup>aB</sup>
MPW, %	−5.13 ± 0.88 <sup>bB</sup>	22.41 ± 0.79 <sup>aA</sup>	30.56 ± 1.40 <sup>aA</sup>	12.15 ± 1.51 <sup>bB</sup>
TMPW, %	31.51 ± 1.64 <sup>bB</sup>	45.69 ± 1.16 <sup>aA</sup>	41.70 ± 1.83 <sup>bA</sup>	48.88 ± 2.33 <sup>aA</sup>
SR, %	37.56 ± 0.13 <sup>bB</sup>	45.78 ± 0.18 <sup>aA</sup>	47.35 ± 0.55 <sup>aA</sup>	45.69 ± 0.65 <sup>bA</sup>

Data expressed as mean ± standard deviation ( $n = 3$ ). \* Within a row, mean values corresponding to the same rice variety, which do not share a superscript lowercase letter are significantly different ( $p < 0.05$ ). Within a row, mean values corresponding to the same type of treatment (raw or frozen), which do not share a superscript uppercase letter are significantly different ( $p < 0.05$ ).



**Figure 1.** Mixolab curves of flours from raw and frozen Basmati and Arborio rice.

The effect of freezing on the starch gelatinization behavior is different for flours obtained from the two rice varieties. Thus, while for the Arborio rice flours (raw and frozen), a similar trend of the Mixolab curves was observed, describing similar starch behavior during heating—maximum gelatinization torque (C3), cooking stability (C3/C4), and breakdown (C3 – C4), in case of flours from Basmati rice variety the trend of the Mixolab curves was different (Figure 1). Thus, for the flour made from frozen Basmati rice, the torque continued to increase constantly after reaching the maximum gelatinization (C3) and temperature was maintained constant at 90 °C. Finally, when the temperature was decreased from 95 to 50 °C and starch retrogradation occurred, an inflection appears and curves tended to flatten. Practically, the decrease in torque after reaching the C3 values was not recorded, as it happens in a typically Mixolab curve. However, the dough prepared with flour from frozen Basmati rice had higher cooking stability (C3/C4), and higher (C5 – C4) and SR values, compared to the flour from raw Basmati rice, but the C3, C4, and C5 values were lower. In case of flour made from Arborio rice variety, one can see from Table 6 that C3, C4, and C5 torques of the dough sample prepared with flour from frozen rice are higher than those from raw rice, and the trend of the Mixolab curves is similar (Figure 1). This difference in dough behavior during heating between the two varieties could be attributed to the fact that, in the case of Arborio variety, the amylose content increases in the frozen sample, as opposed to Basmati variety (Table 4). The common tendencies of the parameters for the two frozen flours, compared to the non-frozen samples, are the higher values of (C5 – C4) and (C3 – C4). According to Yu et al. (2012b), starch retrogradation properties depend on rice variety, but the overall starch architecture, the structure of amylopectin and degree of polymerization had influence on retrogradation properties starch gel. The authors reported that rice amylose content influenced crystallinity degree of starch, and rice with high content of amylose present high retrogradation enthalpy and retrogradation degree.

#### 4. Conclusions

This study showed for the first time the influence of rice variety and grains freezing on the functional properties of flours, gels texture, and the thermo-mechanical properties of dough samples. The freezing and grinding processes followed by sieving allowed obtaining flours with higher volumes of small particles, lower fineness modules, and better swelling power and water absorption index. On the other hand, lower ability of the flours to retain the water during centrifugation was noticed in case of the samples processed through freezing. The changes registered in the damaged starch, amylose content, and gelatinization temperature varied with rice variety subjected to freezing. Both flour gels texture properties and rheological measurements performed on doughs using the Mixolab device indicated that starch behavior depends on the variety and the freezing treatment applied to the rice prior to grinding. On the other hand, regardless of the variety, rice freezing resulted in higher proteins weakening and starch retrogradation. Further investigations are needed to investigate the impact of the freezing time on the technological functionality of the rice flours and the bread making potential.

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