Effect of the rice flour particle size and variety type on water holding capacity and water diffusivity in aqueous dispersions

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Abstract

The aim of this study was to evaluate water binding capacity of selected varieties of rice flours as prospective processing parameter for manufacturing gluten-free products. Water retention capability was determined by measuring the effective diffusivity coefficient, DSC, water absorption index and water solubility index. It was found that with decreasing particles size of flour the water binding capacity was increasing. This phenomenon was dependent also on the saccharides and proteins content of individual materials. There was measured gelatinization temperature and enthalpy of fusion. It was found to be 2.08 J g^{-1} for black and 5.8 J g^{-1} for fine rice flour. Effective moisture diffusivities of 6.167×10^{-10} m^2 s^{-1} for black and of 5.030×10^{-10} m^2 s^{-1} for fine rice flours were found. The latter were of the lowest magnitudes from the set of the studied samples, indicating their highest ability to retain water in their microstructure. There was confirmed structural binding of water based on rheological testing.

Keywords: Rise dispersions; DSC; Thermal analysis; SEM; Rheology

1 Introduction

Rice (*Oryza sativa L.*) is one of the leading food crops in the world and the staple food for more than half the world's population (Champagne, 2004; Shao, Hu, Yu, Mou, Zhu, & Beta, 2018). Rice has taken central stage during last decade, not only as an important provider of nourishment for the world's population, but as a grain now recognized as having many unique nutritional and functional attributes with potential to be captured in a multitude of value-added food and non-food applications due to its easy digestion and hypoallergenic properties (Wu et al., 2019). That is why, the basic, up-to-date knowledge of rice chemistry and technology is vital for developing its new applications and lead rice into the coming decades. Milled rice is used for gluten-free products (Naqash, Gani, Gani, & Masoodi, 2017), however, most of these products are of low micronutrients content, although brown rice has better nutritional value than other rice types. Brown rice is obtained using de-hulling, and the brown colour is due to the presence of bran layers containing high amount of minerals and vitamins. Brown rice contains more nutritional components than other milled rice grains (e.g. dietary fibres, phytic acids, E and B vitamins, and γ-aminobutyric acid (GABA)). All these compounds are present in the bran layers and germ that are removed during polishing or milling (Champagne, 2004). The differences among rice flours are governed by inherent cultivar variations (Tangsrianugul, Wongsagonsup, & Suphantharika, 2019), methods of milling or grinding, and the pre-treatments of rice or flour, as well as by the storage time (Gu, Gong, Gilbert, Yu, Li, & Li, 2019). However, different milling methods affect the properties of rice flour such as the content of damaged starch and the particle size (Wu et al., 2019).

Rice starch granules are the smallest ones (from 3 to 10 μm) among cereal starches. However, higher hierarchy rice starch structures are composed from at least 16 individual granules of angular shape (typically 3 to 5 μm size) (Whistler, BeMiller, & Editors., 1996).

Rice flour is furthermore characterised by the variety or the amylose content, which indicates its inherent properties related to the gel formation (Hu, Chen, Xu, Chen, & Zhao, 2020). Amylose content or amylose-amylopectin ratio, gelatinization, and pasting behaviour are the important properties for describing rice starch (Nishita & Bean, 1979; Nishita & Bean, 1977). Differential scanning calorimetry (DSC) was used to determine the temperature and heat of starch gelatinization. Originally observed single symmetrical endotherm of the phase transition of starch isolated from rice at high water content dispersions exceeding 60 w.% of water was reduced by the development of a second transition at a higher temperature by decreasing water content. They confirmed two stages of swelling and disruption/dissolution of starch granules during gelatinization. It is well known, that the starch granules constitute approximately of 90 % of the dry weight of a milled rice grain. Starch from the chemical point of view, is a polyglucose formed by amylose and amylopectin. Starch determines the physical and cooking properties of rice grains. It contributes to them through interactions with other components of the rice endosperm, e.g. proteins, lipids and water. The ratio of amylose and amylopectin in the starch, the solubility of each, and the structure of each fraction, all contribute to the performance of the rice grain (Champagne, 2004; Hu, Chen, Zhao, Chen, & Wang, 2020). Rapid moisture adsorption causes low-moisture rice grains to crack or fissure. This phenomenon is well known in the rice industry, but neither is it completely understood. Additionally, the handling of rice flour dough in terms of sheeting, flattening and rolling is difficult due to the absence of gluten forming proteins (Dixit & Bhattacharya, 2015). Rice with higher amylose content or higher gelatinization temperature requires more water during cooking to achieve the same degree of doneness (Nishita & Bean, 1979). There was found that the digestion kinetics of different rice flour varieties was markedly retarded with increasing particle size (Farooq, Li, Chen, Fu, Zhang, & Huang, 2018). Data on effective moisture diffusivity of rice dough and bakery products are scarce compared with other foods (Hamdami, Monteau, & Le Bail, 2006). The knowledge of the moisture diffusivity is necessary for proper design and optimisation of food production cycle, including drying, rehydration, extrusion, packaging and storage (Zogzas, Maroulis, & Marinos Kouris, 1996). Starch association with water is realised via hydrogen bonding, where amylopectin was identified as responsible for swelling properties (Tangsrianugul, Wongsagonsup, & Suphantharika, 2019). There was found that the short branch chains of amylopectin are contributing to a more disordered packing of double helices, thus resulting in an easier swelling (Tangsrianugul, Wongsagonsup, & Suphantharika, 2019). Many experimental studies were focused on rheological behaviour of rice dispersions (Ye, Wang, Wang, Zhou, & Liu, 2016; Dixit & Bhattacharya, 2015; Mariotti, Manuela, Caccialanza, Cappa, & Lucisano, 2018; Shanthilal & Bhattacharya, 2015) as well. There was found gel-like viscoelastic behaviour with higher storage modulus compared to the loss modulus (Mariotti, Manuela, Caccialanza, Cappa, & Lucisano, 2018; Shanthilal & Bhattacharya, 2015). Steady-shear results showed that the brown rice flour exhibited a non-Newtonian shear-thinning behaviour (Yoo, 2006). There was found also the hysteresis loop flow curve behaviour, indicating occurrence of the dispersions´ strong thixotropic behaviour (Ye, Wang, Wang, Zhou, & Liu, 2016).

Our focus in this study was aimed on the characterization of the ability of rice flour variety to bind water and on determination, which rice flour and optimum water content are the most suitable for preparation of gluten free products. Our research would like to offer new data evidence for better understanding of the physico–chemical properties of rice flours dispersions, which are critical for effective manufacturing of gluten free products (Wu et al., 2019), based on the mutual close relation between rice dispersion microstructure and its particle size distribution (Zhou, Song, Zhang, Zhao, Hu, & Wang, 2019). As confirmed in the earlier studies (Takei, Maruyama, Washio, Watanabe, & Takahashi, 2019), the primary factor affecting the latter mentioned physicochemical properties are the rice variety and the locality of the raw rice material production, and the secondary factor are production conditions such as milling, kneading, thermal history and water content (Takei, Maruyama, Washio, Watanabe, & Takahashi, 2019).

2 Materials and methods

2.1 Rice flours material characteristics

Six types of rice flours were studied; namely red rice flour, black rice flour, brown rice flour, white sticky rice flour, semi-coarse rice flour and fine rice flour (all purchased from Adveni Medical, Czech Republic). All flours prior to experiments were stored in a dry place at the ambient temperature of (21 ± 1) °C. Basic material characteristics of studied rice flours are given in Table 1. Salt content was lower than 0.1 g/100 g for all samples under study.

2.2 Preparation of rice flour dispersions

For the preparation of rice flour dispersions, a Kitchen robot Spar Mixer SP–800A (SPAR Food Machinery Mfg., Taiwan), was used. This is a planetary type blender with the capacity of 7.6 l of mixture equipped with optional kneader geometry suitable for dough making. Dispersions of rice flour with drinking water were prepared at following weight concentrations of flour/water 0.6:1 (37.5 w.%) and 1:1 (50.0 w.%) respectively (at applied mixing rate of 132 rotations/min for 5 minutes time period). For all experiments drinking water characterized by conductivity of 25 mS/m was used. The quality of drinking water obeyed the EC COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Obtained dispersions of 0.6:1 w/w of stable consistency were suitable for mechanical testing. That is why these samples were used for further rheological analysis. For thermoanalytical measurements, the concentration 1:1 was chosen to observe thermal phenomena of studied samples, because the reduced amount of water is necessary for detection of thermal events. Samples were stored in the plastic bags at the ambient laboratory temperature of (25 ± 1) °C and at 40 % air relative humidity for 12 hours. The latter samples were then stored for additional 12 hours in the refrigerator at the temperature of (4 ± 1) °C.

2.3 Particle size analysis

For the particle size analysis of studied rice flours a vibratory sieve shaker Fritsch Analysette 3 (Fritsch, Germany) was used. Masses of individual fractions retained on sieves screens were determined (applied sieves screen mesh diameters were as follows: 0.56, 0.45, 0.32, 0.22, 0.16, 0.125, and 0.045 mm). The granulation of tested flours corresponds to granulation of fine flour (257 μm / 96 % to 162 μm / 75 %) and semi-coarse flour (366 μm / 96% to 162 μm / 75 %). Weight average particle radius (r_w) was calculated by the following formula: $r_w = \Sigma(r_i.w_i)$ from the particle size distribution, where r_i is the particle radius of the individual fraction and w_i is the weight fraction. Samples were stored in a dry form at the ambient laboratory temperature of (25 ± 1) °C and 40 % air relative humidity.

2.4 Moisture diffusivity and weight loss measurements

Thermogravimetric isothermal measurements (TGA) were performed on DTG 60 simultaneous thermal analyser (Shimadzu, Japan) (at constant temperature of (30.0 ± 0.1) °C for 100 min time scale). Measurements were performed under nitrogen atmosphere (nitrogen flow rate of 50 ml/min was applied). The samples weight was kept constant (25 ± 2) mg at the dispersion layer height of (2.0 ± 0.2) mm. As a reference, empty aluminium pans were used. Water diffusion/desorption processes were quantified by diffusion coefficient and by effective diffusivity D_{eff} (m^2/s) parameters (Vernon-Carter, Garcia-Diaz, Reyes, Carrillo-Navas, & Alvarez-Ramirez, 2017).

2.5 Moisture content and diffusion coefficient calculations

Moisture ratio (MR) parameter was calculated according to the formula (1):

$$MR = \frac{w - w_e}{w_0 - w_e}, \tag{1}$$

where w_0 is the initial weight and w_e the equilibrium weight of the sample. The w_e values were obtained from the drying curves of weight loss vs. time (static TGA) or temperature (dynamic TGA). *MR* value was determined when the sample weight became constant during the drying process.

Differential equation describing drying dynamics of foodstuffs matrix is given:

$$\frac{\partial MR}{\partial t} = \nabla\left[D_{eff}(\nabla MR)\right], \tag{2}$$

where t is the heating time and D_{eff} is the effective diffusivity. If assuming zero shrinkage of the samples and uniformity of the initial moisture content distribution, Eq. (2) allows calculation of the effective diffusivity. A simple approach based on mathematical solution of differential Eq. (2) provides the following approximation:

$$MR(t) \approx \frac{8}{\pi^2} exp\left(-\frac{\pi^2 D_{eff} t}{4L^2}\right), \tag{3}$$

where L is the characteristic sample length (Vernon-Carter, Garcia-Diaz, Reyes, Carrillo-Navas, & Alvarez-Ramirez, 2017). Plotting linear dependency of ln(MR) vs. time (from isothermal heating curve (at 30 °C)) gives slope of $k_{eff} = -\frac{\pi^2 D_{eff}}{4L^2}$, known as the effective diffusion coefficient. The value of k_{eff} was determined in the time interval 0-50 min of heating sequence, which corresponded to a satisfactorily high value of determination coefficient R^2 (no less than 98 %) of the linear dependence. According to the formula (4) (Vernon-Carter, Garcia-Diaz, Reyes, Carrillo-Navas, & Alvarez-Ramirez, 2017), the effective diffusivity was calculated for all samples as follows:

$$D_{eff} = -\frac{4L^2 k_{eff}}{\pi^2}, \tag{4}$$

2.6 Differential scanning calorimetry (DSC) analysis

DSC experiments were performed on differential scanning calorimeter DSC 1 (Mettler-Toledo, Switzerland) instrument (calibrated on indium standard for temperature correction). Approximately 15 mg of rice dispersion of the flour/water mass concentration 1 : 1 was inserted into the aluminium pan (ME-27331, 40 µl pan with pin) and hermetically sealed, empty pan was used as a reference. Under these conditions, the constant moisture level in the measuring pan was kept to evaluate the progress of rice starch gelatinization. Measurements were performed in the temperature range from 20 to 90 °C at the heating rate of 2 °C/min under air atmosphere. Thermally induced structural transitions in rice dispersions were characterized by T_o (onset), T_p (peak), and T_e (endset) temperatures. Enthalpy change associated with rice starch gelatinization was expressed as ΔH_g, and was determined according to the area under DSC curve and expressed in J/g of endothermic process detected in the temperature range of (T_e - T_o) ((Lapcikova, Buresova, Lapcik, Dabash, & Valenta, 2019).

2.7 Water absorption index (WAI) and water solubility index (WSI)

WAI and WSI were determined according to the method of (Kraithong, Lee, & Rawdkuen, 2018). Rice flours (1 g) were dispersed in 10 ml of distilled water and were mixed in a vortex mixer for 1 min. Dispersions were gently stirred and heated in a water bath at 30 °C for 30 min. Subsequently, the samples were centrifuged at 3000 rpm (AVANTI j- 30I centrifuge, Beckman, Germany) at laboratory temperature (25°C) for 10 min. Obtained supernatants were carefully poured into an aluminium moisture dish prior to the heat drying at 105 °C to the constant weight. Collected sediments were carefully weighed. WAI and WSI indices were calculated according to the formulae:

WAI(g/g) = Weight of wet sediment (g)/Dry weight of flour (g)

WSI (%) = Weight of dried supernatant (g)/Dry weight of flour (g) × 100 %

Each test was performed on dispersion samples prepared at three replicates. Observed results were represented as mean values and standard deviation.

2.8 Rheological measurements

For rheological measurements, the Discovery HR-1 rheometer (TA Instruments, USA) was used. It was equipped with 20 mm wide parallel steel plate sensor system (with 2 mm gap height) and Peltier type heating. Dynamic rheological data were collected at 25 °C by frequency sweep measurements at the angular frequency range starting from 0.1 to 100.0 rad s^{-1} and the strain of 0.01 %. There were calculated storage (G′) and loss (G′′) shear moduli. Each test was performed on dispersion samples prepared in three replicates. Observed results were represented as mean values and standard deviation.

2.9 Scanning electron microscopy (SEM) microstructure characterization

Scanning electron microscopy (SEM) was used to visualize shape and size of the studied lyophilized rice flour samples (Wu et al., 2019). The process of lyophilisation was employed to remove moisture content from rice flour samples. The freeze-dried samples were sputter coated with gold-palladium to make them electrically conductive. SEM images were captured using a Hitachi 6600 FEG microscope (Japan) operating in the secondary electron mode using an accelerating voltage of 1 keV.

2.10 Statistical data analysis

Data were analysed using one way analysis of variability (ANOVA) at significance level $P \leq 0.05$ to assess the differences in the mean values among statistical groups if they are greater than would be expected by a chance. Tukey´s test was used for pairwise comparisons (statistic ranking) of the mean responses to different treatment groups. Statistical software SigmaStat version 2.03 was utilized for data testing. All experiments were performed in triplicates.

3 Results and Discussion

3.1 Particle size distribution

Prior to thermal analysis and rheological measurements the particle size of the studied flours was determined by vibrational sieve analysis. It was based on the determined weight of individual rice flours fractions retained on sieves screens as shown in Fig. 1. Calculated weight average radiuses of studied flours are given in Table 2. The widest particle size distribution was found for White sticky (WS) flour with relatively even population of the fractions ranging from 0.0225 to 0.28 mm particles radius reflecting its polydisperse distribution of particles dimensions. The highest fraction of the fine particles was present in the Fine (F) (0.0225 mm to 0.0625 mm) rice flour. The highest fraction of the particles of 0.08 mm to 0.11 mm radius was found for Red (R), Black (B) and Semi-coarse (SC) rice flour samples and of 0.11 mm to 0.16 mm for White sticky (WS) and Brown (BRN) flours. The most narrow polydispersive character was found for the Semi-coarse (SC) sample having two main fractions between 0.0625 mm to 0.16 mm mesh radius. Fine flour (F) particles have the lowest value of weight average particle radius ($r_w = 67.4$ μm) followed by Black flour (B) ($r_w = 95.0$ μm) (Table 2).

The most coarsely grounded flours were the Brown (BRN) ($r_{w} = 143.8$ μm) flour and White sticky (WS) flour ($r_{w} = 124.3$ μm).

3.2 Measurements of water effective diffusivity and of moisture loss

Rice flour is relatively resistant to water molecules due to the complex system of rice flour composition (Arendt & Dal Bello, 2008). Water molecules are located between several phases, e.g. interphase regions between individual starch grains, rice proteins and other phases (Roozendaal, Abu-hardan, & Frazier, 2012). Because the migration of water molecules toward the vaporisation phase depends on the microstructure of the dispersion matrix, i.e. its stability and tendency for the phase separation. The release of water molecules from the rice flour dispersions was considered as a complex process. Furthermore, the molecular organisation of starch granules can be responsible for their different swelling kinetics and extent of starch gelatinization during the heating of samples (Farooq, Li, Chen, Fu, Zhang, & Huang, 2018). Thus, the interaction between particular starch network and water molecules is specific for various flour types, including the rice flour as well (Mariotti, M., Zardi, Lucisano, & Pagani, 2005).

As shown in Fig. 2, continuous isothermal heating (at 30 °C) of rice flour aqueous dispersions represents a process of drying kinetics which is closely tied up to the ability of rice flours to retain water molecules within their complex dispersion structure. As evident from the Fig. 2, the highest liberated water amount of about 52 w.% was observed for brown flour (BRN) dispersion. Brown flour dispersions are characteristic with the presence of relatively high ratio of starch particles of large dimensions, which are characteristic with their limited ability to retain water molecules inside their micro-structure. Calculated tangents of the kinetic curves shown in Fig. 2 read at the zero time (at the initial linear part of the dependency) are directly proportional to the water evaporation rates. Here again the highest evaporation rate was found for Brown (BRN) rise dispersions, followed by White sticky (WS) and Semi-coarse (SC) rice flour dispersions, thus indicating less stable dispersion structure accompanied with the relatively fast phase separation. In opposite to these, Black (B) and Fine (F) rice flour dispersions exhibited relatively mild kinetic process of moisture loss, suggesting that these flours are able to bind water molecules more tightly within their structure. This was interpreted by the presence of small size flour particles (as determined by sieve analysis (Fig. 1)) and small size starch granules (as determined by SEM analysis (Fig. 3)) in Fine (F) and Black (B) rice flours.

Results of the effective diffusivity coefficient (D_{eff}) measurements of water in the studied rice flour dispersions are given in Table 2. There was found the clear correlation between the obtained magnitudes of D_{eff} and flour´s particle size distributions: the lower the particle radius of the rice flour particles present in the dispersion, the lower effective diffusivity coefficient was observed, thus indicating stronger bonding of water in the gel like state of the starch granules. For this reason, the dispersions of Brown (BRN), White sticky (WS) and Semi-coarse (SC) flours showed relatively high values of water diffusivity ranging from 9.250×10^{-10} m^2/s (BRN sample) to 8.114×10^{-10} m^2/s (SC sample) as given in Table 2, because of their flour coarse character. On the other hand, Fine (F) and Black (B) rice flour dispersions were characteristic with the substantially lower D_{eff} of 5.030×10^{-10} m^2/s (F sample) and of 6.167×10^{-10} m^2/s (B sample) which might be related to their high phase stability indicating existence of the gel like structure in the system. Latter mentioned diffusivity data were in excellent agreement with the previous rice hydration experiments (Bhattacharya & Sowbhagya, 1971), indicating dominating effect of the surface area per unit weight of the rice on its swelling.

3.3 *Differential scanning calorimetry analysis*

Differential scanning calorimetry (DSC) was used gelatinization process characterization of the studied rice flour aqueous dispersions. Onset of the gelatinization temperature (T_o) was observed in the temperature range from 59.1 to 66.0 °C, the peak gelatinization temperature (T_p) between 64.4 and 70.2 °C, and the endset gelatinization temperature (T_e) in the temperature range of 68.3 to 82.3 °C (Table 3). It is well known, that the gelatinization temperature varies with variable composition of the rice flour varieties. It was ascribed to the varying saccharides and amylose content in the starch granules (Varavinit, Shobsngob, Varanyanond, Chinachoti, & Naivikul, 2003; Ye, Wang, Wang, Zhou, & Liu, 2016; Hu, Chen, Zhao, Chen, & Wang, 2020). Moreover, lipids and proteins contents, as well as milling process (Hasjim, Li, & Dhital, 2013) are directly affecting the average starch granules particle size as well as their crystallinity. These parameters significantly affect the starch gelatinization temperatures, as well as the gelatinization enthalpy (Leewatchararongjaroen & Anuntagool, 2016; Marco & Rosell, 2008; Suksomboon & Naivikul, 2006). Additionally to the above mentioned parameters, starch gelatinization is closely related also to the starch/water content ratio, amylose/amylopectin ratio, and applied heating rate (Figura, 2007; Fessas & Schiraldi, 2000; Qian & Zhang, 2013). It was found, that the higher amylose content or higher T_p required more water addition during cooking of rice products (Nishita & Bean, 1979).

For the Red (R) and the Semi-coarse (SC) flour dispersions, the values of T_o and T_p were shifted to relatively low temperatures due to the proceeding retarded process of starch gelatinization (Farooq, Li, Chen, Fu, Zhang, & Huang, 2018). A relatively high value of the endset gelatinization temperature of 82.3 °C was detected for Fine (F) flour dispersion, which was clearly distinct from T_e data of other samples (see Table 3). This phenomenon was interpreted as the confirmation of the occurrence of the prolonged gelatinization process. The small particle size of rice flour justifies lower gelatinisation temperature, because of large surface area available for binding of adjacent water molecules, as evident from the results of Red (R) and Fine (F) rice flours (see Table 2 and Table 3). Moreover, Fine (F) rice flour has a high ability to absorb water and swell, the factors, which might promote gelatinisation as well (Kraithong, Lee, & Rawdkuen, 2018). Brown (BRN) rice flour exhibited the highest T_p and the lowest gelatinization enthalpy due to the presence of the large flour and bran particles (Table 2).

Gelatinization enthalpy ΔH_g represents an endothermic effect of the thermal energy intake related to the molecular structure of dispersion and its ability to bind water. This is directly related to the swelling capacity of the individual starch granules. It was found in our previous study of wheat flour doughs that with increasing water content present in the system the corresponding gelatinization enthalpy ΔH_g increase as well (Lapcikova, Buresova, Lapcik, Dabash, & Valenta, 2019). The gelatinization enthalpy of rice flour dispersions varied in the range from 0.5 to 5.8 J/g per dry matter. These values were in agreement with ΔH_g determined by (Leewatchararongjaroen & Anuntagool, 2016) for dry-milled rice flours.

In comparison with the other studied samples, gelatinization enthalpy of White sticky (WS) rice flour was substantially lower of about 0.53 J/g per dry matter. This finding is in excellent agreement with the declared relatively low content of saccharides (in this sample of 42 w.%). Dispersion of White sticky (WS) flour was of incoherent structure characterized by the rapid phase separation. This was consistent with observed relatively high value of effective diffusivity, as given in Table 2. In other words, the diffusion of water molecules from the matrix of White sticky (WS) rice flour dispersion was relatively intense, as reflected in low plastification of starch molecules, thus in the limited process of starch gelatinization.

Brown (BRN) and Black (B) rice flours dispersions were characteristic with observed relatively low values of ΔH_g of 2.08 J/g and 2.41 J/g per dry matter. These low values were affected again by the chemical composition and by the capacity of water molecules retention within the dispersion structure. Because the main fraction of Brown (BRN) flour consisted of relatively large particles, the structure of Brown flour (BRN)/water dispersion was not able to retain water molecules in a sufficient amount, as confirmed by the observed highest D_{eff} of the studied samples (approx. 9.3×10^{-10} $m^2.s^{-1}$). Moreover, Brown (BRN) flour was characteristic also by the presence of bran particles in the flour, which were competing with starch granules present within the dispersion system for water molecules uptake. This might consequently lead to the lack of water molecules available for starch swelling (Ahmed & Al-Attar, 2015). This might explain observed relatively low value of ΔH_g of Brown (BRN) flour dispersion. In contrary to this, Black (B) flour dispersion exhibited relatively stable structure with a good retention of water molecules, owing to the presence of small flour particles. However, the content of saccharides declared by the producer was evidently lower (only 51 w.%) in comparison to the majority of the other rice flours studied. For this reason, the observed process of starch gelatinization was relatively mild in this case.

On the other hand, Semi-coarse (SC) and Fine (F) flours dispersions showed relatively high values of gelatinization enthalpy of 4.95 J/g and 5.80 J/g per dry matter, respectively. In the case of Semi-coarse (SC) flour, relatively high content of saccharides (79 w.%) was associated with the proceeding intensive process of starch gelatinization. For Fine (F) rice flour, the high content of saccharides (79 w.%) and presence of the high ratio of small flour particles enabled, to a large extent, the retention of water molecules inside the dispersion structure, which facilitated the swelling of the starch granules. As a result, a prolonged and energy intensive process of starch gelatinization characterized by observed high value of ΔH_g was detected.

3.4 Water absorption index (WAI) and water solubility index (WSI) measurements

WAI reflects the capability of rice flour to associate with water molecules (Kraithong, Lee, & Rawdkuen, 2018). The highest value of WAI was found for Fine (F) rice flour, reflecting the presence of the high number of hydrophilic groups within starch molecules in the system. As a result, this brings softness, smoothness and viscosity of the food products (Table 2). High contents of carbohydrates and proteins in Fine (F) rice flour tend to encourage a strong hydrogen bonding because of the presence of the polar or charged side chains (Prasad et al., 2012) in the chemical structure. Lower values of the WAI were found for White sticky (WS) and brown (BRN) rice flours. This behaviour attributed to the relatively large size of the individual particles. Similarly, this effect was found also for the Semi-coarse (SC) flour. There was found, that the water solubility index was the highest for Black (B) rice flour (6.13 %) followed by Red (R) (3.41 %) and Fine (F) (2.94 %) rice flours dispersions thus indicating the presence of the high amount of water soluble components in the aqueous phase (Kraithong, Lee, & Rawdkuen, 2018).

3.5 Scanning Electron Microscopy characterization

Results of the SEM analysis of the studied rice flours are shown in Fig. 3. There were identified granular starch structures, which were closely organized in irregular cube shape-like structures of about 55 μm width as observed for Fine (F), Black (B) and Red (R) flours, to about 75 μm for White sticky (WS), Semi-coarse (SC) and Brown (BRN) flours with larger bran particles in their structure. Based on the captured SEM images, there was obtained a clear evidence of the saccharide/lipid complex presence in the inter-starch space of the Black (B) rice flour as well as of the bran particles in the Brown (BRN) rice flour matrix. Our results correspond to the observations of Tangsrianugul et al. (Tangsrianugul, Wongsagonsup, & Suphantharika, 2019) who found a typical 5 μm diameter (of the circumscribed circle) rectangular starch granular structures of the Thai rice varieties. There was found polyhedral shape about 55 μm wide in diameter in rice flour samples studied (Tangsrianugul, Wongsagonsup, & Suphantharika, 2019).

3.6 Rheological measurements

Results of the rheological measurements are shown in Fig. 4. Studied samples of rice flour dispersions (0.6:1 w/w flour : water) exhibited pseudo-plastic flow behaviour. Mechanical properties of studied dispersions were characterized as both the solid-like typical for weak gels (sample Black (B)) and dissipative flow as well (samples Brown (BRN), Fine (F), Red (R), Semi-coarse (SC) and White sticky (WS). The point of gelation was determined in the frequency range of about 3 rad.s^{-1}. There was found for all samples exceeding loss modulus G´´ the storage modulus G´ in the frequency range from 0.1 to 3 rad.s^{-1}. The highest magnitudes of the storage modulus were found for Black (B) rice flour dispersions reflecting their elastic gel-like character due to the presence of higher amount of water soluble components in the aqueous phase as reflected in the observed highest value of the WSI index (6.13 %). This behaviour was different in comparison with the other rice flour dispersions under study. Observed differences in magnitudes of the storage modulus (G´) were minor at the angular frequencies exceeding 3 rad.s^{-1}. Here the organized structure of rice dispersions was destroyed by the high oscillatory frequencies accompanied by the appearance of the liquid enhancement (Wen-Xuan Hu, 2020). For Red (R) and White sticky (WS) rice flour dispersions water separation was observed during experimental measurements as well.

4 Conclusions

Suitability of the different rice flour types and different rice varieties for gluten-free products preparation was evaluated by water diffusivity, water solubility index, water absorption index, differential scanning calorimetry and rheological measurements. It was found, that the visco-elastic behaviour of the rice flour aqueous dispersions depends both on rice variety selection, the particle size of the flour and the amount of water used. Obtained water transport properties were reflecting differences in the intrinsic rice compositions. Two-stage kinetics of the water transport was confirmed by thermogravimetric measurements. It was found, that the flour granulation strongly affects water swelling behaviour of the rice flours. There were found closely organized granular starch structures in the form of the irregular cube shape by scanning electron microscopy measurements. The obtained water diffusivity coefficient was the highest for Brown (BRN) rice flour dispersion confirming its low water retaining capacity and indicating the presence of the water molecules as free water, thus allowing faster water evaporation. On the other hand, the lowest values of water diffusivity coefficient were obtained for Black (B) and Fine (F) flour dispersions reflecting their high water retention capacity. The latter conclusions were supported also by obtained water absorption index data, where the highest water absorption index was found for Fine (F), Red (R) and Black (B) rice flours dispersions indicating their ability to associate with water molecules. There was found, that the water solubility index was the highest for Black (B) rice flour dispersions followed by Red (R) and Fine (F) flours dispersions indicating presence of the high amount of water soluble components in the aqueous phase. This indicates their increased potential to form higher adhesiveness and higher stickiness in the final food product. That is why, for the preparation of the gluten free products the use of the Black (B) and Fine (F) rice flours in the mass ratio of 0.6 : 1 (flour : water) seems to be the most advantageous due to their better ability to retain water in their structure in comparison with the other rice varieties under this study.

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Figures caption

Fig. 1. Weight fraction of the remaining particles on the sieve mash radius of the studied rice flours as obtained by sieve analysis.

Fig. 2. Observed thermogravimetric patterns of rice flour dispersions (1:1 rice flour/water mass concentration) measured at (30.0 ± 0.2) °C under air atmosphere.

Fig. 3. SEM images of the lyophilized rice flours studied. Inset: sample identification.

Fig. 4. Observed frequency sweep patterns of shear storage (G´) and loss (G´´) moduli of the studied rice flour dispersions of 0.6 : 1 flour/water mass concentration (37.5 w.%). Measured at the temperature of 25 °C in the frequency range from 0.1 to 100 rad/s at 1 % deformation strain. Inset: samples labelling.

Table caption

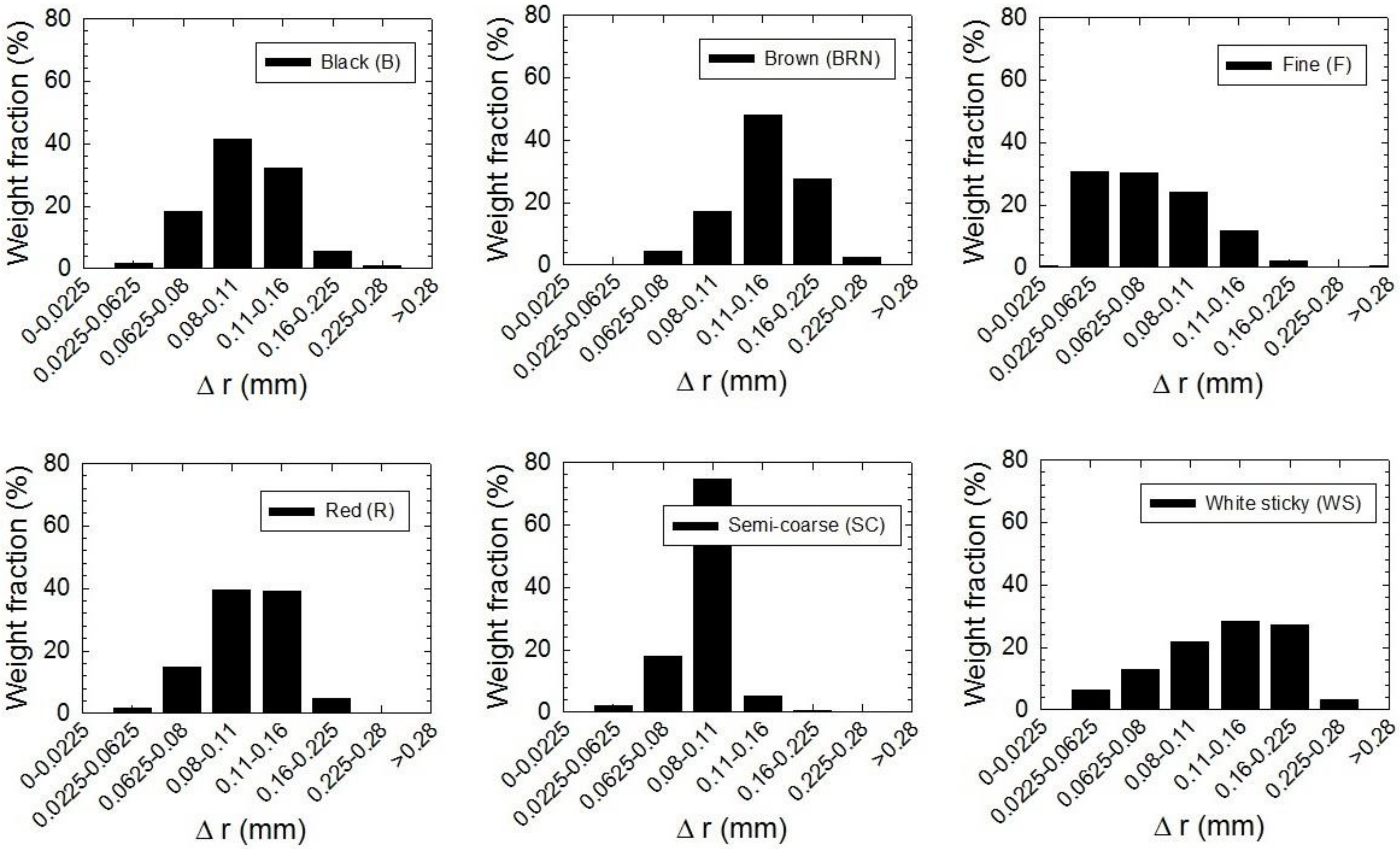
Table 1. Samples labelling and the nutritional values of studied rice flours related to 100 g of the products according to manufacturer´s data sheet (Adveni Medical, Czech Republic).

Table 2. Particle size of rice flours, effective diffusivity of flour dispersions (1:1 rice flour/water mass concentration) and water solubility of rice samples.

Table 3. DSC results of studied rice flour dispersions (1:1 flour/water mass concentration) performed in the temperature range from 20 to 90 °C.

Credit Author Statement

Barbora Lapcikova: Funding acquisition; Investigation; Methodology; Data curation; Formal analysis; Roles/Writing - original draft. **Lubomir Lapcik:** Conceptualization; Data curation; Formal analysis; Funding acquisition; Investigation; Methodology; Writing - original draft; Writing - review & editing. **Tomas Valenta:** Investigation; Software; Data curation; Formal analysis. **Petr Majar:** Investigation. **Kristyna Ondrouskova:** Investigation; Data curation.



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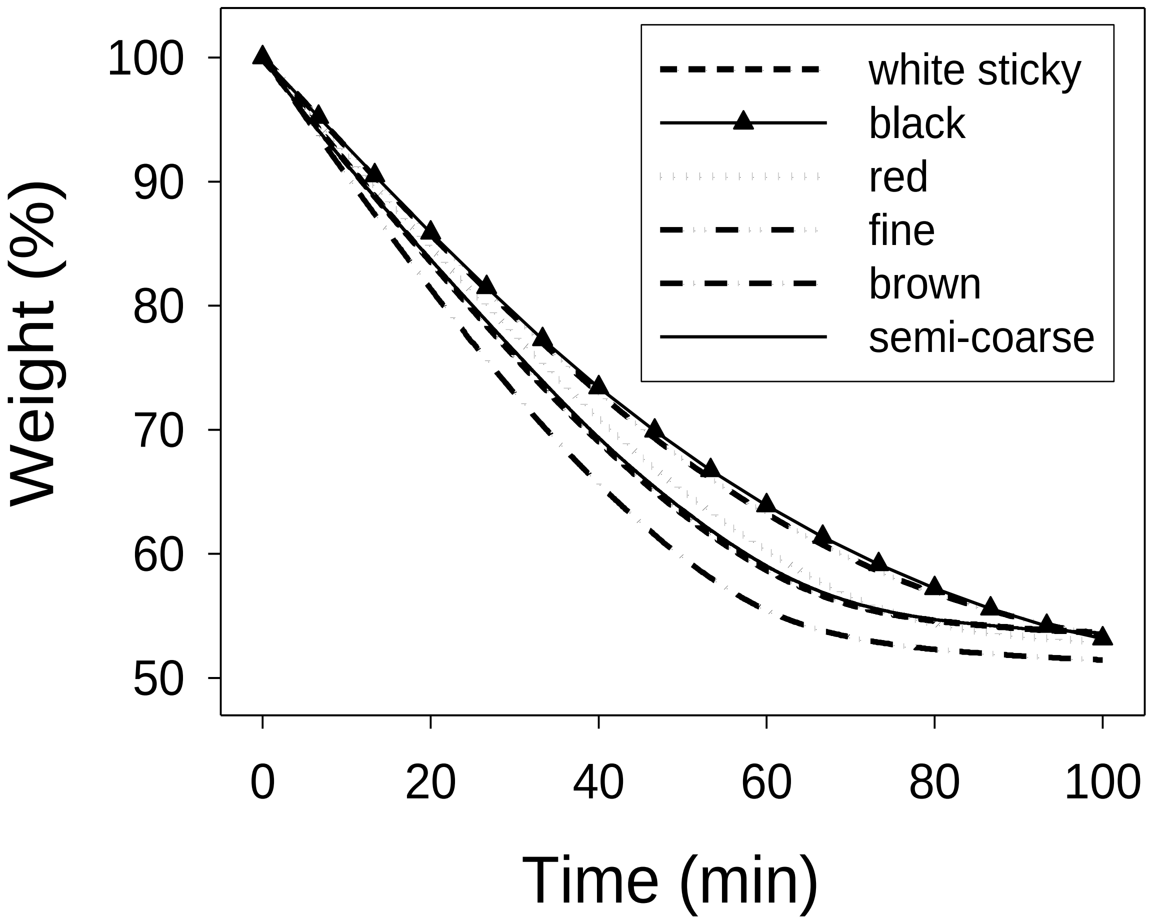

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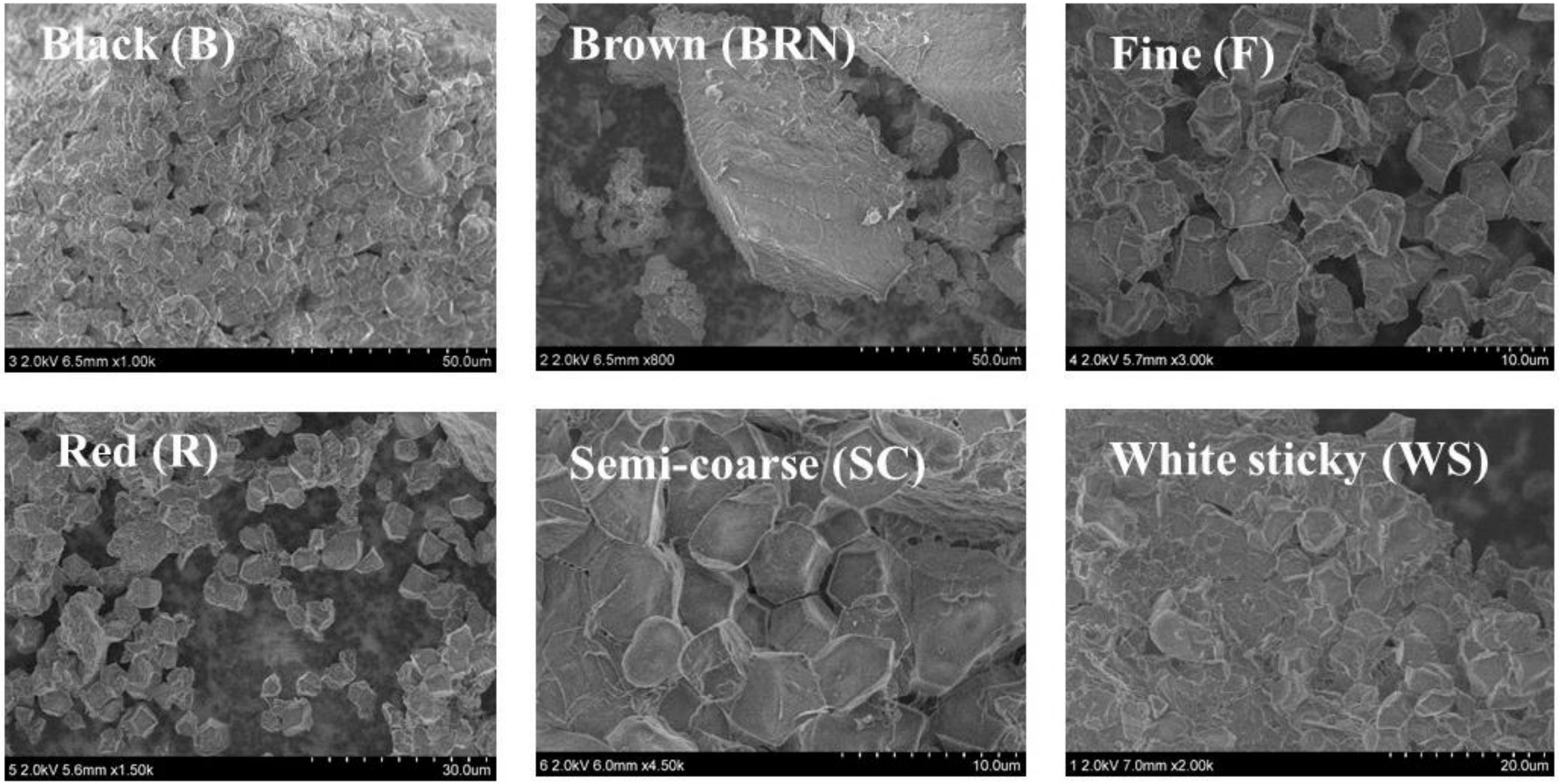

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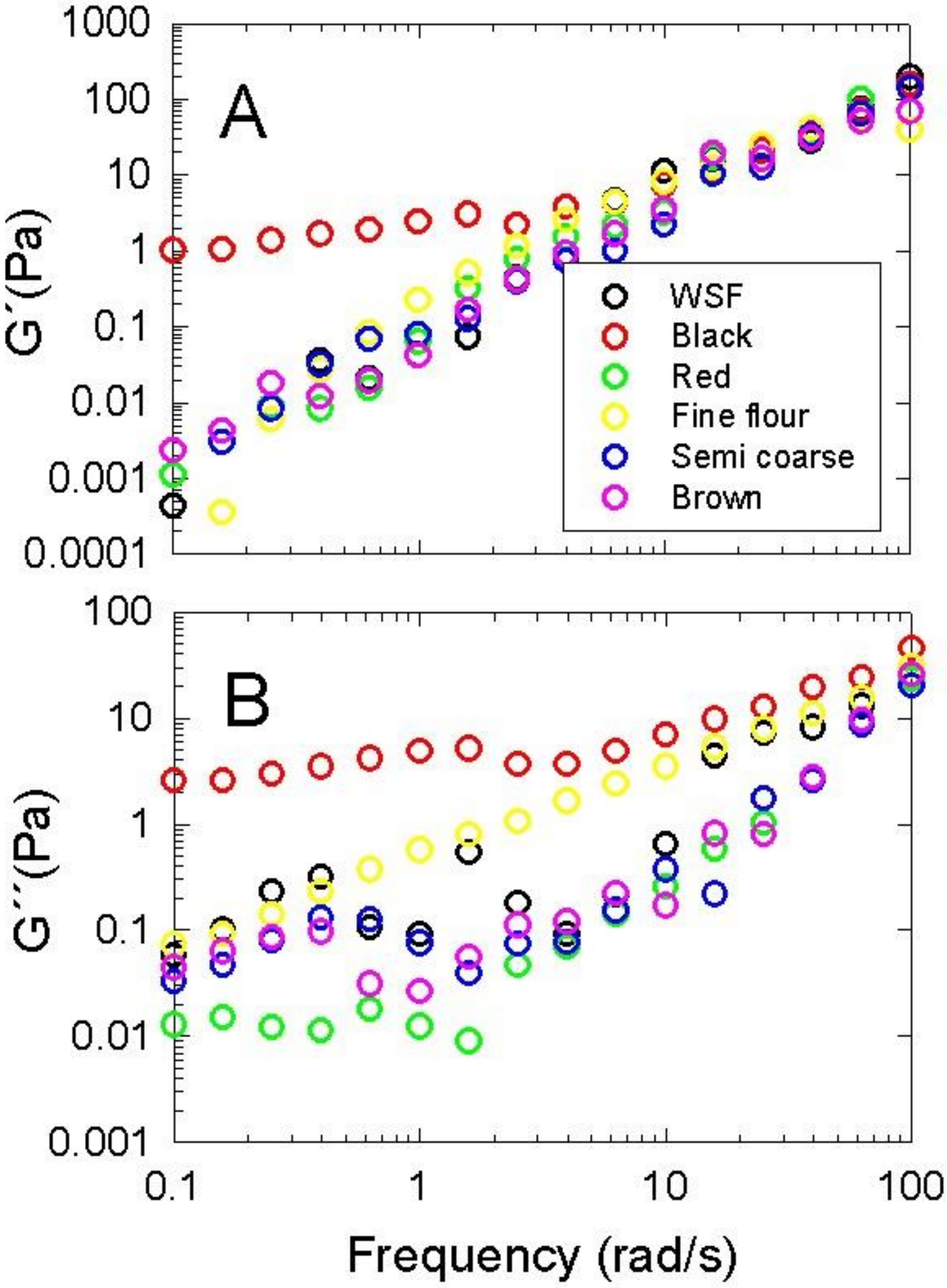

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Table 1. Samples labelling and the nutritional values of studied rice flours related to 100 g of the products according to manufacturer´s data sheet (Adveni Medical, Czech Republic).

Rice flour type (Labelling)	Dietary Energy (kJ)	Saccharides /Sugars (g/g)	Proteins (g)	Lipids (g)
Black (B)	1207	51 / 0	< 0.01	9.2
Brown (BRN)	1578	80 / 0	7.4	2.5
Fine (F)	1484	79 / 0	7.0	0.6
Red (R)	1502	74 / 0	10	2.0
Semi-coarse (SC)	1484	79 / 0	7.0	0.6
White sticky (WS)	797	42 / 0.2	4.0	0.4

Table 2. Particle size of rice flours, effective diffusivity of flour dispersions (1:1 rice flour/water mass concentration), water absorption index and water solubility of rice samples. [*]

Rice flour type	r_w [**] (µm)	D_{eff} [**] (m^2/s)	WAI [**] (g/g)	WSI [**] (%)
Black (B)	95.0	$(6.167 \pm 0.068)\times10^{-10\ a}$	2.42 ± 0.05^{a}	6.13 ± 0.38^{a}
Brown (BRN)	143.8	$(9.250 \pm 0.101)\times10^{-10\ b}$	2.31 ± 0.05^{a}	2.75 ± 0.03^{b}
Fine (F)	67.4	$(5.030 \pm 0.055)\times10^{-10\ c}$	2.76 ± 0.10^{c}	2.94 ± 0.07^{c}
Red (R)	107.1	$(7.140 \pm 0.083)\times10^{-10\ d}$	2.53 ± 0.08^{d}	3.41 ± 0.30^{d}
Semi-coarse (SC)	104.1	$(8.114 \pm 0.091)\times10^{-10\ e}$	2.38 ± 0.04^{a}	1.27 ± 0.21^{e}
White sticky (WS)	124.3	$(8.276 \pm 0.097)\times10^{-10\ e}$	2.30 ± 0.06^{a}	2.85 ± 0.10^{c}

[*] Values are expressed as mean ± standard deviation (n = 3); means within a column (the difference between the different rice flour types) followed by different superscript letters differ significantly ($P < 0.05$); each tested parameter was evaluated separately.

[**] Abbreviations are r_w – weight average particle radius; D_{eff} - effective diffusivity; WAI - water absorption index; WSI - water solubility index.

Table 3. DSC results of studied rice flour dispersions (1:1 flour/water mass concentration) performed in the temperature range from 20 to 90 °C.*

Rice flour type	T_o** (°C)	T_p** (°C)	T_e** (°C)	ΔH_g** (J/g)	ΔH_g (dry)** (J/g)
Black (B)	64.4 ± 0.3 ^{a}	69.2 ± 0.2 ^{a}	74.6 ± 0.2 ^{a}	1.12 ± 0.07 ^{a}	2.41 ± 0.07 ^{a}
Brown (BRN)	66.0 ± 0.4 ^{b}	70.2 ± 0.1 ^{b}	75.6 ± 0.4 ^{b}	0.99 ± 0.03 ^{b}	2.08 ± 0.10 ^{b}
Fine (F)	61.7 ± 0.3 ^{c}	67.1 ± 0.2 ^{c}	82.3 ± 0.5 ^{c}	2.86 ± 0.06 ^{c}	5.80 ± 0.09 ^{c}
Red (R)	59.3 ± 0.1 ^{d}	64.4 ± 0.3 ^{d}	68.3 ± 0.2 ^{d}	1.75 ± 0.07 ^{d}	3.66 ± 0.06 ^{d}
Semi-coarse (SC)	59.1 ± 0.1 ^{d}	65.3 ± 0.2 ^{e}	73.6 ± 0.2 ^{e}	2.50 ± 0.08 ^{e}	4.95 ± 0.07 ^{e}
White sticky (WS)	63.5 ± 0.2 ^{e}	67.7 ± 0.1 ^{f}	68.6 ± 0.1 ^{d}	0.25 ± 0.03 ^{f}	0.53 ± 0.02 ^{f}

* Values are expressed as mean ± standard deviation (**n = 6**); means within a column (the difference between the different rice flour types) followed by different superscript letters differ significantly ($P < 0.05$); each tested parameter was evaluated separately.

** Abbreviations are ΔH_g - gelatinization enthalpy; ΔH_g (dry) - gelatinization enthalpy per dry matter; T_o - onset gelatinization temperature; T_p - peak gelatinization temperature; T_e - endset gelatinization temperature.

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White sticky (WS)	63.5 ± 0.2 ^{e}	67.7 ± 0.1 ^{f}	68.6 ± 0.1 ^{d}	0.25 ± 0.03 ^{f}	0.54 ± 0.02 ^{f}

* Values are expressed as mean ± standard deviation (**n = 3**); means within a column (the difference between the different rice flour types) followed by different superscript letters differ significantly ($P < 0.05$); each tested parameter was evaluated separately.

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Highlights

There was analyzed water diffusivity in the variety of rice flours.

Effect of particle granulometry and rice variety was followed by rheology testing.

DSC quantified effect of flour coarseness on starch gelatinization temperature.

SEM imaging confirmed complex character of starch rice flour granules.