

Effects of gamma radiation on the thermoanalytical, structural and pasting properties of black rice (*Oryza sativa* L.) flour

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Abstract The effects of different doses of gamma radiation on the thermoanalytical, structural and pasting properties of black rice (*Oryza sativa* L.) flour were studied using thermogravimetry and derivative thermogravimetry (TG–DTG), differential scanning calorimetry, X-ray diffraction (XRD), field emission gun–scanning electron microscopy (FEG–SEM) and pasting properties (RVA) analysis. The thermogravimetric curves showed four mass losses. A small displacement was observed for the second loss, which occurred for the irradiated flours, compared to the control sample. The irradiated samples showed a slight decrease in the thermal parameters: initial temperature (T_o), peak temperature (T_p) and gelatinisation enthalpy (ΔH). All the black rice flours exhibited A-type crystallinity pattern, and the gamma radiation did not change the XRD patterns or the degree of crystallinity. The micro-images obtained using FEG–SEM showed a composite of organic and heterogeneous material; after gamma radiation, some changes occurred, such as cracks, pores and smaller fragments. The pasting properties decreased significantly with irradiation. The decrease in setback and breakdown viscosity after irradiation suggested an indication that it may be possible to improve the quality of food

based on black rice flours. Gamma radiation can be a useful tool to modify rice flours in order to suit various functionalities and to help meet the growing demands of the food industry.

Keywords Black rice · Irradiation · Thermal analysis · Gelatinisation · Morphology · Crystallinity

Introduction

Rice is one of the most widely consumed foods in the world, feeding almost one-third of the world's population [1]; it represents a major source of energy owing to its high concentration of starch and proteins, as well as containing minerals and B vitamins [2]. In recent years, pigmented rice varieties, such as black rice, have received increased attention from researchers and have become popular with consumers, due to their health-promoting properties [3].

Black rice contains high amounts of phenolic compounds, such as anthocyanins, which are associated with numerous health benefits due to their antioxidant activity; they also help to reduce the risk of developing chronic diseases such as cardiovascular disease, type II diabetes, obesity and cancer [4]. The natural colourants found in black rice, which can be used in the food industry as synthetic dye replacements, are dark purple anthocyanin pigments. Consequently, this pigmented rice can be used as a valuable ingredient for gluten-free cereal products with higher nutritional value, thereby providing extra health benefits to consumers.

Starch, which is the main carbohydrate present in rice, can be used to confer texture, structure and consistency to many food products. However, the uses of native starches are limited by their low solubility, high viscosity, thermal

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decomposition and high retrogradation tendency [5]. Thus, conventional sources of flours and starches (such as wheat, corn and rice) are modified to suit the specific needs of industries by adapting their physicochemical and functional properties, which are not available in their native form [6, 7]. Chemical modification is commonly used but there is also a growing trend for the physical modification of starch [8].

Food irradiation represents an effective and environmentally friendly technology [9] that is aimed at improving food safety. In recent years, this technique has been widely researched. Its effects are known to preserve, reduce microbial load or sterilise, thereby increasing the shelf life of products and above all maintaining food quality. Its efficacy and safety are proven by official agencies including the Food and Agricultural Organisation (FAO), International Atomic Energy Agency (IAEA) and the World Health Organisation (WHO) [10].

Furthermore, irradiation has been used as a physical method to modify flours and starches in order to replace chemical or enzymatic modifications. According to Bhat and Karim [11], gamma radiation can alter the molecular structures, mainly of starch, causing its fragmentation by the penetration of ionising energy into the granules [12].

Starch plays an important role in the properties of rice and rice products. Gamma irradiation can provide different characteristics for rice flour, which need to be studied according to the final properties obtained. To date, there are few studies in the literature regarding the effect of irradiation on the degree of crystallinity, morphology, viscosity and thermal properties of pigmented rice varieties. Thus, the aim of this study was to understand the effects of gamma radiation on the thermoanalytical, structural and pasting properties of black rice flour.

Experimental

Materials and sample preparation

The black rice used in the experiments was purchased in the local supermarket in the city of Curitiba (25° 25' 40" S 49° 16' 23" W), Paraná, Brazil. The samples were ground and sieved through 60 mesh (particle size up to 250 µm) to obtain the black rice flour (BRF). This flour was separated and vacuum-packed in samples of about 200 g in small non-toxic metallic polyester bags with hermetic sealing and with light protection. The BRF had 10.64% moisture, 76.20% carbohydrate, 9.61% protein, 2.15% fat, 4.32% total dietary fibre and 1.41% ash, based on dry matter. All the samples were stored at 25 °C for further analysis.

Radiation of the BRF

The black rice flour was subjected to gamma radiation at doses of 0, 1, 2 and 3 kGy at 0.221 kGy h⁻¹ dose rate. The irradiation source was Cobalt 60 (Gammacell Excell 220 - MDS Nordion), which was located in the Centre for Nuclear Energy in Agriculture at the University of São Paulo, Brazil (CENA/USP). Harwell Amber 3042 dosimeters were used to measure the radiation dose, and the uncertainty dose was less than 1% [13].

Thermal analysis

The thermogravimetric and derivative thermogravimetric curves (TG/DTG) were obtained as previously described [14] using a TGA-50 thermal analysis system (Shimadzu, Japan) under an oxidative atmosphere (synthetic air) flow of 150 mL min⁻¹ with a heating rate of 10 °C min⁻¹ from 30 to 600 °C. The initial sample mass was about 6 mg, which was weighed in open alumina crucibles. All the mass loss percentages were determined using TA-60WS data analysis software.

The DSC curves were recorded according to Hornung et al. [15], using a DSC-Q200 model thermal analysis system (TA-Instruments) under airflow of 50 mL min⁻¹ and at a heating rate of 10 °C min⁻¹. Each sample (approximately 2.5 mg) was weighed directly in an aluminium crucible, and a volume of distilled water was added (1:4 w/v) using a micropipette. The crucible was hermetically sealed and allowed to equilibrate for 60 min before testing. In order to obtain the DSC curves, the instrument was calibrated with 99.99% purity standard indium, m.p. = 156.6 °C, $\Delta H = 28.71 \text{ J g}^{-1}$, and an empty aluminium crucible was used as reference. TA Universal Analysis 2000 software was used to analyse the main endotherm of the DSC curves for the initial (T_o), peak (T_p) and conclusion (T_c) temperatures, as well as the gelatinisation enthalpy (ΔH). The measurements were performed in triplicate.

Morphological analysis

The micro-images were obtained using a field emission gun-scanning electron microscope (FEG-SEM) (MIRA 3, Tescan, Czech Republic). The parameters were as follows: reading scale of 5 and 50 µm with a tension of 15 kV of field emission gun, which was generated by a lamp with a tungsten filament. The black rice flour samples were pulverised over a carbon tape. As flour is not conductive, it was necessary to metallise the samples with gold and palladium to promote the passage of electrons and to obtain the images using Image J software (Image J 1.47 to WindowsTM) [16].

X-ray diffractometry (XRD)

The X-ray diffractograms (XRD) were obtained using an X-ray diffractometer (Ultima IV, Rigaku, Japan) with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), a tension of 40 kV and an electric current of 30 mA. The analysis was performed at 20 °C in an angular range of 5–40° (2θ), scanning speed of 2° min^{-1} and a step of 0.02° . Equation (1) was used to calculate the relative crystallinity [7].

$$X_c = \frac{A_p}{(A_p + A_b)} \times 100 \quad (1)$$

where X_c refers to the relative crystallinity; A_p refers to the crystallinity area of the X-ray diffractogram and A_b refers to the amorphous area of the diffractogram.

Pasting properties

Prior to determining the pasting properties of each sample, it was necessary to determine their moisture content in order to calculate the exact amount of dry matter to prepare a suspension with 8% of flour. An infrared moisture analyser (Sartorius AG, MA35 M, Germany) was used for the moisture determination. The pasting properties of the black rice flour samples were determined using a RVA-4 viscoamylograph (Newport Scientific Pvt. Ltd., Australia). A total mass of 28 g of the flour suspension was submitted to a controlled heating and cooling cycle under constant stirring, where it was held at 50 °C for 2 min, heated from 50 to 95 °C at 6 °C/min and held at 95 °C for 5 min, cooled to 50 at 6 °C/min and held at 50 °C for 2 min [17].

Statistical analysis

The results are expressed as the mean \pm standard deviation and were analysed using STATISTICA 10 software (Stat-Soft Inc., Tulsa, OK, USA). One-way analysis of variance was used to study the effect of the gamma radiation on DSC, X-ray diffraction and pasting properties. Tukey's tests were conducted to determine differences between the means at 95% confidence level ($p < 0.05$). Pearson's products (r) were used to evaluate the strength of correlation between the response variables [10].

Results and discussion

Thermogravimetry and derivative thermogravimetry (TG/DTG)

Thermogravimetry is a thermoanalytical technique where the mass variation of a substance that is subjected to a

controlled temperature variation is evaluated. The data that are obtained make it possible to study the decomposition of the matter and the periods of thermal stability [18]. The TG/DTG curves are presented in Fig. 1.

Flour is a complex mixture of different components, such as starch, non-starch polysaccharides, lipids, sugars, minerals and proteins, which influence its industrial use [19]. In addition, black rice flour contains a high content of fibres, minerals and phytochemicals, which are mainly flavonoids and anthocyanins [4]. These components present specific temperature ranges of thermal decomposition; thus, it is possible degradation occurs during different mass loss steps, which are detected by thermogravimetry.

Four mass losses were detected for the black rice flour samples, different from the characteristic behaviour of thermal decomposition of starches, which usually involves only three steps [16, 17]. A slight displacement was observed for the second loss which occurred for the irradiated flours, compared to the control sample (0 kGy). The values obtained from the TG/DTG curves are shown in Table 1.

The first loss occurred at similar temperatures for all the samples and corresponded to the loss of water and volatile compounds, as discussed by Bet et al. [16].

A slight increase in the thermal stability range was observed for the irradiated sample at a dose of 2 kGy (until 189 °C). The second loss, with a mass loss between 4.01 and 4.56%, started soon after the stability and was related to the thermal-oxidative decomposition, mainly of lipids [20]. The peak temperatures calculated by DTG were between 213 and 216 °C, corresponding to the maximum rate of loss. Darfour et al. [21] reported that after the irradiation of cowpea meal at doses between 0.25 and 1.5 kGy, the flour had a greater capacity to absorb oil. In the present study, this may have been associated with the second loss, where there was an increase in the temperature range in which this event occurred in relation to the control sample.

The third and fourth losses referred to the decomposition and oxidation of organic matter, as reported by Lopes et al. [22], and occurred at similar temperatures for the control flour and the flours subjected to gamma irradiation. Corradini et al. [23] have suggested that the degradation of compounds such as fibres, proteins, cellulose (310–360 °C) and hemicellulose (240–310 °C) occurs during the third step. In addition, as pointed out by Beninca et al. [24], the depolymerisation of the starch chains that make up the flours occurs. The final residue contents after the thermal decomposition (ash) of the black rice flour were 1.41% for the control sample (0 kGy) and 1.48, 1.40 and 1.68% for the samples submitted to gamma radiation at doses of 1, 2 and 3 kGy, respectively.

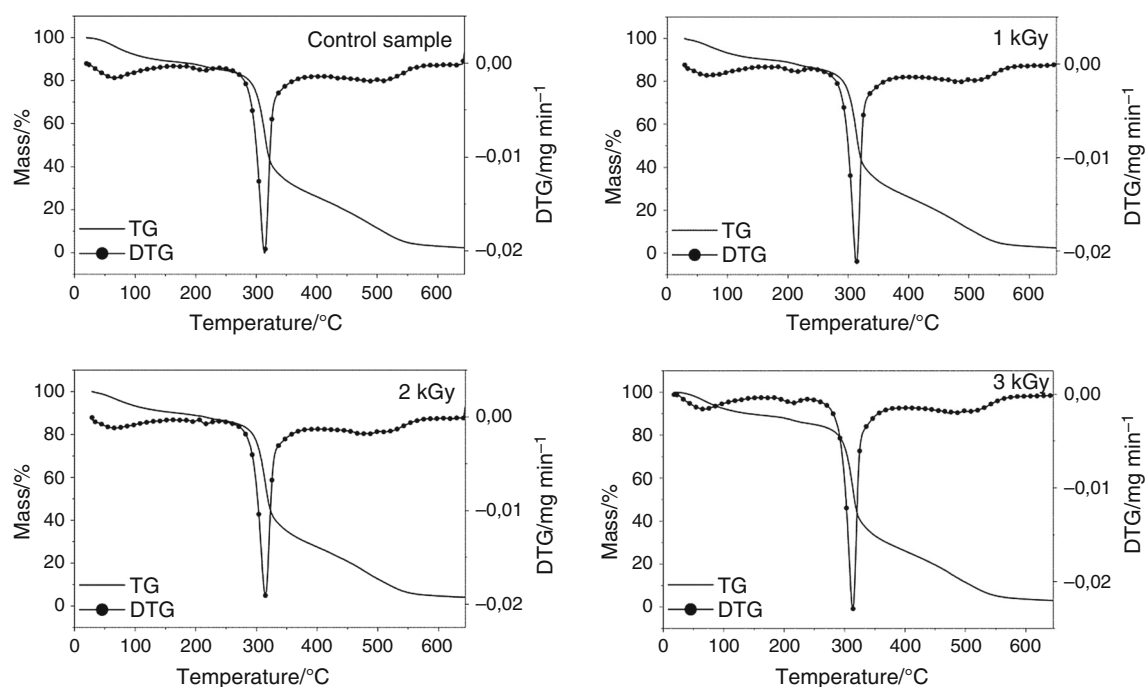


Fig. 1 TG/DTG curves of untreated and irradiated samples of black rice flour

Table 1 TG/DTG results of untreated and treated samples of black rice flour

| Samples | TG results | | DTG results | |
|----------------|------------|---------------|---------------------------|----------------------|
| | Step | $\Delta m/\%$ | $\Delta T/^\circ\text{C}$ | $T_p/^\circ\text{C}$ |
| Control sample | 1st | 10.64 | 30–148 | 67.13 |
| | Stability | – | 148–186 | – |
| | 2nd | 4.01 | 186–238 | 214.06 |
| | 3rd | 61.79 | 238–406 | 313.93 |
| | 4th | 22.15 | 406–593 | 488.06 |
| 1 kGy | 1st | 9.08 | 30–144 | 71.00 |
| | Stability | – | 144–183 | – |
| | 2nd | 4.56 | 183–244 | 213.56 |
| | 3rd | 62.64 | 244–404 | 313.51 |
| | 4th | 22.24 | 404–592 | 487.64 |
| 2 kGy | 1st | 9.14 | 30–146 | 67.35 |
| | Stability | – | 146–189 | – |
| | 2nd | 4.32 | 189–247 | 216.21 |
| | 3rd | 61.75 | 247–394 | 314.60 |
| | 4th | 23.39 | 394–593 | 472.41 |
| 3 kGy | 1st | 10.07 | 30–145 | 69.03 |
| | Stability | – | 145–184 | – |
| | 2nd | 4.41 | 184–240 | 215.38 |
| | 3rd | 61.35 | 240–400 | 313.54 |
| | 4th | 22.49 | 400–597 | 472.29 |

Δm mass loss/%, ΔT temperature range, T_p peak temperature

Differential scanning calorimetry (DSC)

Starch is an ingredient widely used in food systems to impart better texture, consistency and viscosity; it is the main component found in rice and confers important characteristics in the use of this cereal in a process known as gelatinisation [12]. This phenomenon can be studied using DSC to study the temperatures and the enthalpy involved in this endothermic event.

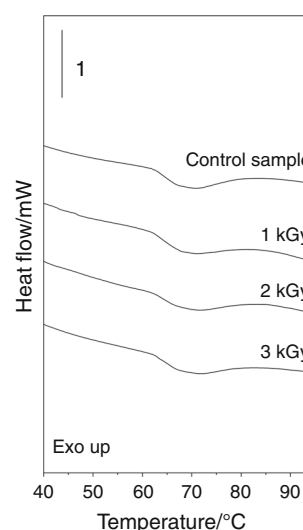


Fig. 2 DSC curves of untreated and irradiated samples of black rice flour

The DSC curves of the black rice flour samples are presented in Fig. 2. All the samples showed slight changes in the thermal parameters (T_o , T_c , T_p , and ΔH). For the irradiated samples (1, 2 and 3 kGy), T_c remained unchanged ($p > 0.05$), whereas T_o , T_p and ΔH displayed a slight decrease when compared to the control sample (0 kGy) (Table 2).

The dose of 1 kGy showed the lowest T_o (62.1 °C) and T_p (68.4), whereas the control sample (0 kGy) displayed the highest T_o (62.5 °C) and T_p (69.7 °C). Regarding the behaviour of ΔH , it decreased continuously with the increase in the irradiation dose ($p < 0.05$). Bao et al. [12] also concluded that the ΔH decreased in white rice flour after gamma irradiation. The enthalpy value was reported to decrease in wheat starches [25]. Rombo et al. [26] studied different flours and concluded that a decrease in required energy may have been due to the difference in starch granule sizes, or possibly to a difference in polymer chain lengths of the starch.

In the present study, the gamma irradiation caused a rupture in the black rice flour components, promoting a small variation in the gelatinisation temperature of the starch fraction. The samples submitted to 1 and 2 kGy presented a slight decrease in the onset temperature (T_o). The reduction in the gelatinisation temperature is due to the cleavage of the amylopectin, which results in short chains and a reduction in the crystalline phase [27].

A slight decrease in the crystallinity, although without significant difference ($p > 0.05$) in relation to the non-irradiated flour shown by XRD (Table 2), may also have influenced the decrease in the gelatinisation enthalpy that was observed for the irradiated samples, which was due to the loss of the crystalline domain and double helices [6]. Furthermore, the ΔH and crystallinity parameters showed a positive correlation ($r = 0.84$), suggesting that ΔH was influenced by the crystallinity of the starch [28].

X-Ray diffractograms (XRD)

The X-ray diffractograms (Fig. 3) were used to verify the main peaks and to calculate the relative degree of crystallinity (%) of each sample (Table 2). All the samples had clear A-type diffraction patterns with main reflections at $2\theta \approx 15^\circ$, 17° , 18° and 23° . Minor peak intensities were also observed at $2\theta \approx 20^\circ$ and 27° . According to Ocloo et al. [29], this peak observed at $2\theta \approx 20^\circ$ indicates the presence of some V-type starch crystals in rice varieties.

In the present study, the gamma irradiation did not change the XRD patterns of the black rice flours, which was in agreement with other studies, such as [12] with white rice flour [29], with rice cultivars from Ghana [6], with rice starch and [5, 30] with cornstarch.

The non-irradiated flour showed a relative crystallinity higher than values reported for rice flour by Yu et al. [31]. Those authors reported that the differences found in the degree of relative crystallinity could have been associated with the presence of other components in the flour, such as proteins and lipids.

The relative crystallinity values obtained for the analysed samples ranged from 19.7 to 23.1% (Table 1). All the irradiated flour samples (1, 2 and 3 kGy) had decreased crystallinity compared with that of the non-irradiated flour sample (0 kGy). Chung and Liu [30] found lower crystallinity values with increasing doses of gamma radiation, and they attributed this fact to breaks in the crystalline regions inside the starch granules. However, the present study did not find significant ($p > 0.05$) effects of gamma irradiation on the relative crystallinity of the black rice flour samples.

According to Polesi et al. [6], many studies have found varying results for crystallinity. Irradiation degrades both the crystalline structure and the amorphous region of the starch granules, which leads to an increase or decrease in crystallinity depending on which region is most affected by

Table 2 DSC and relative crystallinity results of untreated and treated samples of black rice flour

| Sample | DSC gelatinisation | | | | XRD |
|--------|----------------------|----------------------|----------------------|---|------------------------------------|
| | $T_o/^\circ\text{C}$ | $T_p/^\circ\text{C}$ | $T_c/^\circ\text{C}$ | $\Delta H_{\text{gel}}/\text{J g}^{-1}$ | Degree of relative crystallinity/% |
| 0 kGy | 62.5 ± 0.04^a | 69.7 ± 0.23^a | 77.8 ± 0.30^a | 4.4 ± 0.12^a | 23.1 ± 0.05^a |
| 1 kGy | 62.1 ± 0.03^b | 68.4 ± 0.47^b | 77.3 ± 0.82^a | 3.7 ± 0.37^b | 22.5 ± 3.41^a |
| 2 kGy | 62.2 ± 0.05^b | 69.7 ± 0.09^a | 77.6 ± 0.15^a | 3.3 ± 0.07^b | 21.2 ± 0.60^a |
| 3 kGy | 62.5 ± 0.06^a | 68.6 ± 0.17^b | 77.1 ± 0.10^a | 3.3 ± 0.05^b | 19.7 ± 2.08^a |

T_o “onset” initial temperature, T_p peak temperature, T_c “endset” conclusion temperature, ΔH_{gel} gelatinisation enthalpy, the degree of crystallinity was calculated as a percentage, and peaks are determined in 2θ

Averages followed by the same letters in the same column do not differ statistically by Tukey’s test ($p < 0.05$)

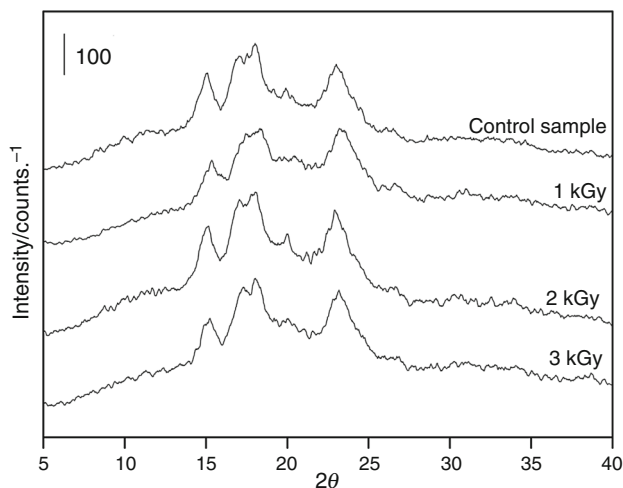


Fig. 3 X-ray diffraction patterns of untreated and irradiated samples of black rice flour

each dose. In addition to the botanical source, the dose rate plays an important role in crystallinity because greater recombination occurs among the starch molecules at low dosage rates [30].

Field emission gun–scanning electron microscopy (FEG–SEM)

The micro-images in Fig. 4 show an organic and heterogeneous composition, with particle agglomerates presenting irregular shapes and sizes that are characteristic of the samples of black rice flour. For the non-irradiated sample (0 kGy), the black rice flour was characterised by having a continuous structure with the starch granules surrounded by protein bodies and embedded in a cementing matrix [32]. Some changes occurred after gamma radiation such as cracks, pores and smaller fragments.

In the control sample (0 kGy), the particles were larger, and surface cracking increased in line with increasing radiation doses; at the doses of 1, 2 and 3 kGy, there was an accumulation of smaller fragments, which resulted from cracks, pores and irregularities on the surface.

Ashwar et al. [33] reported that cracks on the surface could be due to the effect of highly energetic and penetrating gamma radiation. These changes were associated with free radicals generated by gamma irradiation cleaving the glycosidic linkages of the large starch molecules, and some starch granules were fractured along the cleaved molecules, which may contribute to the formation of dextrin [34]. This kind of breakage resulted in increased numbers of small-sized particles in samples of the black rice flour.

Pasting properties

The pasting properties of the non-irradiated and irradiated black rice flour samples are presented in Fig. 5. Significant ($p < 0.05$) differences in the pasting properties were found in terms of temperature, peak viscosity, setback, breakdown and final viscosities in all the samples (Table 3). These results agreed with previous reports of the effects of irradiation on the pasting properties of flours made with rice cultivars [12, 29].

In the present study, the pasting properties decreased continuously with the increase in irradiation dose, except for the pasting temperature, which proportionally increased with the gamma radiation (Table 3). The pasting temperature was negatively correlated with peak, break, setback and final viscosity, which was in line with a previous study by Singh et al. [28]. Free radicals generated during the modification by irradiation of flour can promote the cleavage of the amylose and amylopectin glycosidic bonds, which are major components of starch, reducing its molecular mass and consequently decreasing the paste viscosity, thereby requiring higher temperatures for the formation of gel [6]. As found by Singh et al. [28], the pasting temperatures were higher than the T_o obtained by DSC.

The decrease in these characteristic features (peak viscosity, setback, breakdown and final viscosities) of black rice flour samples after gamma irradiation can be associated with partial depolymerisation of the rice starch molecules due to chain ruptures [29]. This can be correlated with the results found by microscopy and X-ray powder diffraction analysis. According to Chung and Liu [30], a reduction in peak viscosity after irradiation might be due to the degradation of starch after irradiation, as well as the reduction in its swelling power.

Liu et al. [5] reported that the breakdown viscosity provides an indication of the stability of starch pastes and the tendency of starch granules to resist shear force during the heating process. However, the higher breakdown viscosity of the irradiated flour samples might indicate a disruption or weakening of the bonding forces (hydrogen bonds) in the starch granules [35].

According to Bhat et al. [35], the decrease in setback and final viscosities mainly occurs due to the reordering or polymerisation of leached amylose and amylopectin. This might decrease due to the degradation, as well as the shortening of the amylopectin branch chains. It is worth noting that setback and final viscosities are important parameters for the food industry. The lower viscosities of the studied samples suggest that irradiated black rice flours could be used in infant foods, for example.

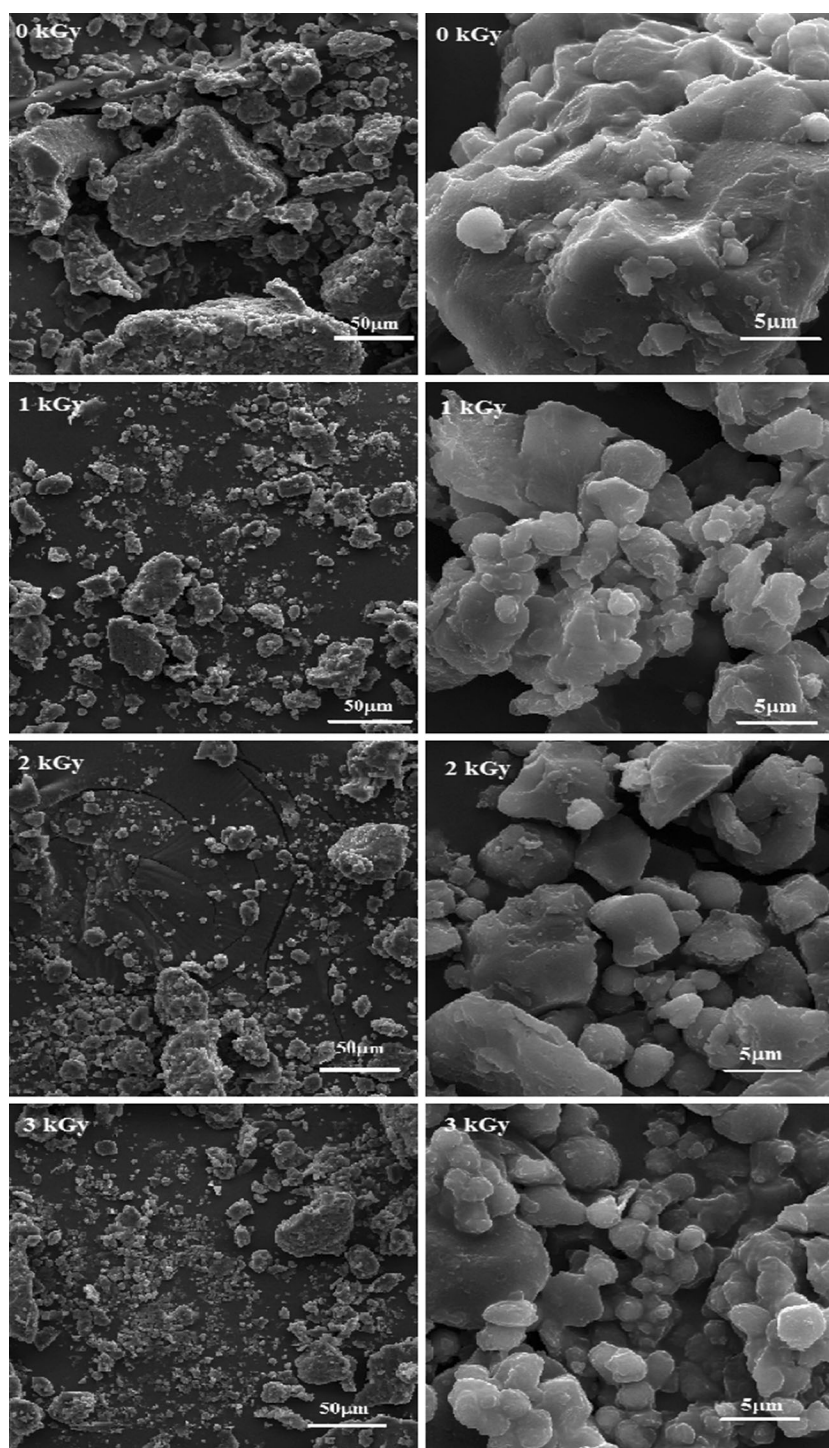


Fig. 4 FEG-SEM micro-images of untreated and irradiated samples of black rice flour

Conclusion

The effects of gamma radioisotope ^{60}Co on black rice flour were investigated considering thermoanalytical, structural and pasting properties. The thermogravimetric curves showed four mass losses. A small displacement was

observed for the second loss, which occurred for the irradiated flours compared to the control sample. All the samples showed slight changes regarding thermal parameters (T_o , T_c , T_p and ΔH). For the irradiated samples, the T_o , T_p and ΔH displayed a small decrease.

Fig. 5 RVA pasting curves of untreated and irradiated samples of black rice flour

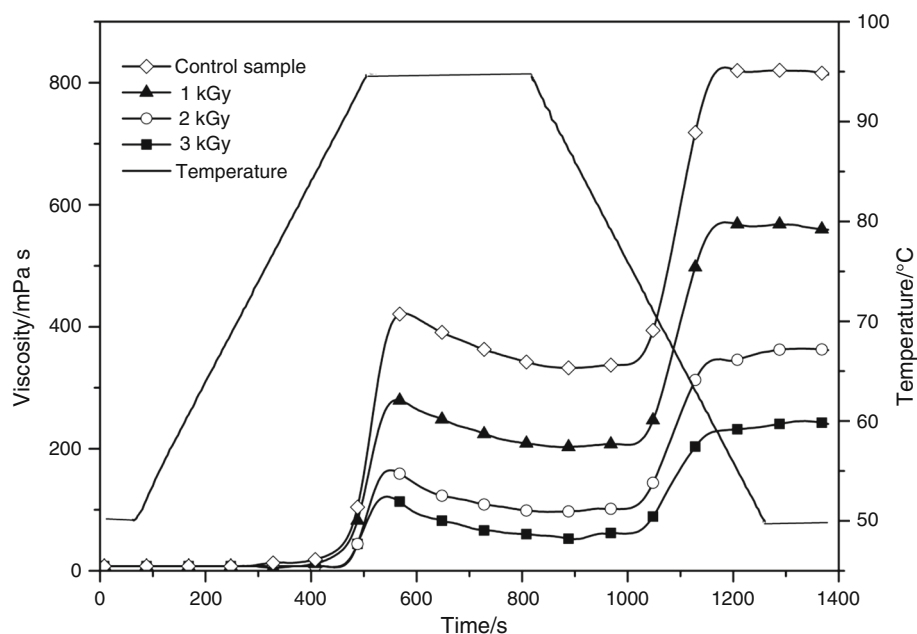


Table 3 RVA results of untreated and treated samples of black rice flour

| Sample | Pasting temperature/°C | Viscosity peak/mPa s | Setback/mPa s | Break/mPa s | Final viscosity/mPa s |
|--------|---------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| 0 kGy | 92.9 ± 0.21 ^c | 422 ± 2.82 ^a | 481 ± 0.41 ^a | 90 ± 1.20 ^a | 813 ± 0.21 ^a |
| 1 kGy | 93.7 ± 0.28 ^{bc} | 281 ± 1.41 ^b | 358 ± 0.40 ^b | 80 ± 1.40 ^b | 559 ± 0.25 ^b |
| 2 kGy | 94.8 ± 0.27 ^{ab} | 166 ± 2.83 ^c | 267 ± 0.28 ^c | 71 ± 1.21 ^{bc} | 362 ± 0.28 ^c |
| 3 kGy | 95.0 ± 0.28 ^a | 124 ± 1.21 ^d | 191 ± 0.08 ^d | 74 ± 2.12 ^c | 241 ± 0.58 ^d |

mPa s “millipascal-second”, s “second”

Averages followed by the same letters in the same column do not differ statistically by Tukey’s test ($p < 0.05$)

All the black rice flours exhibited A-type crystallinity pattern, and the gamma radiation did not change the XRD pattern or the degree of crystallinity. The micro-images obtained using FEG–SEM showed a composite of organic and heterogeneous material: after gamma radiation, some changes occurred such as cracks, pores and smaller fragments. The pasting properties (viscosity) decreased significantly with irradiation. The decrease in setback and breakdown viscosities after irradiation suggested the possibility of improving the quality of foods based on black rice flours.

Gamma radiation can be a useful tool to modify rice flours to suit various functionalities and to help to meet the growing demands of the food industry. Black rice is known as a potential source of anthocyanins, as well as being used as a natural colourant. This study showed that flours from gamma-irradiated black rice have the potential to be used in food formulations that require low viscosity such as porridges and infant foods. However, it also can be a valuable ingredient in gluten-free, cereal products with

higher nutritional value, thereby providing extra health benefits to consumers.

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