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Physicochemical characterization of irradiated arrowroot starch

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ABSTRACT

The term arrowroot is used for the starch obtained from the rhizomes of *Maranta arundinacea*. In the present work effects of ^{60}Co radiation treatment (dose up to 15 kGy) on structural characteristics and pasting properties of arrowroot starch were evaluated. Thermal properties, granule size and shape and size distribution, by means of optical and scanning electron microscopy and Fourier transform IR (FTIR) spectra were also obtained. On pasting properties strong decrease in peak and final viscosities, as well as breakdown, were observed. In the dose range applied, minimal changes in crystallinity, molecular composition and structure of arrowroot starch were found.

1. Introduction

Arrowroot or araruta (*Maranta arundinacea*) is a tropical herb probably native to South American rainforest habitats from which a very fine and extremely white flour is extracted. It has a 7.7% protein content and their starch contains 21.9% amylose and 62.3% amylopectin (Aprianita et al., 2014).

There are numerous applications of ionizing radiation on food safety (Inamura et al., 2012). Also, the action of radiation treatment on most commercially important starches is well documented (Sujka et al., 2015; Teixeira et al., 2018). Except by an investigation about X-ray diffraction patterns of arrowroot starch (Barroso et al., 2019, in press), this starch was seldom studied. Arrowroot starch presents great potential for multiple applications in the food industry as it is highly digestible and gluten-free, and can be use by people with dietary restrictions (Jyothi et al., 2009). The objective of this work was to establish physicochemical and structural characteristics of arrowroot starch when treated by ionizing radiation in the dose range mostly applied for dried food products.

2. Material and methods

2.1. Material

Arrowroot or araruta starch was obtained from local food market as a fine powder.

2.2. Irradiation

Starch samples were gamma irradiated in polyethylene bags, at doses of 0–15 kGy, dose rate about 1 kGy h^{-1} using a ^{60}Co Gammacell 220, Atomic Energy of Canada Ltd (AECL), dose uniformity factor of 1.13 at room temperature.

2.3. Fourier transform infrared spectroscopy (FTIR)

Arrowroot starch was characterized using a FTIR spectrometer (Nicolet iS50 FT-IR); samples were prepared using the attenuated total reflection standard (ATR). Spectra were recorded in transmission mode from 4000 to 650 cm^{-1}, with spectral resolution of 4 cm^{-1}, at room temperature. Spectra were averaged over 32 scans.

2.4. Particle size distribution

The particle size of arrowroot starch granules was determined using a Nikon Eclipse 80i microscope. Samples of 100 mg of starch were dispersed in 10 mL water by using ultrasound (Hielscher's ultrasonicator model UP50H, 50 W, 30 kHz) at room temperature for 1 min, avoiding the swelling of the granules. Digital image analysis (IA) coupled with light microscopy was used to determine starch size distributions where the volume of granules was calculated as spherical particles. A magnification of 40x was employed for granules observation using a NIS-Elements software for the analysis.

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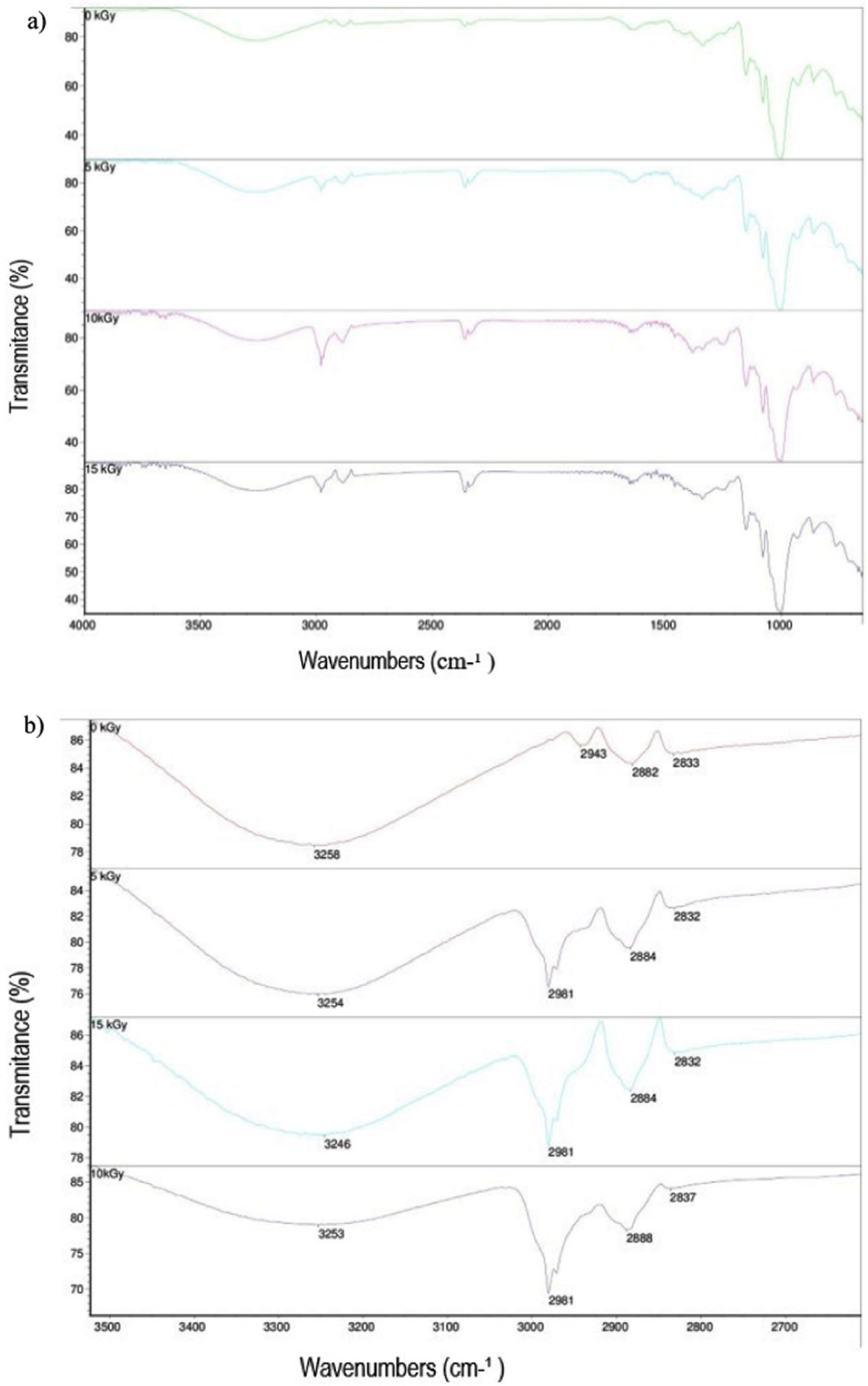

Fig. 1. a) FTRI spectra of arrowroot starch samples. b) Spectrum zoom image.

2.5. Morphology

The granules were observed by scanning electron microscopy (SEM Hitachi, TM3000) suspended in a carbon tape and previously coated with a fin layer of gold. The microphotographs were subjected to an accelerating analyse mode.

2.6. Differential scanning calorimetry (DSC)

The heat flow curves for the starches under study were determined using a DSC 6000 Perkin Elmer differential scanning calorimeter. Arrowroot starch was weighed in aluminum pan and mixed with distilled water in ratio 1:1. A sample weight of approximately 6,5 mg was packed and sealed hermetically. An empty aluminum pan was used as

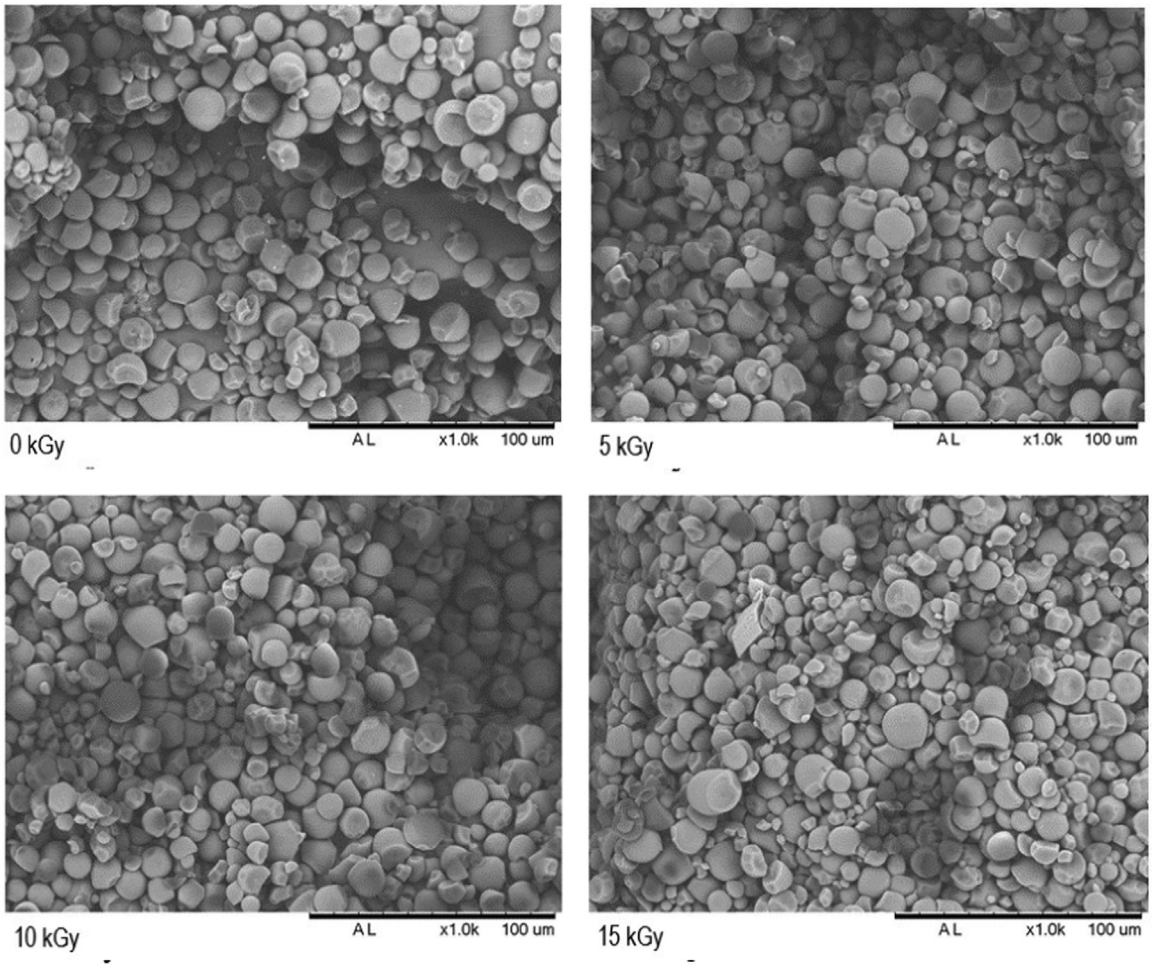

Fig. 2. SEM images of control and irradiated arrowroot granules.

Table 1
Granule size (mean ± SD) versus absorbed dose.

Absorbed dose (kGy)	Mean Diameter (μm)	N*
0	$28.7^{a} \pm 8.6$	1333
5	$24.7^{b} \pm 6.6$	2284
10	$27.5^{c} \pm 8.5$	3025
15	$24.6^{b} \pm 7.3$	3368

* N indicates the number of granules measured. Values with different superscripts are different statistically ($p < 0.05$).

Table 2
Differential scanning calorimeter (DSC) parameters for irradiated (0–15 kGy) arrowroot starch.

Sample	DSC Parameters			
	T_{onset} (°C)	T_p (°C)	T_{endset} (°C)	ΔH (J/g)
Control	63.9^{a}	71.0^{a}	81.3^{a}	4.2^{a}
5 kGy	66.5^{b}	74.0^{b}	84.7^{b}	22.0^{b}
10 kGy	66.7^{c}	74.0^{c}	83.9^{c}	23.4^{c}
15 kGy	67.9^{d}	74.1^{d}	83.9^{d}	22.3^{d}

Values with different superscripts (a, b, c and d) within each column are significantly different ($p < 0.05$).

reference. Pans were heated from 0 to 200 °C at a scanning rate of 10 °C/min, under a flow of dry N2 (50 mL/min). Thermal events such as onset (To), peak (Tp), final (Tf) temperatures and enthalpy gelatinization (ΔH) were determined from the thermograms. The enthalpy of gelatinization (ΔH) was expressed per gram of dry starch.

2.7. Thermogravimetric analysis (TGA)

The arrowroot starch was characterized by TGA using a thermogravimetric analyser (Artisan Technology Group, TA Instrument SDT Q600), under a flow of air dry (100 $mL.\ min^{-1}$). The samples (5,0 mg) were weighed in a platinum and heated from 25 to 450 °C at a rate of 20 $°C.\ min^{-1}$. The TGA curves were determined by means of the Universal Analysis 2000 software provided by TA Instruments.

2.8. Pasting properties

The pasting properties were determined using a Rapid Visco Analyser RVA-4500, Perten Instruments, and a Thermocline program for Windows version 3, according to Ferrari et al. (2005).

2.9. Statistical analysis

The data reported are the average of triplicate observations and expressed as means ± standard deviations (SD) or standard error of the mean (SEM) when adequate. The data were subjected to one-way analysis of variance (ANOVA) with a significance level of 5% and Tukey's test was applied to determine the differences between the means. For this purpose, the software Minitab 18 was used.

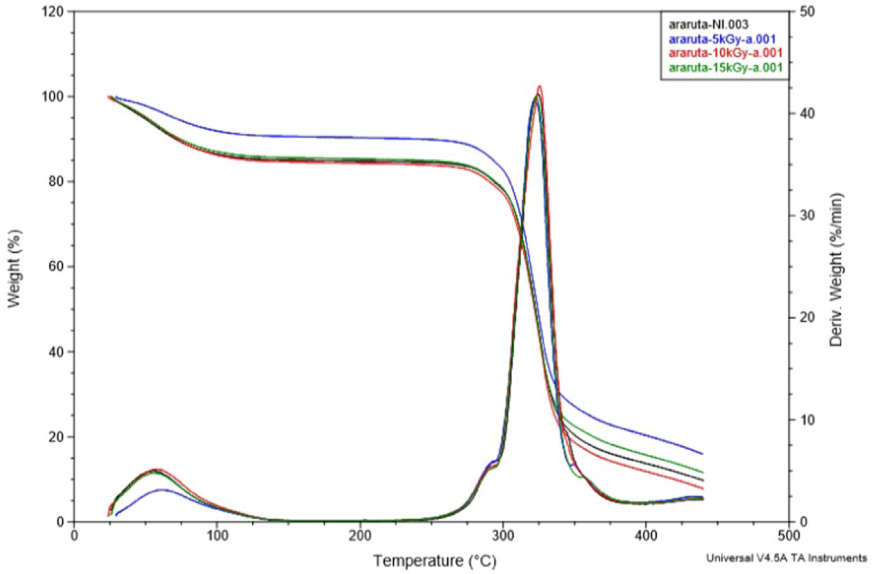

Fig. 3. TGA thermograms of irradiated arrowroot starch samples.

Table 3
Pasting properties of irradiated (0–15 kGy) arrowroot starches (means ± SD of triplicates). Values with different superscripts (a, b, c and d) within each line are significantly different ($p < 0.05$).

Parameters/Doses	0 kGy	5 kGy	10 kGy	15 kGy
Pasting Temp. (°C)	$67.2^{b} \pm 0.2$	$68.1^{a} \pm 0.2$	$68.3^{a} \pm 0.1$	$68.3^{a} \pm 0.1$
Peak Viscosity (RVU)	$173.1^{a} \pm 0.3$	$146.9^{b} \pm 0.3$	$110.5^{c} \pm 0.9$	$82.0^{d} \pm 1.0$
Final Viscosity (RVU)	$57.6^{a} \pm 1.9$	$22.0^{b} \pm 0.1$	$9.6^{c} \pm 0.1$	$5.4^{d} \pm 0.1$
Breakdown (RVU)	$124.8^{a} \pm 1.4$	$130.2^{b} \pm 0.3$	$101.6^{c} \pm 1.0$	$77.0^{d} \pm 1.2$
Setback (RVU)	$9.2^{a} \pm 0.6$	$5.3^{b} \pm 0.1$	$0.7^{c} \pm 0.0$	$0.5^{c} \pm 0.0$

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

Arrowroot starch treated with different gamma radiation doses were analyzed by FTIR spectroscopy (Fig. 1). The spectra did not change substantially upon irradiation, although the zoom image indicates the presence of a peak at 2981 for irradiated samples inexistent in the non-irradiated ones, remaining uncertain whether the new peak could be revealing the transformation of any specific functional group (Fig. 1b). An extremely broad band at 3200 cm^{-1} was ascribed to O-H stretching vibrations. Li et al. (2018), studying maize starch, also observed that the band referred to the O-H group decreases with increasing dose, attributing this fact to the action of gamma radiation inducing chemical changes in starch macromolecules and decreasing their ordered structure (Dar et al., 2018; Noor et al., 2018). The absorption band in the region 1336 cm^{-1} is a bending of the carboxylic group CO_2. Bands in the spectra region between 950 and 810 cm^{-1} were associated C-O-C vibrations (Gordillo et al., 2014).

3.2. Optical and scanning electron microscopies

The morphology and the granule size distribution were studied through scanning electron microscopy (SEM) and optical microscopy respectively, as granule size, size distribution and shape are among the most important factors of starches from different origins. It is observed spherical shape as predominant format of the granules of both native and irradiated arrowroot starch, with smooth surfaces, few irregularities and no porosities (Fig. 2).

Mean granule diameter for the unirradiated samples was 28.7 μm; the irradiated ones presented a slight decrease in size with the absorbed dose. The samples irradiated with 5 kGy and 15 kGy presented unexpectedly no differences among them (Table 1). The size and shape of granules are generally quite variable among starches. Present results are in agreement with the report from Peroni et al. (2006). They found that the average size of granules from tuber and root starches varies from 13.9 to 42.3 μm.

As Chung and Liu (2009) pointed out, radiation is able to break starch macromolecules disrupting crystalline and especially amorphous regions of the granules. The fine structure of amylose and amylopectin as crystalline components could influence the supramolecular arrangements in the starch that could affect the granule size (Perez and Bertolf, 2010). Barroso et al. (2017) had already reported that the relative crystallinity of irradiated arrowroot starch increased slightly but no significantly with irradiation. They found crystalline index of 29.0 ± 1.6; 30.6 ± 1.0; 29.5 ± 1.0 e 29.5 ± 1.2 for araruta starch samples irradiated with 0, 5, 10 e 15 kGy respectively, being that effect more noticeable at the lower dose assayed, 5 kGy. Anyway, radiolysis of solids with small absorbed dose like those applied in the present study was not expected to lead to stronger structural changes.

3.3. Thermal analysis

The results of the differential scanning calorimetry (DSC) with endothermic profiles of arrowroot starch are displayed in Table 2. The gelatinization temperatures, when the granules begin to swell, increased with the radiation dose as well as the enthalpy. It is well known that during gelatinization the processes involved are granule swelling, crystal or double helical melting, and amylose leaching. Lower enthalpy values were associated with higher levels of amylose (Hernandez-Medina et al., 2008) and usually endothermic enthalpy and final gelatinization temperature measured by differential scanning calorimetry correlated negatively with amylose content. The increase of the enthalpy could indicate a degradation of the amorphous part of the starch after the irradiation, as validated by XRD results (Barroso et al., 2017).

Fig. 3 shows the thermogravimetric analysis (TGA) spectra of arrowroot starch irradiated with doses from 0 to 15 kGy. All samples presented three main weight loss regions (Valencia et al., 2012). The first region in the 23–140 °C temperature range is attributed to water evaporation. The second and third events were attributed to the thermal degradation of starch. It is in this second event that the largest

loss of starch mass occurs (about 68%) and the degradation begins around 250 °C. Samples irradiated at 10 kGy and 15 kGy did not present significant differences in mass loss when compared to the control, but the sample irradiated with 5 kGy presented a small deviation, which occurred in other analyses as well (Barroso et al., 2017).

3.4. Pasting properties

The humidity content of arrowroot starch was 13.1 ± 0.2 and remained almost unchanged after the irradiation process. It is well known that amylose contents and amylopectin branch chain length distributions affect the pasting properties of starch. The results obtained from triplicate assays of rapid visco analyser measurements of irradiated arrowroot starch can be visualized in Table 3.

The peak viscosity of the samples decreased with the increase of radiation dose. All the samples presented this acute peak, characteristic of granules with structural homogeneity, typical of arrowroot starch. The samples presented a high breakdown value, indicating low pulp stability and brittleness of the granules (Ferrari et al., 2005). When the temperature is lowered, the dissociated amylose and amylopectin polymers begin to re-associate by increasing the viscosity, called setback. With the increase of the radiation dose the tendency for retrogradation was diminished, indicating the degradation of starch macromolecules, reduction of the crystallization capacity and disruption of molecular structures (Valencia et al., 2012). It was observed that the final viscosity of all samples decreased with increasing radiation dose. Setback and final viscosity probably correlated with amylose content. It must be considered that in the present case, oxidation, as air was present during irradiation, may be playing also a significant role as other radiolytic effects on radiation-induced pasting properties changes.

4. Conclusions

The radiation treatment with doses up to 15 kGy of arrowroot starch produced some modifications on starch granules. All irradiated samples presented size distribution differences in relation to the unirradiated ones. The FTIR spectra presented the same characteristic bands, with small variations in band intensities as a result of irradiation. There was an increase in the enthalpy that is probably due to the degradation of the amorphous part of the starch after irradiation, but thermogravimetry showed no differences in mass loss. The high breakdown value in pasting properties indicates low stability of the arrowroot starch granule, and the low setback value indicates a low tendency to retrograde, important characteristic for cold and frozen foods.

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