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Comparison of gamma radiation effects on natural corn and potato starches and modified cassava starch

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ABSTRACT

The objective of this work was to evaluate the effect of irradiation treatment on physicochemical properties of three natural polymers, i.e. native potato and corn starches and a typical Brazilian product, cassava starch modified through fermentation -sour cassava- and also to prepare composite hydrocolloid films based on them. Starches were irradiated in a ^{60}Co irradiation chamber in doses up to 15 kGy, dose rate about 1 kGy/h. Differences were found in granule size distribution upon irradiation, mainly for corn and cassava starch but radiation did not cause significant changes in granule morphology. The viscosity of the potato, corn and cassava starches hydrogels decreased as a function of absorbed dose. Comparing non-irradiated and irradiated starches, changes in the Fourier transform infrared (FTIR) spectra in the 2000–1500 cm^{-1} region for potato and corn starches were observed but not for the cassava starch. Maximum rupture force of the starch-based films was affected differently for each starch type; color analysis showed that doses of 15 kGy promoted a slight rise in the parameter b* (yellow color) while the parameter L* (lightness) was not significantly affected; X-ray diffraction patterns remained almost unchanged by irradiation.

1. Introduction

Starches from different botanical origin have different biosynthetic mechanisms and may exhibit distinct molecular structure and characteristics as well as diversity in granule shape, size, composition, and other constituents (Jenking et al., 1993). Biodegradable plastics are a solution to the environmental pollution derived the accumulation of plastic waste. Biodegradable films can be manufactured based on different starches and can include specific additives encapsulation (Gutierrez et al., 2015; Li et al., 2016).

Corn starch represents over 75% of the world's starch market (Demiate and Kotovicz, 2011). Potato starch is a very refined starch, containing minimal protein or fat. Cassava starch production in Latin America is located mainly in Southern Brazil. The production process for making starch from cassava is simple because cassava is a purer starch source than potato or cereals. These important sources of starch differ significantly in composition, morphology, thermal, rheological and retrogradation properties. Cereal starches contain a significant quantity of phospholipids, while potato starch is rich in esterified phosphorus. Potato starch exhibits higher swelling power, solubility, paste clarity and viscosity than wheat, rice or corn starch. Although native starches can be used as gelling agents in many gelling products depending on their source and availability, in many industrial utilizations physical and chemically modified starches are commonly used.

Gamma-irradiation is a non-thermal process that has been used as method for food preservation and functional modification of polymer. The dose dependent capability of gamma-irradiation to degrade glycoside bonds results in conversion of large starch molecules into smaller fragments that may affect the physicochemical properties of starches (Kang et al., 1999; Kong et al., 2016). Then, the purpose of the present investigation was to compare the effect of irradiation on corn, potato and fermented manioc or sour cassava starches by using different characterization methods.

2. Material and methods

Samples of corn, potato and cassava starches were obtained in bulk from local food market. Starches were gamma irradiated at doses of 0–15 kGy, dose rate about 1 kGy/h, using a ^{60}Co Gammacell 220, Atomic Energy of Canada Ltd (AECL) in polyethylene bags at room temperature, dose uniformity factor of 1.13. Starch hydrogels were prepared with 5% starch, 3% glycerol and 0.5% Ca propionate by heating. Starch-based films were prepared by the casting technique in glass containers, thickness range 1.5–1.7 mm. A Nikon Eclipse 80i microscope was employed together with NIS-Elements software for

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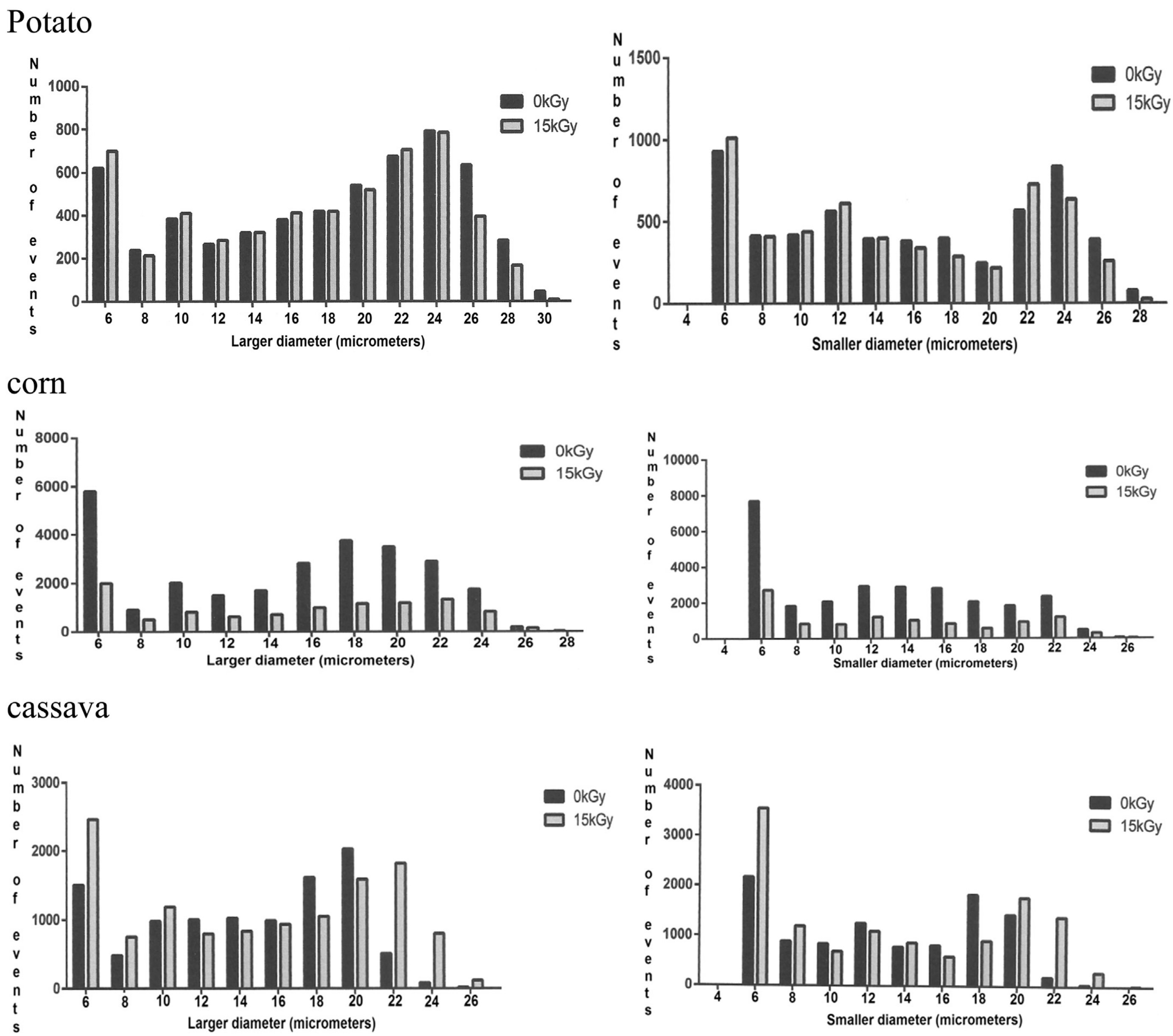

Fig. 1. Granule size distribution of starch granules of (top to bottom) potato, corn and fermented cassava irradiated with 0 and 15 kGy.

assessment of granule size distribution. Five different pictures were made from each slide and analyzed with *ImageJ* program. Granule characterization was made by scanning electronic microscopy (SEM) using a Hitachi, TM3000, photographs of 1000× magnification. A Brookfield LVDV-III viscometer, spindle SC4-18, with an adapter ULA coupled with a Neslab water bath model RTE-210, precision ± 0,1 °C was employed for viscosity measurements of starch hydrogels and the results are the means of at least 3 experiments. A Bruker D8 Advance diffractometer, equipped with Cu tube operating in 40 kV and 30 mA, graphite monochromator and scintillation detector was used for X-ray diffraction (XRD) studies on the starches. Relative crystallinity has been determined using the method of Nara and Komiya (1983) through computational plotting between peaks and total areas, with the aid of software Bruker EVA®, using Cu-kα radiation, two theta from 5° to 45°, stepsize of 0.04° and 10 s per step. The crystallinity index (CI) was calculated dividing the value of the crystalline area (obtained from the difference of total and amorphous area) by the total area of the diffractogram. Amorphous area was determined using the background function at EVA software, with curvature and threshold parameters equal to unity. FTIR-spectra of starches were taken in a Perkin-Elmer Spectrum 1000 infrared spectrometer with Fourier transform (FTIR). Films color was established using a hand-held Minolta chroma meter J (CR-400 Minolta Camera Co. Ltd.). The instrument was calibrated with a white tile (Minolta color values recorded as L*, a*, and b*). Coordinates L represented the lightness of color (0 = black; 100 = white), -a/+a greenness or redness, and –b/+b blueness or yellowness. Chroma and Hue angle were calculated using the following equations: $C = \sqrt{(a)^2+(b)^2}$ and $H = 180^\circ + \tan-1(b/a) for\, a < 0$. Textural properties of films (pieces of 30 × 30 mm) were measured by means of a Stable Micro Systems TA-XT2 analyzer, compression capability of 50 kg, using a stainless steel cylinder probe of 35 mm diameter (P/35). Samples were compressed at 1 mm/s. The rupture maximal force (N) was determined, in 15 samples for each one of the starch samples, all in triplicate.

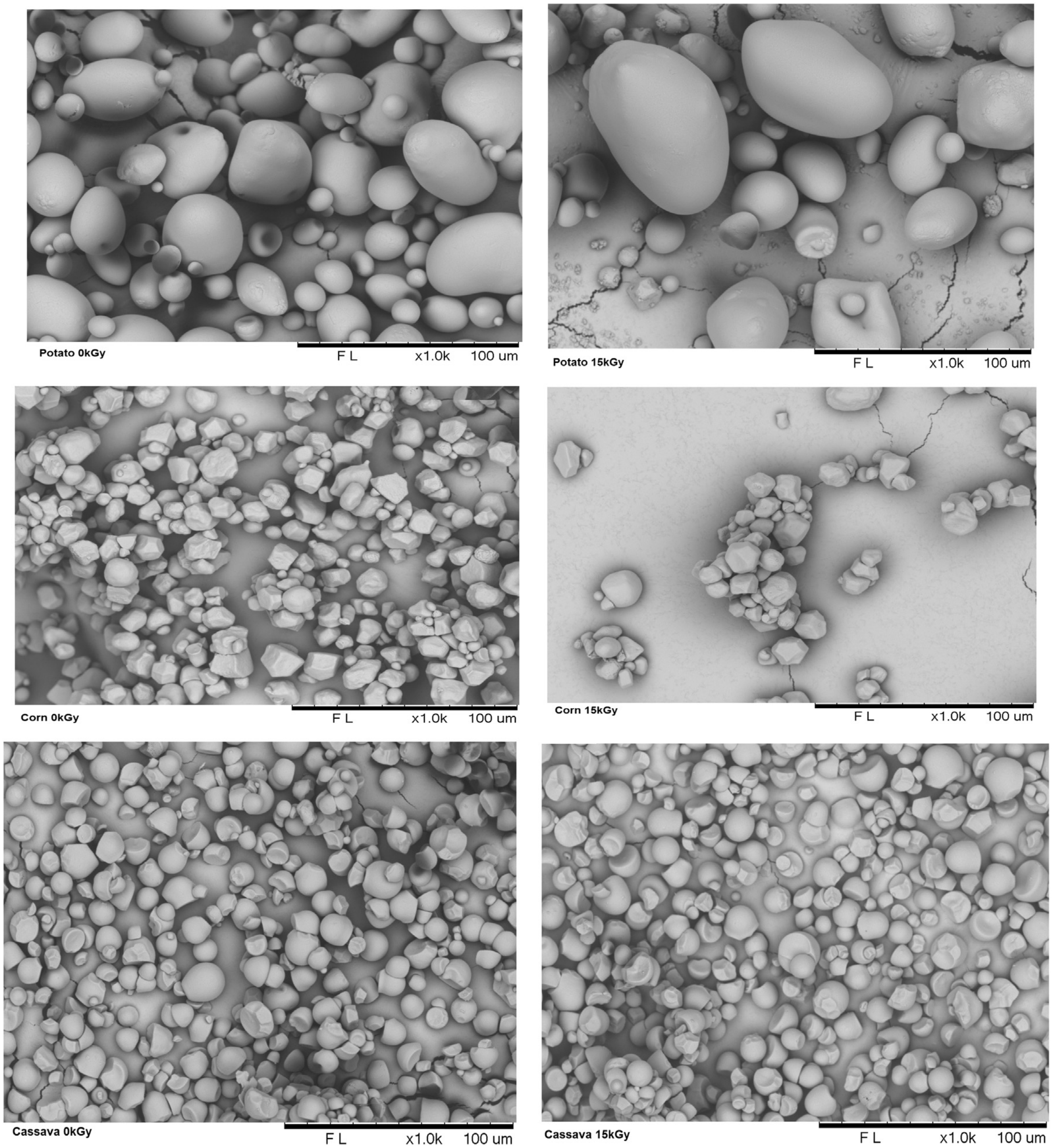

Fig. 2. SEM microphotographs of starch granules isolated from control (a) and 15 kGy irradiated (b) of potato, corn and sour cassava, from top to bottom (1000×).

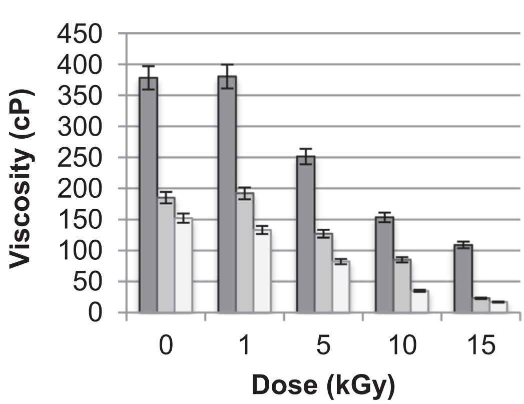

Fig. 3. Viscosity of starch hydrogels versus irradiation dose for potato (dark grey), corn (grey) and sour cassava (white) starches.

3. Results and discussion

The size and shape of starch granules are species specific. In this study the starch granules from the three different starches showed great variability mainly in size but also in shape. Fig. 1 displays the maximal and minimal granule size distribution of starch granules of potato, corn and cassava starches respectively. It is evident a mainly trimodal distribution of granule sizes: small granules, midsize granules, and large granules for the starch samples. Raeker et al. (1998), working with soft wheat starch, had also found a trimodal distribution of granule sizes. In the present work, potato starch presented the largest granules, and remained almost unchanged by 15 kGy absorbed dose. Cornstarch was strongly affected by radiation, suffered a significant reduction in the granule size as a consequence of radiation treatment. The effect was higher particularly on the small particles. Granule size distribution of fermented cassava starch showed some radiation effects, although no as

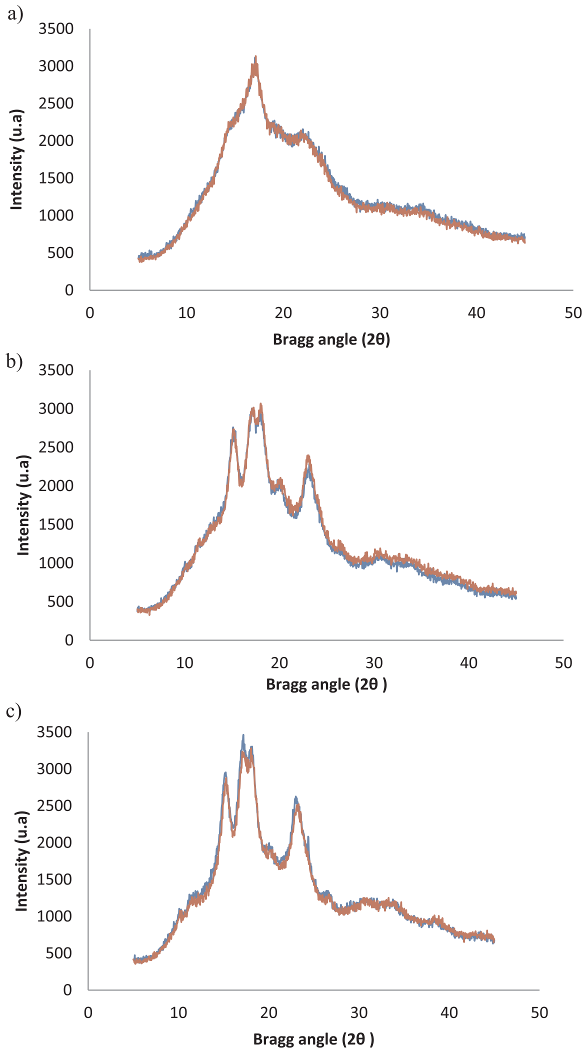

Fig. 4. XRD. Relationship between the intensity and the Bragg angle of 0 kGy (blue) to 15 kGy (red) irradiated potato, corn and sour cassava starches, from top to bottom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

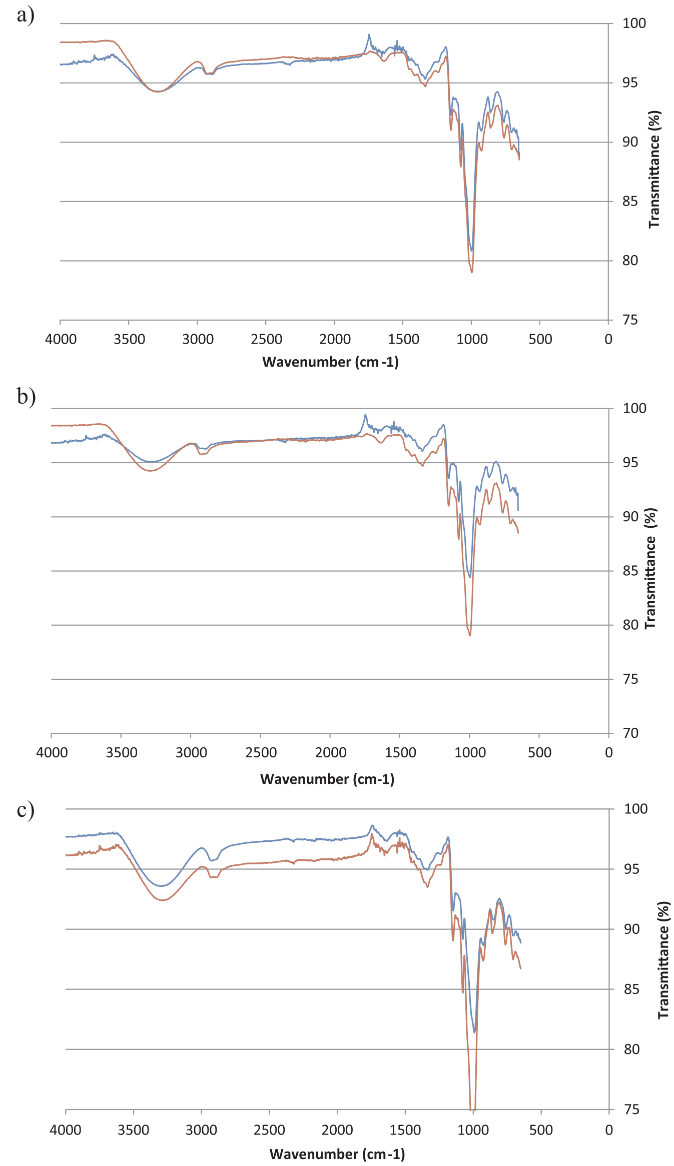

Fig. 5. FTIR spectra of 0 kGy (blue) to 15 kGy (red) irradiated corn (a), potato (b) and sour cassava (c) starches. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Relative crystallinity (%) of irradiated starches.

Starch	Dose (kGy)	
	0	15
Potato	20.6 ± 0.1^{a}	21.5 ± 0.5^{b}
Corn	23.4 ± 0.3^{c}	22.9 ± 0.6^{d}
Sour cassava	23.1 ± 0.5^{e}	21.8 ± 0.3^{f}

Values represent means ± standard deviation. Letters same in the same row (lowcase) or in the same column (upper case) indicated no significant difference between the results ($P \leq 0.05$).

much as that of corn and presenting at times even an increase in size. As established by Jenking et al. (1993) starch samples coming from different botanical species present different features in either structure or function: for example both the amylose/amylopectin ratio and the amylopectin chain length are found to vary extensively with botanic source. In the starches employed in the present study the amylase content of cornstarch (24%) was described as higher than that from cassava (17%) and potato (20%) starches (Ciacco and Cruz, 1982).

Starch granules particle size can determine physical, chemical and functional properties (Chiotelli and Le Meste, 2002; Savlak et al., 2016; Wang et al., 2016). Bhat and Karim (2009) had already suggested that starch research for commercial applications must focus on normalizing the particle size for irradiation treatments to obtain uniformity, along with setting standardized doses for each of the starch molecules. The starch granule size and shape were examined by scanning electron microscopy (SEM). Fig. 2 displays the microphotographs of irradiated and non-irradiated potato, corn and cassava starches. Morphological characteristics, such as shape and size of the starch granules, exhibit significant differences among starches. Potato starch granules are smooth–surfaced, oval and irregular or cuboidal-shaped while corn granules are spherical and angular–shaped. Cornstarch granules are less smooth–surfaced than potato starch granules. Potato starch granules are the largest in size followed by cornstarch and cassava ones. No radiation modification in the granule shape was observed by SEM, similarly as reported by others for gamma-irradiated wheat and potato starches with doses up to 50 kGy (Atrous et al., 2016).

The comparison of viscosity of potato, corn and cassava starch hydrogels is displayed in Fig. 3. As starch is a predominantly chain-scissioning polymer, irradiation resulted in substantial decrease in viscosity values with the increase with the absorbed doses starting from 5 kGy;

Table 2
Minolta color values (L*, a*, b*, C and Hue angle) for 0–15 kGy irradiated starch films.

Attribute	Starch film	Dose (kGy)				
		0	1	5	10	15
L*	Potato	95.6 ± 0.5^{aA}	95.7 ± 0.7^{aA}	95.6 ± 0.5^{aA}	95.5 ± 0.4^{aA}	95.6 ± 0.5^{aA}
	Corn	95.7 ± 0.5^{aA}	96.1 ± 0.5^{aA}	95.4 ± 0.5^{aA}	95.2 ± 0.6^{aA}	95.3 ± 0.5^{aA}
	Sour cassava	94.5 ± 0.6^{aA}	94.4 ± 0.6^{aA}	94.1 ± 0.4^{aB}	94 ± 0.6^{aA}	93.5 ± 0.6^{aB}
a*	Potato	− 0.1 ± 0.2^{aA}	− 0.2 ± 0.2^{aA}	− 0.4 ± 0.1^{aA}	− 0.4 ± 0.1^{aA}	− 0.6 ± 0.1^{aA}
	Corn	− 0.5 ± 0.2^{aA}	− 0.6 ± 0.1^{aB}	− 0.7 ± 0.1^{aB}	− 0.9 ± 0.1^{aB}	− 1.0 ± 0.3^{aA}
	Sour cassava	− 0.1 ± 0.1^{aA}	− 0.2 ± 0.1^{aA}	− 0.3 ± 0.1^{aA}	− 0.6 ± 0.1^{bA}	− 0.7 ± 0.1^{bA}
b*	Potato	3.2 ± 0.3^{aA}	3.5 ± 0.8^{aA}	3.6 ± 0.3^{aA}	4.5 ± 0.4^{bA}	5.2 ± 0.5^{bA}
	Corn	4.1 ± 0.1^{aB}	4.1 ± 0.3^{aA}	5.3 ± 0.6^{bB}	6.2 ± 0.7^{bB}	7.0 ± 0.7^{cB}
	Sour cassava	5 ± 0.6^{aB}	6 ± 0.6^{aB}	6.7 ± 1^{aB}	7.6 ± 1.1^{aB}	9.2 ± 1.3^{bC}
Chroma	Potato	3.2 ± 0.3^{aA}	3.6 ± 0.9^{aA}	3.6 ± 0.3^{aA}	4.6 ± 0.4^{aA}	5.3 ± 0.5^{aA}
	Corn	4.2 ± 0.3^{aA}	4.1 ± 0.3^{aA}	5.4 ± 0.6^{bB}	6.3 ± 0.9^{bB}	7.1 ± 0.7^{bA}
	Sour cassava	5.0 ± 0.6^{aA}	6.0 ± 0.6^{aB}	6.7 ± 0.5^{aC}	7.6 ± 0.6^{bB}	9.2 ± 1.3^{bB}
Hue angle	Potato	91.3 ± 0.8^{aA}	95.5 ± 0.9^{bA}	93 ± 0.9^{bA}	95.5 ± 0.9^{bA}	96.3 ± 1.0^{bA}
	Corn	98.3 ± 0.7^{aB}	97 ± 1.0^{aA}	98 ± 1.0^{aB}	98.6 ± 1.0^{aB}	98.3 ± 1.2^{aA}
	Sour cassava	91.6 ± 0.5^{aA}	91.6 ± 0.8^{aB}	93 ± 1.0^{aA}	94.6 ± 0.8^{aA}	94.7 ± 0.7^{bA}

Table 3
Resistance to breakage (N) of films prepared with irradiated starches.

Starch film	Resistance to breakage (N) of starch-based films				
	0 kGy	1 kGy	5 kGy	10 kGy	15 kGy
Potato	3.7 ± 0.66	4.9 ± 0.17	4.1 ± 0.17	3.6 ± 0.12	3.3 ± 0.24
Corn	2.8 ± 0.12	2.7 ± 0.10	2.4 ± 0.10	1.9 ± 0.10	2.4 ± 0.10
Sour cassava	1.5 ± 0.10	1.6 ± 0.10	1.7 ± 0.10	2.3 ± 0.10	2.3 ± 0.10

no significant difference was found among the unirradiated and those irradiated with 1 kGy for potato and corn starches. Among them, potato starch showed the highest viscosity (375 cP), followed by corn and cassava; that correlated to the highest size of potato starch granules.

X-ray diffraction is one of the various ways employed to classify native starches (Sajilata et al., 2006). Three types of starches, designated as type A, type B, and type C, have been identified based on X-ray diffraction patterns. These depend partly on the chain lengths making up the amylopectin lattice, the density of packing within the granules, and the presence of water. Although type A and type B are real crystalline modifications, type C is a mixed form. The type A structure has amylopectin of chain lengths of 23–29 glucose units. The hydrogen bonding between the hydroxyl groups of the chains of amylopectin molecules results in the formation of outer double helical structure. In between these micelles, linear chains of amylose moieties are packed by forming hydrogen bonds with outer linear chains of amylopectin. This pattern is very common in cereals. The type B structure consists of amylopectin of chain lengths of 30–44 glucose molecules with water inter-spread. This is the usual pattern of starches in raw potato and banana. The type C structure is made up of amylopectin of chain lengths of 26–29 glucose molecules, a combination of type A and type B, which is typical of tubers, peas and beans. An additional form, called type V, occurs in swollen granules. XRD diffractograms of studied starches are shown in Fig. 4. Potato starch presented B pattern, revealing the presence of two peaks at $2\theta = 17.2^\circ$ and 21.7°. Corn starch displayed the A crystalline type with weak peak at $2\theta = 19.4^\circ$, and 15.8° and a strong one at the doublet 17–17.4°. The diffractogram from cassava starch, was type C, where a strong predominance of type A was perceived with peaks at $2\theta = 15.3^\circ$ and 23° and strong one at 17–17.6°. For all the starches assayed, irradiation with 15 kGy did not affect XRD diffractograms.

Table 1 presents the relative crystallinity (%) of potato, corn and sour cassava starches. Irradiation at 15 kGy seems to affect crystallinity in a limited extend, showing small decrease for corn and fermented cassava and increase for potato starch. Shawrang et al. (2013) applied 15 kGy of electron beam irradiation on barley resulting in 6% decrease in starch crystallinity index. On the other hand, increased crystallinity index of starches, determined by X-ray diffraction techniques, has been reported in wheat (MacArthur and D'Appolonia, 1984) and rice (Wootton et al., 1988) starches. The crystalline content of common starches, usually in the range of 20–45%, are actually not well describes assuming that relatively perfect crystalline domains are interspersed with amorphous regions. Some authors consider necessary taking in account irregularities in crystals that are expected to exist in semi-crystalline materials (Lopez-Rubio et al., 2008).

The structural characterization of native and irradiated starch samples was carried out using FTIR. Ramazan et al. (2002) used FTIR for characterization and also classification of irradiated starch samples. Fig. 5 displays the spectrograms from potato, corn and cassava starches. The O–H (3000–3600 cm^{-1}) stretch, C–H (2800–3000 cm^{-1}) stretch, the skeletal mode vibration of the glycoside linkage (900–950 cm^{-1}) in infrared spectra, and the infrared band of water adsorbed in the amorphous parts of starches (1550–1750 cm^{-1}) are employed in classification analysis of irradiated starches. Spectral data related to water adsorbed in the noncrystalline regions of starches provided also a sort of classification of irradiated starches.

In the present work irradiation did not change the FTIR spectra, but irradiation increased intensities of absorbance mainly for potato and corn starches, as previously seen for other starches as well (Bashir et al., 2017). According to Ciesla et al. (2010), radiation-induced improvement of hydrophobic properties of the films prepared using potato and wheat starch and selected potato starch-surfactant compositions. Improvement of strength and flexibility was obtained in the case of potato starch films, while in the case of wheat starch films the increase of strength was accompanied by a decrease in flexibility. Improvement of the functional properties of potato starch films corresponds to the improvement of their structural properties. Present results do not permit corroborate such affirmative, and for detailed explanation concerning the relationship between physicochemical and functional properties of the films further studies are needed.

Color of starch-based films is an important sensory attribute since it affects the decision to buy a product. Color analysis using a Minolta chroma meter of potato, corn and sour cassava starches films showed that doses of 15 kGy promoted a slight rise in the parameter b* (yellow color) while the parameter L* (lightness) was not significantly affected on any starch-based films (Table 2).

Texture analyses were performed by the determination of resistance to breakage of prepared starch films. A progressive firmness of sour cassava starch films with the increase of absorbed doses was observed. On the other hand, no simple correlation between resistance to breakage and absorbed dose was possible to establish for potato and corn starches (Table 3).

4. Conclusion

An apparent trimodal size granules distribution of the three studied starches was obtained depending on the botanical variety. Highest granule size was presented by potato starch. The ranking in granule size was potato, corn and fermented cassava starches. Morphology of starch granules did not change with gamma radiation dose up to 15 kGy. However, the size distribution of corn and cassava starch granules was reduced but not that of potato starch. Viscosity values follow the same relationship as the size of granules. Nevertheless, viscosity of irradiated starch samples, starting from 5 kGy, decreased upon irradiation for all three starches and samples from potato and corn starches irradiated with 1 kGy remained unchanged. Amorphous region of all the starch structures was slightly affected by the applied 15 kGy absorbed dose. Irradiation did not change FTIR spectra, although increased intensities of absorbance were found at 1000 cm^{-1} and on the broadband around 2904 cm^{-1}. Inherent differences among starches behavior found in the present work must be take into account whenever gamma irradiation were applied trying to obtain desired properties or to create novel functionality for diverse food and non-food applications.

References

Atrous, H., Benbettaieb, N., Chouaibi, M., Ghorbel, D., 2016. Changes in wheat and potato starches induced by gamma irradiation: a comparative macro and microscopic study. J. Food Prop(Published online 08 Sep 2016. Available from: ⟨http://dx.doi.org/10.1080/10942912.2016.1213740⟩ (Accessed 19 September 2016).
Bashir, K., Jan, K., Aggarwal, M., 2017. Thermo-rheological and functional properties of gamma-irradiated wholewheat flour. Int. J. Food Sci. Technol. 52, 927–935.
Bhat, R., Karim, A.A., 2009. Impact of radiation processing on starch. Compr. Rev. Food Sci. Food Saf. 8, 44–58.
Chiotelli, E., Le Meste, M., 2002. Effect of small and large wheat starch granules on thermomechanical behavior of starch. Cereal Chem. 79 (2), 286–293.
Ciacco, C.F., Cruz, R., 1982. Fabricação do amido e sua utilização. São Paulo, Secretaria da Indústria, Comércio. Ciênc. Tecnol. Estado de São Paulo 152 (In portuguese).
Ciesla, K., Nowicki, A., Buczkowski, M., 2010. Preliminary studies of the influence of starch irradiation on physicochemical properties of films prepared using starch and starch-surfactant systems. Nukleonika 55 (2), 233–242.
Demiate, I.M., Kotovicz, V., 2011. Cassava starch in the Brazilian food industry. Cienc. Tecnol. Aliment. Camp. 31 (2), 388–397.
Gutierrez, T.J., Tapia, M.S., Perez, E., Famá, L., 2015. Structural and mechanical properties of edible films made from native and modified cush-cush yam and cassava starch. Food Hydrocoll. 45, 211–217.
Jenking, P.J., Cameron, R.E., Donald, A.M., 1993. A universal feature in the structure of starch granules from different botanical sources. Starch 45 (12), 417–420.
Kang, I.J., Byunm, M.W., Yook, H.Y., 1999. Production of modified starches by gamma irradiation. Radiat. Phys. Chem. 54, 425–530.
Kong, X.L., Zhou, X., Sui, Z.Q., Bao, J.S., 2016. Effects of gamma irradiation on physicochemical properties of native and acetylated wheat starches. J. Biol. Macromol. 91, 1141–1150.
Li, H.T., Ho, V.T.T., Turner, M.S., Dhital, S., 2016. Encapsulation of *Lactobacillus plantarum* in porous maize starch. LWT-Food Sci. Technol. 74, 542–549.
Lopez-Rubio, A., Flanagan, B.M., Gilbert, E.P., Gidley, M.J., 2008. A novel approach for calculating starch crystallinity and its correlation with double helix content: a combined XRD and NMR study. Biopolymers 89 (9), 761–768.
MacArthur, L.A., D'Appolonia, B.L., 1984. Gamma radiation of wheat. II. Effects of low-dosage radiations on starch properties. Cereal Chem. 61, 321–326.
Nara, S., Komiya, T., 1983. On the relation between the water saturated state and the crystallinity of moistened potato starch, using the X-ray diffraction method. Bull. Fac. Agric. Mie Univ. 67, 81–86.
Raeker, M.O., Gaines, C.S., Finney, P.L., Donelson, T., 1998. Granule size distribution and chemical composition of starches from 12 soft wheat cultivars. Cereal Chem. 75 (5), 721–728.
Ramazan, K., Irudayaraj, J., Seetharaman, K., 2002. Characterization of irradiated starches by using FT-Raman and FTIR spectroscopy. J. Agric. Food Chem. 50 (14), 3912–3918.
Sajilata, M.G., Rekha, S., Singhal, R.S., Kulkarn, P.R., 2006. Resistant starch— a review. Compr. Rev. Food Sci. Food Saf. 5, 1–17.
Savlak, N., Turker, B., Yesilkanat, N., 2016. Effects of particle size distribution on some physical, chemical and functional properties of unripe banana flour. Food Chem. 213, 180–186.
Shawrang, P., Sadeghi, A.A., Ghorbani, B., 2013. The effect of electron beam irradiation on beta-glucan content, X-ray diffraction of starch, protein subunit patterns, and in vivo digestibility of barley grain in cockerels. Vet. Anim. Sci. 37 (4), 443–448.
Wang, C., Tang, C.H., Fu, X., Huang, Q., Zhang, B., 2016. Granular size of potato starch affects structural properties, octenylsuccinic anhydride modification and flowability. Food Chem. 212, 453–459.
Wootton, M., Djojonegoro, H., Driscoll, R., 1988. The effect of gamma-irradiation on the quality of Australian rice. J. Cereal Sci. 7, 309–315.