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Physicochemical and structural characteristics of rice starch modified by irradiation

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ABSTRACT

This work evaluated the physicochemical and structural properties of rice starch of the cultivars IAC 202 and IRGA 417 modified by irradiation. Starch samples were irradiated by ^{60}Co in doses 1, 2 and 5 kGy, on a rate of 0.4 kGy/h. A control not irradiated was used for comparison. The granule morphology and A-type X-ray diffraction pattern were not altered by irradiation. There was an increase in amylose content, carboxyl content and acidity with irradiation. Gamma radiation did not affect the thermal properties of IAC 202, but increased gelatinization temperature of IRGA 417, in the higher dose (5 kGy). The number of long chains of amylopectin was reduced and short chains were increased for IAC 202, whereas for IRGA 417, the opposite was observed, probably due to cross-linking of starch chains. Starches had their physicochemical and structural properties modified by irradiation differently.

1. Introduction

Rice is the second most produced cereal in the world, with Brazil being the largest producer and consumer in the west (FAO, 2014). This cereal is rich in carbohydrates, of which starch is the component in greater proportion, participating of 65% in brown rice, up to 90% in polished rice (Zhou, Robards, Helliwell, & Blanchard, 2002). Starch is composed of amylose, linear chains of glucose units linked by α-1,4 glycosidic bonds, and amylopectin, branched chains of α 1,4 and α 1,6-linked glucose units. Variations in the proportions amylose/amylopectin ratio and the chain size of each one, contribute to differences in physicochemical, functional and nutritional properties of starch for each cultivar (Chung, Liu, Lee, & Wei, 2011; Chávez-Murillo, Méndez-Montealvo, Wang, & Bello-Pérez, 2012).

Cooked rice with low amylose is soft and sticky, while rice with high amylose is firm and fluffy (Jayamani, Negrao, Brites, & Oliveira, 2007). For this reason rice cultivars with higher amylose content are preferred by Brazilian consumers. IRGA 417 and IAC 202 are rice cultivars marketed in Brazil, and the first show cooked grains with higher hardness and less stickiness compared to the second (Polesi et al., 2014).

Irradiation is a non-thermal treatment used for food preservation because it eliminates insects, insect eggs and microorganisms, improving the hygienic quality and maintaining nutritional value of food. Ionizing radiation can improve a food by inactivating the antinutritional factors and inhibiting the allergenic compounds. Moreover, it is a quick treatment that requires minimal sample preparation and not depends on reagents (Bhat & Karim, 2009).

Gamma radiation generates free radicals capable of breaking chemical bonds, thus promoting reduction in the molecular mass of both amylose and amylopectin, which affects the starch behavior in various irradiated foods in which it is present (Chung & Liu, 2009).

In recent years, irradiation has been used as alternative technique to modify starch to replace standard techniques of chemical and physical modifications. The conventional sources of starches are modified to suit the specific needs of industries by physicochemical and functional properties not offered by them. These changes may be chemical, physical or enzymatic. Irradiation is a physical treatment which alters the starches physical and chemically (Bhat & Karim, 2009).

The modified starch by gamma radiation shows agreement in changing some properties such as, reduction in viscosity and

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molecular weight of amylose and amylopectin and increase in solubility and carboxyl content, regardless of source (Bao, Ao, & Jane, 2005; Chung & Liu, 2009, 2010; Falade, Ighravwe, & Ikoyo, 2011; Gani, Bashir, Wani, & Masoodi, 2012; Liu, Ma, Xue, & Shi, 2012; Singh, Singh, Ezekiel, & Kaur, 2011). However, other properties have shown different results depending on the botanical source of starch and irradiation conditions (Chung & Liu, 2009). The granule crystalline structure, granule morphology, thermal properties and amylopectin fine structure are some parameters of starch subjected to irradiation that shows distinct behaviors (Chung & Liu, 2009; Liu et al., 2012).

Thus, the aim of this study was to evaluate the physicochemical and structural properties of starch isolated from two rice cultivars (IAC 202 and IRGA 417) subjected to modification by irradiation.

2. Materials and methods

Polished rice grains of two commercial cultivars were used for starch isolation, IAC 202, acquired from Instituto Agronômico de Campinas (IAC), and IRGA 417, courtesy of the Instituto Rio Grandense do Arroz (IRGA), both the 2010/2011 crop.

2.1. Starch isolation

Starch was extracted according to the alkaline method of Patindol, Wang, Siebenmorgen, and Jane (2003) with modifications. Polished rice grains were soaked in 0.1% NaOH in the ratio 1:2 (w/v) for 24 h. After that, the grains were ground and sieved (63 μm). The material that passed through the sieve was centrifuged for 15 min at 1500g, the supernatant was discarded and the protein upper layer (yellowish) carefully removed with a spatula. The starch was again suspended in 0.1% NaOH solution, centrifuged for 15 min at 1500g, the supernatant was discarded and the upper layer removed carefully with a spatula. The decanted starch was suspended in distilled water, pH adjusted to 6.5 with 0.2 M HCl and centrifuged for 15 min at 1500g. The supernatant was discarded and decanted starch was suspended in distilled water and centrifuged for 15 min at 1500g. This procedure was repeated 3 times. Starch was dried in air circulating oven at 40 °C, ground in a mortar, sieved (150 μm) and stored in a sealed glass flask.

2.2. Irradiation of samples

Samples of 200 g of starch (approximately 9% moisture) were packed in polyethylene bags and subjected to gamma radiation doses of 1, 2 and 5 kGy at a dose rate of 0.4 kGy/h in ^{60}Co gamma irradiator (Gammacell, 220 Excel, GC-220E, Nordion Inc., Ottawa, ON, Canada) at room temperature. These doses were based on previous studies (data not shown) and doses necessary to ensure higher shelf life by insect disinfestation. The samples did not show changes in temperature and moisture content during the process. The irradiation treatments were performed at Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, SP, Brazil. A non-irradiated sample (dose 0) was used for comparison.

2.3. Morphology and size of starch granules

The scanning electron microscopy (SEM) was used to observe general morphology of the starches granules. The samples were fixed on stubs with double-sided adhesive tape and covered with a gold layer of 20 nm in a sputter coater (FDU 010, Bal-Tec, Balzers, Liechtenstein). The metallic samples were observed in a scanning electron microscope (LEO 435 VP, LEO Electron Microscopy Ltd, Cambridge, England) with an amperage of 80 mA and acceleration voltage of 20 kV.

To assess the granules size, the starch samples were placed on microscope slides, added a drop of glycerin (50%), mixed and covered with coverslip. The microscope slide (3 per sample) were observed by optical microscope (Jenamed 2, Carl Zeiss, Jena, Germany) and images captured by coupled camera (MA88-300, Premiere® Camera Eyepieces, Microscopes America Inc., Cumming, GA, EUA). The Image Tool© software (Wilcox, Dove, David, & Greer, 2002) was used to measure the granules (200 per microscope slide). Due to the irregularity in the granules shapes, the larger and the smaller axis of each granule were measured.

2.4. Amylose content

The amylose content was determined using amylose/amylopectin assay kit (K-AMYL 07/11, Megazyme International Ireland Ltd., Wicklow, Ireland) according to the methodology proposed by the manufacturer. This method is based on the amylopectin precipitation by lectin concanavalin-A, which is removed from the process to not interfere with the quantification of amylose which is enzymatically hydrolyzed to glucose and measured (Gibson, Solah, & Mccleary, 1997; Yun & Matheson, 1990).

2.5. Carboxyl content

The carboxyl content was determined according to the methodology described by Chattopadhyay, Singhal, and Kulkarni (1997) with modifications. In 2 g of starch sample were added 25 mL of 0.1 M HCl and stirred for 30 min at 25 °C. The suspension was filtered through a fritted funnel and the solid residue was washed with 400 mL of distilled water. The starch was transferred to a beaker, added 300 mL of distilled water and brought to boiling water bath for 15 min. Then, the sample was titrated while still hot with 0.1 M NaOH in an automatic titrator (Titrino plus 848, Metrohm, Herisau, Switzerland) to pH 8.3. A sample of the non-irradiated starch was analyzed and considered blank. The carboxyl content (%) was calculated as: {[(titrated volume of sample − titrated volume of blank) × NaOH molarity × 0.045 × 100]/weight of the sample}.

2.6. Acidity and pH

The acidity was determined in a starch slurry (5 g/50 mL) titrated with 0.01 M NaOH to pH 8.3 (Instituto Adolfo Lutz, 2008, chap. IV). The result was expressed in percentage of acidity (v/m). The pH was determined in a starch slurry (5 g/50 mL) using a digital pH meter (Instituto Adolfo Lutz, 2008).

2.7. Molecular weight distribution

The molecular weight distribution profiles of the starches were determined by gel permeation chromatography (GPC) as described previously (Alves, Polesi, Aguiar, & Sarmento, 2014). The total carbohydrate content (CHO) was analyzed using the phenol–sulfuric method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) adapted to be measured using a microplate reader (Asys Expert Plus, Asys Hitech, Eugendorf, Áustria), at 492 nm.

2.8. Amylopectin branch chain length distributions

The starches were debranched by isoamylase (3 U, Megazyme International, Ireland) and the branch chain length distributions were determined using a high performance anion exchange chromatography with pulsed amperometric detector (HPAEC-PAD) system (ICS 3000, Dionex Corporation, Sunnyvale, CA, USA) equipped

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