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Gamma irradiation induced modification of bean polysaccharides: Impact on physicochemical, morphological and antioxidant properties

Peerzada R. Hussain[a,*], Idrees A. Wani[b], Prashant P. Suradkar[a], Mohd A. Dar[a]

[a] Astrophysical Sciences Division, Nuclear Research Laboratory, Bhabha Atomic Research Centre, Zakura, Srinagar 190006, India
[b] Department of Food Science and Technology, University of Kashmir, Srinagar 190006, India

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ABSTRACT

In the present study starches from four bean varieties viz. red, yellow, black and white, were gamma irradiated in the dose range of 5–25 kGy to investigate the effect of radiation processing on physicochemical, morphological and antioxidant properties. Studies revealed positive correlation between gamma irradiation and solubility ($r = 0.91$), irradiation and water absorption capacity ($r = 0.82$) and negative correlations between irradiation and swelling power ($r = -0.92$), irradiation and pasting properties ($r = -0.91$) and irradiation and thermal properties ($r = -0.89$). Microscopic observation under scanning electron microscope indicated the development of surface cracking and fractures on the surface of starch granules with increase in dose. X-ray diffractometry revealed no significant change in diffraction patterns between control and irradiated starches, except a decrease in relative crystallinity. Irradiation increased the proportions of both rapidly digestible starch and enzyme resistant starch of bean starches and significantly prevented the retrogradation of bean starches during storage. Results of the DPPH radical scavenging activity and ferric reducing power indicated significant ($p \leq 0.05$) increase in antioxidant activity of all irradiated bean starches with increase in dose.

1. Introduction

Gamma irradiation is a non-thermal method of preservation and has been extensively studied to extend the shelf-life of perishable foods and food products. It has also been used to protect the grain seeds from insect infestation and microbial contamination during storage and has proved to be an efficient alternative to the use to chemical preservatives like methyl bromide, ethylene dibromide and ethylene oxide, in addition to its use as quarantine treatment for export purposes and development of radiation induced mutants for improvement of crop yield and disease resistance (Kume, Furuta, Todoriki, Uenoyama, & Kobayashi, 2009; Liu & Chung, 2010; Liu, Ma, Xue, & Shi, 2012; Sabato et al., 2009). In addition to the above applications, gamma irradiation has also been used to bring about the modifications of polysaccharides like starch through crosslinking (Choi et al., 2009; Nagasawa, Yagi, Kume, & Yoshi, 2004), grafting (Kiatkamjornwong, Mongkolsawat, & Sonsuk, 2002) and degradation (Bertolini, Mestres, Colonna, & Raffi, 2001; Kim et al., 2008). The versatility and edge of gamma irradiation over other modification techniques, such as pre-gelatinization, chemical crosslinking and oxidation; which are complex and time consuming, lies in the fact that gamma irradiation is a low cost and environmentally-friendly alternative to produce modified polymer materials (Xu, Sun, Yang, Ding, & Pang, 2007; Zainol, Akil, & Mastor, 2009). It has been reported that polysaccharide modification through degradation by gamma irradiation leads to the cleavage of the glycosidic bonds (Byun et al., 2008; Cho, Kim, & Rhim, 2003). The basic advantage of the degradation of polysaccharides by radiation is the ability to produce changes which are both reproducible and quantitative in nature (Choi et al., 2009).

Among the major legumes, beans occupy an important place and constitute a rich and inexpensive source of protein and carbohydrate. Carbohydrate represents the main fraction of beans, accounting up to 50–80% of the dry matter; of these starch and non-starch polysaccharides (dietary fiber) are the major constituents (Hoover & Sosulski, 1991). As a major ingredient, starch can be used to control structure, texture, consistency and appeal to many food and non-food products (Jobling, 2004). However the properties of starch like low solubility, high viscosity, shear resistance, thermal resistance, thermal decomposition, high resistance toward swelling and rupture and tendency toward retrogradation limit its use in food applications (Liu et al., 2012). The literature review reveals that extensive work has been done on modification of starch from maize (Liu et al., 2012), rice (Yu & Wang, 2007),

* Corresponding author. Tel.: +91 1942422420; fax: +91 1942422420.
E-mail address: hussainpr@rediffmail.com (P.R. Hussain).

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cassava (Bertolini et al., 2001), corn (Yoon et al., 2010) and potato (Ezekiel, Rana, Singh, & Singh, 2007; Luo, Huang, Fu, Zhang, & Yu, 2009) in relation to their morphological and physicochemical properties. However, such studies on radiation induced modification of starch are limited in case of beans and other legumes (Hoover, Hughes, Chung, & Liu, 2010). Further studies on radiation induced enhancement of antioxidant activity of bean polysaccharides, i.e., starch are also limited in the literature. Therefore, the present study was undertaken to investigate the effect of gamma irradiation on physicochemical and morphological modification of bean starch and enhancement of antioxidant properties so as to increase its food applications.

2. Materials and methods

2.1. Materials

Seeds of red, white, black and yellow kidney beans (*Phaseolus vulgaris*) harvested during 2012 were procured from Seed Research Centre of Sheri Kashmir University of Agricultural Sciences and Technology, Shalimar, Jammu and Kashmir, India. Seeds were cleaned from dust and foreign materials manually and stored at room temperature till further use.

2.2. Starch extraction

Two kilogram sample in duplicates of each bean seed was soaked in 4 L of double distilled water for 24 h at room temperature. After soaking, the coats of the seeds were removed and slurry was prepared along with water using a mixer blender. The slurry obtained was again diluted ten times with distilled water and pH of the slurry was raised to 10 with 0.5 N sodium hydroxide. After pH adjustment, the slurry was continuously mixed for 1 h using magnetic shaker followed by filtration through a 75 μ mesh sieve to separate fiber. The filtered slurry was then centrifuged at 5000 × g for 45 min at 10 °C using Eppendorf Centrifuge (5810R, Germany). The aqueous phase obtained on centrifugation was discarded and the white sediment portion was recovered as starch. The starch obtained was dried to a constant weight at 45 °C in a hot air oven. The percentage of starch recovery was about 75–80%.

2.3. Gamma irradiation

The starch samples were packed in polyethylene bags and irradiated in the dose range of 5–25 kGy using PANBIT irradiator having Co-60 as the gamma-ray source. The samples were irradiated at a dose rate of 185 Gy/h. To ensure that starch samples received the exact dose, the dosimeters were placed along with the samples. A ceric-cerous dosimeter was used to measure the absorbed dose of gamma irradiation by the samples. The samples that received no radiation treatment were considered as control. For all the irradiation treatments including control, the sample size used was approximately 150 g of starch in duplicate. After irradiation treatment, the samples were kept at 10 ± 2 °C till further use.

2.4. Solubility and swelling power

Solubility and swelling power were determined by the method of Subramanian, Hoseney, and Bramel-Cox (1994). Starch (0.5 g) was mixed with 30 ml of distilled water and heated with constant stirring at 80 °C for 30 min. After heating to desired temperature, the sample was centrifuged for 30 min at 1500 × *g*. The supernatant was decanted and dried at 120 °C in an oven to a constant weight (M_1). The settled and swollen starch was carefully taken out and weighed as (M_2). The solubility and swelling power were determined by mass balance equations as under

$$\text{Solubility (g/100 g)} = \left(\frac{M_1}{M_0}\right) \times 100$$

$$\text{Swelling power (g/g)} = \frac{M_2}{M_0}$$

where M_0 is the initial weight of starch taken.

2.5. Carboxyl content and pH

The carboxyl content of the irradiated and control starch samples were determined using the method of Chattopadhyay, Singhal, and Kulkarni (1997). To 0.5–1.0 g of starch, 25 ml of 0.1 N HCl was added and the mixture was allowed to stand for 30 min with occasional stirring. The slurry was filtered through a fritted glass crucible and washed with distilled water until it was free from chlorine. The starch was then transferred to a 500 ml beaker to which 300 ml distilled water was added. It was then boiled for 5–10 min for complete gelatinization, followed by titration with 0.1 N NaOH using phenolphthalein as indicator. A blank test was also performed with unmodified starch. Carboxyl content was calculated as follows:

$$\text{Milli-Eq. of acid/100 g starch} = (A - B) \times 0.1\,\text{N NaOH} \times 100/W$$

where A is titer value for sample; B is titer value for blank; and W is weight of sample in grams.

Apparent percent carboxyl

= Milli-equivalents of acid/100 g starch × 0.045.

pH of the starch slurry (30 g/100 ml) was determined using a digital pH meter (Eutech Instruments, USA) calibrated using buffer pH 4.

2.6. Starch retro-gradation

Starch retro-gradation was determined indirectly as a function of light transmitted by an aqueous solution of starch. An aqueous solution of starch (0.5%, w/v) was prepared by heating at 90 °C in a water bath for 45 min with constant stirring. The solution was cooled to room temperature and stored for 5 days at refrigeration temperature. Absorbance of the solution was taken every day at 640 nm using UV–vis spectrophotometer (Hitachi 330, Japan) and the percent transmittance values were calculated using absorbance–transmittance relationship.

2.7. Apparent amylose content and amylose leaching

Apparent amylase content was determined as per the method of Williams, Kuzina, and Hlynka (1970). A starch suspension was made by dissolving 20 mg of starch in 10 ml of 0.5 N KOH and the contents were mixed thoroughly. The samples were then transferred to a 100 ml volumetric flask and the volume was made up to the mark with distilled water. An aliquot (10 ml) of the sample was taken into 50 ml volumetric flask and 5 ml of 0.1 N HCl were added followed by 0.5 ml of iodine reagent. The contents were again diluted to 50 ml and the absorbance was measured at 625 nm. The content of amylase was determined from the standard curve of amylose and amylopectin blends from potato starch.

For determining amylose leaching, a starch suspension of (0.5%, w/v) was heated at temperature range of 60–80 °C for 30 min followed by centrifugation at 1500 × *g* for 30 min. The amount of leached amylose was estimated by determining the amount of amylose in the resultant solution as above.