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Pasting characteristics and *in vitro* digestibility of γ-irradiated RS_4 waxy maize starches

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ABSTRACT

The effect of γ-irradiation on the physicochemical properties of cross-linked waxy maize resistant starches was examined. The cross-linked waxy maize starches contained resistant starch (RS) of 56.1 and 63.5%, respectively for 5 and 10% sodium trimetaphosphate (STMP)/sodium tripolyphosphate (STPP) cross-linking, and the RS contents slightly decreased as the irradiation dose increased whereas the RS content in unmodified waxy maize starch increased with an increase in irradiation dose. For both native and cross-linked starches, the rapidly digestible starch (RDS) content increased and the slowly digestible starch (SDS) content decreased by the irradiation. The solubility of the native and cross-linked starches increased as the irradiation dose increased. The cross-linked starches did not swell in boiling water without showing pasting viscosity. However, the starches became swellable, forming pastes by irradiation, and the pasting viscosity gradually increased with an increase in irradiation dose. The crystallinity as determined by an X-ray diffraction analysis remained unchanged upon cross-linking and γ-irradiation. However, the gelatinization enthalpy of the cross-linked starches decreased in proportion with irradiation dose. The melting temperatures of cross-linked starches gradually decreased and the temperature range for melting increased with an increase in irradiation dose.

1. Introduction

Starch has been used as a food ingredient to control the structure, texture and consistency of many types of food. It is often chemically, physically or enzymatically modified to control its physical and nutritional properties as an ingredient to optimize the food applications (Eliasson and Gudmundsson, 1996; Thomas and Atwell, 1999).

Gamma-irradiation has been used to extend the shelf-life or to ensure the safety of foods by reducing spoilage and the number of pathogenic microorganisms. Irradiated foods in the markets have been confirmed to be nutritionally adequate and safe for human consumption (Yu and Wang, 2007). It has also been shown to be a useful method for producing modified starch since it generates free radicals that can alter the structure of starch molecules (Sokhey and Hanna, 1993). The major effect of γ-irradiation on starch has been reported to be depolymerizing or degrading starch chains, resulting in progressive reduction in molecular size of amylose and amylopectin. This structure change induces a decrease in viscosity, an increase in solubility, and an increase in acidity (Sokhey and Hanna, 1993; Tomasik and Zaranyika, 1995). However, these effects on physicochemical properties of starch (granule structure, crystallinity, gelatinization enthalpy, retrogradation extent, etc.) and starch digestibility are not consistent and depend on the botanical source and irradiation conditions. The surface of starch granule remained unchanged when maize starch was irradiated at 40 kGy (Lee et al., 2006), whereas it became rough when acorn starch was irradiated at a lower dose of 10 kGy (Kweon et al., 2002). Crystallinity of rice starch was increased by irradiation (Bao et al., 2005), but that of maize starch was decreased (Chung and Liu, 2009). Under a DSC analysis, gelatinization enthalpy was reported to increase for bean starch but decrease for major cereal and root starches (Bao et al., 2005; Ciesla and Eliasson, 2002; Lee et al., 2006). The effect on retrogradation of maize starch appeared dependent on the irradiation conditions (Chung and Liu, 2009; Lee et al., 2006). Starch digestibility could be changed by irradiation but the change was not proportional to the irradiation dose (Chung and Liu, 2009; Rombo et al., 2004).

Cross-linking, one of the most common chemical modifications for starch, may control the degree of granular swelling by making starch resistant to heating, and mechanical shear (Wurzburg, 1986). Cross-linking of starch has also been used to provide stability to acidic conditions. However, the level of cross-linking used to

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produce starches as thickeners in foods may not comprise the resistance to enzymes (Ostergard et al., 1988). Woo and Seib (2002) reported that highly cross-linked starches were more resistant to amylase digestion than native starch.

Based on digestion behavior, starch may be classified into rapidly digestible starch (RDS) which causes a sudden increase in blood glucose level after ingestion, slowly digestible starch (SDS) which is slowly but completely digested in the small intestine, and resistant starch (RS) which is not digested in the small intestine but is fermented in the large intestine, depending on the rate and extent of digestion (Englyst et al., 1992). The RS is subdivided into four categories depending on its origin: RS_1, physically inaccessible starch due to entrapment in a non-digestible matrix; RS_2, raw starch granules with a degree of crystallinity; RS_3 retrograded amylose; and RS_4, chemically modified starch. RS_4 products are commonly produced by cross-linking the starch in granule state using various chemical reagents, and contain 30–70% of RS when assayed with the *in vitro* starch digestion procedure described by Englyst et al. (1992) (Woo and Seib, 2002). However, the RS_4 products have no swelling property even by heating in water, and lack the ability of paste formation due to the rigid granule matrix by cross-linkages among starch chains (Alexander, 1995). Consequently, RS_4 products may not function as thickeners in food systems which require adequate swelling and viscosity formation.

The objective of this study was to produce food-grade resistant starches (RS_4) from waxy maize starch which were capable of swelling and forming pastes during aqueous heating, using chemical cross-linking agents and consequent γ-irradiation. The level of resistant starch and various physicochemical properties of the irradiated RS_4 were evaluated.

2. Materials and methods

2.1. Materials

Waxy maze starch was provided by Samyang Genex Company (Seoul, South Korea). Sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), pancreatin (P-7545), and amyloglucosidase (A-9913) were obtained from Sigma and Aldrich Chemical Company (St. Louis, MO).

2.2. Preparation of cross-linked starch

Cross-linking of waxy maize starch was performed according to the method of Woo and Seib (2002). Waxy maize starch (500 g, dry basis [db]), sodium sulfate (50 g, 10%, starch basis [sb]), and different amounts (25 or 50 g, 5% or 10%, sb) of a 99:1 mixture of STMP and STPP were mixed in water (700 ml). The mixture was adjusted to pH 11.5 by adding 1.0 M NaOH, and then stirred continuously for 3 h at 45 °C. The starch slurry was adjusted to pH 6.5 by adding 1.0 M HCl, and then centrifuged (3000×*g*, 10 min). Extensive washing with distilled water (300 ml, 7×) was done to ensure the removal of un-reacted inorganic salts. After drying overnight at 40 °C in a convection oven, the cross-linked starch was ground and sieved (100 mesh).

According to the United States Code of Federal Regulations (CFR, 2001), when the starch was modified with a mixture of STMP and STPP, the residual phosphate must not exceed 0.4% calculated as phosphorous. As reported by Woo and Seib (2002) and Chung et al. (2004), cross-linking of various starches in an aqueous slurry (33% starch solids, w/w) with 1–19% (sb) of a 99:1 (w/w) mixture of STMP and STPP in 10% sodium sulfate for 3 h at 45 °C and pH 11.5 gave less than 0.4% of residual phosphorous (maximum permissible level). In this experiment, the residual phosphorus was not determined since the cross-linking reactions were done exactly in the same manner as those reported by Woo and Seib (2002) and Chung et al. (2004).

2.3. Gamma-irradiation of cross-linked starch

Native and cross-linked waxy maize starches (100 g) were packed in polyethylene bags and irradiated using a ^{60}Co gamma source (AECL, IR-79, MDS Nordion International Co. Ltd., Ottawa, ON, Canada) at the Korea Atomic Energy Research Institute (Jeongeup, South Korea). The different doses were controlled at 10, 20, 40, and 100 kGy with a dose rate of 10 kGy/h at 15 °C. The absorbed dose was monitored using an alanine dosimeter (5 mm, Bruker Instruments, Rheinstetten, Germany).

2.4. Solubility in water

The solubility of starch was measured according to the method of Schoch (1964) with modification. The starch (1.0 g, db) was placed in a centrifuge tube and mixed with 10 ml of water. The starch solution was gently stirred for 1 h at room temperature and centrifuged at 1500×*g* for 10 min. Solubility was determined as follow: solubility = (weight of dissolved solids in supernatant)/(weight of dry solids in the original sample).

2.5. X-ray diffraction

The X-ray diffraction patterns of cross-linked and γ-irradiated waxy maize starches were obtained with an X-ray diffractometer (MAC Science Co., Japan) operated at 40 kV and 40 mA. The scanning range and rate were 3–35° (2θ) and 2.0 °/min, respectively.

2.6. Thermal properties

The thermal properties of cross-linked and γ-irradiated waxy maize starches were measured using a differential scanning calorimeter (DSC6100, Seiko Instruments, Chiba, Japan). A starch sample (3 mg, db) was placed in an aluminum pan (Seiko Instruments, Chiba, Japan) and distilled water (4.5 μl) was added. The sample pan was then sealed, allowed to equilibrate at room temperature for 1 h, and heated from 10 to 130 °C at a rate of 5 °C/min. An empty pan was used as a reference. The onset (T_o), peak (T_p) and conclusion (T_c) temperatures and melting enthalpy (ΔH) of gelatinization were determined from the thermograms.

2.7. Pasting properties

The pasting properties of cross-linked and γ-irradiated waxy maize starches were determined using a Rapid Visco-Analyzer (RVA-3D, Newport Scientific, Warriewood, Australia). Starch (12% w/w, db) was dispersed in a sodium phosphate buffer solution (0.1 M, pH 6.5). Starch slurries were held at 50 °C for 1 min, heated to 95 °C at a rate of 12.2 °C/min, held at 95 °C for 2.5 min, cooled to 50 °C at 12.2 °C/min, and held at 50 °C for 2 min. Peak viscosity, breakdown, setback, final viscosity and pasting temperature were obtained from viscograms.

2.8. In vitro starch digestibility

In vitro starch digestibility was determined according to the procedure of Englyst et al. (1992) with modifications. Porcine pancreatic α-amylase (3.89 g, activity 8 × USP/g) was dispersed in water (25.7 ml) by magnetic stirring for 10 min and the dispersion was centrifuged at 1500×*g* for 10 min. Supernatant (18.7 ml) was collected and amyloglucosidase (1.46 ml, activity; 5000–8000 units/ml) was