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Short communication

In vitro digestibility of gamma-irradiated corn starches

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ABSTRACT

The digestibility of gamma-irradiated corn starches was investigated. Gamma-irradiation (5–20 kGy) decreased the average molecular size of waxy and normal corn starches, but increased the proportions of both rapidly digestible (RDS) starch and enzyme-resistant starch (RS). The residual moisture in starch affected the susceptibility of the starches to the irradiation. Waxy corn starch was more susceptible to the irradiation than normal corn starch. The increase in RS content indicates that the irradiation induced the structural modification besides the chain degradation.

1. Introduction

Gamma-irradiation has been used to extend the shelf-life of food products and is often applied for the modification of food materials to change their physical properties (Waje & Kwon, 2007). The irradiation may generate active radicals which readily react with food components to change their molecular structure (Ciesla, Zoltowaski, & Mogilevski, 1991; Yu & Wang, 2007).

Native starch has amylose and amylopectin existing in heterogeneous semi-crystalline granules (Srichuwang & Jane, 2007). Gamma irradiation modifies the structure in both amorphous and crystal regions inducing physical and rheological changes in starch. Irradiation often resulted in increase in solubility but decrease in viscosity of starch by degrading the glycosidic linkages (Tollier & Guilbot, 1970). It was reported that the ratio of amylose and amylopectin affected the sensitivity to gamma-irradiation (Chung & Liu, 2009; Kong, Kasapis, Bao, & Corke, 2009; Wu, Shu, Wang, & Xia, 2002). Degradation by gamma-irradiation occurs through two types of interactions (Jackson, Corey, Frederick, & Picken, 1967): direct interaction in which the gamma-ray energy is absorbed to starch cleaving glycosidic linkages and indirect interaction in which gamma-ray firstly interacts with water producing free radicals and peroxides, the reactants inducing the cleavage of glycosidic linkages.

Compared to the physical and rheological changes, the effect of gamma irradiation on starch digestibility has been rarely investigated. It was reported that irradiated starches might exhibit different digestibility depending on irradiation dose (Rombo et al., 2001; Zuleta, Dyner, Sambucetti, & Francisco, 2006). In this study, waxy and normal corn starches were gamma-irradiated up to 20 kGy, and the changes in digestibility were determined using an *in vitro* analysis.

2. Materials and methods

2.1. Preparation of irradiated starch

Waxy and normal corn starches (12 ± 0.1% moisture) were provided by Samyang Genex Company (Seoul, Korea). Starches of 5 ± 0.1% moisture were also prepared by drying in a convection oven at 45 °C to compare with those of 12% moisture. Starches in polyethylene bags were irradiated using a 100 kCi gamma irradiator (^{60}Co, Korea Atomic Energy Research Institute, KAERI) at a dose rate of 10 kGy h^{-1} at 15 °C. The total doses were adjusted to 5, 10, and 20 kGy, which were confirmed by alanine dosimeter (5 mm, Bruker Instruments, Rheinstetten, Germany).

2.2. Molecular characteristics

The molecular structure of the irradiated starch was analyzed using a high performance size-exclusion column chromatography connected to a multi-angle laser light scattering (DAWN DSP-F, Wyatt Technology, Santa Barbara, CA) and a refractive index (Optical DSP, Wyatt Technology, Santa Barbara, CA) detector following

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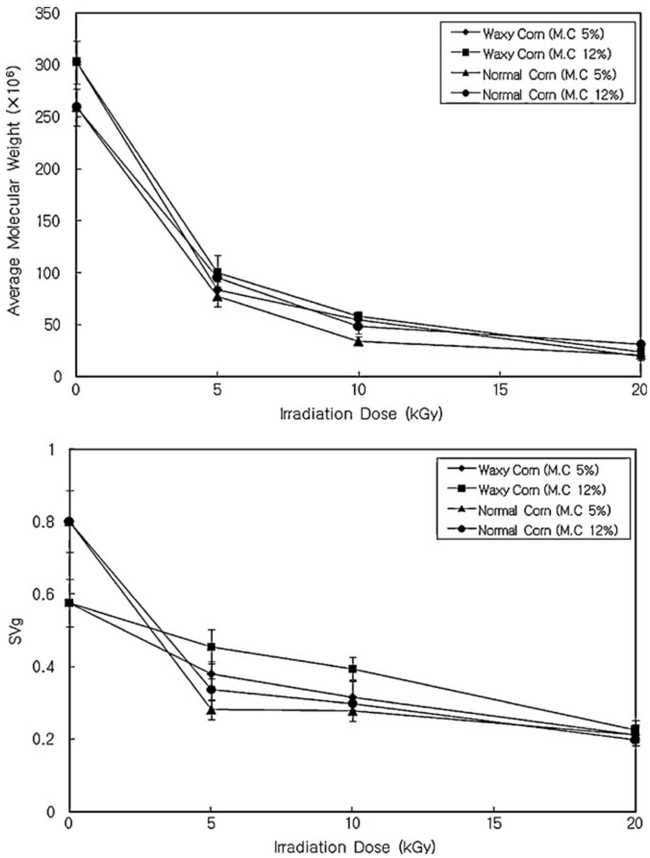

Fig. 1. Average molecular weight (*Mw*) and specific volume for gyration (*SVg*) of waxy and normal corn starches irradiated at different doses and moisture contents (5% and 12%) ($n = 3$).

the method of Han and Lim (2004). The flow rate and pump pressure were 1.5 mL/min and 2.8 kg/cm^2, respectively.

2.3. In vitro digestibility

In vitro digestibility was determined according to the procedure of Chung, Lim, and Lim (2006). The classification of starch based on its digestibility was consistent with that described by Englyst, Kingman, and Cummings (1992).

2.4. Statistical analysis

All measurements were performed in triplicate. Significant differences between means were detected by the Duncan's multiple range test ($P < 0.05$). Statistical analysis was performed using the SAS software package (2001).

3. Results and discussion

Molecular weight (*Mw*) of waxy and normal starch decreased by irradiation, and the decrease was significant during the irradiation up to 5 kGy (Fig. 1). A specific volume for gyration (*SVg*) that indicated molecular compactness of starch was calculated as $2.522Rg^3/Mw$. The *SVg* also decreased by irradiation, indicating that the starch molecules became smaller and denser (Han & Lim, 2004). These structural changes were more significant when the moisture content of the irradiated starch was 5% than the changes at 12%. A similar result was reported showing an increased sensitivity to a gamma irradiation of guar gum with decreased moisture content (Gupta, Shah, Sanyal, Variyar, & Sharma, 2009). The differences in *Mw* and *SVg* induced by moisture content became less as the irradiation dose increased. The starch degradation by gamma-irradiation undergoes by radical oxidation unlike the hydrolysis with acids or enzymes (Ciesla et al., 1991). The enhanced degradation with reduced moisture content might indicate that the chain degradation by the irradiation occurred through direct interaction of irradiation energy on starch, unlike the hydrolysis assisted by water.

The chain degradation appeared more significant for waxy corn starch than for normal corn starch (Fig. 1). Higher sensitivity of waxy starch to gamma-irradiation was reported in a previous study (Chung & Liu, 2009) which showed a decrease in *Mw* and an increase in the content of short chains ($6 \leq DP \leq 12$) of amylopectin. The difference in the compactness might be attributed to the difference in irradiation susceptibility between waxy and normal corn starches tested.

The *in vitro* digestibility of the irradiated starches is summarized in Table 1. There was 4.3–9.3% increase in the proportion of RDS in waxy corn starch by irradiation treatment at various doses, and 0.4–2.7% increase in normal corn starch. The digestibility increase was induced by structural degradations in both granules and molecules of starch which allowed easy access of the digestive enzymes to starch. However, no consistent changes in the proportion of RDS in both starches were observed as the irradiation dose increased. The irradiation decreased SDS contents in both starches although irradiation dose effect was not evident. It was assumed that SDS might be partially transformed to RS by the irradiation. It was expected that free radicals produced by the irradiation might induce chain associations resulting in the formation of more stable matrices which had an increased resistance against digestive enzymes. The irradiated starches at lower moisture content (5% *vs* 12%) mostly exhibited lower proportion of SDS in both waxy and normal corn starches. The proportion of RS was significantly increased by irradiations, with exception of a normal corn

Table 1
Proportions of rapidly digestible, slowly digestible and resistant starches in waxy and normal corn starches irradiated at 12 or 5% moisture content.[a].

Irradiation doses	Moisture (%)	Waxy starch			Normal starch		
		Rapidly digestible (%)	Slowly digestible (%)	Resistant (%)	Rapidly digestible (%)	Slowly digestible (%)	Resistant (%)
Native		32.8 ± 0.6^{e}	53.4 ± 0.3^{a}	13.8 ± 0.9^{d}	25.2 ± 1.2^{b}	47.1 ± 0.6^{a}	$27.7 \pm 0.5d^{e}$
5 kGy	12	37.1 ± 0.7^{d}	43.0 ± 0.4^{c}	19.9 ± 1.1^{bc}	26.0 ± 0.5^{b}	46.9 ± 0.4^{a}	27.1 ± 1.0^{e}
	5	38.2 ± 0.7^{ad}	35.4 ± 0.6^{f}	26.3 ± 1.5^{a}	26.1 ± 0.1^{b}	42.7 ± 1.0^{b}	$31.2 \pm 1.1b^{c}$
10 kGy	12	42.1 ± 0.4^{a}	40.4 ± 0.1^{d}	18.5 ± 0.5^{c}	27.9 ± 0.3^{a}	40.9 ± 0.6^{c}	30.0 ± 0.8^{cd}
	5	40.7 ± 0.1^{ab}	37.2 ± 1.6^{ef}	22.0 ± 1.7^{b}	25.7 ± 0.5^{b}	40.6 ± 0.3^{c}	33.7 ± 0.6^{a}
20 kGy	12	39.2 ± 1.2^{bc}	45.8 ± 1.0^{b}	15.0 ± 1.0^{d}	25.6 ± 0.4^{b}	43.5 ± 1.5^{b}	30.9 ± 1.8^{bc}
	5	38.3 ± 1.5^{cd}	38.9 ± 2.4^{de}	22.8 ± 3.5^{b}	27.9 ± 0.1^{a}	39.1 ± 1.8^{c}	33.0 ± 2.4^{a}

Values not sharing common letter within the column differ significantly ($p < 0.05$).
[a] Results are means of three measurements.

starch (5 kGy at 12% moisture). The increase in RS content was more evident in waxy starch than in normal starch. However, the proportion of RS in waxy starch was decreased as the irradiation dose increased. In both waxy and normal corn starches, the irradiation at 5% moisture resulted in greater RS contents than those at 12% moisture in all irradiation levels. It was reported that starch digestibility was increased when the irradiation doses were relatively low (up to 2 kGy) but decreased as the dose increased (Rombo et al., 2001; Zuleta et al., 2006) in accordance with our result.

The cleavage of anhydrous glycosidic linkages increases the accessibility of the digestive enzymes and thus decreases RS content. The increase of RS thus indicates that there were structural changes besides the chain cleavage. The starch chains might have increased mobility by the cleavage of glycosidic linkages and thus readily aligned to packed starch matrices. In this case, the starch chains in the packed matrices were physically less accessible to digestive enzymes. The physical association of the starch chains might be limited as the starch was irradiated in dry powers. It has been reported that the irradiation might induce the formation of new chemical bonds between anhydrous glucose units as a result of transglucosidation (Rombo, Taylor, & Minnaar, 2004) which was resistant to enzymatic hydrolysis. In addition, the formation of carbonyl and carboxyl groups through oxidation (Wu et al., 2002; Yadav, Mahadevamma, Tharanthan, & Ramteke, 2007) was also reported. These chemical changes for the formations of new linkages and functional groups are more feasible during the irradiation of dry starches.

As physical ways to raise RS content, hydrothermal treatments such as heat-moisture treatment and annealing are applied (Jacobs & Delcour, 1998; Kurakake, Tachibana, Masaki, & Komaki, 1996; Würsh, 1999). Similarly to the hydrothermal treatments, gamma irradiation may be used to increase RS content in starch without the disruption of granule structure.

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