Effects of pH and Gamma Irradiation on the Physicochemical Properties of Corn Starch

Il-Jun Kang[†], Cha-Kwon Chung and Jeong-In Sohn*

Division of Life Sciences, Hallym University, Chunchon 200-702, Korea *Department of Chemistry, Hallym University, Chunchon 200-702, Korea

Abstract

To develop a production method for modified starches with less pollution, pH adjustment and gamma irradiation were applied to commercial corn starch. Blue values were significantly decreased, while alkali number, optical transmittance and solubility markedly increased when gamma irradiation was applied to pH 2 adjusted corn starch. Water binding capacity and swelling power at pH 5 were the highest among the samples. Gelatinization viscosity was considerably affected by gamma irradiation and pH of the starch. Gamma irradiation of pH 2 adjusted starch showed the lowest peak viscosity and the best cooling stability among the tested samples. Therefore, the production of modified starch with low viscosity as well as with sufficient viscosity stability seems feasible by controlling the pH of the starch and gamma irradiation.

Key words: gamma irradiation, pH, corn starch, physicochemical property

INTRODUCTION

Various modified starches have been produced for the purpose of improving gelatinization and gelatinization properties, reducing retrogradation and water-holding capacities at low temperature. Corn starch, in particular, one of the most abundant natural starches, is available in the industry at the most reasonable cost (1,2). Currently, the demand for modified starch in the industry is increasing annually. The production of oxidized low-viscosity starch and acid-treated starch for local pulp sizing and textile sizing has reached 120,000 tons per year. Approximately 90% of the oxidized starch is used for pulp and produced domestically (3). However, recent environmental regulations make the production of modified starch more difficult than ever and the quantity as well as the quality of the modified starch is known to run short (4).

As a useful method for the production of modified starch, gamma irradiation produces free radicals on the starch molecules that can alter their size and structure (5,6). Several studies have been done on the effects of ionizing radiation on wheat starch and barley endosperm (7,8). Gamma irradiation is capable of hydrolyzing chemical bonds, thereby cleaving large molecules of starch into smaller fragments of dextrin that may be either electrically charged or uncharged as free radicals. These changes may affect the physical and rheological properties of irradiated starches, resulting in increased solubility of starch, decreased swelling power, and decreased relative viscosity of starch paste (9,10). Other effects of irradiation include structural changes of starch molecules resulting in changes in sensitivity to enzymes, lowering of the melting point, changes of the absorption spectrum and cleavage of the α -1,4 chain of starch molecule (11).

Although starch irradiated at 100 kGy revealed a similar gelatinization properties with the oxidized starch in the market, high dose irradiation seems necessary for improvement in starch properties, in spite of the existence of the efficiency problems in the economy (12). Therefore, this study has examined the physicochemical properties of gamma irradiated $(0 \sim 50 \text{ kGy})$ corn starch at different pHs as a basis for the economic and less-pollutive techniques of modifying starch production.

MATERIALS AND METHODS

Sample preparation

The corn starch specimen used in this study was obtained from Samyang Genex Co., which contains 12% moisture, 0.1% ash, 0.38% protein and 37 ppm of SO₂. In order to adjust pH, corn starch was suspended in water and pH was then set at 2, 5, 7 and 9 with HCl and NaOH, vortex mixed for an hour, dehydrated and dried.

Gamma irradiation

Corn starch was packed in PVC bags (\emptyset 5×H 8 cm) to reduce dose variations among samples. The gamma radiation flux from the gamma irradiator of 100,000 Ci (60 Co, Korea Atomic Energy Research Institute) to the sample was 1 kGy per hour at ambient temperature(15 $^{\circ}$ C±0.5) and the total dose applied was 0~50 kGy, which was confirmed by ceric cerous dosimeter.

Physicochemical properties of the starch

The blue value was determined by the method of Gilbert and Spragg (13), alkali number by Schoch (14) and water binding capacity by Medcalf and Gilles (15). Solubility was deter-

[†]Corresponding author. E-mail: ijkang@sun.hallym.ac.kr Phone: 82-361-240-1478, Fax: 82-361-255-4787 mined by weighing the residual dissolved starch, and the swelling power at 90° C was calculated by the method of Schoch (16). Transmittance of the starch solution (0.2%) was analyzed using a spectrophotometer (Bausch & Lomb, Spectronic 70) at 625 nm at the temperature ranges of $50 \sim 95^{\circ}$ C (17).

Characteristics of gelatinization by amylograph

Gelatinization characteristics of 12% of corn starch (dry weight basis) was measured by Brabender viscograph (E Type, Brabender Co., West Germany) and by the method of Medcalf and Gilles (15). The suspension of 500 ml of starch sample was gently stir-mixed for a minute, put in amylograph bowl, heated slowly from 25°C to 95°C at a speed of 1.5°C/min, maintained for 30 min at 95°C and then cooled to 50°C or 30°C at a speed of 1.5°C/min. The temperature of initial gelatinization was measured when the curve reached 20 B.U.

RESULTS AND DISCUSSION

Blue value and alkali number

The changes in the blue value of the irradiated starch at 50 kGy after pH adjustment at 2, 5, 7, and 9 were shown in Fig. 1. Iodine binding capacity of the starch was shown to be the highest at pH 5. As pH approached neutral (pH 7) it began to gradually decrease and further decrease was observed at pH 9. Iodine binding value was 0.136 at pH 2, which was lower than that of the starch irradiated at much higher doses of 110 kGy without pH adjustment (12). This result indicates that iodine binding capacity (blue value) of the gamma irradiated starch is affected by pH and greatly reduced under acidic conditions.

The alkali number of the starch adjusted to pH 2 showed the highest among the starches gamma irradiated at 50 kGy (Fig. 1). Although the alkali number at pH $5\sim9$ was not different among samples and remained in the range of $29.4\sim32$, it drastically increased to 43.6 at pH 2, which was higher

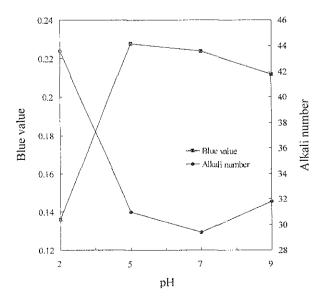


Fig. 1. Changes in blue value and alkali number of pH adjusted corn starches irradiated at 50 kGy.

than that (41.8) of the starch irradiated at 110 kGy without pH adjustment (12).

Subsequently, the effects of gamma irradiation in the range of $10\sim50$ kGy on the starch adjusted to pH 2 were examined (Fig. 2). The blue value was reduced as irradiation dose increased. It was drastically reduced at doses above 40 kGy. On the other hand, the alkali number of the starch adjusted to pH 2 linearly increased as irradiation dose increased ($10\sim50$ kGy) (Fig. 2).

The blue value of the starch irradiated at 50 kGy, pH 5 (Fig. 1) was similar to that of the starch irradiated at 10 kGy, pH 2 (Fig. 2). The alkali number of the starch irradiated at 10 kGy, pH 2 was also slightly higher than that of 50 kGy at pH 5, 7 and 9 (Fig. 1, 2). The above results indicate that gamma irradiation at acidic conditions (pH 2) causes structural changes in the starch molecule, thereby reducing iodine binding capacity and increasing the number of terminal aldehyde groups.

Optical transmittance pattern

Clarity, turbidity and whiteness of starch solutions are very critical in the application of starch for food or for pulp. Also, the content and structure of amylose, amylopectin, lipid, sugar and salt affect the optical transmittance pattern of starch (18). Optical transmittance pattern of starch irradiated at 50 kGy, pH 2 revealed the highest value at all temperature ranges $(50 \sim 95^{\circ}\text{C})$, secondly, the optical transmittance at pH 9. Optical transmittance at pH 7 and 5 showed the lowest values (Fig. 3). Therefore, gamma irradiation after acidic treatment turned out to be effective for improving optical transmittance. On the other hand, as irradiation dose increased, optical transmittance of starch at pH 2 linearly increased until the heating temperature reached 85°C, slowly increased between 85 and 95°C and then plateaued at temperatures above 95°C (Fig. 4). The above results indicate that high optical transmittance was preserved at low temperatures.

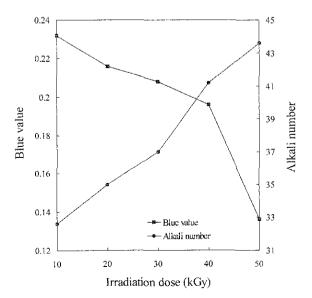


Fig. 2. Effects of gamma irradiation on blue value and alkali number of pH 2 adjusted corn starch.

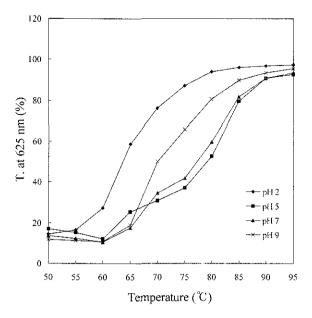


Fig. 3. Changes in transmittance of pH adjusted corn starch suspensions (0.2%) by gamma irradiation at 50 kGy.

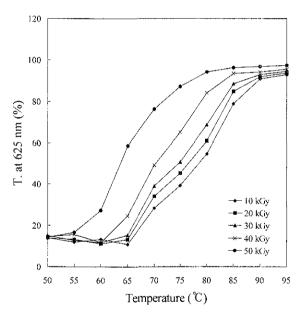


Fig. 4. Effects of gamma irradiation dose levels on transmittance of pH 2 adjusted corn starch suspensions (0.2%).

Water-binding capacity and swelling power

Water-binding capacity and swelling power of starch irradiated at 50 kGy showed the highest value at pH 5 with minimum changes in the structure of the starch molecule. However, those of the starch at pH 2 and 9 showed relatively low values (Fig. 5). Water-binding capacity of the starch irradiated at dose of 30 kGy or less was not different among groups at pH 2, but at dose of 50 kGy, it showed only 82% of the initial value (Fig. 6).

Swelling power of the starch was gradually reduced as irradiation dose increased. It drastically decreased at doses above 30 kGy, and it showed 4.5% of the initial value at 50 kGy (Fig. 6).

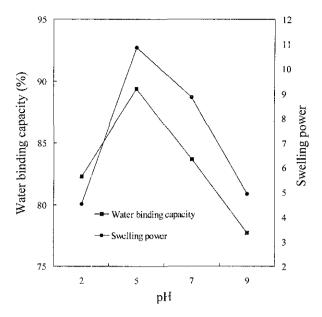


Fig. 5. Changes in water binding capacity and swelling power of pH adjusted corn starches irradiated at 50 kGy.

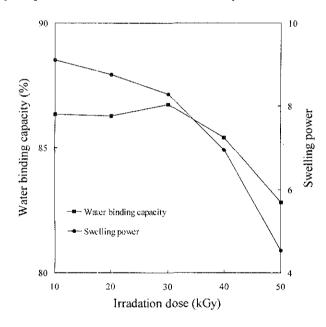


Fig. 6. Effects of gamma irradiation dose levels on water binding capacity and swelling power of pH 2 adjusted corn starches.

Water-binding capacity and swelling power depend upon the existence and amounts of the soluble components and unionizing granules of the starch (19). The structural changes in the starch by gamma irradiation resulted in water-binding capacity to be kept within a certain range, but it dropped at doses above 30 kGy due to the destruction of the amylose structure of the starch molecule.

Solubility

The solubility of starch irradiated at 50 kGy after pH adjustment at pH 5 to 9 was not different among samples. However, it increased to 82% as pH was adjusted to 2, which was higher than that of the starch irradiated at 110 kGy without pH adjustment (Fig. 7). In addition, solubility linearly in-

creased with the increase of the irradiation dose under acidic conditions (Fig. 8). These results exhibit a similar trend to those observed above in alkali number that the damage to the starch chain affects its solubility.

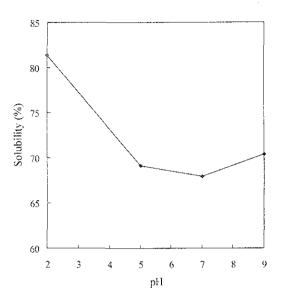


Fig. 7. Changes in solubility of pH adjusted corn starches irradiated at 50 kGy.

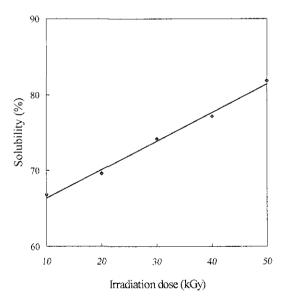


Fig. 8. Effects of gamma irradiation dose levels on solubility of pH 2 adjusted corn starches.

Gelatinization properties

Physical property of starch gelatinization after pH adjustment was examined. Gelatinization at 50 kGy irradiation after pH adjustment to acidic or alkali states revealed similar results to that of the commercial oxidized starch. The peak and cooling viscosity of the starch irradiated at 50 kGy at pH 2 was lower than that of the oxidized starch and showed excellent gelatinization property (Table 1).

This was largely due to the acid hydrolysis, the reduction of amylose content, and subsequent low binding power and easy expansion between the molecules. So far, starch only irradiated at higher doses, 100 kGy, has been commercially available as a substitute for oxidized starch. However, the technique of adjustment of the starch to acidic conditions along with the reduction of irradiation dose allows economical benefits and improvement of the physicochemical property.

ACKNOWLEDGEMENTS

This study was supported in part by the Hallym University Research Fund, for which the authors appreciate deeply.

REFERENCES

- Swinkles, J. J. M.: Sources of starch, its chemistry and physics. In "Starch conversion technology" Van Beynum, G.M.A. and Roels, J.A. (eds.), Marcel Dekker Inc., New York, p.18 (1985)
- Ohtaka, T.: Resources of starch-corn, wheat, tapioca and Sago. J. Jap. Soc. Starch Sci., 27, 244 (1980)
- Miwa, T.: Corn wet milling industry. J. Jap. Soc. Starch Sci., 27, 256 (1980)
- Galliard, T.: Starch availability and utilization. In "Starch: Properties and potential" Galliard, T. (ed.), John Wiley & Sons, Chichester, p.1 (1987)
- Ciesla, K., Zoltowski, T. and Mogilevsky, L. Y.: Detection of starch transformation under gamma-irradiation by small-angle X-ray scattering. Starch/Staerke, 43, 11 (1991)
- Grant, L. A. and D'Appolonia, B. L.: Effect of low-level gamma irradiation on water-soluble non-starchy polysaccharides isolated from hard red spring wheat flour and bran. *Cereal Chem.*, 68, 651 (1991)
- Lai, S. P., Finney, K. F. and Milner, M.: Treatment of wheat with ionizing radiations. 4. Oxidative, physical and biochemical changes. *Cereal Chem.*, 36, 401 (1959)
- Faust, M. and Massey, L. M. Jr.: The effect of ionizing radiation on starch breakdown in barley endosperm. *Rad. Research*, 29, 33 (1966)
- Ananthaswamy, H. N., Vakil, U. K. and Sreenivasan, A.: Effect of gamma radiation on wheat starch and its components. J. Food

Table 1. Effects of pH on the amylograph indices of 50 kGy irradiated corn starch¹⁾

pН	Initial pasting temp. (°C)	Peak temp. (°C)	Peak viscosity (B.U)	Viscosity after 30 min at 95°C (B.U)	Viscosity at 50°C (B.U)	Viscosity after 30 min at 50°C (B.U)	Viscosity at 30°C (B.U)	Viscosity after 30 min at 30°C (B.U)
2	ND	69.0	10	18	21	20	20	20
5	65.0	69.0	760	39	110	220	720	700
7	67.0	71.5	236	29	114	205	670	620
9	68.0	72.0	100	22	70	110	360	320
OX ²⁾	65.0	69.0	76	18	40	35	50	45

¹⁾12% dry basis, 350 cmg torque. ²⁾Oxidized starch.

- Sci., 35, 795 (1970)
- Deschreider, A. R.: Systematic study of flour treated with gamma rays. 1. Action on polysaccharides. Fermentatio., 1, 31 (1959)
- 11. Tollier, M. T. and Guilbot, A.: Development of certain physicochemical properties of the starch granule as a function of irradiation conditions. *Starke*, **2**, 296 (1970)
- Kang, I. J. and Byun, M. W.: Development of modified starch by gamma irradiation. Korean J. Food Sci. Technol., 28, 514 (1996)
- Gilbert, G. A. and Spragg, S. P.: Iodimetric determination of amylose. In "Methods in carbohydrate chemistry" Whistler, R. L. (ed.), Academic Press, New York, Vol. 4, p.168 (1964)
- 14. Schoch, T. J.: Determination of alkali number. In "Methods in carbohydrate chemistry" Whistler, R. L. (ed.), Academic Press,

- New York, Vol. 4, p.61 (1964)
- Medcalf, D. G. and Gilles, K. A.: Wheat starches. I. Comparison of physicochemical properties. *Cereal Chem.*, 42, 558 (1965)
- Schoch, T. J.: Swelling power and solubility of granular starches. In "Methods in carbohydrate chemistry" Whistler, R. L. (ed.), Academic Press, New York, Vol. 4, p.106 (1964)
- Wilson, L. A., Birmungham, V. A., Moon, D. P. and Snyder, H. E.: Isolation and characterization of starch from mature soybeans. *Cereal Chem.*, 55, 661 (1978)
- Craig, S. A. S., Maningat, C. C., Seid, P. A. and Hoseney,
 R. C.: Starch paste clarity. Cereal Chem., 66, 173 (1989)
- Roach, R. R. and Hoseney, R. C.: Effect of certain surfactants on the swelling, solubility and amylograph consistency of starch. *Cereal Chem.*, 72, 571 (1995)

(Received July 24, 1999)