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Effect of Irradiation on pH, Color, and Sensory Quality of Cooked Pork Sausage with Added Chitosan Oligomer

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Abstract

The combined effect of water-soluble chitosan oligomer and irradiation on changes in quality of pork sausage made with (156 ppm) or without $NaNO_2$ was determined. The pH of nonirradiated sausage without $NaNO_2$ decreased significantly during 3 wks of storage, but the pH of irradiated sausage did not. Irradiation at 4.5 kGy did not increase the Hunter color a-value but 10 and 20 kGy showed significantly higher a-values in the sausage with chitosan oligomer ($p < 0.05$). The sausage with $NaNO_2$ had higher sensory scores than that without $NaNO_2$, and irradiated sausage had lower scores in overall acceptance. Results indicate that further research is needed to achieve consumers sensory standards for irradiating cooked meat products.

Key words: gamma irradiation, pork sausage, chitosan oligomer, sodium nitrite

INTRODUCTION

Chitin, a polymer of *N*-acetylglucosamine, is a cellulose-like biopolymer present in the exoskeleton of crustaceans and in cell walls of fungi, insects and yeast (1). Chitin, chitosan, and their oligomers are known to have many beneficial biological effects, such as antimicrobial (2), antitumor (3), antioxidant (4), and hypocholesterolemic (5) activities. The absorption of chitosan in the human intestine, however, is a little difficult because of its high viscosity and high molecular weight (1). Recently, therefore, increasing attention has been given to chitosan oligomer which is prepared from chitosan by enzymatic or chemical hydrolysis (6). In addition, the chitosan oligomers are soluble in aqueous solution, thus may be readily absorbed *in vivo* and be more applicable for industrial uses.

The residual NO_2 from $NaNO_2$ in processed meat products can react with amines and amino acids to form N-nitrosamine which is known to cause certain types of cancer (7). However, the various beneficial effects of $NaNO_2$ in meat processing, such as desirable color, flavor, and the inhibitory effect on toxic spores of *Clostridium botulinum* make it difficult to find alternatives. Byun et al. (8) reported, however, that the ham made from gamma-irradiated raw pork loin showed a desirable color and kept an acceptable microbial level without addition of $NaNO_2$. Moreover, Jo et al. (9) and Jo et al. (10) reported that the Hunter color a-value of the cooked pork sausage prepared from different fat contents or fat sources increased by electron-beam irradiation when vacuum-packaged. The authors also found that the changed color a-value was maintained regardless of fat content or fat source used during storage in a 4°C refrigerator for 4 wks. Byun et al. (8) reported that a dose of 5 kGy was as effective as the use of 200 ppm of $NaNO_2$.

However, information of the combined effect of irradiation and chitosan oligomer on the quality of emulsion-type smoked sausage is very limited. Based on the hypothesis that irradiation of pork sausage will have a desirable color without sodium nitrite, and chitosan will give beneficial functions to cooked pork sausage, the present study was to determine the effect of water-soluble chitosan oligomer combined with irradiation on the quality change of cooked pork sausage.

MATERIALS AND METHODS

Sample preparation

Vacuum-packaged, refrigerated lean pork and frozen pork backfat, were obtained within 48 hrs of slaughtering from a local meat packer and ground (Model 160, Fatosa, Barcelona, Spain) twice through a 9-mm and a 3-mm plate, respectively. An emulsion-type pork product was prepared using ground meat, and sodium nitrite ($NaNO_2$, 156 ppm) or chitosan oligomer (0.2%, m.w. = 5,000, pH = 7.2, Shinyoung Chitosan Co. Ltd, Seoul, Korea) were selectively added to products to investigate the irradiation effect on quality changes in sausage (Table 1); without chitosan oligomer and $NaNO_2$ (T1), without chitosan oligomer but with $NaNO_2$ (T2), with chitosan oligomer but without $NaNO_2$ (T3), and with both

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Table 1. Formula of the smoked pork sausage

Materials	Composition (%)
Pork	60
Pork backfat	20
Ice water	20
NaCl[1)]	1.5
Trisodium phosphate[1)]	0.3
Ascorbic acid[1)]	0.01
Monosodium glutamate[1)]	0.02
Spice mix[1),2)]	0.5
$NaNO_2$[1)]	156 ppm or none
Chitosan oligomer[1)]	0.2 or none

[1)] *Composition of each material other than pork, pork backfat and ice water is a percentage of total weight of pork, pork backfat and ice water.*
[2)] Spice mix contained coriander, glucose, red pepper, and onion powder.

chitosan oligomer and $NaNO_2$ (T4). All ingredients were purchased from Sewoo Co. Ltd. (Seoul, Korea), and the spice mix contained coriander, glucose, red pepper, and onion powder. Lean pork, salt and phosphate were placed in a silent cutter (C-75, Fatosa, Barcelona, Spain) and mixed for about 1 min after which 50% of ice was added and mixed at high speed. When the temperature of mixture decreased by about 1~2°C, ground pork backfat was added and mixed until the temperature of the mixture reached 10°C. The remainder, 50% of ice and other spices were added and mixed until the temperature of mixture reached 13°C. Total emulsification time was about 10 min and the processing room temperature was 13°C. The sausages were stuffed (Patron Sausage Filler MWF 591, MADO, Nederland) into a collagen casing (2.5 cm of diameter, Woosung Co. Ltd., Seoul, Korea), dried (45°C for 30 min), smoked (55°C for 40 min) by sawdust, and cooked to 70°C of internal temperature (about 1 hr) using a smokehouse (Fracomat 1200, Franke Gm bH & Co., Germany). For color measurement, a fibrous casing (3.2 cm of diameter) was used to avoid interference of smoke rings. The cooked sausage was water-spray cooled for 5 min, dried at room temperature for 30 min, and cut into pieces (about 100 g each). The samples were vacuum-packaged (75 cmHg pulled) in oxygen-impermeable nylon bags (2 mL $O_2/m^2/24$ h at 0°C; 20 cm × 30 cm; Sunkyung Co. Ltd, Seoul, Korea) with a vacuum packaging machine (Leepack, Hanguk Electronic, Kyungi, Korea) and then stored overnight in a 4°C refrigerator.

Irradiation

Irradiation was performed next morning using a Co-60 gamma irradiator (point source, AECL, IR-79, Nordion International Co., Ltd, Ontario, Canada) with a source strength of 100 kCi. The dose rate was 70 Gy/min at 16±0.5°C and the absorbed dose was 0 and 4.5 kGy. For color measurement, additional 10 and 20 kGy of irradiation were applied. Dosimetry was performed using 5 mm-diameter alanine dosimeters (Bruker Instruments, Rjeomstettem, Germany), and the free radical signal was measured using a Bruker EMS 104 EPR Analyzer. The actual dose was within ±2% of the target dose. The irradiated pork sausages were transferred to a 4°C refrigerator and analyses were started 3 hrs later.

pH and color measurement

pH was measured by pH meter (Model 520A, Orion Research Inc., Boston, MA 02129, USA) adding 9 parts of deionized distilled water (DDW) into 1 part of the sample.

For color measurement, samples were cut into 2 cm-thick pieces and measured on the plate of the Color Difference Meter (Spectrophotometer CM-3500d, Minolta Co., Ltd., Osaka, Japan). The instrument was calibrated to standard black and white tiles before analysis. Eight pieces per treatment were measured and mean values were used for replication. A medium size aperture was used and the measurement was duplicated. The Hunter color L-, a-, and b-, C-, and h°- values were reported through the computerized system using a Spectra Magic software (version 2.11, Minolta Cyberchrom Inc., Osaka, Japan).

Lipid oxidation

Lipid oxidation was determined as a 2-thiobarbituric acid reactive substances (TBARS) value by using a spectrophotometer (UV 1600 PC, Shimadzu, Tokyo, Japan) as described by Turner et al. (11). Sausage was homogenized in a blender and 1 g of sample was added into a 50 mL test tube with 5 mL of 20% trichloroacetic acid in 2 M phosphoric acid and 10 mL of 0.01 M TBA. The sample was vortexed and heated in boiling water for 30 min, then chilled in icewater for 10 min. Mixture of isoamylalcohol and pyridine (2 : 1, v/v, 15 mL) was added into the test tube and vigorously vortexed for 2 min. Then, the sample was centrifuged for 15 min at 2,400 rpm. The upper layer of the mixture was used for spectorphotometric reading at 538 nm.

Sensory evaluation

Sensory analysis was performed with 15 panel members, who were trained and accustomed to the color, flavor, and texture of the normal nonirradiated sausage with sodium nitrite (156 ppm) before analysis. Sensory scores were evaluated with a 5-point scale : 1, very poor; 2, poor; 3, average; 4, good; 5, very good. The sausage was reheated to 70°C internal temperature in an oven at 180°C for about 15 min, sliced into 2 cm-thick pieces, and served to the panels individually. The sensory parameters including flavor, color, texture, and overall acceptance, were evaluated independently by the panel members 3 different times.

Statistical analysis

Analyses of Variance were performed using SAS software (12) and the Student-Newman-Keuls multiple range test was used to compare differences among mean values. Mean values and pooled standard errors of the mean (SEM) were reported, and the significance was defined at $p<0.05$.

RESULTS AND DISCUSSION

pH and lipid oxidation

The pH of nonirradiated sausage decreased by storage re-

Table 2. Changes in pH of gamma-irradiated and vacuum-packaged sausage during storage at 4°C

Irradiation dose (kGy)	Treatment[1)]	0 wk	1 wk	2 wk	3 wk	SEM[2)]
0	T1	6.39^{bz}	6.43^{ay}	6.08^{cy}	5.93^{dz}	0.008
	T2	6.43^{ayz}	6.29^{bz}	6.29^{bz}	5.99^{cy}	0.012
	T3	6.47^{by}	6.49^{bx}	6.41^{bx}	6.53^{aw}	0.012
	T4	6.59^{x}	6.53^{w}	6.51^{w}	6.41^{x}	0.055
	SEM[3)]	0.010	0.007	0.008	0.007	
4.5	T1	6.42^{b}	6.49^{ayz}	6.36^{cz}	6.38^{cz}	0.008
	T2	6.59	6.47^{z}	6.47^{x}	6.47^{y}	0.056
	T3	6.47	6.51^{y}	6.41^{y}	6.56^{x}	0.056
	T4	6.50^{c}	6.58^{ax}	6.50^{cx}	6.54^{bx}	0.008
	SEM[3)]	0.056	0.007	0.009	0.011	

a-d Different letters within a same row differ significantly ($p<0.05$).
x-z Different letters within a same column with same irradiation dose differ significantly ($p<0.05$).
1) Treatment : T1, No addition of both chitosan oligomer and $NaNO_2$; T2, chitosan oligomer (0.2%) added but no $NaNO_2$; T3, No chitosan oligomer but $NaNO_2$ (156 ppm) added; T4, both chitosan oliogmer (0.2%) and $NaNO_2$ (156 ppm) added.
2) Pooled standard errors of the mean (n = 8).
3) Pooled standard errors of the mean (n = 8).

gardless of treatment combinations (Table 2), but the decreasing rate was faster in T1 and T2 than in T3 and T4. Sausage prepared without chitosan and $NaNO_2$ (T1) showed the fastest decline in pH and the final pH at 3 wk was 5.93. The decreasing order of pH of the sausage was generally T4 > T3 > T2 > T1 in nonirradiated sample regardless of storage. The pH of sausage irradiated at 4.5 kGy did not change significantly but still the sausage with T4 was the highest (Table 2). The rapid reduction in pH was observed in the nonirradiated sausage with T1 and T2, but others were steady. The pH decrease can be related to microbial change, because acid-producing bacterial growth may result in the pH decline. This indicates that microbial controls by irradiation help the pH to remain constant in the cooked pork sausage.

The lipid oxidation development was measured by the TBARS method but no significant difference was observed by storage, irradiation dose or treatment combinations (data not shown). However, Darmadji and Izumimoto (4) reported that addition of chitosan at 0.2, 0.5, and 1% resulted in decreases of 10, 25, and 40% in the TBA values of meat in aerobic conditions. Generally, aerobic packaged raw meat or meat products (8) accelerated the lipid oxidation, but without oxygen, such as modified atmosphere packaging (13) or vacuum packaging (14), the lipid oxidation was inhibited in raw meat or cooked pork sausage. Ahn et al. (15) concluded that exposure to oxygen was a more important factor than irradiation in the development of lipid oxidation in meat products during storage.

Color

When color measurement was performed with small diameter-collagen casing (1.8 cm), the smoke ring interfered the accuracy of data, thus, the present study used a larger casing (3.2 cm). The nonirradiated sausage with T4 showed the highest Hunter color L-value, and a higher irradiation dose caused an increase in the L-value in the sausage with T1 (Table 3). Jo et al. (10) reported that the Hunter color L-value of irradiated cooked pork sausage did not change by irradiation at 2.5 and 4.5 kGy, but they reported that the after 8-days of storage, the L-value decreased in the sausage with vacuum packaging.

Cornforth (16) reported that consumers prefer bright-red fresh meats, brown-gray cooked meats, and pink cured meats. Therefore, the a-value is one of the most important factors in the color of meat products. The Hunter color a-value was higher in the sausage with $NaNO_2$ (T4) added than that without it (T1 and T2, Table 3). The results from Darmadji and Izumimoto (4) indicated that the Hunter color a-value of raw meat patties increased by chitosan addition, but with the chitosan oligomer in the present study, the a-value was lower in the nonirradiated sausage with T2 than T1. The a-value of the sausage with only the chitosan oligomer (T2) was lower in the nonirradiated control but increased by irradiation at 10 and 20 kGy, resulting in a much higher a-value than that of the sausage with T1. Jo et al. (10) reported that irradiation with electron-beam increased redness in vacuum-packaged cooked pork sausage regardless of fat sources used, and the increase in redness was dose dependent. Additives to sausage may interact with pigment molecules, resulting in different a-values in irradiated sausage since Jo

Table 3. Changes in Hunter color value of vacuum-packaged sausage 3-hour after gamma irradiation

Parameters	Treatment[1)]	Irradiation dose (kGy) 0	4.5	10	20	SEM[2)]
L-value	T1	69.58^{cy}	70.03^{b}	70.33^{bx}	70.78^{ax}	0.150
	T2	69.34^{y}	70.34	69.70^{y}	70.32^{y}	0.296
	T4	70.37^{abx}	70.16^{b}	70.48^{abx}	70.98^{ax}	0.190
	SEM[3)]	0.250	0.304	0.160	0.123	
a-value	T1	6.39^{ay}	5.49^{cz}	6.47^{az}	5.88^{bz}	0.074
	T2	5.97^{cz}	5.83^{cy}	8.50^{ay}	8.00^{by}	0.120
	T4	9.21^{ax}	7.77^{dx}	8.90^{bx}	8.31^{cx}	0.905
	SEM[3)]	0.135	0.092	0.055	0.088	
b-value	T1	13.46^{y}	13.72^{x}	13.72^{x}	13.30^{x}	0.205
	T2	14.98^{ax}	13.69^{bx}	12.39^{cy}	12.62^{cy}	0.200
	T4	11.94^{bcz}	11.70^{cy}	12.81^{ay}	12.42^{aby}	0.188
	SEM[3)]	0.173	0.306	0.139	0.115	
C-value	T1	14.89^{y}	14.78	15.17^{y}	14.54^{y}	0.198
	T2	16.14^{ax}	14.88^{b}	15.03^{by}	14.95^{bx}	0.201
	T4	15.08^{ay}	14.05^{b}	15.60^{ax}	14.95^{ax}	0.197
	SEM[3)]	0.195	0.305	0.123	0.111	
h°-value	T1	64.59^{cy}	68.14^{ax}	64.71^{cx}	66.13^{bx}	0.345
	T2	68.30^{ax}	66.87^{by}	55.53^{dy}	57.63^{cy}	0.443
	T4	52.35^{cz}	56.38^{az}	55.19^{by}	56.16^{az}	0.257
	SEM[3)]	0.368	0.375	0.322	0.360	

a-c Different letters within a same row differ significantly ($p<0.05$).
x-z Different letters within a same column with same storage differ significantly ($p<0.05$).
1) All notations represent the same of those in Table 1.
2) Pooled standard errors of the mean (n = 32).
3) Pooled standard errors of the mean with same storage (n = 24).

et al. used only pork, fat, and ice water to make sausage (10). Moreover, the a-value change induced by irradiation did not reach the same level of a-value in the sausage with $NaNO_2$. Byun et al. (8), however, successfully made the pork loin ham without $NaNO_2$ by 5 kGy of irradiation to raw pork loin. The results they provided indicated that the color characteristics of irradiated meats were comparable to the NO_2-cured products. It also suggested that irradiation to the meat products before and after cooking may interact differently to the redness of end products.

The Hunter color b-value of the sausage with nitrite (T4) was always lower than that of T1 or T2. The addition of chitosan oligomer (T2) increased yellowness in the nonirradiated sample but irradiation at 10 and 20 kGy resulted in a lower b-value in the sausage. Youn et al. (17) reported that 0.5% of chitosan addition increased the color b-value, indicating that the own color of chitosan affected on the surface color of sausage. Irradiation at 10 and 20 kGy increased the b-value in the sausage with T4. Nanke (18) reported that Hunter color b-value of vacuum-packaged pork and turkey increased as irradiation dose increased from 0 to 4.5 kGy but it remained unchanged at 7.5 and 10.5 kGy. With aerobic packaging, the b-value for the exterior surface of irradiated pork was significantly higher than that of nonirradiated control at 4°C for 6 and 7 days of storage (19).

C-values and h°-values were significantly different and the sausage with T2 had higher C-values and the sausage with T1 had higher h°-values than other treatments (Table 3).

Table 4. Sensory scores of vacuum-packaged sausage 3-hour after gamma irradiation[1)]

Sensory parameters	Irradiation dose (kGy)	Treatment[2)] T1	T2	T3	T4	SEM[3)]
Color	0	2.7[b]	2.7[b]	4.4[ax]	4.1[a]	0.72
	4.5	2.7[b]	2.8[b]	3.4[ay]	3.7[a]	0.19
	SEM[4)]	0.17	0.17	0.22	0.16	
Flavor	0	2.9[b]	3.0[b]	3.9[ax]	3.7[ax]	0.22
	4.5	2.5[ab]	2.4[ab]	2.1[by]	3.1[ay]	0.22
	SEM[4)]	0.25	0.21	0.21	0.22	
Texture	0	3.1[b]	2.9[b]	4.0[ax]	4.0[a]	0.18
	4.5	2.6[b]	2.6[b]	2.9[by]	3.5[a]	0.19
	SEM[4)]	0.19	0.22	0.16	0.16	
Overall acceptance	0	2.9[bx]	2.9[bx]	4.5[ax]	4.1[ax]	0.16
	4.5	2.0[by]	2.3[by]	2.5[by]	3.5[ay]	0.19
	SEM[4)]	0.17	0.18	0.18	0.16	

[a,b]Different letters within a same row differ significantly ($p<0.05$).
[x,y]Different letters within a same column and same sensory parameter differ significantly ($p<0.05$).
[1)]Sausage was reheated to 70°C and served to the 15-trained panel members. Sensory score was evaluated with a 5-point scale : 1, very poor; 2, poor; 3, common; 4, good; 5, very good. Same panels were conducted 3 different times.
[2)]All notations represent the same of those in Table 1.
[3)]Pooled standard errors of the mean (n = 180).
[4)]Pooled standard errors of the mean (n = 90).

Sensory qualities

The surface color of the sausage with $NaNO_2$ (T3 and T4) was preferred by panels to that without $NaNO_2$ (T1 and T2) regardless of irradiation treatment (Table 4). Sensory panels scored lower on irradiated sausage with T3 than nonirradiated for color evaluation. The sausage with T3 and T4 also obtained higher scores on flavor and texture, which suggests that the $NaNO_2$ is an important additive in processing the smoked pork sausage for sensory besides the purpose of microbiological and color concerns. In the sausage with T3, the irradiation effect was clearly shown in color, flavor, and texture, resulting in lower scores when the sausage was irradiated. Some panel members detected characteristic off-odors from irradiated samples that was not detected from nonirradiated controls, describing it as "burnt feathers or burnt plastic films". Heath et al. (20) reported that irradiated uncooked chicken breast and leg at 2 or 3 kGy produced a "hot fat", "burnt oil", or "burnt feathers" odor that remained after the thighs were cooked. Ahn et al. (15) reported, however, that panelists detected irradiation odor from irradiated pork loin and described it as a "barbecued corn-like" odor but no objection was observed.

CONCLUSION

Results indicate that the surface color of cooked sausage cannot be achieved to present consumer standard by 4.5 kGy of irradiation without adding $NaNO_2$. Further research to protect sensory quality changes is necessary to get consumer acceptance for irradiated processed meat.

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