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ARTICLE

Egg Shell and Oyster Shell Powder as Alternatives for Synthetic Phosphate: Effects on the Quality of Cooked Ground Pork Products

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Abstract

This study aimed to determine the optimal ratio of natural calcium powders (oyster shell and egg shell calcium) as synthetic phosphate replacers in pork products. Ground pork samples were subjected to six treatments, as follows: control (–) (no phosphate added), control (+) (0.3% phosphate blend added), treatment 1 (0.5% oyster shell calcium powder added), treatment 2 (0.3% oyster shell calcium powder and 0.2% egg shell calcium powder added), treatment 3 (0.2% oyster shell calcium powder and 0.3% egg shell calcium powder added), and treatment 4 (0.5% egg shell calcium powder added). The addition of natural calcium powders resulted in an increase in the pH values of meat products, regardless of whether they were used individually or mixed. The highest cooking loss was observed ($p<0.05$) in the negative control samples, whereas the cooking loss in samples with natural calcium powder added was similar ($p>0.05$) to that in the positive control samples. CIE L* values decreased as the amount of added egg shell calcium powder increased. CIE a* values were higher ($p<0.05$) in samples containing natural calcium powder (treatments 1, 2, 3, and 4) than in the positive control. The combination of oyster shell calcium powder and egg shell powder (treatment 2 or 3) was effective for the improvement of textural properties of the pork products. The findings show that the combined use of 0.2% oyster shell calcium and 0.3% egg shell calcium should enable the replacement of synthetic phosphate in the production of cooked pork products with desirable qualities.

Keywords pork products, egg shell powder, oyster shell powder, phosphate replacer

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Introduction

Phosphates are salts of phosphoric acid and sodium or potassium that are widely used in the meat industry (Long *et al*., 2011; Petracci *et al*., 2013) for adjustment of pH, providing buffering capacity, and improvement of product yields, as well as for enhancing the tenderness, juiciness, and water-binding capacity by increasing the ionic strength of the meat, along with the addition of salts (McKee and Alvarado, 2004; Petracci *et al*., 2013; Sebranek, 2009; Sebranek, 2015). However, the usage of synthetic phosphates in meat products has declined, as consumers have negative perceptions of their effects on health (Petracci *et al*., 2013). In recent years, changing consumer interests and demands have driven an increase in the popularity of processed meats with natural, organic, and/or clean labels. However, no direct replacement for phosphate has been discovered (Sindelar, 2015). The identification and application of new phosphate replacers, especially those from natural sources, is therefore of great interest.

The application of solubilized proteins (Vann *et al*., 2007), plum ingredients (Hooshmand and Arjmandi, 2009; Jarvis *et al*., 2012; Jarvis *et al*., 2015), protein hydrolysates (Shahidi and Synowiecki, 1997), functional carbohydrates (Park *et al*., 2008), and natural calcium powders (Bae *et al*., 2017; Choi *et al*., 2014; Lee *et al*., 2011, Park, 2011) as phosphate substitutes in meat products has been investigated in several studies. Oyster shell calcium and egg shell calcium, which may be obtained from the byproducts of eggs or shellfish, are considered new candidates for the substitution of synthetic phosphates in meat products (Bae *et al*., 2017). Oyster shell calcium is produced by calcining of shellfish such as oyster, marsh clam, and scallops. The main compound present in oyster shell is calcium carbonate ($CaCO_3$), which is used not only as additive in various foods but also as a calcium source (Furuhashi *et al*., 2009; Kim *et al*., 2003; Kim *et al*., 2015; Lee *et al*., 2011). Egg shell calcium, a powdered product derived from calcination of egg shells that are byproducts generated during the manufacture of egg products, has a high calcium content because the main compound is also calcium carbonate and is used as a raw material in foods, medicines, and cosmetics (Lee and Park, 2002; Shin and Kim, 1997; Shin *et al*., 1998). Lee *et al*. (2011) and Choi *et al*. (2014) suggested that oyster calcium powder may serve as a suitable substitute for sodium tripolyphosphate in emulsion-type pork sausages or restructured pork hams. Recently, Bae *et al*. (2017) investigated the potential utility of egg shell calcium, oyster shell calcium, marine algae calcium, or milk calcium as natural calcium-based alternatives for phosphates in cooked pork products. They found that products with egg shell calcium was the most optimal candidate for phosphate substitution, as it minimized cooking loss and contributed to the textural properties of the products. However, the combined effects of oyster shell and egg shell calcium as phosphate alternatives in meat products have not been examined to date.

Therefore, the objective of this study was to determine the effects of oyster shell calcium and egg shell calcium on the quality properties of cooked ground pork products when used alone or in combination as synthetic phosphate replacers.

Materials and Methods

Preparation and processing of pork products

Raw pork ham (*M. biceps femoirs*, *M. semitendinosus*, and *M. semimembranosus*) used in this study was purchased from a local meat processor (Pukyung Pig Farmers Livestock Cooperatives, Korea) at 24-48 h postmortem. After removing subcutaneous and intermuscular fat and visible connective tissues from the fresh ham, lean pork meat was cut in a square shape of approximately 4-5 cm, vacuum-packaged in nylon/PE film bags, and stored in a freezer at -18°C until processing. Pork back fat was prepared in the same manner. A phosphate blend (mixture of sodium tripolyphosphate, tetrasodium pyrophosphate, and sodium hexametaphosphate) (Polymix-CS, SDBNI Co. Ltd., Korea) was used as the synthetic phosphate. The natural calcium powders were prepared from commercially available products in Korea. Egg shell calcium (egg shell calcium 50, Essentron Co. Ltd., Korea) used in this study contained 51.6% calcium, 0.4% magnesium, 0.2% sodium, and less than 0.1% iron and potassium, and oyster shell calcium (oyster shell calcium, JK Biochem Co. Ltd., Korea) had 39.6% calcium and less than 0.1% magnesium, sodium, iron, and potassium. The formulation of the pork meat products with the various natural calcium powders, used individually or in combination, is shown in Table 1.

Table 1. Formulations for ground pork meat products with natural calcium powders

Materials (%)	Treatments[1)]					
	Control (–)	Control (+)	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Ground pork	68.5	68.2	68.0	68.0	68.0	68.0
Back fat	15.0	15.0	15.0	15.0	15.0	15.0
Ice	15.0	15.0	15.0	15.0	15.0	15.0
Salt	1.5	1.5	1.5	1.5	1.5	1.5
Phosphate blend		0.3	-	-	-	-
Oyster shell calcium powder	-	-	0.5	0.3	0.2	
Egg shell calcium powder	-	-	-	0.2	0.3	0.5
Total	100.0	100.0	100.0	100.0	100.0	100.0

[1)]Control (–), no phosphate added; Control (+), 0.3% phosphate blend added; Treatment 1, 0.5% oyster shell calcium powder added; Treatment 2, 0.3% oyster shell and 0.2% egg shell calcium powder added; Treatment 3, 0.2% oyster shell and 0.3% egg shell calcium powder added; Treatment 4, 0.5% egg shell calcium powder added.

The frozen pork ham and back fat were stored at 2-3°C for 24-36 h before processing meat products. The thawed raw materials were ground in a chopper (TC-22 Elegant plus, Tre Spade, Italy) equipped with an 8-mm plate and then with a 3-mm plate. The negative control (–) was prepared by mixing ground pork meat and back fat with ice water and salt (1.5%). In the positive control (+), phosphate blend (0.3%) was additionally added into ground meat mixtures in a mixer (KitchenAid 5K5SS, Whirlpool Corp., USA) for 5 min (Fig. 1). For the natural calcium treatments, samples were prepared by adding 0.5% oyster shell calcium (treatment 1), 0.3% oyster shell calcium and 0.2% egg shell calcium (treatment 2), 0.2% oyster shell calcium and 0.3% egg shell calcium (treatment 3), or 0.5% egg shell calcium (treatment 4), with ice water and salt (1.5%) to the ground pork meat and back fat. The meat mixtures from each batch (controls and natural calcium-treated products) were stuffed into conical tubes (50 g each) using a stuffer (MOD.5/V Deluxe, Tre Spade, Italy). The stuffed tubes were centrifuged at 2000 × g for 10 min in a centrifuge (FELTA5, Hanil Scientific Inc., Korea) to remove air pockets. The tubes were then transferred into a 90°C water bath (CB60L, Dong Won Scientific System, Korea) and cooked until the internal temperature reached 75°C. Changes in temperature were monitored by inserting a K-type thermocouple attached to a digital thermometer (TES-1384, Ketech Scientific Instrument Co., Ltd., Taiwan) into the center of the samples. After cooking, the samples were immediately cooled on ice slurry for 20 min and placed at 2-3°C overnight prior

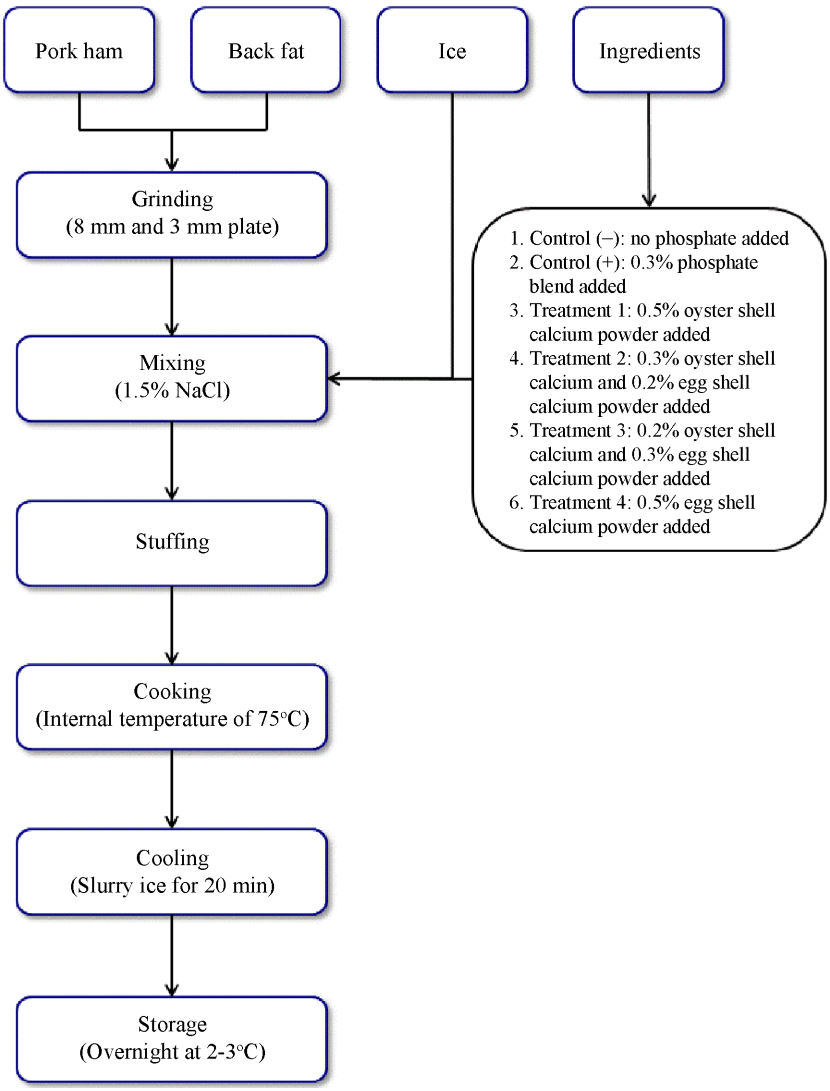

Fig. 1. Schematic diagram of manufacturing process for ground pork meat products with natural calcium powders.

to measuring cooking loss. The samples were further stored for 2 d at 2-3°C until analysis. The experiments were performed in triplicate.

Determination of pH values

From each treatment, 5 g of sample was collected before and after cooking, and then homogenized with 20 mL of distilled water for 1 min in a homogenizer (DI 25 basic, IKA®-Werke GmbH & Co. KG, Germany). Measurements were obtained using a glass electrode pH meter (Fisher Scientific Accumet AB150, Thermo Fisher Scientific, Inc., Singapore).

Determination of moisture content

For cooked products, moisture content was measured using the drying method (AOAC, 2007). After drying the samples in a 105°C dry oven (CB60L, Dongwon Scientific System, Korea) for 12 h, the difference between the weight of each sample before and after drying was calculated.

Determination of cooking loss

As previously described, the weight of each sample in the conical tubes was measured prior to cooking and then again after cooking and cooling to determine the cooking loss. The difference between the weights before and after cooking was calculated as shown below:

$$\text{Cooking loss (\%)} = \frac{\text{Weight before cooking} \\ -\text{Weight after cooking}}{\text{Weight before cooking}} \times 100$$

Instrumental color measurement

A colorimeter (Chroma Meter CR-400, illuminant C; Konica Minolta Sensing Inc., Japan) was used to measure the CIE L* values (indicating lightness), CIE a* values (indicating redness), and CIE b* values (indicating yellowness) of the freshly cut surface of the cooked samples. Two slices from each cooked sample were cut in half, parallel to the longitudinal axis, and three CIE L*a*b* readings per slice were taken immediately following cutting. The colorimeter was standardized against a white calibration plate (CIE L* +94.90, a* -0.39, and b* +3.88).

Texture profile analysis

After cutting the samples at a width of 2.5 cm perpendicular to the longitudinal axis, the hardness, springiness, cohesiveness, gumminess, and chewiness of the samples were measured using a texture analyzer (TA-XT2*i*, Stable Micro System, UK) equipped with a 50-mm diameter aluminum cylinder (Bourne, 1978). The cross-head speed for measurement was 5 mm/s.

Statistical analysis

All experiments were performed in triplicate. Statistical analysis of the results was conducted using the generalized linear model (GLM) procedure of the SAS package program (SAS, 2012). When the analysis of variance showed a significant difference between the means of different samples, the significance of the differences was further analyzed by the Duncan's multiple range test ($p<0.05$).

Results and Discussion

pH values, moisture content, and cooking loss

The pH values, moisture content, and cooking loss of the ground pork products formulated with oyster shell calcium or egg shell calcium powder are presented in Table 2. Before and after cooking, the pH value showed a similar trend. As expected, control samples formulated without synthetic phosphate or natural calcium had the lowest ($p<0.05$) pH values. Further, the pH value of the control (+) was increased as a result of the addition of a 0.3% phosphate blend, as also reported by Trout and Schmidt (1984) and Alvarado and McKee (2007). The addition of natural calcium powders to the ground pork products resulted in an increase in pH; this increase was significant ($p<0.05$) for added egg shell calcium compared with that for oyster shell calcium powder. Therefore, treatment 4 (addition of 0.5% egg shell calcium alone) had the highest pH values ($p<0.05$). These results were in agreement with those of the study by Bae *et al.* (2017), who reported that samples with egg shell calcium resulted in the highest pH values among pork products treated with various natural calcium powders. It is possible that egg shell calcium, which is ionized, is responsible for elevating pH values in meat products owing to its strong alkaline effects (Cho and Jeong, 2016; Shin and Kim, 1997).

Increased pH as a result of the addition of alkaline phosphate blend or higher level of egg shell calcium may exert positive effects on water retention in cooked ground pork products (Bae *et al.*, 2017; Long *et al.*, 2011; McKee and Alvarado, 2004; Trout and Schmidt, 1983). In this study, moisture contents were higher ($p<0.05$) in the control (+) and treatments 3 and 4 compared with those in the

Table 2. pH values, moisture contents, and cooking loss of ground pork meat products with natural calcium powders

Traits	Treatments[1)]					
	Control (–)	Control (+)	Treatment 1	Treatment 2	Treatment 3	Treatment 4
pH (uncooked)	5.98±0.07^{E}	6.26±0.06^{D}	6.42±0.05^{D}	6.90±0.06^{C}	7.48±0.05^{B}	9.04±0.06^{A}
pH (cooked)	6.27±0.04^{F}	6.41±0.03^{E}	6.60±0.03^{D}	7.06±0.03^{C}	7.40±0.04^{B}	8.75±0.05^{A}
Moisture content (%)	65.95±0.24^{B}	67.27±0.24^{A}	66.18±0.15^{B}	66.14±0.47^{B}	67.77±0.16^{A}	67.40±0.15^{A}
Cooking loss (%)	11.64±0.70^{A}	1.67±0.28^{CD}	5.93±0.31^{B}	2.60±0.25^{C}	1.40±0.16^{D}	1.37±0.15^{D}

[1)]Control (–), no phosphate added; Control (+), 0.3% phosphate blend added; Treatment 1, 0.5% oyster shell calcium powder added; Treatment 2, 0.3% oyster shell and 0.2% egg shell calcium powder added; Treatment 3, 0.2% oyster shell and 0.3% egg shell calcium powder added; Treatment 4, 0.5% egg shell calcium powder added.

All values are presented as means ± standard error of triplicates.

[A-F]Means within the same row with different superscript letters are significantly different ($p<0.05$).

control (–) and treatments 1 and 2. However, treatments 3 and 4 were found to have moisture contents ($p>0.05$) similar to those of the control (+) samples.

As expected, cooking loss was the highest ($p<0.05$) in the control (–) without phosphate. However, except for treatment 1, all natural calcium treatments ranged from 1.37% to 2.60%, had lower ($p<0.05$) cooking loss than the control (–), but cooking loss of treatments 2, 3, and 4 were not different ($p>0.05$) from the control (+). These results indicate that use of egg shell calcium alone or combination with oyster shell calcium powder rather than oyster shell calcium alone to ground meat products is capable to increasing water holding properties during cooking. These results disagree with those of Lee *et al*. (2011), who found that pork sausage formulated with 0.5% whey protein and 0.3% oyster shell calcium exhibited significantly improved water holding capacity and cooking loss. However, Bae *et al*. (2017) reported that the cooking loss in pork products formulated with egg shell calcium was the lowest among the natural calcium-treated products formulated with oyster shell, egg shell, marine algae, or milk calcium. These results are in agreement with the present findings. Therefore, egg shell calcium or a blend of egg shell and oyster shell calcium would serve as suitable synthetic phosphate replacers with positive effects on the reduction of cooking loss in meat products.

Instrumental color

Instrumental color values of ground pork products formulated with oyster shell calcium or egg shell calcium powder are shown in Table 3. There were no differences ($p>0.05$) in CIE L* values between the negative control (–), the positive control (+), or treatment 1. However, samples with egg shell calcium (treatments 2, 3, or 4) had lower CIE L* values ($p< 0.05$) than the negative control (–), the positive control (+), or treatment 1, and the CIE L* values decreased as the addition ratio of egg shell calcium increased. pH values are related to color (lightness) of cooked meat products, as the higher the pH value, the darker the color (Barbut, 2009; Casco *et al*., 2013; Sams and Alvarado, 2004). In the current study, products formulated with natural calcium powders (treatments 1, 2, 3, and 4) were redder (higher CIE a* values; $p<0.05$) than the positive control (+) and the highest CIE a* values were observed ($p<0.05$) in treatment 4 (0.5% egg shell calcium added). It is likely that the more intense red color resulting from an increased level of egg shell calcium may be attributable to pH-dependent effects. At a high pH, cooked meat products have been shown to be redder in color because of incomplete myoglobin denaturation at such pH values (Trout, 1989). CIE b* values were lower ($p<0.05$) in natural calcium treatments (treatments 1, 2, 3, and 4) than in the positive (–) and negative control (+). Similarly, Lee *et al*. (2011) reported that samples containing 0.5% whey protein and 0.3% oyster calcium powder showed significantly less yellowness than phosphate-free restructured pork hams or products with 0.3% sodium tripolyphosphate. Among the natural calcium treatments, treatment 2 had the lowest ($p<0.05$) CIE b* values, while treatments 2 and 3, those treated with a combination of oyster shell calcium and egg shell calcium powder, had similar ($p>0.05$) CIE b* values (Table 3).

Textural properties

Table 4 shows the results of texture profile analysis of cooked ground pork products formulated with oyster shell calcium or egg shell calcium powder. The control (–) had the lowest ($p<0.05$) hardness among the samples tested in this study. Products formulated using each natural calcium treatment showed lower ($p<0.05$) hardness than the positive control (+) and treatment 4 had the lowest ($p<$ 0.05) hardness. Similar trends were reported by Bae *et al*.

Table 3. Instrumental color values of ground pork meat products formulated with various natural calcium powders

Traits	Treatments[1)]					
	Control (–)	Control (+)	Treatment 1	Treatment 2	Treatment 3	Treatment 4
CIE L*	69.78±0.16^{A}	69.79±0.21^{A}	69.70±0.11^{A}	68.36±0.20^{B}	68.03±0.25^{BC}	67.51±0.18^{C}
CIE a*	5.67±0.25^{C}	4.19±0.36^{D}	6.57±0.15^{B}	6.35±0.14^{BC}	6.23±0.13^{BC}	8.16±0.32^{A}
CIE b*	9.51±0.19^{A}	9.07±0.15^{B}	8.29±0.15^{CD}	7.78±0.11^{E}	7.90±0.09^{DE}	8.61±0.13^{C}

[1)]Control (–), no phosphate added; Control (+), 0.3% phosphate blend added; Treatment 1, 0.5% oyster shell calcium powder added; Treatment 2, 0.3% oyster shell and 0.2% egg shell calcium powder added; Treatment 3, 0.2% oyster shell and 0.3% egg shell calcium powder added; Treatment 4, 0.5% egg shell calcium powder added.
All values are presented as means ± standard error of triplicates.
$^{A-E}$Means within the same row with different superscript letters are significantly different (p<0.05).

Table 4. Textural properties of ground pork meat products formulated with various natural calcium powders

Traits	Treatments[1)]					
	Control (–)	Control (+)	Treatment 1	Treatment 2	Treatment 3	Treatment 4
Hardness (kg)	3.286±0.170^{D}	6.214±0.137^{A}	5.007±0.092^{B}	4.796±0.108^{B}	4.901±0.087^{B}	4.418±0.109^{C}
Springiness	0.860±0.010^{C}	0.950±0.000^{A}	0.920±0.010^{B}	0.930±0.000^{B}	0.950±0.000^{A}	0.940±0.000^{A}
Cohesiveness	0.510±0.010^{D}	0.760±0.010^{A}	0.640±0.020^{C}	0.700±0.010^{B}	0.730±0.010^{A}	0.750±0.010^{A}
Gumminess (kg)	1.718±0.126^{D}	4.698±0.107^{A}	3.246±0.120^{C}	3.357±0.109^{BC}	3.579±0.067^{B}	3.314±0.089^{BC}
Chewiness (kg)	1.503±0.121^{D}	4.445±0.104^{A}	3.001±0.125^{C}	3.116±0.107^{BC}	3.389±0.064^{B}	3.127±0.087^{BC}

[1)]Control (–), no phosphate added; Control (+), 0.3% phosphate blend added; Treatment 1, 0.5% oyster shell calcium powder added; Treatment 2, 0.3% oyster shell and 0.2% egg shell calcium powder added; Treatment 3, 0.2% oyster shell and 0.3% egg shell calcium powder added; Treatment 4, 0.5% egg shell calcium powder added.
All values are presented as means ± standard error of triplicates.
$^{A-D}$Means within the same row with different superscript letters are significantly different (p<0.05).

(2017), following the addition of various natural calcium powders to ground pork products. These results indicate that the addition of egg shell calcium powder alone did not increase hardness of cooked meat products. However, in the present study, treatment 4 had higher moisture contents and lower cooking loss. Thus, the increased tenderness of these samples may be attributed to the lower cooking loss, as was found by Casco *et al*. (2013). However, springiness and cohesiveness were enhanced with increasing amount of added egg shell calcium in the present study. Springiness and cohesiveness of treatments 3 and 4 did not differ significantly (p>0.05) from those of the positive control (+), but were higher (p<0.05) than those of the negative control (–). Among the natural calcium treatments, treatment 1 had the lowest (p<0.05) cohesiveness. Gumminess and chewiness were the highest (p< 0.05) in the positive control (+). Treatment 3 (formulated with a combination of 0.2% oyster shell and 0.3% egg shell calcium) showed increased gumminess and chewiness (p<0.05) compared to treatment 1 (formulated with 0.5% oyster calcium power alone). In the present work, the addition of synthetic phosphate to the pork products resulted in improved textural properties compared with all other samples, including the negative control (–). These findings are similar to those of Bae *et al*. (2017), who reported that hardness, gumminess, and chewiness were significantly higher in the control samples with synthetic phosphate than in samples with the natural calcium powders. Overall, the combination or mixed use of oyster shell and egg shell calcium, rather than the addition of each natural calcium alone, may complement the texture of pork products when compared with products containing synthetic phosphate.

Conclusions

In conclusion, oyster shell calcium and egg shell calcium were found to serve as suitable substitutes for synthetic phosphate owing to the improved quality characteristics compared to the negative control (–), which was processed without phosphate. Although the use of egg shell calcium alone may minimize the cooking loss as a result of the increased pH, the hardness of products formulated with egg shell calcium alone tended to be lower than that of those subjected to synthetic phosphate treatment (positive control (+)). Therefore, the combined use of oyster shell calcium and egg shell calcium as substitutes for synthetic phosphate should enable the processing of meat products with desirable qualities. Further research is necessary to explore for food ingredients that can complement these textural properties in phosphate-free meat products.

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