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Quality of walleye pollack frozen *surimi* by adding carboxylic acid salt in place of sugar compounds

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Abstract

Sugar compounds and polyphosphates are typically added to frozen *surimi* for the maintenance of its quality. To create healthier, low-calorie frozen *surimi*, frozen *surimi* using carboxylic acid and amino acid salts as preservatives in place of sugar compounds was prepared. After thawing, the *surimi* was salted, followed by preheating at 30°C for either 40 min or between 0 and 40 min, and then heating it at 90°C for 30 min. The breaking strength (BS) and breaking strain (bs) of the heat-induced gels of the *surimi* were then measured using a rheometer, and the gel strength (Gs = BS / bs) and jelly strength (JS = BS × bs) were calculated. The quality of the *surimi* was evaluated by assessing the physical properties of the heat-induced gels made from it, as well as the relationship between the BS and Gs during preheating for two-step heated gels. Results showed that the frozen *surimi* preparations made with 5% sodium gluconate and 3% sodium gluconate + 2% sodium glutamate, each with the addition of 0.1% Na_3PO_4, were comparable in quality to the typical preparation with 5.7% sugar compounds, remaining stable at -23°C for seven months or at -45°C for ten months. It was also found that, when comparing samples with equal BS values, the heat-induced gels of the 5% sodium gluconate and 3% sodium gluconate + 2% sodium glutamate preparations had slightly lower bs values as compared to typical frozen *surimi* with sugar compounds, thus exhibiting a slightly more brittle texture.

Introduction

Frozen *surimi* (minced fish paste) is a general term referring to fish protein products made through the mechanical separation (mincing) of edible fish meat. The minced fish is washed and dehydrated, after which it is mixed with preservatives and frozen.

The shelf life of frozen *surimi* is considered to be approximately one year, and the product's quality is most prominently evaluated when it becomes a commercial product. When it is used as a raw ingredient for making fish paste-based items, the properties of the heat-induced gel made from the *surimi* are used as markers of the product's quality and texture (Okada, 1999a; 1999b; Shiba, 2016; Kato *et al.,* 2016). In Japan, the heat-induced gels used for testing are made at a standard size, and the shape of the plunger used to do so is also standardised. A rheometer is then used to determine the load (g) and strain (cm) under which the gel sample breaks. This so-called punch test has been used for many years, and we previously conducted a detailed study demonstrating its general applicability (Kato *et al.,* 2016).

As is well-known, sugar compounds and polyphosphate have traditionally been used to prevent the denaturation of *surimi* proteins during freezing. In particular, sugar compounds are thought to contribute the most to extending the shelf life of *surimi* by preventing the denaturation of unstable fish meat proteins during freezing (Okada, 1999a; Shiba, 2016; Kato *et al.,* 2016). On the other hand, adding sodium polyphosphate to *surimi* slightly raises its pH, which has been reported to enhance the effects of the added sugar compounds by creating a neutral to slightly alkaline environment (Kumazawa *et al.,* 1990; Kato *et al.,* 2012). However, once the *surimi* is thawed, salt is added, and the surimi made into a heat-induced gel such as a meat paste, it is possible that the above two additives may exert some effects that influence the properties of the product. We examined this question in a previous study, and found that sugar compounds had an inhibitory effect on heat-induced gel formation, and affected the quantitative physical properties of such gels; in particular, they significantly decreased the gel's breaking strain (cm). Further, we found that the addition of sodium polyphosphate reversed the effects of sugar

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compounds on the product's physical properties (reversal of inhibition) (Kato *et al.,* 2012).

As long-term freezing of *surimi* has become feasible, planned production of fish paste-based products has become possible, and most fish paste-based products now utilise frozen *surimi* as their raw ingredient. However, this has also led to the homogenisation of the quality, flavour, and texture of these products throughout Japan, which some have said is diminishing the appeal of this Japanese traditional regional product. In addition, due to the addition of 5 - 10% sugar compounds, these frozen *surimi* products have become sweeter, and producing saltier products has become more difficult. In the future, it will be necessary to find proactive solutions to these problems (Okada, 1999b).

In recent years, low-carbohydrate diets have become more popular, not only in Japan but on a worldwide scale with increasing coverage of these on television and in print media. There is increasing demand for protein sources such as fish paste-based products, which are made without the addition of sugar compounds (low-calorie products), particularly among consumers with diabetes or prediabetes.

Similar to sugar compounds, salt compounds containing amino acids and carboxylic acids are also known to inhibit fish protein denaturation. Ooizumi (1991) previously compared the effects of sorbitol, 24 amino acids, and 11 carboxylic acids; but, this study was done in the context of the heat denaturation of myofibril Ca-ATPase. Few amino acids have been tested for their effects on the denaturation of fish protein products during freezing, and the available data on this topic are limited (Matsumoto and Arai, 1987; Ooizumi, 1991). Noguchi *et al.* (1975) studied the effects of six amino acids and seven carboxylic acids on the physical properties of *kamaboko* fish cakes, in addition to the effects of sugar compounds mixed with amino acids, but this was only done for directly heated gels, while two-step heated gels (*suwari* gels) were not studied. Even so, the results of those studies suggested that molecules with many -COOH and -OH groups are the most likely to exert a strong inhibitory effect on the denaturation of *surimi* proteins during freezing.

Based on this reasoning, in the present work, we chose to study the effects of the addition of two carboxylic acid salts namely sodium citrate and sodium gluconate, as well as the amino acid salt, sodium glutamate, on the quality and shelf life of frozen *surimi*. The resulting frozen *surimi* preparations containing these additives were frozen, and their heat-induced gel formation ability was tested over the course of approximately one year (ten months). Further, their quality was compared with that of the typical frozen *surimi* prepared with sugar compound additives (added sugar).

Materials and methods

Frozen surimi

The frozen *surimi* tested in the present work was composed of grade 2 and special grade A domestic-caught walleye pollack. The typical *surimi* to which the test preparations were compared to had a sugar compound content of 5.7% (4.73% sucrose + 0.97% sorbitol) and 0.2% sodium polyphosphate. Raw *surimi* was produced with a similar percent content of sodium citrate, sodium gluconate, or sodium glutamate (either alone or in combination) in place of the sugar compounds in the typical *surimi*, and these mixtures were then frozen to produce the tested frozen *surimi* preparations. In addition to those additives, 0.1% Na_3PO_4 was also added to the preparations. The compositions and quantities of each of the additives in the frozen *surimi* are shown in Table 1. Polyphosphate was purchased from Ueno Food Techno Industry as an equal mixture of sodium pyrophosphate acid and sodium tripolyphosphate. Sodium citrate was purchased from Fuso Chemical, sodium gluconate from MC Food Specialties, sodium glutamate from Ajinomoto, and Na_3PO_4 from MC Food Specialties.

Preparation of the heat-induced gels

After the frozen *surimi* was partially thawed, it was thinly sliced using a high-speed refrigerated vacuum cutter (Stephan, UM-5 Universal, Germany). Without adding water, 2.5% (w/w) solar salt was added, and the mixture was ground up to make fish

Table 1. Compositions of the additives used for different preparations of frozen *surimi*.

Frozen surimi	Na-citrate	Na-gluconate	Na-glutamate	Na_3PO_4	Sucrose	Sorbitol	Na-polyphosphate
①	1%	0%	3%	0.10%	0%	0%	0.20%
②	0%	3%	2%	0.10%	0%	0%	0.20%
③	0%	5%	0%	0.10%	0%	0%	0.20%
④	0%	0%	0%	0%	4.73%	0.97%	0.20%

paste. The finished fish paste was maintained below 8°C. A 48-mm diameter polyvinylidene chloride tube was filled with the prepared paste, and was then preheated in a constant-temperature bath for 20 and 40 min at 30°C. The preheated gel was then heated at 90°C for 30 min to create the two-step heated gel, or else the preparation was directly heated to 90°C for 30 min without preheating to create the directly heated gel. The preheating conditions (temperature and time) needed to maximise the physical properties of a two-step heated gel (*suwari* gel) are known to vary based on the type of fish used to make the *surimi*; in the present work, these conditions were set at 30°C for 40 min (Sato *et al.,* 2014).

Measurement of the properties of the heat-induced gels

Each of the prepared heat-induced gels was placed in a 25°C constant-temperature bath for over 2 h, and a columnar sample (30 mm diameter × 25 mm height) was taken with a rheometer (Sun Scientific Co., Ltd., CR-200D) by using a 5-mm diameter spherical plunger that advanced at a speed of 6 cm/min. The stress and deformation of the gel sample at the time it broke were quantified as its breaking strength (BS; g) and breaking strain (bs; cm), respectively, and these were used to calculate the gel stiffness (Gs = BS / bs; g/cm) and jelly strength (JS = BS × bs; g･cm). Correlations between these physical parameters were quantified using least-squares regressions (Samejima, 1977), which were plotted as straight, best-fit lines in Figures 2 and 3.

Evaluation of the suwari heat-induced gelling ability of frozen surimi

The ability to produce a *suwari* (two-step heated) heat-induced gel is a characteristic of fish *surimi. Suwari* refers to the phenomenon in which, following salting and preheating at a low temperature, the two-step heated gel progressively displays marked improvements in its physical properties. During this process, the BS and Gs (BS / bs) vary proportionally to one another, exhibiting a first-order relationship as follows: BS = a × Gs - b, where a and b are fitted constants. Therefore, BS and Gs exhibit a linear relationship with each other when plotted. Gels that are brought to a high temperature without first preheating them (directly heated gels), as well as the *surimi* of fish whose meat does not possess *suwari* gelling properties (e.g., arabesque greenling) do not exhibit this relationship (Suzuki *et al.,* 2008). When the *surimi* deteriorates or changes due to the use of additives, the above first-order relationship changes, thus allowing for direct graphical comparisons of the linear relationships to be made. Herein, *surimi* quality was comparatively evaluated between the newly prepared frozen *surimi* with carboxylic acid and amino acid salt additives, and the typical frozen *surimi* to which sugar compounds were added.

To outline the rheological properties of heat-induced gels, Kim and Park (2005) used the punch test (non-breakage testing) to plot a stress-strain curve, dividing the heat-induced gels' physical characteristics into several groups from a rheological perspective. With this in mind, Park (2000) created a texture profiling map based on these stress and strain relationships (Park, 2000; Kim and Park, 2005). In the present work, we focused on the fact that preheating leads to a dynamic improvement of the physical properties of two-step heated gels, and therefore aimed to identify the physical properties of the prepared heat-induced gels. For rheological properties, we adopted Kim and Park (2005)'s terminology of distinguishing BS vs. Gs, noting these in the Figures we produced, thus allowing for the texture profiling of our gels. When gels break without resisting deformation but need sufficient force, they are described as brittle. When gels strongly resist deformation, but do not require a large force, they are described as rubbery. When gels are both brittle and rubbery, they are tough. When gels are neither brittle nor rubbery, they are mushy.

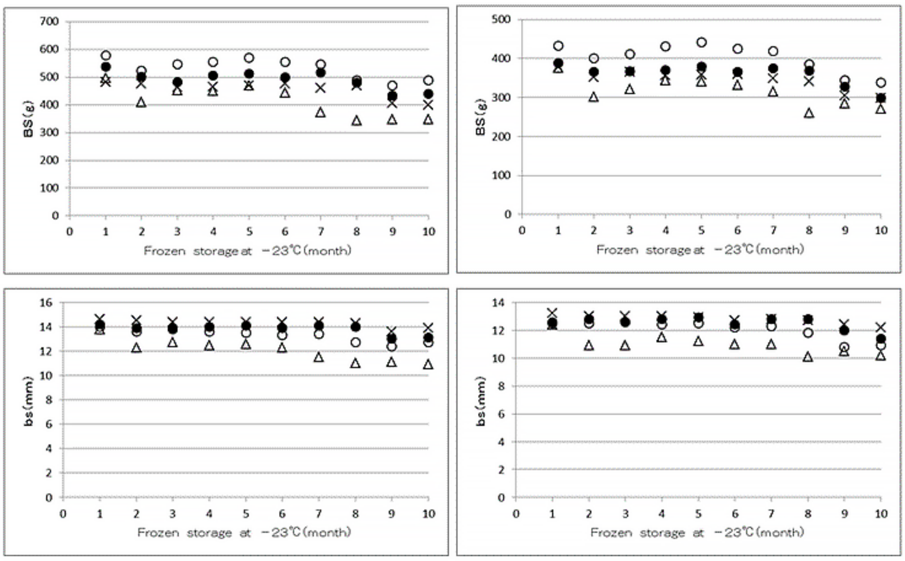
Results

Shelf life of frozen surimi with added carboxylic acid and amino acid salts

The additive compositions of the frozen *surimi* prepared in the present work are shown in Table 1. The four preparations we made were composed of: (1) 1% sodium citrate + 3% sodium glutamate; (2) 3% sodium gluconate + 2% sodium glutamate; (3) 5% sodium gluconate; and (4) 5.7% adjusted sugar compounds. All preparations included 0.2% sodium polyphosphate, which was added concurrently with all other additives. We also added 0.1% Na_3PO_4, as this additive was recently found to improve *suwari* gelling. As the frozen *surimi* sold in stores contains sugar compounds and sodium polyphosphate, but not Na_3PO_4, the comparison sample used herein did not include Na_3PO_4. After the frozen *surimi* was frozen at -23°C, a sample was taken each month thereafter, and a heat-induced gel was prepared from it under identical conditions each time. The breaking strength (BS; g) and breaking strain (bs; cm) of the gel were measured, and the gel stiffness (Gs = BS / bs; g/cm) and jelly strength (JS = BS × bs; g･cm) were then calculated. Measurements were made for ten months, and the statistical analysis was performed. The mean values of the BS and the bs (each 9~10 times tests) are shown in Figures 1(A) and 1(B), while the standard deviations are not shown in the figure, because it was difficult to discriminate between four samples. The standard deviations were between 11~21 g on BS and 0.2~0.5 mm on bs of the gel from the *surimi* with 1% Na-citrate + 3% Na-glutamate, 10~33 g on BS and 0.1~0.5 mm on bs of the gel from the *surimi* with 3% Na-gluconate + 2% Na-glutamate, 11~24 g on BS and 0.1~0.5 mm on bs of the gel from the *surimi* with 5% Na-gluconate, and 19~42 g on BS, and 0.3~0.6 mm on bs of the gel from the *surimi* with 5.7% sugar compounds. Based on these results, with the exception of the 1% sodium citrate + 3% sodium glutamate frozen *surimi, surimi* quality was maintained for seven months without degradation for all preparations. Gs and JS calculations are not displayed herein, because they showed similar patterns as Figure 1(A).

However, when comparing the physical properties of the heat-induced gels, they were found to vary according to their additives. The heat-induced gel of the 3% sodium gluconate + 2% sodium glutamate frozen *surimi* had the highest BS value, followed by the 5% sodium gluconate sample, which was in turn closely followed by the typical samples with sugar compounds. The 1% sodium citrate + 3% sodium glutamate *surimi* had the lowest BS value, and this was thought to be due to the accelerated degradation of this preparation. On the other hand, for bs values, the samples differed in the following order: typical sugar compounds > 5% sodium gluconate > 3% sodium gluconate + 2% sodium glutamate > 1% sodium citrate + 3% sodium glutamate. For Gs values, the samples differed in a different order, as follows: 3% sodium gluconate + 2% sodium glutamate > 5% sodium gluconate ≈ 1% sodium citrate + 3% sodium glutamate > typical sugar compounds. For JS values, the order of differences among the samples was: 3% sodium gluconate + 2% sodium glutamate > 5% sodium gluconate > typical sugar compounds > 1% sodium citrate + 3% sodium glutamate. The 1% sodium citrate + 3% sodium glutamate samples scored the lowest in all physical properties, thus suggesting that this preparation yielded lower-quality frozen *surimi* than all the others. While the physical properties of the other three heat-induced gels were fairly similar, there were some differences in the BS, bs, Gs, and JS values among them, thus suggesting that the textures of these three heat-induced gels might have been slightly different. Our results suggest that, among gels with the same BS value, 3% sodium gluconate + 2% sodium glutamate added had a relatively lower bs value; similarly, those to which 5% sodium gluconate was added also had a slightly lower bs value.

The same four mixtures were also prepared as directly heated gels and frozen, with samples taken and measurements made over the course of ten months.



(A) (B)

Figure 1. Changes in the quality of walleye pollack frozen *surimi* prepared with various additives during storage at -23°C. The frozen *surimi* was thawed, ground up with 3% NaCl, and heated at 90°C for 30 min, with or without preheating at 30°C for 40 min. The quality of the frozen *surimi* was evaluated by measuring the physical properties of the heat-induced gel prepared from it. Breaking strength (BS) and breaking strain (bs) were measured with a rheometer. (A) Two-step heated gel, and (B) Directly heated gel. Additives in the tested frozen *surimi* were: (○) 3% sodium gluconate + 2% sodium glutamate + 0.1% Na_3PO_4; (●) 5% sodium gluconate + 0.1% Na_3PO_4; (△) 1% sodium citrate + 3% sodium glutamate + 0.1% Na_3PO_4; (×) 5.7% sugar compounds (4.73% sucrose + 0.97% sorbitol); and (∗) 0.2% sodium polyphosphate. The quality of the frozen *surimi* prepared with 5.7% sugar compounds was equal to that of grade 2 product in the market.

Results for these preparations are shown in Figure 1 (B). While the values of the physical properties of these directly heated gels were all lower than those of the *suwari* gels, it was found that the relative stability of their quality, relative effects of each additive on the samples' physical properties, and differences in texture were all similar to those found for the *suwari* gels.

Furthermore, after frozen storage for over eight months, all four frozen *surimi* samples were found to have deteriorated in quality. This was seen in the samples to which carboxylic acid salts and sodium glutamate were added, as well as in the commonly sold typical sample to which sugar compounds were added, thus suggesting that deterioration is most likely linked to the temperature at which the *surimi* is stored. For this reason, the 3% sodium gluconate + 2% sodium glutamate and 5% sodium gluconate sample were also stored at -45°C, and their resultant heat-induced gels were sampled for the assessment of their physical properties over another ten months. These results are not shown herein, but did show that the stability of the quality of both the two-step heated gels and directly heated gels was increased by this treatment.

Textural characteristics of heat-induced gels prepared from frozen surimi with added carboxylic acid and amino acid salts

The three frozen surimi preparations with carboxylic acid and amino acid salt additives formed *suwari* gels similar to those of the frozen *surimi* to which sugar compounds were added. As they were preheated, the two-step heated gels maintained a constant BS to Gs ratio, thus demonstrating a first-order linear relationship between these properties (BS = a × Gs - b). To determine and compare these linear relationships for the *surimi* with each of the four compositions of additives earlier discussed, these were all displayed on the same Figure. Figure 2 shows the linear relationships for the four frozen surimi preparations when stored at -23°C for seven months. It can be seen that the plot for the 5.7% sugar compounds sample is the furthest to the left in the Figure, with the next line to the right representing the 5% sodium gluconate sample, followed by the 3% sodium gluconate + 2% sodium glutamate sample. The line representing the 1% sodium citrate + 3% sodium glutamate sample nearly overlaps the rightmost line in the figure. The slopes of the above lines ('a' in the linear regression equation) represent the rate of change in the *suwari* gel's physical properties, so they can be considered to represent their abilities to form *suwari* gels (Kato *et al,* 2016). As the four lines in the Figure are parallel, the abilities of the different preparations to form *suwari* gels were roughly equal, meaning that the *suwari* gelling ability of the newly prepared *surimi* matched that of the standard frozen *surimi* with sugar compounds added to it. In contrast, the maximum values of the physical properties of the gels differed slightly with the frozen *surimi* to which sugar compounds were added, and had slightly lower values than the others. However, this was thought to potentially be due to the fact that 0.1% Na_3PO_4 was not added to this *surimi*, so a new sample with 0.1% Na_3PO_4 added was also prepared. This new sample displayed increases in its physical characteristics similar to those in the other tested samples. Further, it was found that the improvements in physical

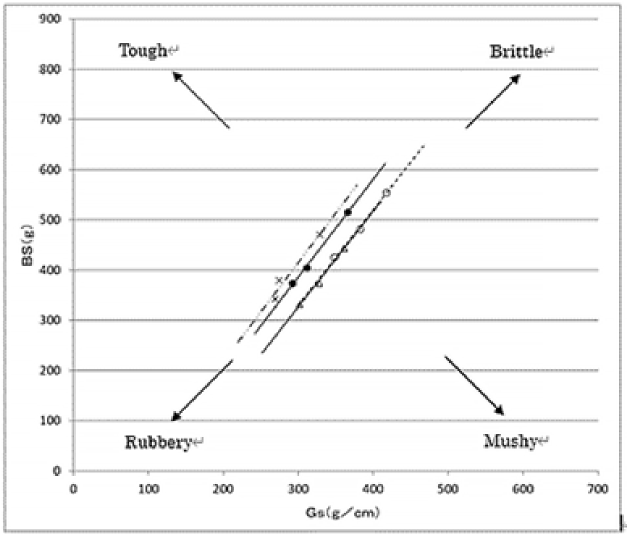


Figure 2. Effect of sodium carboxylate and sodium glutamate on the physical properties and texture characteristics of two-step heated gels. The frozen *surimi* was thawed, ground up with 3% NaCl, and preheated at 30°C for 0 - 40 min, and subsequently heated at 90°C for 30 min. The physical properties were measured as in Figure 1, and preheating induced linear increases in the BS vs. Gs (BS / bs) plots of the two-step heated gels were represented. From the results of the regression lines relating the BS to the bs determined by the punch test, the rate of increase in the BS vs. Gs ratio of the two-step heated gel induced by preheating was determined, and the sensory textural characteristics of the gel were identified as: tough, brittle, rubbery, or mushy. Relationships between physical parameters and typical texture characteristics are also shown in this Figure. Additives in the tested frozen *surimi* were: (○) 3% sodium gluconate + 2% sodium glutamate + 0.1% Na_3PO_4; (●) 5% sodium gluconate + 0.1% Na_3PO_4; (△) 1% sodium citrate + 2% sodium glutamate + 0.1% Na_3PO_4; and (×) 5.7% sugar compounds (4.73% sucrose + 0.97% sorbitol).

properties seen with the addition of 0.1% Na_3PO_4 were equal when the addition was made during the production of the frozen *surimi* and during thawing and salting.

The amounts of carboxylic acid and amino acid salts added to the raw surimi were limited to 5% because if greater amounts were added, the concentration of protein in the salted meat paste would decrease, which we hoped to avoid. It has already been reported that a decrease in the protein concentration (C) of the meat paste affects the physical properties of the resultant heat-induced gel, particularly causing marked decreases in its BS and Gs. The relationship is exhibited as BS (and Gs) = a × C^n, where a and n are constants specific to the gel, and n is 2 - 3 (Kitakami *et al.,* 2005), potentially negating the positive effects of the additives.

The dual effects of carboxylic acid and amino acid salts

We found that the heated-induced gel forming ability of frozen *surimi*, to which carboxylic acid or carboxylic acid + amino acid salts were added remained stable during long-term frozen storage in similar manner to that of traditional frozen *surimi* with sugar compounds added to it. We hoped to explore whether these chemicals exerted a stronger effect on the *surimi*'s ability to withstand frozen storage or its ability to form a heat-induced gel. Therefore, we compared the effects of the above additives when they were added at the time of preparation of the frozen surimi vs. when they were added at the time of salting.

We prepared frozen *surimi* with (1) 3% sodium gluconate and (2) 3% sodium gluconate + 2% sodium glutamate + 0.1% Na_3PO_4, and these preparations were frozen at -23°C for one month before thawed. These samples were then tested for their ability to form heat-induced gels. Next, during salting the preparation, an additional preparation was made by adding 2% sodium glutamate + 0.1% Na_3PO_4 to it to assess its ability to form heat-induced gels after addition at this stage. The BS to Gs ratios of these preparations were then plotted over time (Figure 3) to show whether progressive changes occurred during the preparation of the two-step heated gels with preheating. It was found that as compared to 3% sodium gluconate sample, the heat-induced gel derived from 3% sodium gluconate + 2% sodium glutamate + 0.1% Na_3PO_4 sample had higher physical property values than all the others, and thus superior quality, with the line representing this preparation being the furthest to the left on the plot in Figure 3. In contrast, when 2% sodium glutamate + 0.1% Na_3PO_4 was added at the time of salting to the sample with only

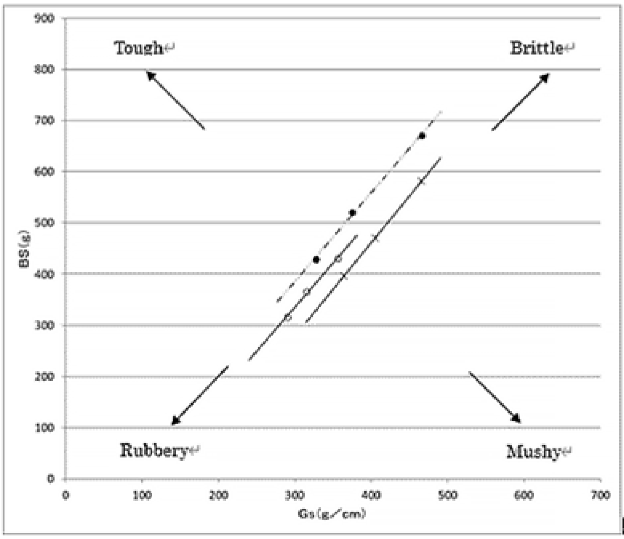


Figure 3. Dual effects of sodium gluconate and sodium glutamate on the physical properties and texture characteristics of two-step heated gels. The measurement of the physical properties and representation of the linear relationships between the increase in the BS vs. Gs ratio induced by preheating in plots of two-step heated gel results were conducted in the same manner as described in Figure 2. The texture profiling analysis of the two-step heated gel was also performed and represented in the same manner as in Figure 2. Additives in the tested frozen *surimi* were: (○) 3% sodium gluconate; (●) 3% sodium gluconate + 2% sodium glutamate + 0.1% Na_3PO_4; (×) 3% sodium gluconate + (2% sodium glutamate + 0.1% Na_3PO_4); and (∗) 0.2% sodium polyphosphate. The frozen *surimi* prepared with 3% sodium gluconate and 3% sodium gluconate + 2% sodium glutamate + 0.1% Na_3PO_4 was stored at -23°C for six months, and then subjected to these tests.

3% sodium gluconate, the properties of the heat-induced gel did not improve to the level of those in the sample, including all three additives at the time of initial production, thus failing to show significant increases in physical properties. These findings show that the combination of these three additives prevented the deterioration of *surimi* during frozen storage, but did not inhibit the deterioration of its ability to form heat-induced gels, of which recovered rate of the bs was less than that of the BS. Furthermore, while these results are not shown in the Figure, the addition of sodium citrate and sodium gluconate at the time of salting, similarly to the addition of sodium glutamate, did not result in the same recovery of the superior gel-forming ability of the *surimi* as in if they were added at the time of initial production.

These results suggest that, while sodium gluconate and sodium glutamate improved the ability of frozen *surimi* to withstand freezing, thus leading to the improved maintenance of its quality, they clearly inhibited the *surimi*'s ability to form heat-induced gels. In other words, the effects of these additives on the quality of the frozen *surimi* represented dual positive and negative effects, with them giving the *surimi* increased ability to withstand freezing and decreased ability to form heat-induced gels, and ultimately affecting the stability of the *surimi*'s quality.

It has been previously reported that, even in the typical *surimi* to which sugar compounds are added, the addition of sorbitol increases *surimi*'s ability to withstand freezing, but decreases its ability to form heat-induced gels (Kato *et al.,* 2012). However, the latter decrease in gelling ability induced by sorbitol is eliminated with the addition of sodium polyphosphate (reversal of inhibition), but this phenomenon was not seen for sodium gluconate or sodium glutamate in the present work, thus representing a marked difference from the effects of sugar compounds. The basic mechanisms by which sodium gluconate and sodium glutamate exert these dual effects are not yet known.

Discussion

We found that the addition of carboxylic acid salts, in particular sodium gluconate or the replacement of a portion of sodium gluconate with sodium glutamate, increased the stability of walleye pollack frozen *surimi*, allowing for the maintenance of its heat-induced-gel-forming ability for nearly one year. Although these additives improved the ability of the *surimi* to withstand freezing, they in fact had an inhibitory effect on its gelling ability following salting and heating, and thus exhibited dual, overlapping effects. Based on the additives' effects on the physical properties of the resultant gels, we found that 5% sodium gluconate was a superior additive that might be used to replace sugar compounds, with 3% sodium gluconate + 2% sodium glutamate being the next most efficient combination of additives tested. However, 1% sodium citrate + 3% sodium glutamate was found to have inferior preservative ability, leading to an unstable frozen *surimi* with its quality deteriorated quickly. Modifying this preparation to include 2% sodium citrate or adding additional sodium glutamate did not improve this result.

When compared with heat-induced gels derived from the typical *surimi* to which sugar compounds were added, the bs values found for the 5% sodium gluconate preparation samples with similar BS values were slightly lower. Similarly, the 3% sodium gluconate + 2% sodium glutamate preparation also had a slightly lower bs value. When 0.1% Na_3PO_4 was added, there was no difference in the ability of the *suwari* gel formation, and both the BS and bs increased. It has been previously reported that adding water to form a gel at the time of salting could be an effective method of raising a heat-induced gel's bs value (Kato *et al.,* 2011); so, we also examined the effects of the addition of water on the carboxylic acid salt and amino acid salt preparations. While these findings are not shown in the present work, we found that the addition of water caused a decrease in the BS value as seen in typical *surimi*, alongside an increase in the bs value. Using this method, it was possible for the test preparations to approach the bs value of the heat-induced gels of typical frozen *surimi*.

We found (Figure 3) that the addition of sodium glutamate to sodium gluconate preparations improved the quality of frozen *surimi*, and markedly increased its ability to form heat-induced gels. When the content of sodium gluconate, on its own, was increased from 0 to 5% in the sample, the quality of the frozen *surimi* increased, and the gelling ability of its heat-induced gel improved (in fact, when the additive content of the surimi increased, both of the BS and bs value of the heated-induced gel made from it showed higher values); the same result was also seen for sodium glutamate. Further, the addition of sodium glutamate (or replacement of a portion thereof with sodium glutamate) led to improved physical properties in the gel, suggesting that carboxylic acid and amino acid salts might affect the quality of frozen *surimi* through various mechanisms. As the addition of 1% or more sodium citrate clearly caused the deterioration of the quality of frozen *surimi*, the differences in the effects of the three additives tested in the present work might be attributable to the negative ions in these salts according to the Hofmeister series (Okada, 1999b), that is, sodium citrate is known for its strong salting-out effects, but at low concentrations, its salting-in effects are prominent (JPO, 2010). At concentrations above 1%, the heat-induced gel-forming ability of the surimi would be affected, thus leading to differing physical properties. The salting-out effect of sodium gluconate is not known, and this effect is weaker for sodium glutamate than for sodium citrate, meaning that its salting-in effects are not prominent (JPO, 2010). The ability of *surimi* to form heat-induced gels was found only at high concentrations (3 - 5%) of these salt additives, at which improved physical properties also began to be observed in the *surimi*.

In general, it is thought that the ions derived from carboxylic acid salts bind ionically to *surimi* proteins, thus affecting the water molecules bound to the protein surface; but at higher salt concentrations the surface-bound water molecules are removed, and this affects the internal structure of the proteins, thus leading to their denaturation. The magnitude of these effects differs depending on the type of carboxylic acid salt. Further, the stability of *surimi* proteins differs among different types of fish, and it is important to consider that this might, in turn, affect the impacts of carboxylic acid salt additives on them. While Takeshita *et al.* (2000) previously studied the effects of sodium gluconate on the physical properties of walleye pollack *surimi* heat-induced gels, their study compared the gel-forming ability of *surimi* with 4 and 8% sodium gluconate added to the preparations with 8% sorbitol added, and did not study the effects of these additives on the freezing resistance of the heat-induced gel-forming ability of *surimi*.

Gluconic acid is not only found in natural products, such as honey and royal jelly, but also in fermented foods. It is known for its health-promoting effects, as it is largely not absorbed in the small intestine, reaching the large intestine and increasing the colonic flora, thereby maintaining bowel health and moderating digestion by increasing the levels of short-chain fatty acids in the intestinal environment. Gluconic acid salts act similarly to this, and their safety has been established. Further, they are known to help in the maintenance and improvement of human health, as well as to help improve the flavour of food and mask unpleasant odours (Nagai, 2003).

Therefore, the development of stable frozen *surimi* without the addition of sugar compounds (sugar-free) should have major benefits to the fish paste industry, which uses *surimi* as a primary ingredient.

Conclusion

To create sugar-free frozen *surimi* from walleye pollack, we prepared frozen *surimi* by using carboxylic acid and amino acid salts in place of sugar compounds, and subjected to long-term frozen storage. It was found that the frozen *surimi* preparation made with 5% Na-gluconate and 3% Na-gluconate + 2% Na-glutamate were comparable in quality to the frozen *surimi* preparation with 5.7% sugar compounds. The quality of the frozen *surimi* was assessed in the maximal values of breaking strength (BS; g) and breaking strain (bs; mm) of the gel formed from it, as well as the relationship between the BS and gel stiffness (Gs = BS / bs; g/mm) in the process of two-step heat-induced gelation of salted *surimi*, which exhibited *suwari*-gel forming ability of the *surimi*. Furthermore, the quality of all three frozen *surimi* made with Na-gluconate, Na-gluconate + Na-glutamate, and sugar compounds remained stable during the storage at -23°C for seven to eight months, as well as the storage at -45°C for ten months or over. It was apparent that the frozen *surimi* made with Na-carboxylate / Na-carboxylate + Na-glutamate could be well utilised as raw material for the production of healthier, low-calorie, and heat-induced gel food (*kamaboko*).

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