Technical paper

Effect of Curdlan on Retort Stability of a Pork Meat Gel System

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Effect of curdlan with or without trehalose on retort stability of a minced-pork gel system was investigated. The addition of curdlan suppressed the deterioration of physical properties as well as the water-holding capacity of the gel system upon retorting. Effect of the addition of curdlan at the same concentration on the suppression of deterioration was larger by its addition in pre-suspended form via a brine solution than by dry addition; in the case of pre-suspended addition, 1% curdlan was sufficient to suppress deterioration of the above properties significantly, while in the case of dry addition, 2% curdlan was required. The addition of 0.5% curdlan and 10% trehalose also had a significant effect on the suppression of deterioration of these properties. The addition of trehalose did not cause browning of the gel surface through Maillard's reaction.

Keywords: curdlan, retort, minced-pork gel, trehalose

Curdlan is a thermal gelling polysaccharide produced by a microorganism, *Alcaligenes faecalis* var. *myxogenes* (Harada *et al.*, 1966). Curdlan is an ingredient recently approved by the U.S. Food and Drug Administration as a direct food additive (Anonymous, 1996a). It is insoluble in water but its aqueous suspension forms gels by heating. Curdlan forms two types of heat-induced gels depending on the heating temperature (Harada *et al.*, 1987). One is obtained when its aqueous suspension is heated to between 55 and 60°C and then cooled to below 40°C. This gel is thermo-reversible and termed a low-set gel. The other is obtained when the aqueous suspension is heated above 80°C; this gel is thermo-irreversible and termed a high-set gel. The molecular mechanism of high-set gel formation is different from that of low-set gel formation (Konno *et al.*, 1994). For the high-set gel, cross-linking within a three-dimensional network is accompanied by hydrophobic interactions, whereas for the low-set gel, cross-linking within a three-dimensional network is accompanied by hydrogen bonding. The high-set gel is characteristically stable against high temperature treatment such as retorting (Nakao, 1996), and remains tasteless, odorless and colorless after such treatment (Nakao, 1991).

This heat stable property of the curdlan gel enables manufacturers to create new types of foods that were technically impossible to retort, such as traditional Japanese tofu. Tofu is rarely used in retorted foods because it hardens due to syneresis during the retort processing (Nonaka *et al.*, 1996). Retort conditions are too severe for tofu to retain its prior texture as the structure is destroyed by protein denaturation. However, new formulations and preparation methods have been introduced to develop tofu products suitable for retort

utilizing curdlan (Miwa *et al.*, 1994).

Curdlan has been studied and used in Japan as a key ingredient in various types of processed foods since 1966 (Harada *et al.*, 1993; Miwa *et al.*, 1994). Especially in meat processing, it is widely used for texture modification and to improve water-holding capacity (Kimura *et al.*, 1973). The effects of curdlan have been reported on some basic rheological properties of model meat gels using pork (Funami & Nakao, 1996), and its application as a main ingredient in a fat mimetic system have also been reported using reduced fat sausage (Funami *et al.*, 1998a).

It is general knowledge in the meat processing industry that meat products including ham and sausage lose their original texture accompanied by syneresis upon retort processing.

Our objective here was to investigate the practical usage of curdlan for retorted meat products, taking advantage of its thermal gelling properties. The initial phase of this study involved the comparison of retort stability of curdlan gel with those of food protein gels which are commonly used in processed meat products to clarify the advantage of curdlan as a texture modifier in retorted meat products. The secondary phase involved investigations of the effect of curdlan alone and curdlan in combination with trehalose on retort stability of a minced-pork gel system, an experimental model for meat products.

Materials and Methods

Materials Frozen pork (ham) was obtained from a local wholesaler. The pork was thawed in a refrigerator overnight; visible fat and connective tissue were manually removed and the pork was cut into 25 mm cubes. Cubes were ground through a 3 mm grinder plate. Curdlan and lactalbumin were obtained from Takeda Chemical Ind., Ltd. (Osaka). Soy protein isolate and egg white powder were obtained from Fuji Seiyu, Ltd. (Osaka) and Taiyo Chemical

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Ltd. (Mie), respectively. Commercial trehalose was obtained from Hayashibara Co., Ltd. (Okayama). As a control reducing sugar, reagent grade glucose was obtained from Wako Pure Chemical Ind., Ltd. (Osaka). A curing agent mixture [47% sodium polyphosphate, 15% acidic sodium pyrophosphate, 8% L-sodium ascorbate, 8% sodium pyrophosphate (anhydride) and 1.3% sodium nitrite] and corn syrup solids (dextrose equivalent-25) were also obtained from Takeda Chemical Ind., Ltd. Pronase was obtained from Wako Pure Chemical Ind., Ltd.

Gel preparation Concentrations were reported using weight per weight percentage in this paper.

1) **Soy protein isolate** Soy protein isolate powder was dispersed in deionized water first by hand stirring and then mixing thoroughly with a vacuum grinder (Model 18Z, Ishikawa Kozyo, Tokyo) for 15 min. Concentration of soy protein isolate in the mixture was 20%. The mixture was stuffed into a 30 mm diameter vinylidene chloride casing tube (100 g/tube) and heated at 100, 110, 120 and 130°C for 30 min.

2) **Egg white and lactalbumin** Egg white or lactalbumin powder was dissolved in deionized water and then deaerated under vacuum. Concentration of egg white or lactalbumin in the mixture was 15%. Each mixture was stuffed and heated in the same manner as soy protein isolate.

3) **Curdlan** Curdlan powder was dispersed in deionized water with a homogenizer (AM-8, Nihon Seiki Co., Ltd., Tokyo) for 10 min and deaerated under vacuum. Concentration of curdlan in the mixture was 2%. The mixture was stuffed into a casing tube (100 g/tube) and heated at 100 and 120°C for 30 min.

After being cooled under running water to 25°C, these gels were refrigerated overnight at 4°C. The following day the preparations were subjected to measurements.

Retorted minced-pork gel preparation Brine solutions (Table 1) containing curdlan were prepared in two ways. One was addition to the brines as a dry ingredient: curdlan was added to water together with other dry ingredients and mixed for 5 min without shear using a magnetic stirrer. The other was pre-suspended addition via the brine solution: curdlan was homogenized in water with the homogenizer prior to

mixing with other dry ingredients. Brines were stored overnight at 4°C before use. Brine solutions (Table 2) containing curdlan and sugar (trehalose or glucose) were also prepared. Glucose was used as a reference to compare its effect on the browning of minced-pork gel during retorting with that of trehalose. In this case, curdlan was added to the brines as a dry ingredient. Brines were stored overnight at 4°C before use. Prepared brine solutions were mixed with minced pork at a ratio of 50% brine: 100% meat using a food processor (Model FC-27D, Aiho, Aichi). Concentration of sugar in the mixture of the brine and meat was fixed at 10% (Anonymous, 1996b). After the mixture was stored in a refrigerator at 4°C overnight, it was stuffed into a casing tube (100 g/tube) and heated at 75°C for 60 min, followed by retorting at 120°C for 20 min. After being cooled under running water to 25°C, the retorted minced-pork gel was refrigerated overnight at 4°C. The following day the preparation was subjected to measurements.

Physical measurements Physical properties of curdlan or food protein gels and retorted minced-pork gels were investigated by texture profile analysis or with puncture tests using a rheometer (Sun Scientific Co., Ltd., Tokyo). For texture profile analysis, the gel samples (30 mm in height and 30 mm in diameter) were compressed at 1 mm/s twice with a disk plunger (40 mm in diameter) in a reciprocating motion which is a slow model simulation of the action of the human jaw. From the force vs. time curve, four textural parameters (hardness, cohesiveness, springiness and chewiness) were determined. Data for these parameters upon retorting were expressed in percentages calculated by dividing the values obtained after retort with those measured prior to the process. In this analysis the degree of compression was 85% (Bourne,

Table 1. Formulations of brine solution with curdlan.

Ingredient	Weight (%)			
	Curdlan 0% ^{a)}	Curdlan 0.5% ^{a)}	Curdlan 1.0% ^{a)}	Curdlan 2.0% ^{a)}
Corn syrup solids ^{b)}	7.5	7.5	7.5	7.5
Salt	6.0	6.0	6.0	6.0
Curing mix ^{c)}	2.4	2.4	2.4	2.4
MSG ^{d)}	0.6	0.6	0.6	0.6
Curdlan		1.5	3.0	6.0
Water	83.5	82.0	80.5	77.5
Total	100	100	100	100

^{a)}Curdlan was added to the brines in pre-suspended form (at 0, 1.5 and 3% (w/w)) or as a dry ingredient (at 0, 1.5, 3 and 6%). Concentration in the mixture of minced pork and the brine. The brines were mixed with minced pork at a ratio of 50% brine: 100% meat.

^{b)}Dextrose equivalent-25.

^{c)}47% sodium polyphosphate, 15% acidic sodium pyrophosphate, 8% L-sodium ascorbate, 8% sodium pyrophosphate (anhydride) and 1.3% sodium nitrite.

^{d)}Monosodium glutamate.

Table 2. Formulations of brine solution with curdlan and sugar.

Ingredient	Weight (%)		
	CUD 0% SUG 0% ^{a)}	CUD 0.25% SUG 0% ^{a)}	CUD 0.5% SUG 0% ^{a)}
Salt	6.0	6.0	6.0
Curing mix ^{b)}	2.4	2.4	2.4
MSG ^{c)}	0.6	0.6	0.6
Sugar ^{d)}			
Curdlan		0.75	1.5
Water	91.0	90.25	89.5
Total	100	100	100

Ingredient	Weight (%)		
	CUD 0% SUG 10% ^{a)}	CUD 0.25% SUG 10% ^{a)}	CUD 0.5% SUG 10% ^{a)}
Salt	6.0	6.0	6.0
Curing mix ^{b)}	2.4	2.4	2.4
MSG ^{c)}	0.6	0.6	0.6
Sugar ^{d)}	30.0	30.0	30.0
Curdlan		0.75	1.5
Water	61.0	60.25	59.5
Total	100	100	100

^{a)}Curdlan was added to the brines as a dry ingredient (at 0, 0.75 and 1.5%). Concentration in the mixture of minced pork and the brine. The brines were mixed with minced pork at a ratio of 50% brine: 100% meat. CUD and SUG represent curdlan and sugar, respectively.

^{b)}See footnotes in Table 1.

^{d)}Trehalose or glucose.

1993). As a puncture test, gel samples of the same size were compressed with a cylindrical plunger (10 mm in diameter) at 1 mm/s. From the stress vs. strain curves, apparent breaking stress, breaking strain and breaking energy were determined. These data upon retorting were calculated in the same manner as in the texture profile analysis. Each measurement was performed at 25°C.

Water-holding capacity For retorted minced-pork gels, apparent water exudation from the gel before and after retorting was represented by the weight loss resulting from wiping the gel with a lint free paper towel (Nakao *et al.*, 1991). Percentage of exudative water was calculated as the ratio of apparent exudative-water to total moisture content of the mixture of the brine and meat before heating to negate the difference of solid content between each treatment. Apparent water released from the gel by pressure was measured as the weight loss resulting from compression of a gel slice (10 mm thick, still 30 mm in diameter) between double layers of filter paper (Toyo Roshi, No. 2, 110 mm in diameter) at 10 kg/cm² for 1 min. Percentage of released water was represented by the ratio of apparent released-water to total moisture content. For the food protein gels, percentage of water exuded from the gel was also measured as the weight loss resulting from wiping the gel with a lint free paper towel.

Viscosity measurement Viscosity of the brine solution was measured with a Brookfield type viscometer. One hundred and fifty milliliter of the brine solution was poured into a cylindrical glass beaker (40 mm in diameter, 150 mm in height) and apparent viscosity of the brines was measured at various rotating speeds with a fixed spindle at 25°C.

Browning reaction Browning caused primarily by Maillard's reaction within the retorted minced-pork gel, which may occur before, during or after retorting, was measured by the concentration of peptide pigment released during pronase digestion (Kim *et al.*, 1984). A 50 mg-aliquot of the gel was suspended in 2 ml of 0.1 M NH₄HCO₃ (pH 8.0). One milligram of pronase was added to the suspension and incubated at 37°C for 24 h with occasional stirring. One milliliter of CHCl₃ was then added to remove lipid material from the suspension. The suspension was mixed in a vortex mixer and left standing overnight at 25°C. Absorbance of the upper clear aqueous phase was measured at 420 nm to determine the degree of development of color through Maillard's reaction.

Color determination Surface color (*L**, *a** and *b**) of minced-pork gels was measured before and after retorting using a Chroma Meter CR-200 instrument (Minolta Camera Co., Ltd., Osaka) calibrated with a standard white plate prior to each measurement.

Statistics Experiments for retorted minced-pork gels were randomized designs and replicated three times using different meat sources. Statistical analysis of physical properties and water-holding capacity data for the triplicates was performed using the software program, StatView (Abacus Concepts, Inc., Berkeley, CA). When analysis of variance (ANOVA) revealed a significant effect (*p*<0.05), data means were compared with least significant differences (LSD) test to identify significant differences (*p*<0.05) among treatments.

Results and Discussion

Retort stability of gels None of the food protein gels: egg white, lactalbumin or soy protein isolate disintegrated upon heating to above 100°C (Table 3). However, apparent breaking stress for the lactalbumin gel increased with increased heating temperature, whereas that for the soy protein isolate gel decreased. Increase in breaking stress for the lactalbumin gel was most likely due to increase in syneresis. Apparent breaking strain for both gels, especially the soy protein gel, decreased with increasing heating temperature. The ratio of breaking stress to strain for the lactalbumin gel increased with heating temperature, whereas that for the soy protein gel decreased. Physical properties of the egg white gel were less changeable upon heating to above 100°C than those of the lactalbumin or soy protein gel, but the flavor was altered and had deteriorated. Carrageenan, a representative polysaccharide widely used in processed meat products, is thermally reversible, so it does not possess retort-resistance. On the other hand, although both breaking stress and strain for the curdlan gel slightly increased with heating temperature (stress: 66.0±2.4×10³ Pa at 100°C and 74.1±2.9×10³ Pa at 120°C, strain: 56.2±2.5% at 100°C and 62.8±2.8% at 120°C), the ratio of the former to the latter was almost constant, suggesting that the quality of curdlan gel changed little upon retorting. In addition, curdlan gel was tasteless, odorless and colorless after retorting as aforementioned. Therefore, the addition of curdlan to retorted meat products was thought to be more advantageous than the addition of food protein.

Effect of curdlan on retorted minced-pork gel Physical properties of minced-pork gels with curdlan were determined by texture profile analysis before and after retorting. Among four independent textural parameters, the result of chewiness, a parameter obtained through calculations using values from the other three parameters, was shown as representative (Fig. 1). Curdlan contributed to suppressing the deterioration of chewiness during retorting. When suspended uniformly in the brine solution prior to mixing with meat, curdlan significantly exhibited its effect at 1%. When added to the brine as a dry ingredient, 2% curdlan was required to achieve the same result. The other three parameters exhibited the same result as in the case of chewiness except for springiness: the addition of curdlan as a dry ingredient

Table 3. Effect of retorting on properties of food protein gels.

Treatment	Temperature (°C)	Syneresis (%)	Breaking stress (×10 ³ Pa)	Breaking strain (%)
Egg white	100	<1	99.9±3.8	39.5±1.5
	110	<1	107.3±4.7	43.9±1.8
	120	<1	114.7±4.5	40.5±1.4
	130	<1	130.7±5.1	43.3±1.8
Lactalbumin	100	<1	117.8±4.7	28.6±1.4
	110	1.20±0.05	149.7±5.4	30.6±1.1
	120	6.45±0.29	178.6±7.1	25.2±1.2
	130	12.51±0.46	220.6±9.0	26.0±1.2
Soy protein isolate	100	<1	78.4±3.5	57.1±2.5
	110	<1	71.8±3.2	57.2±2.8
	120	<1	54.4±2.9	49.1±2.4
	130	<1	21.5±1.4	35.7±1.1

Values are means±SD of duplicates.

suppressed the deterioration of springiness, but not significantly even at 2%. These results suggested that pre-suspended curdlan could give better retort stability to meat than curdlan powder at the same concentration. The structure of the retorted minced-pork gel system could be reinforced by curdlan gel particles existing throughout the system (Funami

Table 4. Changes in physical properties of minced-pork gels upon retorting from puncture tests.

Treatment	Breaking stress ^a (%)	Breaking strain ^a (%)	Breaking energy ^a (%)
Curdlan 0% +Trehalose 0%	50.2±3.9 ^a	65.1±5.3 ^a	35.5±2.1 ^a
Curdlan 0.25%+Trehalose 0%	50.0±3.3 ^a	65.5±4.0 ^a	35.4±2.4 ^a
Curdlan 0.5% +Trehalose 0%	50.3±2.8 ^a	66.5±3.5 ^a	36.6±2.0 ^a
Curdlan 0% +Trehalose 10%	51.7±1.9 ^a	65.7±3.6 ^a	35.8±2.4 ^a
Curdlan 0.25%+Trehalose 10%	52.9±3.2 ^{ab}	69.8±3.9 ^a	38.4±2.7 ^{ab}
Curdlan 0.5% +Trehalose 10%	56.4±3.0 ^b	70.9±3.8 ^a	43.0±3.0 ^b

Values are means±SD of triplicates.

^{a,b}Values in the same column with different superscripts are significantly different ($p<0.05$).

^cThese values are expressed relative to the values measured before retorting, and the latter was arbitrarily assigned 100%.

Table 5. Water-holding capacity of minced-pork gels after retorting.

Treatment	Exudative water (%)	Water released by pressure (%)
Curdlan 0% +Trehalose 0%	5.9±0.3 ^a	47.4±1.8 ^a
Curdlan 0.25%+Trehalose 0%	5.8±0.3 ^a	47.2±1.7 ^a
Curdlan 0.5% +Trehalose 0%	5.2±0.3 ^{ab}	42.8±1.8 ^b
Curdlan 0% +Trehalose 10%	5.3±0.3 ^{ab}	42.9±1.8 ^b
Curdlan 0.25%+Trehalose 10%	4.6±0.1 ^b	41.9±1.1 ^b
Curdlan 0.5% +Trehalose 10%	3.7±0.2 ^c	38.7±2.0 ^c

Values are means±SD of triplicates.

^{a-c}Values in the same column with different superscripts are significantly different ($p<0.05$).

et al., 1998b). Pre-suspended curdlan could form a hydro-gel more completely by absorbing and entrapping a larger amount of released moisture from meat in its gel structure (Funami *et al.*, 1998c) than the dry powder at the same concentration during retorting, leading to better suppression of the deterioration of physical properties upon retorting. Other than this physical reinforcement effect, the molecular interaction between curdlan and meat protein, especially myosin, is also possible, so further investigations are needed in this respect. Addition of curdlan did not change the surface color or the flavor of the gel system at all. However, a practical problem with the brine containing suspended curdlan was high viscosity; apparent viscosity of the brine containing 1.5% suspended curdlan, for instance, was 1500 mPa·s at 12.9 s⁻¹, which might pose a problem for injection using actual injectors for processing. Pre-suspended curdlan in the brine is

Fig. 2. Effect of addition of sugar on browning of minced-pork gels. Each datum represents mean of triplicates. □: before retorting, ■: after retorting.

Fig. 1. Effect of addition of curdlan on chewiness of minced-pork gels after retorting. (a): dry ingredient addition, (b): pre-suspended addition. Each datum represents mean±SD of triplicates and means with different superscripts are significantly different ($p<0.05$).

Fig. 3. Effect of addition of sugar on surface color of minced-pork gels. Each datum represents mean $\pm$ SD of triplicates. $\square$: before retorting, $\blacksquare$: after retorting.

applicable to some types of retorted meat products such as sausage or beef patties which do not require brine injection, but is not suitable for meat products which require needle injection in the manufacture.

Effect of curdlan in combination with trehalose on retorted minced-pork gel The addition of curdlan as a dry ingredient was necessary to decrease viscosity of the brine solution containing curdlan. However, the addition of curdlan alone as a dry ingredient was not effective in suppressing the deterioration of physical properties of retorted minced-pork gel until 2% was used in the mixture of the brine and meat. To decrease this effective addition level of curdlan, the combination of curdlan and sugar was investigated. This was because sugars have been reported to prevent denaturation of meat protein during heating and drying (Matsuura *et al.*, 1990) and also do not contribute to increase viscosity of the brine solution because of their water solubility. Among non-reducing sugars, which cause less deterioration of color and taste (especially sweetness) than reducing-sugars, trehalose was selected because it reportedly prevented meat protein denaturation during heating and drying (Okada & Sugimoto, 1995). In this section, physical properties of the minced-pork gel system were determined from a puncture test. Deterioration of physical properties of the gels during retorting was suppressed by the addition of curdlan and trehalose; their effect strengthened with increase in curdlan (Table 4). The combination of 0.5% curdlan and 10% trehalose suppressed the deterioration of physical properties significantly compared to the treatments of 0% curdlan+0% trehalose, 0% curdlan+10% trehalose and 0.5% curdlan+0% trehalose, especially those of breaking stress and breaking energy. In this case, apparent viscosity of the brine was 14.5 mPa·s at 15.2 s⁻¹, which was lower than that of the brine containing 6% soy protein isolate, 3% egg white powder and 3% lactalbumin, one of the most popular brine formulations for cured ham in Japan: 36.6 mPa·s at 15.2 s⁻¹. Actually, injection of the brine for the treatment of 0.5% curdlan+10% trehalose into pork was not a problem at all. Although corn syrup solids were added to the brines in place of trehalose at the same concentration, no significant suppression of the deterioration of physical properties was observed even with 0.5% or 1% curdlan (data not shown). Since relatively low

concentration of curdlan (0.5%) suppressed the deterioration of physical properties of retorted minced-pork gels with trehalose while trehalose itself did not do so, synergism might exist between the two substances. The percentage of exudative water and water released by pressure for retorted minced-pork gels decreased with increasing concentration of curdlan (Table 5). These values for the treatment of 0.25% curdlan+10% trehalose or 0.5% curdlan+10% trehalose were smaller than those in other treatments. This also suggested that curdlan absorbed and entrapped water released during retorting in its gel structure, resulting in higher water-holding capacity of the gel system. No browning reaction occurred in retorted minced-pork gel with 0.5% curdlan and 10% trehalose (Fig. 2). When glucose was added as a reducing sugar in place of trehalose, however, significant browning as a result of Maillard's reaction occurred upon retorting. Addition of trehalose hardly affected the surface color of the gels during retorting (Fig. 3), while the addition of glucose, in contrast, deteriorated it significantly: *L** value decreased, *a** and *b** values increased, and browning of the meat gel was very visible. In summary, in combination with trehalose, a lower concentration of curdlan was required to suppress the deterioration of physical properties of retorted minced-pork gel compared to the use of curdlan alone. The sugar did not deteriorate the surface color nor the taste of the gel system. Also, in this case it was not necessary to homogenize curdlan in the brine solution prior to mixing with meat, which prevented the increase in brine viscosity.

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