Effects of Temperature on the Breaking Functions of Kamaboko

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The temperature dependence of the breaking functions of kamaboko such as breaking force and breaking strain in the puncture test was assessed from 10 to 80℃, and the effects of starch content on the relation of breaking functions to temperature were also examined. Breaking force and breaking strain were expressed as the force and the depth required to push a spherical plunger into kamaboko until irreversible crushing occurred, respectively. The kamaboko samples contained starch at three different contents in the range 0. 62-7. 70％. Breaking force decreased with the rise in temperature for any sample. Temperature dependence of the breaking force was similar to that of the previously reported dynamic modulus, G'. That of the breaking strain, however, decreased as an increase in the starch content. Based on the present and previous results, the kinds of cross linkages and physical entanglement in the network structure of salt soluble proteins are discussed along with the mechanism for the appearance of tensile strength in elongated kamaboko.

When kamaboko is elongated or compressed up to the breaking point, breaking functions such as breaking force, breaking strain, and jelly strength (the product of breaking force and breaking strain) usually serve as indices of the commercial quality of kamaboko[1-5] and for basic research to elucidate the gellation mechanism of salt soluble fish proteins.[6-12] Little attention, however, has so far been given to the effects of temperature on these functions.

The present paper reports the effects of temperature on the breaking functions of kamaboko in the puncture test with a spherical plunger, and together with that of starch content of kamaboko on the temperature dependence of these functions.

1 Materials and methods

Sample Kamaboko

Three commercially available grades of kamaboko (A, B, and C) were used. Their quality was evaluated by kamaboko textural test. Kamaboko A had the highest quality, followed by B and C. They were all prepared from frozen surimi, or frozen raw fish meat paste of walleye pollack *Theragra chalcogramma*. Kamaboko A was made by heating with a gas burner and B and C, with steam.

Measurements of the Breaking Functions by Puncture Test

The kamaboko sample was cut into pieces 3

cm in height, and their breaking functions were measured at every 10℃ from 10 to 80℃. Breaking force and/or breaking strain, that is the force and the depth required to push a spherical plunger 5 mm in diameter into kamaboko to cause irreversible crushing, were measured, using a NRM-2002J Rheometer (Fudoh Kogyo Co., Japan). The plunger was driven at a constant rate of 2 cm/min.

In preliminary experiments, the test pieces were immersed in a temperature-controlled 2.5% NaCl solution and variation in temperature against immersion period was measured. At least a 15 min period was required for the measurements of the solution temperature of 39, 58 or 80℃. Consequently, the test pieces were immersed in a 2.5% NaCl solution for 15 min, and thereafter breaking functions were measured under the same conditions as those under which the test pieces had been immersed in the solution. Five test pieces were used for each measuring temperature for every kamaboko sample. Each piece was tested three times.

Measurement of Starch Content

Five grams of the comminuted kamaboko sample was heated with 40 ml of a 8% KOH-95% ethanol solution on a hot water bath (90-95℃) for 30-40 min with occasional shaking.[13] The precipitated starch was collected by centrifugation and washed twice with 4% KOH-50% ethanol solution, then twice with 50% ethanol solution, and hydrolyzed with 200 ml of 2.5% HCl. Sugar content was determined by the Somogyi method.[14] Starch content was calculated by multiplying the

reducing sugar content by the starch conversion factor 0.9.

2 Results

Starch Content of Kamaboko

Starch contents of the three kamaboko samples, together with the results of recovery test of potato starch added to the kamaboko are shown in Table 1. Recovery was about 102% for every sample, and accordingly, the observed starch content was taken as the actual value of starch. The starch content of kamaboko A was calculated at 0.62% (grams starch / 100g kamaboko), and that of samples B and C, at 4.76% and 7.70%, respectively. Consequently, the commercial quality of kamaboko was inversely proportional to the starch content.

Effects of Immersion of Test Pieces in 2.5% NaCl Solution on Breaking Functions

To control the temperature of the test pieces of kamaboko, they were immersed in a temperature-controlled 2.5% NaCl solution for 15 min. The values of the breaking functions when the test pieces were immersed in the NaCl solution appeared to differ somewhat from those of the temperature-controlled test pieces not immersed in the NaCl solution. Accordingly, the effects of immersion of the test pieces in the NaCl solution on the breaking force and the breaking strain were examined. Two kinds of kamaboko, one of low starch content (kamaboko A) and other, high starch content (kamaboko C), were immersed in NaCl solution controlled to 80℃. The test pieces

Table 1. Starch content of the kamaboko sample and the result of recovery test of added starch

Kamaboko sample	Starch analyzed (mg/5g kamaboko) (Ⅰ)	Starch added (mg) (Ⅱ)	Starch content (mg / 5g kamaboko)		
			Sum (Ⅰ + Ⅱ)	Found	Recovery (%)
A	31	74	105	108	102.9
B	238	934	1,172	1,192	101.7
C	385	133	518	531	102.5

of kamaboko were divided into two groups, one directly immersed in the 80℃-controlled 2.5% NaCl solution (direct heating method), and the other immersed after the test pieces were wrapped with polychlorovinylidene-resin film (indirect breaking force and the breaking strain for different heating methods were shown in Table 2. As heating methods are shown in Table 2. As indicated in the table, the absolute values of the Student's t_0 were less than the t value at 0.01 level for any breaking function. Thus statistically, there was no significant difference between the direct and indirect heating methods regardless of

starch content. The temperature of the test pieces can thus be simply controlled by the direct heating method.

Temperature Dependence of the Breaking Functions.
Variations in the breaking functions with rise in temperature are shown in Fig. 1. The magnitudes of the breaking force of kamaboko A and B were almost the same in the range of experimental temperature, whereas that of kamaboko C was somewhat lower. Temperature dependence of the breaking force and the extent of decrease in the breaking force within the

Table 2. Comparison of the breaking force and the breaking strain between direct and indirect heating methods for kamaboko sample of different starch content

Kamaboko sample	Method of heating	Breaking force in g	Breaking strain in cm	t test[*1] Breaking force	Breaking strain
A[*2]	Direct	276±65	1.52±0.22	$|t_0|=1.00$	$|t_0|=1.24$
	Indirect	255±49	1.42±0.14		
C[*2]	Direct	113±13	1.22±0.10	$|t_0|=0.15$	$|t_0|=0.63$
	Indirect	112±18	1.05±0.13		

*1 t $(n_1+n_2-2) = t$ $(28, 0.01)=2.763$
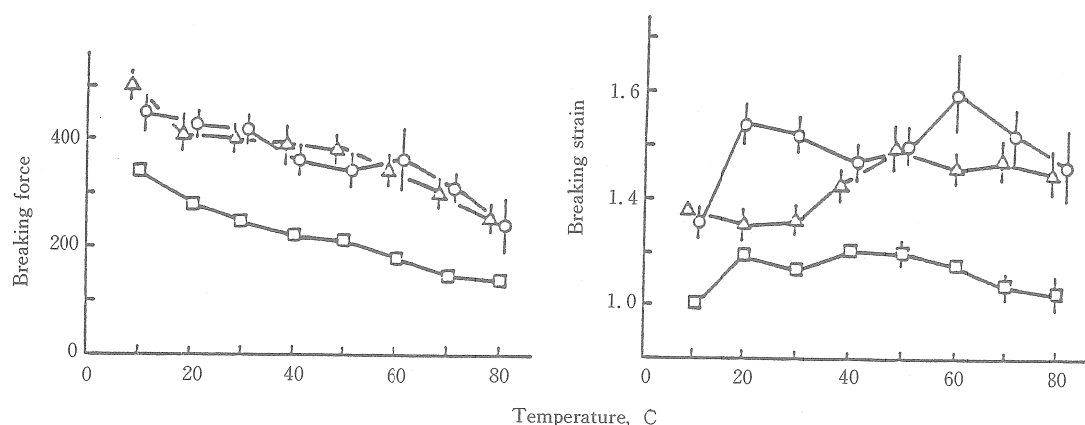*2 Starch content: A, 0.62% (0.62g starch / 100g kamaboko); C, 7.70%.

Fig. 1. Temperature dependence of the breaking force and the breaking strain of kamaboko in the puncture test.
○, sample A (0.62g starch/100g kamaboko); △, sample B (4.76g starch/100g kamaboko); □, sample C (7.70g starch/100g kamaboko).

measuring temperature range, however, were almost the same in spite of the difference in starch content. That is, the breaking force decreased gradually with rise in temperature for kamaboko, as was also noted for dynamic modulus G'.[15, 16] and instantaneous compression modulus.[17] According to Niwa et al.[18], the temperature dependence of the breaking force was quite different from present results as shown by a curve with a maximum temperature at about 40℃ in the temperature range of 20-80℃.

The temperature dependence of the breaking strain differed according to starch content. For a low starch content, it was expressed as a complicated curve with two peak-temperatures at 20℃ and 60℃. For high starch content, it showed a gentle, upward curve. The difference between maximum and minimum breaking strain was 0. 5 for kamaboko A with a low starch content and 0. 3 and 0. 2 for kamaboko B and C, respectively. Thus the magnitude of the difference was inversely proportional to starch content.

3 Discussion

The breaking force and G'[15, 16] of kamaboko were measured under large and small deformation, respectively. They represent different physical properties of kamaboko. The temperature dependence of the breaking force of three different kamaboko, however, resembled each other, and was comparable to G'. Since the network structure of kamaboko is accepted as consisting of some kinds of cross linkages and physical entanglement, the temperature dependence of these cross linkages appears to function similarly even under large or small deformation. One main cross linkage which decreases with rise in temperature is hydrogen bond,[19, 20] and is thought to play a major role in forming the network structure.

The breaking functions of kamaboko, however, are not necessarily lowered nearly to zero even st 80℃, where hydrogen bond cannot function. Accordingly, some cross linkages and physical entanglement in the network structure are fairly stable at high temperatures. That is,

chemically stable cross linkages and physical entanglement are responsible for the stability of the network structure at high temperatures.

The temperature dependence of the breaking strain was quite different from that of the breaking force and differed among the different kamaboko as shown in Fig. 1. The reason is not clear, but may possibly be the presence of air bubbles in the test pieces. This is because the deformation of a substance is affected by the volume and distribution of empty spaces in a substance.[21]

Based on the temperature dependence of the breaking functions, the commercial quality of kamaboko may be related to the breaking strain rather than the breaking force. But the latter appears a more suitable index for investigating the kinds of cross linkages or physical entanglement of the network structure regardless of starch content or magnitude of deformation, because the temperature dependence is simple for kamaboko sample.

The elasticity of a substance such as energy- or entropy-elasticity can be analyzed from the temperature dependence of tensile force. However, the temperature dependence of the breaking force cannot be used for the analysis of elasticity. Because, the breaking force is not necessarily proportional to the breaking strain, and breaking occurs irregularly at a bubble in kamaboko.

Now, the breaking force is presumed to be proportional to the tensile strength of kamaboko under large elongation, and we can discuss this as follows. As the breaking force decreased with the rise in temperature in the range of 10-80℃ as shown in Fig. 1, the relation of the breaking force to temperature was applied to the following equation as derived from thermodynamics[21]

$$f = (\partial E/\partial e)_T - T(\partial S/\partial e)_T$$

where f is the tensile force, E the inner energy, S entropy, e strain, and T, absolute temperature.

The slope or the negative sign of $(\partial S/\partial e)_T$ was negative as shown in Fig. 1, and accordingly $(\partial S/\partial e)_T$ was positive. Thus the entropy of kamaboko may increase with the elongation.

Since natural phenomena inevitably proceed in the direction of increased entropy, the elongated state is more stable than that before elongation. However, this interpretation does not permit understanding the reason for the increase in the tensile strength as kamaboko was elongated. Consequently, the elasticity of kamaboko may not be entropy elasticity. This notion is consistent with the temperature dependence of G'[22], even assuming the breaking force to be proportional to the tensile force at large elongation.

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かまぼこの破断特性に及ぼす測定温度の影響

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　かまぼこの破断特性値の温度依存性ならびにそれとでんぷん含量との関係を，でんぷん含量が0.62～7.70％の3種類の市販かまぼこを用いて10～80℃で検討した。テクスチャーから判定したかまぼこの品質は，でんぷん含量と逆の関係であった。球形プランジャーを用いて得られた破断荷重は測定温度の上昇に伴って低下し，そのパターンはでんぷん含量によらずほぼ同一であった。破断歪の温度依存性はでんぷん含量が低い時には大きく，高い時には小さかった。これらの結果をもとに，ミクロおよびマクロなレベルで網状構造について考察を加えた。