かまぼこのレオロジー的物性と構造に関する研究II.

誌名	日本水産學會誌
ISSN	00215392
著者	高木, 一郎 清水, 亘
巻/号	38巻5号
掲載ページ	p. 471-474
発行年月	1972年5月

On Rheological Properties and Structure of Kamaboko—II. Influence of Starch Contents upon Stress-Strain Relation of Kamaboko*

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(Received October 27, 1971)

In the previous paper the relation between stress and extension ratio of kamaboko which does not contain starch has been discussed on the basis of the theory of rubber elasticity.

In this paper are considered the stress-strain relations of kamaboko which contains various amounts of starch. An experiment concerning the influence of difference of raw fish on this relation is also included.

The results obtained are analysed as follows:

(1) Starch contained in kamaboko has a 'filler reinforcement effect' similar to that of the filler contained in elastic rubber.

(2) The deviation of experimental data from the theoretical curve expressed by

$$f = K(\alpha - \alpha^{-2}) = \tfrac{1}{3}E(\alpha - \alpha^{-2})$$

may be closely related to the texture, chewiness, elasticity and firmness of kamaboko.

In a previous paper[1], it was considered that the elasticity of kamaboko can be explained well by application of the rubber elasticity theory. In the case of kamaboko which made from various raw fish without starch, the stress-strain behavior was expressed by the equation as follows:

$$f = K(\alpha - \alpha^{-2}) = \frac{1}{3}E(\alpha - \alpha^{-2}),$$

where f(dyn/cm^2) is the stress, α is the extension ratio and E(dyn/cm^2) is the initial Young's modulus.

Most kamaboko sold at markets contain more or less starch for the purpose of reinforcing *ashi* or increasing quantity. A number of studies were reported about the mechanical properties of kamaboko which contains various amounts of starch in connection with *ashi*,[2-6] but there is no discussion from the polymer-scientific point of view.

In the present paper, influence of starch contents on the stress-strain behavior was examined, and the meaning of existence of starch as gel component was also discussed.

Materials and Methods

Kamaboko Kamaboko were prepared in order to obtain the reqirered potato starch

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* Presented at the Annual Meeting of the Kinki branch of the Japanese Society of Scientific Fisheries, Akashi City, Jan. 23, 1971.

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contents for this experiment by the usual method. Raw fish used were jack mackerel, *Trachurus japonicus*, and lizard fish, *Saurida argyrophanes*, the former was very fresh and the latter was transported under icing after caught in East China Sea. Moisture and potato starch contents of prepared kamaboko are shown in Table 1. Physical measurements of their kamaboko were carried out after storage for 24 hours at 25°C.

Table 1. Tension-compression tester measurements on kamaboko made with various amounts of potato starch.

Sample	Raw fish	Starch (%)	Moisture (%)	Initial Young's modulus* E (dyn/cm^2)	Ultimate extension ratio* α_B	Ultimate stress* f_B (dyn/cm^2)	Toughness** (erg/cm^3)
				$\times 10^5$		$\times 10^5$	$\times 10^5$
a	Lizard	none	71.4	11.1	2.50	8.66	7.5
b	fish	6.0	69.8	11.3	2.30	7.92	6.5
c	(*maeso*)	11.0	69.1	11.7	2.25	7.90	6.1
a'	Jack	none	70.6	12.9	1.95	6.75	2.9
b'	mackerel	6.0	70.6	14.7	1.80	7.33	3.0
c'	(*maaji*)	12.0	70.0	16.2	1.60	6.55	2.2

* at tension side

** Toughness $= \int_{\alpha=1}^{\alpha_B} f(\alpha)d\alpha$

Measuring apparatus The tension-compression tester which was reported in the previous paper[1)] was used. The measuring conditions were as follows: 5.00×10^{-2} cm/sec in stretching and compressing rates, 25.00±0.05°C, 98–100% humidity, shape and size of the test specimen were the same as the previous paper[1)].

Results and Discussion

Results obtained such as the initial Young's modulus, the tensile ultimate extension ratio, the tensile ultimate stress and the toughness are shown in Table 1. The stress *vs.* extension ratio curves are shown in Fig. 1 and Fig. 2, where the solid lines are theoretical curves[1)] which are given from the mode of frequency distribution of initial Young's moduli at tension side and the extension ratio. The difference between Fig. 1 and Fig. 2 is little significant, though different kinds of fish were used as raw material.

It is seen from these results that in case of stretching the stress *vs.* extension ratio curves agree well with the theoretical scheme independently of starch contents, while in case of compression the deviation of these experimental data from the theoretical curves becomes considerable in proportion to increasing of starch contents. Moreover, it is seen from Table 1 that the initial Young's modulus and the ultimate stress have a tendency to become more in proportion as starch contents increase.

These results suggest an idea on the meaning of existence of starch in kamaboko as follows: From the essential difference of behavior between the tension side and the compression side, small lumps of starch gel (about 35 μ in diameter) do not take part directly in the micro-network structure which constitutes heat coagulated proteins gel, and do not serve as the vulcanizing agent. From the tendency obtained on the tensile ultimate stress, the dimension of protein molecules must be smaller than that of starch lumps, in analogous to the estimation described by BUECHE[7] with regard to the rupture for rubber containing the impurities. Further, as indicated by FLORY[8] with regard to the gel forming for polymers, two or more cross-linkings per each gel forming proteins molecule may be necessary in order to form gel network structure. Therefore, starch lumps can not be packed into the micro-network structure which constitutes heat coagulated proteins gel. It may be given as a conclusion that these small lumps of starch gel contained in kamaboko play 'filler reinforcement effect' as if the filler contained in elastic rubbers behaves so[9,10]. That is, small lumps of starch gel may squeeze itself as the filler in the macro-structure of optical-microscopical dimensions which consists of sizable gathering of micro-network structure of heat coagulated proteins gel.

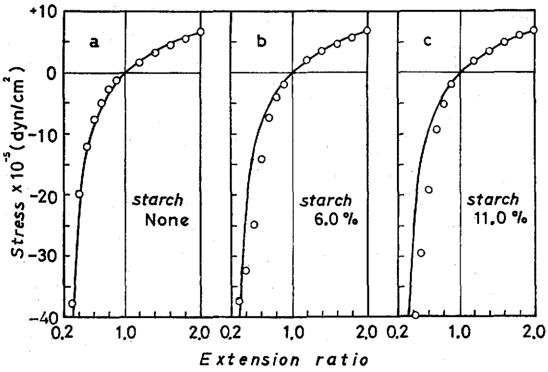

Fig. 1. Stress *vs.* extension ratio curves for samples *a*, *b* and *c* at 25°C, 98–100% humidity. Solid lines represent theoretical curves which are expressed by $f = K(\alpha - \alpha^{-2})$. Open circles indicate experimentals.

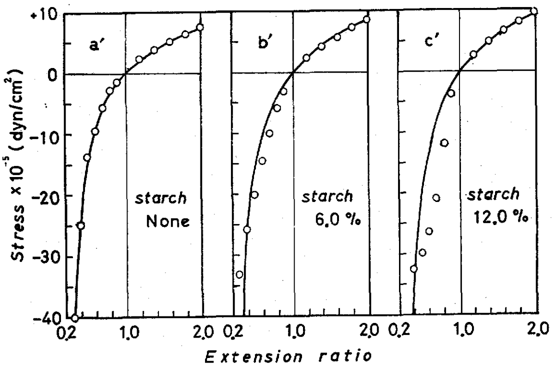

Fig. 2. Stress *vs.* extension ratio curves for samples *a'*, *b'* and *c'* at 25°C, 98–100% humidity. Solid lines represent theoretical curves which are expressed by $f = K(\alpha - \alpha^{-2})$. Open circles indicate experimentals.

This presumption, that starch behaves as the filler in kamaboko, is supported with following mentions. Firstly, the initial Young's modulus has a tendency to become more in proportion as starch contents increase. Secondly, the ultimate stress is affected by starch contents. Thirdly, in case of stretching any curve conforms well to the theoretical equation based on the rubber elasticity theory, but in case of compressing the deviation from the theoretical becomes more in proportion as starch contents increase. These phenomena observed in kamaboko bear a close resemblance to the filled rubbers.[7,11,12]

Although small starch lumps do not behave to connect directly with micro-network structure, there is no denying to speculate upon existing chemical or secondary bond between starch gel surface and protein molecules.[13]

Moreover, when we consider the texture of kamaboko from the food scientific point of view on the basis of these experimental results, the difference of texture such as chewiness, elasticity and firmness between non-starch kamaboko and kamaboko containing starch may be caused by the deviation of behavior at compressed deformation side from the theoretical curve.

Acknowledgements

The authors wish to express thanks to Prof. Shizunori IKEDA of Kyoto Univ., for his continued advice and encouragement in this work.

The technical assistance of Mr. Kengo UCHIDA is also acknowledged.

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