On Rheological Properties and Structure of Kamaboko—XIII Relation between *Ashi* and Distribution Function of Relaxation Times for Kamaboko

Ichiro TAKAGI*

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The tensile relaxation modulus reduced to 25°C in the time scale range from 3×10^{-2} sec to 1×10^6 sec was determined, and the relaxation spectrum was calculated for kamaboko.

A comparison of the relaxation spectra for various kamaboko varying in tensile toughness (*i.e.*, the strength of *ashi*) gives the following information: (1) There is a very good parallelism between the magnitude of tensile toughness and the absolute value of the differential coefficient of the relaxation spectrum at 1×10^{-1} sec of relaxation time. (2) There is also good parallelism between the magnitude of tensile toughness and the width of the distribution range of the relaxation times of Maxwell units which are able to relax under applied strain.

In the previous papers, the relations between the quality of kamaboko and the physical properties such as the stress-strain relation in both sides of tension and compression^{1,2)}, the thermodynamical property for contractile force^{3,4)}, and the instantaneous and equilibrium moduli⁵⁾ for kamaboko have been reported.

This paper is undertaken to determine the relaxation spectrum for kamaboko, and to obtain the informations about the relation between the spectrum and the quality of kamaboko.

Materials and Methods

Kamaboko Six commercial kamaboko used in this experiment were as shown in Table 1.

Tension-compression tester measurement The measurement was carried out in the method as described in the previous papers.^{1,2)}

Tensile stress relaxation measurement The relaxation modulus was determined during a period from 1×10^{-1} sec to 4×10^4 sec at an extension ratio of 1.20 at various fixed temperatures of 0, 20, 40, 60, and 80°C at fixed humidity of 98% for various kamaboko, and the master curve of relaxation modulus reduced to 25°C over the time scale range from 10^{-2} sec to 10^8 sec was obtained. Details for relaxation measurement was as previously described.^{6,7)}

The relaxation spectrum, $H(\log_e \tau)$, was calculated according to Eq. (6).

Relaxation spectrum Previously⁸⁾, we indicated that the relaxation behavior of

* Ayabe Higher School, Ayabe City, Kyoto, 623, Japan. (高木一郎: 京都府立綾部高校)

Table 1. Results with both tension-compression tester and relaxometer on six commercial kamaboko.

Sample	Locality	Moisture (%)	Starch*	T_T^{**} (erg/cm ³)	$E(t)_{\text{red., } 25^\circ\text{C}}^{***}$ (dyn/cm ²)		$\left[\frac{E(10^{-1}) - E(10^7)}{E(10^{-1})} \right] \times 100$ (%)
					$t=10^{-1}$	$t=10^7$	
				$\times 10^5$	$\times 10^5$	$\times 10^5$	
A	Hagi	73.0	±	6.6	18.5	1.8	90
B	Odawara	69.9	+	6.0	12.1	2.3	81
C	Nagato	78.0	—	5.9	16.3	2.8	80
D	Kyoto	67.0	+	5.7	11.1	3.0	73
E	Maizuru	69.5	++	4.0	11.2	3.4	70
F	Maizuru	71.4	+	3.0	13.4	4.4	67

* Iodostarch reaction.

** Tensile toughness.

*** Tensile stress relaxation modulus reduced to 25°C.

kamaboko may be interpreted by the generalized Maxwell model. Let the distribution of relaxation times be infinite and continual, then the tensile stress relaxation modulus for kamaboko, $E(t)$, is written as

$$E(t) = \int_0^\infty E(\tau) e^{-t/\tau} d\tau + E(\infty), \quad (1)$$

where τ is a relaxation time of a Maxwell unit in the viscoelastic network structure in kamaboko and $E(\infty)$ is the equilibrium modulus for kamaboko.

Because the width of distribution range of τ is large, $E(\tau)$ is usually expressed as a function of $\log_e \tau$:

$$H(\log_e \tau) = \tau \cdot E(\tau) \quad (2)$$

where $H(\log_e \tau)$ is called the relaxation spectrum or the distribution function of relaxation times. Then Eq. (1) can be given as

$$E(t) = \int_{-\infty}^{+\infty} H(\log_e \tau) e^{-t/\tau} d(\log_e \tau) + E(\infty). \quad (3)$$

There have been many studies on calculating $H(\log_e \tau)$ from the experimental result about $E(t)$.⁸⁻¹⁰⁾ Considering the accuracy of calculation, let us introduce SCHWARZL-STAUERMAN's third approximation equation¹⁰⁾ expressed by

$$H(\log_e \tau) = \left[-\frac{dG(3t)}{d(\log_e t)} + \frac{3}{2} \frac{d^2 G(3t)}{d(\log_e t)^2} - \frac{1}{2} \frac{d^3 G(3t)}{d(\log_e t)^3} \right]_{t=\tau}. \quad (4)$$

The relaxation modulus determined in this experiment is not the shearing relaxation modulus, $G(t)$, but the tensile relaxation modulus, $E(t)$. We have obtained experimentally a following relation between $G(t)$ and $E(t)$ for kamaboko⁹⁾:

$$3 \cdot G(t) \simeq E(t). \quad (5)$$

Therefore Eq. (4) may be also written in the form:

$$H(\log_e \tau) = -\frac{1}{3} \left[\frac{dE(3t)}{d(\log_e t)} - \frac{3}{2} \frac{d^2 E(3t)}{d(\log_e t)^2} + \frac{1}{2} \frac{d^3 E(3t)}{d(\log_e t)^3} \right]_{t=\tau}. \quad (6)$$

Results and Discussion

Quality of kamaboko The quality of kamaboko, the strength of *ashi* of kamaboko, can be evaluated by the instrumental value of the tensile toughness, T_t , as often pointed out.^{1,2,11)} The order of the quality of kamaboko, or of the strength of *ashi* of kamaboko, used in this experiment was therefore $A > B > C > D > E > F$.

Relaxation modulus As described in the previous paper⁵⁾, the 10^{-1} sec relaxation modulus for kamaboko, $E(10^{-1})$, is considered approximately to be the instantaneous modulus, $E(0)$, and, the 10^7 sec one, $E(10^7)$, is considered certainly to be the equilibrium one, $E(\infty)$. $E(10^{-1})$, $E(10^7)$, and $\{E(10^{-1}) - E(10^7)\}/E(10^{-1})$ are shown in Table 1. There is good parallelism between the ratio of $\{E(10^{-1}) - E(10^7)\}$ to $E(10^{-1})$ and the magnitude of tensile toughness. This fact suggests that the contribution of Maxwell units being able to relax in stress under applying strain to the tensile toughness is significant. That is to say, the entanglement and friction between chain segments in kamaboko network structure contribute to the tensile toughness of kamaboko. On the contrary, the clear correlations between each the magnitude of $E(10^{-1})$, $E(10^7)$ and the magnitude of tensile toughness are not observed respectively, though logarithm of $E(10^{-1})$ and logarithm of $E(10^7)$ are proportional to logarithm of the myofibrillar protein content in kamaboko as reported previously⁵⁾.

Fig. 1. Relaxation spectra for six commercial kamaboko at 25°C.

Fig. 2. Relations between tensile toughness of kamaboko and various rheological values.

Relaxation spectrum As shown in Fig. 1, the relaxation spectra obtained have been plotted on not the natural logarithm scales but the common logarithm scales, *i.e.*, $\log_{10}$

$H(\log_e \tau)$ and $\log_{10} \tau$, in order to compare these spectra with the results of relaxation experiment reported in the previous papers^{6,7)}. A relation between the relaxation time $\log_{10} \tau$ corresponding to a magnitude of 3 of relaxation spectrum $\log_{10}\{H(\log_e \tau), (\log \tau)_{\log H=3}\}$, and the tensile toughness, T_T , is shown in Fig. 2. Since the value of $(\log \tau)_{\log H=3}$ is proportional to the magnitude of tensile toughness, it seems that the amount of Maxwell relaxation units in longer time scale region in kamaboko of good quality is larger than that in kamaboko of poor quality.

As shown in Fig. 1, there is tendency that the larger the magnitude of tensile toughness the larger the magnitude of relaxation spectrum in $\log_{10} \tau \leq 0$. This tendency supports that the distribution of Maxwell units having relaxation times of 10^0 sec and below in kamaboko of good quality is more plentiful than that in kamaboko of poor quality.

Moreover, a proportional relation between the absolute value of $[d(\log_{10} H)/d(\log_{10} \tau)]_{\log_{10} \tau=-1}$ and the magnitude of T_T (Fig. 2) supports that the distribution of Maxwell units having relaxation times of 1×10^{-1} sec and below in kamaboko of good quality may be more plentiful than that in kamaboko of poor quality.

From the facts described above we may conclude that the width of distribution range of relaxation times of Maxwell units in viscoelastic network structure of kamaboko is proportional to the strength of *ashi* of kamaboko, and the degree of contribution of Maxwell units being able to relax to the strength of *ashi* is also proportional to the strength of *ashi* of kamaboko.

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