The Change of the Rheological Properties of Surimi (Minced Fish-Meat) by Heating

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The change of the rheological properties of surimi which accompanied heat-processing was examined by stress-relaxation experiment. Samples were made from the frozen surimi of Alaska pollack. The instantaneous compression modulus showed the measuring temperature dependence, and the results could be analyzed by the theory of rubber elasticity. All the samples except those produced by heating at 40°C showed the thermo-rheological simplicity. Although the elastic modulus of all the samples except those of 0% NaCl generally increased with the heating temperature, the viscosity was almost independent of the heating temperature.

In the course of our study concerning the change in texture which accompanies heat-processing, the rheological properties of surimi have so far been ignored. This work, however, is concerned with the change of the rheological properties; namely, the instantaneous compression modulus, elastic modulus, viscosity, and relaxation time, of surimi by heating.

When a surimi sample has been completely heated, it has the same texture as the so-called "kamaboko", which is a kind of fish-meat gel. The rheology of kamaboko has been studied by many investigators,1-12 and it is clear that the rheological properties of kamaboko are essentially the rubber-like elasticity, which results mainly from the network structure of the protein chains.

Moreover, the properties of surimi and minced meat have been reported by several researchers.14,15 However, few studies concerning the variation of the rheological properties of surimi when undergoing heat-processing have been carried out, although there have been some works on "suwari" (thermo-setting) and "modori" (thermo-disintegration).1,12,13

In this work, we examined the rheological properties of surimi samples that had been heated to between 40°C and 95°C by stress-relaxation experiments.

Experimental

Materials

Samples were made from the frozen surimi of Alaska pollack which was purchased at a market. The frozen surimi was ground for ca. 14 min with water (21 %) and sodium chloride (0, 1.0, 2.5, and 4.0%). Then the paste was inserted in a poly (vinylidene chloride) casing (55 mm x 220 mm) and heated for 1 h at 40°C, 55°C, 70°C, and 85°C.

Stress-relaxation Experiments

The stress-relaxation experiments were carried out by using a TENSIPRESSOR Model TTP-50 BX (TAKETOMO DENKI) at 0°C, 16°C, 20°C, 30°C, 40°C, 50°C, and 63°C. The plunger was a cylinder of 18 mm in diameter. A constant strain of 0.25 was selected. Five measurements were taken with the samples heated at the same temperature.

Analysis of Stress-relaxation Curve

The equation of the stress-relaxation curve can be expressed approximately as follow:

\[ p(t) = e_0 \sum_{i=1}^{n} E_i \exp\left(-t/\tau_i\right) \]

\[ p(t) \] is stress, \( e_0 \) the constant strain, \( t \) the time, \( E_i \) the elastic modulus of \( i \)-th element, and \( \tau_i \) the stress-relaxation time of \( i \)-th element. The stress-relaxation time of \( i \)-th element, \( \tau_i \), is related to the viscosity, \( \eta_i \), and elasticity, \( E_i \), of \( i \)-th element as eq. (2).

\[ \tau_i = \eta_i / E_i \]  

The instantaneous compression modulus, \( E_0 \), is defined as follows:

\[ E_0 = E_1 + E_2 + \cdots + E_n \]
The stress-relaxation curve was analyzed by using the progressive approximate method.\textsuperscript{16)}

Results and Discussion

Fig. 1 shows the measuring temperature dependence of the instantaneous compression modulus on the sample of 0\% NaCl. The instantaneous compressive modulus decreased linearly with the measuring temperature as shown in Fig. 1. The other samples, which contained NaCl, showed the same tendency.

According to the theory of rubber elasticity, the stress-tension strain curve of ideal rubber is expressed as follows:\textsuperscript{17)}

\begin{equation}
\bar{f} = \frac{\nu RT}{L} \frac{L_u^2}{L^2} - \frac{L_u}{L}, \tag{4}
\end{equation}

where $R$ is the gas constant, $\nu$ the number of chains per unit volume (mol/cm$^3$), and $T$ the absolute temperature. The $L_u$ is the undeformed sample length, and $L$ is the deformed one. We have assumed that the theory of rubber elasticity can be applied to the compression-strain. On the assumption, eq. (4) must be replaced to the following equation,

\begin{equation}
\bar{f} = -\nu RT \left( \frac{L}{L_u} \right)^2 - 1. \tag{4'}
\end{equation}

Since the compression elastic modulus, $E$, is defined as

\begin{equation}
E = L \left( \frac{\partial^2 f}{\partial L^2} \right)_T, \tag{5}
\end{equation}

the combination of eqs. (4') and (5) gives the eq. (6),

\begin{equation}
E = -\nu RT \left( \frac{L}{L_u} \right)^2. \tag{6}
\end{equation}

In this study, the compression ratio is 0.25, i.e. $L/L_u = 0.75$, then we get the following relation,

\begin{equation}
E = -0.4 \nu RT. \tag{7}
\end{equation}

The number of chains per unit volume, $\nu$, can be considered to be the number of crosslinks in the network structure. Fig. 2 shows the relationship between the $\nu$-value and the heating temperature. The $\nu$-value of the sample of 0\% NaCl showed the minimum ($1.5 \times 10^{-4}$ mol/cm$^3$) at the heating temperature of 55° C, and those of the other samples increased with the heating temperature. At a heating temperature of 85° C, the $\nu$-value of all samples attained an almost constant value of ca. $3.0 \times 10^{-4}$ mol/cm$^3$. This result suggests that the number of crosslinks depends on the NaCl contents at a heating temperature below 70° C, and that the crosslink in the fish-meat gel produced below 70° C are less than those in the gel produced at 85° C.

The $\nu$-value can be related to the density, $d$, and the molecular weight of a network chain, $M_c$.

\begin{equation}
M_c = d/\nu. \tag{8}
\end{equation}

In other words, $M_c$ is the molecular weight of the chain between the nearest neighbor crosslinks. The relationship between $M_c$ and the heating temperature is the reverse of that shown in Fig. 2 as clearly stated in eq. (8). Using the density of the fish-meat gel of 1.03 g/cm$^3$, which was measured at room temperature, the $M_c$ value of the sample produced by heating at 85° C was independent of NaCl contents and was estimated to be ca. $0.3 \times 10^4$. The $M_c$ value of $0.3 \times 10^4$ corresponds to 10 amino acid residues on the basis of the assumption that the average molecular weight of amino acid
Fig. 3. The thermo-rheological simplicity of the sample of 0% NaCl and on a heating temperature of 55°C. The right-hand side shows the master curve, of which reference temperature is 30°C.

Residue is 300. From the fact that $M_c$ is near 10,000 for most rubbers, it can be said that the structure of the fish-meat gel is somewhat loose when compared to those of rubbers.

The sample produced by heating at 40°C did not exhibit thermo-rheological simplicity. However, the other samples showed the thermo-rheological simplicity. The thermo-rheological simplicity was reported on some kamabokos.3,10 An example is shown in Fig. 3: the results were on the sample of 0% NaCl and on a heating temperature of 55°C. The right-hand side of Fig. 3 shows the master curve, in which case the reference temperature has been taken arbitrarily to be 30°C. The fact that the sample heated at 40°C did not show the thermo-rheological simplicity can be explained as follows: the heating temperature of 40°C was not sufficient for heat-processing of fish-meat gel, and the structure changes occurred in the measurement at the temperature above 40°C.

The temperature dependence of the shift factor, $a_T$, can be expressed by the Arrhnius equation [eq. (9)] or WLF equation [eq. (10)].

$$\ln a_T = \frac{\Delta H}{T - T_r}$$

where $T$ is the absolute temperature, $T_r$ the reference temperature (in this work 303 K), and $\Delta H$ the activation energy.

$$\ln a_T = -c_1(T - T_r)/(c_2 + T - T_r),$$

where $c_1$ and $c_2$ are constants.

Fig. 4 shows an example of the Arrhenius plot of $\ln a_T$ versus $(1/T)$. As shown in Fig. 4, the Arrhenius equation can be applied to the data in this work, that is, all the data of all the samples except those heated at 40°C can be treated with the Arrhenius equation. However, the WLF equation cannot be applied to all the samples in this work. Hamada and Inamasu have reported that both the Arrhenius equation and the WLF equation cannot be applied to the data on kamaboko (fishmeat gel).10 Therefore this point must be ascertained in future.

The activation energy, $\Delta H$, was estimated to be 25–30 kcal/mol, which was independent of the heating temperature and of the NaCl contents. Although the number of crosslinks increased with the heating temperature, the activation energy was
almost the same. The results may suggest that the relaxation mechanism was not necessarily related to the number of crosslinks in these samples.

Figs. 5 and 6 show the master curves: in the former, the master curves were shown as the function of heating temperature and in the latter as the function of the NaCl contents. As shown in Figs. 5 and 6, the relaxation properties of fish-meat gel were attained to the same level at NaCl 2.5% or 4.0% and at a heating temperature above 70°C.

The analysis of the stress-relaxation curve was done with the progressive approximate method. The three trials gave satisfactory results in each sample, i.e. $n=3$ in eq. (1). The elastic modulus of 1-th element, $E_1$, are shown as the function of heating temperature in Fig. 7. The results of the other elements, $E_2$ and $E_3$, show comparable behavior. Namely, the elastic modulus generally increased with the heating temperature except
those of the sample of 0% NaCl. The elastic modulus of the latter showed a minimum at 55°C, which may correspond to the "modori" (thermodisintegration). On the other hand, the viscosity was almost independent of the heating temperature. Fig. 8 shows the viscosity of 1-th element, \( \eta_1 \), versus the heating temperature plots. The viscosities of the other elements, \( \eta_2 \) and \( \eta_3 \), showed the same behavior. This may result from the fact that the viscosity element in the viscoelastic body is mainly due to the whole deformation which occurs at the loose structure in the whole body.

In other words, the distribution of cross-links in the gel structure was not uniform and the viscosity deformation occurs at the small density of cross-links.

An investigation as to the nature of the crosslinks is one of the most important problems that remain to be solved.

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References