◇◇◇ Original Paper ◇◇◇

Two-element Model Analysis of the Viscoelastic Behavior of Liquid Food Materials by Means of the Non-rotational Concentric Cylinder Method

Kanichi SUZUKI[†], Kenichi IMAOKA, Somchai KEAWKAIKA and Yoshio HAGURA

Graduate School of Biosphere Science, Hiroshima University
1-4-4 Kagamiyama, Higashi-Hiroshima 739-8528, Japan

A new method of analyzing the viscoelastic behavior of liquid food materials is proposed. This new analysis method is based on a non-rotational concentric cylinder (NRCC) method that simultaneously measures the static viscoelastic properties (viscosity and elastic modulus) at a constant shear rate. Mayonnaise and ketchup with or without added water were used as the liquid samples. Two-element models, i.e. a series model comprised of a Newtonian viscous element and a Hookean elastic element (Maxwell model) and a parallel model comprised of these same two elements (Voigt model), were investigated in this study to elucidate the possibility of predicting the static viscoelastic behaviors of the samples, because the dynamic viscoelasticity of liquid food materials have been discussed mostly using these two-element models. Measurements using the NRCC method yielded mainly two types of force-time curves for the liquid samples. One type was a convex force-time curve, and the other was an almost linear curve. The analytical results showed that the former curve corresponds to the Maxwell-model materials, whereas the latter curve corresponds to the Voigt-model materials. The results indicate that the liquid materials with high dispersed-phase content (volumetric ratio $\phi > 0.75$) showed Voigt-model-like behavior, while lower-concentration liquids showed Maxwell-model-like behavior.

Key words: liquid material, viscosity, elastic modulus, NRCC method, two-element model

1. Introduction

Many methods have been proposed for measuring the viscosity or flow behavior of liquid materials [1-3]. Usually, the rheological properties of non-Newtonian liquids are expressed using apparent viscosity or flow parameters, i.e. the yield stress, flow behavior index and consistency factor. On the other hand, it has been known that many non-Newtonian liquid foods show viscoelastic behavior. Thus, viscoelasticity and viscosity are both recognized to be two of the essential physical properties of liquid materials, including liquid foods, in the control of quality and processing conditions. But only dynamic viscoelastic measuring methods have been applied to liquid materials because of their flow properties, even though the viscoelastic properties of solid materials can be evaluated by both static and dynamic methods.

Dynamic viscoelastic properties are quite sophisticated physical parameters, because they depend on the static viscoelastic properties (viscosity and static modulus of elasticity) of materials and on the measuring conditions. Usually, two-element models, i.e. the series model comprised of a Newtonian viscous element and a Hookean elastic element (Maxwell model) and the parallel model comprised of these same two elements (Voigt model), are applied to elucidate the dependence of the dynamic (or complex) viscoelastic properties on the viscosity, static elastic modulus and frequency. Therefore, it is necessary to measure the static modulus of elasticity of liquid materials to clarify the dynamic rheological properties in terms of the static rheological properties and the frequency. To investigate analytically the interrelationship between the dynamic and static viscoelastic properties, it is also important to divide the rheological behavior of liquid materials into two categories: Maxwell-model-like behavior and Voigt-model-like behavior.

Recently, a new method of measuring the viscosity and static elastic modulus of liquid materials was developed [4, 5]. The method, called the "non-rotational concentric cylinder" (NRCC) method, can measure simultaneously the static viscoelastic properties (viscosity and shear modulus of elasticity) of liquid materials within a few seconds (including the computer calculations), during a very short

movement (0.1~0.2 mm) of the cup or cylinder (plunger) along a given axis at a constant speed. The time–force curve at the beginning of the cup or plunger movement which sets the sample into flowing motion is very important for analyzing the viscoelastic properties of liquid materials, because their relaxation time is commonly very short [3]. Also, most of their apparent behavior after the relaxation time has elapsed resembles that of viscous fluids with no elasticity.

From a large number of measurement results, we found that most of the time–force curves obtained by the NRCC method can be classified into two types, as shown in Fig. 1(a) and 1(b). In one type, the force, F, increases convexly during a very short time period after the start of the cup movement, following a sudden increase in the measured force to F_0 at time $t \doteqdot 0$ (Fig. 1(a)). In the other type, the curve is almost linear after the force reaches F_0 followed by a curved line (Fig. 1(b)). These typical measured results are given in the experimental & results section. The value of F_0 is a function of the measuring conditions, the geometric constant of the apparatus and the viscosity of the sample, as explained in the next section.

The objective of this study was to investigate the reason why two types of time–force curves are obtained by the NRCC method, on the supposition that each type of time–force curve can reflect the viscoelastic behavior of the sample. Two-element models were adopted to analyze the viscoelastic properties of liquid materials, because the dynamic viscoelasticity is usually found by means of two-element models.
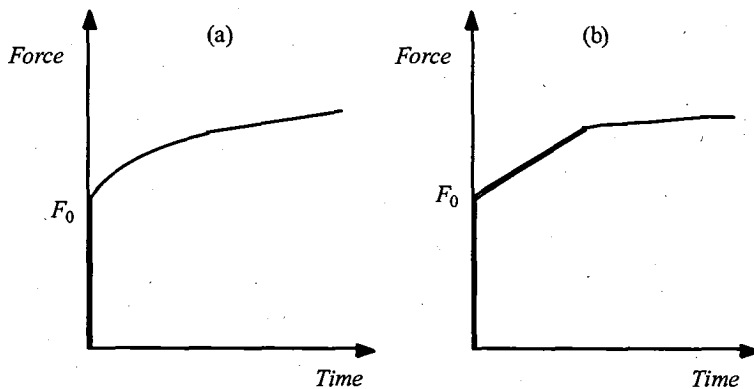
2. Theory of Viscosity and Elastic Modulus Evaluation

Figure 2 shows the theoretical situation of the NRCC method. A plunger (radius: R_i) is dipped initially at a distance, L_0, in the sample liquid which is in a cup (radius: R_o). The initial distance between the plunger's bottom and the cup bottom is L_b. From this initial spatial relationship, the cup is moved upward or the plunger is moved downward for a short distance, ΔL, at a constant speed, V_p. Thus, the movement duration of the cup is $t = \Delta L/V_p$. During this time period, the immersion distance of the plunger in the sample liquid increases from L_0 to L due to the upward flow of the sample caused by the cup movement, as follows:

$$L = L_0 + \{V_p t/(1-\kappa^2)\} \quad (\kappa = R_i/R_o) \quad (1)$$

This method analyzes the change in the force acting on the plunger during the plunger movement. If the sample is a viscous liquid with no elastic property, the total force, F_v, acting on the plunger is the sum of the forces F_s acting on the side wall of the plunger and F_p acting on the bottom area, expressed as follows [4, 7] (see Appendix):

$$F_v = -2\pi\mu V_p \alpha [L_0 + \{V_p t/(1-\kappa^2)\}] \quad (2)$$

where α is a geometric constant of the apparatus defined as follows:

$$\alpha = (1+\kappa^2)/\{(1+\kappa^2)\ln\kappa + (1-\kappa^2)\} \quad (3)$$

The value of α depends only on κ, and the absolute value

Fig. 1   Two types of force–time curves obtained by the NRCC method during a very short time period after the start of the measurement.
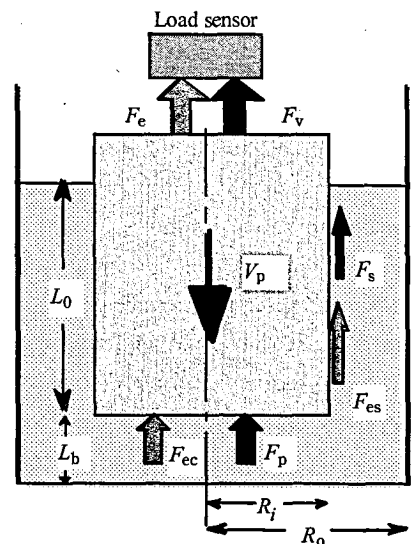

Fig. 2   Schematic explanation for evaluating the viscosity and viscoelasticity of liquid materials by means of a non-rotational concentric cylinder (NRCC) system.

of α increases with increasing κ. The value of F_v changes with time, as shown in Fig. 3(a). Thus, if it is possible to measure the force just at the starting time of the plunger movement ($t \fallingdotseq 0$), the force $F_v = F_0$ is expressed as follows:

$$F_0 = -2\pi \mu V_p \alpha L_0 \qquad (4)$$

The viscosity of the liquid material can be evaluated from Eq. (4) as well as from Eq. (2).

If it is possible to assume that the sample is a perfect elastic body with Young's modulus E ($E=3G$, where G is the shear modulus of elasticity), the total force acting on the plunger, F_e, will be the sum of the shear force on the side wall, F_{es}, and the compressible force on the bottom surface, F_{ec}. Then, the total force is derived as follows [4] (see Appendix):

$$F_e = \{3\pi (\kappa R_0)^2 V_p t G/L_b\}$$
$$-[2\pi L_0 V_p t G/\{(1-\kappa^2)\ln \kappa\}] \qquad (5)$$

Thus, the value of F_e for elastic materials is proportional to the time, as shown in Fig. 3(b).

When the sample is a viscoelastic liquid, stress relaxation affects the force acting on the plunger, as shown in Fig. 3(c), so that it is impossible to simply combine the F_v and F_e to evaluate the viscoelastic properties of the sample. But it is considered that the force at the start of the plunger movement (theoretically, $t \rightarrow 0$) consists of the forces due to viscosity and elasticity, without stress relaxation. Thus, the derivative of the force with time, i.e. the gradient of the force curve, at $t=0$, was derived from Eqs. (2) and (5), and the tangent, F_t, of the force at $t \rightarrow 0$ was obtained as follows:

$$F_t = F_0 - 2\pi\mu V_p^2 \alpha t/(1-\kappa^2) + \{3\pi (\kappa R_0)^2 V_p t G/L_b\}$$
$$-[2\pi L_0 V_p t G/\{(1-\kappa^2)\ln \kappa\}] \qquad (6)$$

When the material is a viscous liquid with no elastic property ($G=0$), Eq. (6) is reduced to Eq. (2).

The viscosity and shear modulus of the sample were evaluated as follows: 1) the tangent at $t=0$ of the measured force values acting on the plunger was estimated, 2) the viscosity (or apparent viscosity), μ, from the intercept, F_0, of the tangent was calculated using Eq. (4), and 3) the shear modulus, G, was evaluated from the F_t value at any time point by substituting the value of μ into Eq. (6) (Fig. 3).

3. Materials and Methods

3.1 Materials

Two kinds of ketchup (KA, KB) and two kinds of mayonnaise (MC, MD) from different producers purchased from a local market were used as the liquid food samples. The initial water content of each liquid food measured by the drying method were as follows: MA=17.5 wt%, MB= 20.0 wt%, KA=72.6 wt%, and KB=73.8 wt%. The water contents (wt%) of the mayonnaise samples were then adjusted to 20, 22, 24, 26, 28, 30, 32%, and of the ketchup to 74, 76 and 78%, by adding water.

3.2 Methods

To evaluate the viscosity and shear modulus of the samples, a rheometer (CR-200, Sun Scientific Co., Japan) was used. The cup diameter was 29.2 mm; the plunger diameter for the mayonnaise samples was 25.1 mm ($\kappa=0.860$) and for the ketchup samples 27.1 mm ($\kappa=0.928$). Both the cup with a jacket for temperature control and the plunger were made of acrylic resin. The initial immersion distance of the plunger in the sample, L_0, was 60 mm, and the upward cup speed, V_p, was 0.333 mm/s (20 mm/min).
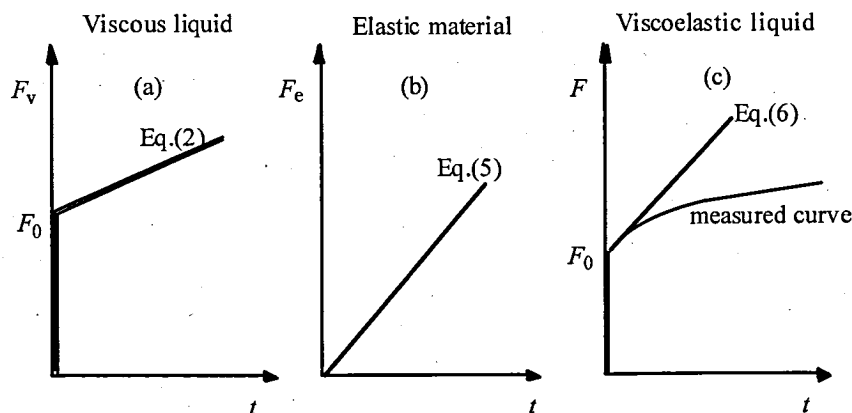

Fig. 3 Force–time curves for a viscous liquid (a), an elastic material (b) and a viscoelastic liquid (c) estimated from the theoretical equations (2), (4), (5) and (6).

All measurements were carried out at 25℃. The accuracy of the viscosity measurement was confirmed by using glycerol and sugar solutions of known viscosity [6]. Average values of the viscosity and shear modulus of elasticity were obtained from 4~6 measurements for each sample. Both the mayonnaise and the ketchup samples showed non-Newtonian flow characteristics. This means that the viscosity and other flow parameters depended on the measurement conditions, such as the shear rate and shear stress. The shear rate at the plunger wall in the present measurement conditions was calculated using the following equation [4, 7]:

$$(d\gamma/dt)_{Ri} = -(1-\kappa^2) \, V_p \, \alpha/\{(1+\kappa^2)R_i\} \qquad (7)$$

In this study, the shear rate for the mayonnaise was 3.51 s^{-1}, and 13.9 s^{-1} for the ketchup.

4. Results and Discussion

4.1 Experimental results

The force–time curves of the ketchup and mayonnaise samples after smoothing in the NRCC measurements are shown in Fig. 4(a) and 4(b). It is obvious from the figure that all of the ketchup samples and mayonnaise samples whose the water contents were higher than 25 wt% had convex force–time curves. However the mayonnaise samples with a water content lower than 25 wt% showed almost linear force–time curves for a very brief time period just after the start of the cup movement.

Figure 5 shows the experimental results for the viscosity and shear modulus of the mayonnaise and ketchup samples evaluated by the NRCC method. The viscosity of both samples decreased almost linearly with the increase in the

moisture content, although the values were somewhat different depending on the producer. The ketchup samples, which had a comparatively high water content, showed a linear viscosity curve for each sample within the water content range (Fig. 5(a)). However, the viscosity curve of mayonnaise bent at a water content of about 25 wt%, and two linear curves were obtained, as shown in Fig. 5(c). The shear modulus of elasticity of the samples decreased more steeply against the water content than the viscosity, and a semi-logarithmic relationship between the elastic modulus and the water content was obtained (Fig. 5(b) and 5(d)). Similarly to the viscosity curves, the elastic modulus curves of the mayonnaise samples bent at a moisture content of about 25 wt%, and two linear curves resulted, although the shear modulus of the ketchup samples was an almost linear curve for each kind of ketchup. These results indicate that the viscoelastic behavior of the samples might change at a moisture content of about 25% or a dispersed-phase content of 75%. Thus the reasons why two types of the force–time curve are obtained by the NRCC method were analyzed as follows. The reason why the viscosity curves and the elastic modulus curves of the mayonnaise samples bent at a moisture content of about 25 wt% was also discussed.

4.2 Analysis of viscoelastic behavior using the two two-element models

The dynamic viscoelasticity or viscoelastic behavior is usually discussed by means of two-element models. Therefore two-element models were adopted to analyze the static viscoelastic properties of liquid materials in this study.
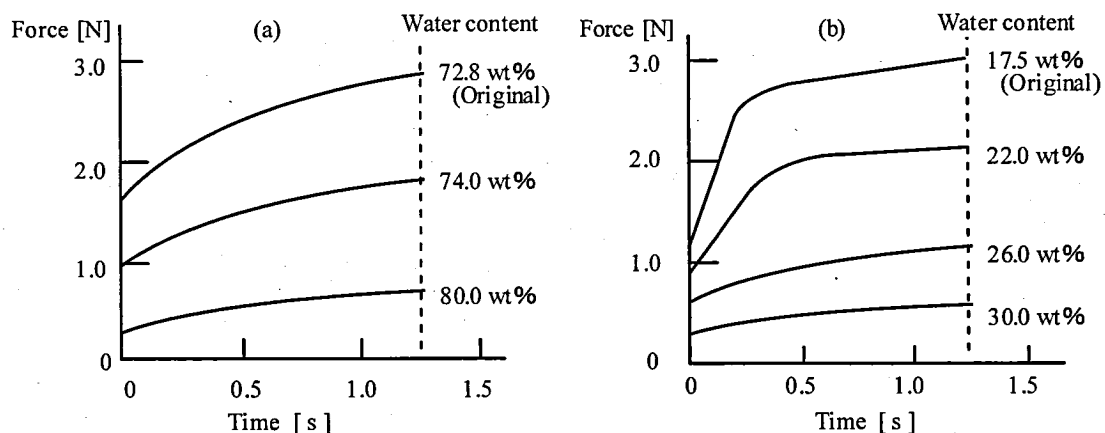

Fig. 4 Force–time curves for ketchup (a) and mayonnaise (b) samples with or without added water, as measured by the NRCC method.
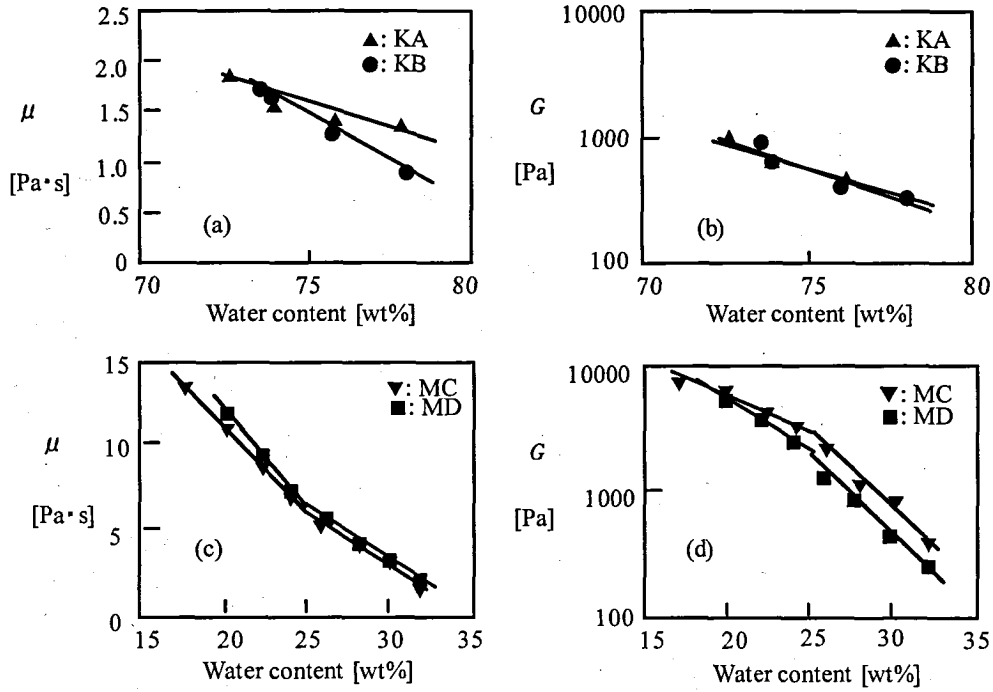
Fig. 5 Water content dependence of the viscosity and shear modulus of elasticity for ketchup ((a), (b)) and mayonnaise ((c), (d)) samples with or without added water, as measured by the NRCC method.

μ[Pa·s]: Viscosity, G [Pa]: Shear modulus of elasticity, KA, KB: Ketchup samples from different producers A and B, MC, MD: Mayonnaise samples from different producers C and D

4.2.1 Series (Maxwell) model

The basic equation of the Maxwell model is as follows:

$$\mathrm{d}\gamma/\mathrm{d}t = \mathrm{d}\gamma_v/\mathrm{d}t + \mathrm{d}\gamma_e/\mathrm{d}t = K \qquad (8)$$

where γ is the shear strain, and the subscripts v and e indicate the viscous element and the elastic element, respectively. The constant shear rate in the NRCC method, K, is assumed to be proportional to V_p, i.e. $K = \beta V_p$. From the basic theory of the dash pot and the spring, the shear stress of the series model, f, is derived as follows:

$$f = K\mu\{1 - \exp(-Gt/\mu)\} \qquad (9)$$

Eq. (8) shows that the force f increases convexly as a result of stress relaxation. But the NRCC method measures a finite value of the force F_0 at $t \to 0$, and the base line of the force increases in proportion to the time, because the immersion distance of the plunger in the sample increases with time, as expressed in Eq. (1). Thus, the increase of the base line of the shear stress, f_b, was approximated by considering Eq. (2), as follows:

$$f_b = \delta K\mu(L_0 + \phi Kt) \qquad (10)$$

where δ is a constant which corresponds to $-2\pi a/\beta$, and ϕ is a constant which corresponds to $1/\{\beta(1-\kappa^2)\}$.

Then, the change in shear stress in the NRCC method was corrected, as the following equation shows:

$$f = \delta K\mu(L_0 + \phi Kt) + K\mu\{1 - \exp(-Gt/\mu)\} \qquad (11)$$

Eq. (11) indicates that the shear stress or shear force changes convexly with increasing time, as shown in Fig. 1(a).

4.2.2 Parallel (Voigt) model

The basic equation of the Voigt model is as follows:

$$f_b = f_v + f_e \qquad (12)$$

$$\mathrm{d}\gamma_v/\mathrm{d}t = \mathrm{d}\gamma_e/\mathrm{d}t = K \qquad (13)$$

From the basic theory of the dash pot and the spring, the shear stress of the parallel model, f, is derived as follows after correcting the base shear stress as in Eq. (10):

$$f = \delta K\mu(L_0 + \phi Kt) + K\mu + KGt \qquad (14)$$

Eq. (14) indicates that the shear stress or shear force changes linearly with increasing time, as shown in Fig. 1(b).

4.3 Classification of viscoelastic behavior and discussion

Though Eqs. (11) and (14) show merely that the changing shape of the force–time curves corresponds to the series model and the parallel model, respectively, the model analysis indicates that the viscoelastic behavior of liquid materials which have a convex force–time curve (Fig. 1(a)) can be classified into Maxwell-model-like behavior, and that the linear force–time curve (Fig. 1(b)) corresponds to Voigt-model-like behavior. The theoretical derivation of the tangent of the force–time curves in the NRCC method at $t \rightarrow 0$ gave Eq. (6) for all liquid materials. Therefore, the gradients of the tangents for both two-element models at $t \rightarrow 0$ have to be equal to enable the evaluation of the elastic modulus from Eq. (6). The results from Eq. (11) and (14) gave the same gradient of the tangent f_t at $t \rightarrow 0$, expressed as follows:

$$f_t = \delta \phi K^2 \mu + KG \qquad (15)$$

Thus, the shear modulus of elasticity can be evaluated from Eq. (6) for both viscoelastic behaviors.

It is obvious from the Fig. 4 that all of the ketchup samples and mayonnaise samples whose the water contents were higher than 25 wt% had convex force–time curves; this means that the samples behaved as Maxwell-model-like viscoelastic materials. However the mayonnaise samples with a water content lower than 25 wt% showed almost linear force–time curves for a very brief time period just after the start of the cup movement. This suggests that mayonnaise, or the mayonnaise sample with a dispersed-phase content higher than 75%, showed Voigt-model-like viscoelastic behavior.

The density of most liquid foods is near to that of water, and their water content expressed in wt% is roughly the volumetric concentration of water. This means that the volumetric concentration of water in liquid foods with a water content of 25 wt% of is very roughly 25%, or that the liquid food in question has a water volumetric ratio of 0.25. The volumetric concentration of the dispersed phase in the most packed state for mono-dispersed particle systems is well known to be 74.05%. Taken together, all of the results mentioned above lead to the conclusion that the viscoelastic behavior of liquid food materials can be divided into two types: Maxwell-model-like behavior and Voigt-model-like behavior. The critical line of division is the volumetric concentration of the dispersed phase in the most packed state. Liquid foods with a lower dispersed-phase concentration than that in the most packed state may behave as Maxwell-model-like viscoelastic materials. The overall movement of liquid materials with a higher dispersed-phase concentration than that in the most packed state might be restricted by the cross-linked structure of the dispersed phase, and this might cause Voigt-model-like viscoelastic behavior. This conclusion has to be confirmed more precisely by comparing the two types of viscoelastic behavior using the dynamic measurement method.

6. Conclusions

The meaning of two types of time–force curves obtained by the non-rotational concentric cylinder (NRCC) method was investigated on the supposition that each type of time–force curve can reflect the viscoelastic behavior of the sample. Two-element models, i.e. a series model comprised of a Newtonian viscous element and a Hookean elastic element (Maxwell model) and a parallel model comprised of these same two elements (Voigt model), were adopted to elucidate the possibility of predicting the static viscoelastic properties of liquid food materials, because the dynamic viscoelasticity of liquid materials have been discussed mostly using these two-element models. Mayonnaise and ketchup with or without added water were used as the liquid samples.

One type of the force–time curve was a convex force–time curve during a very short time period after the start of the cup movement, following a sudden increase in the measured force, and the other was an almost linear curve. The mayonnaise samples with the water content larger than 25% and all ketchup samles showed the convex force–time curves. On the other hand, the mayonnaise samples with the water content less than 25% showed the linear force–time curves. The analytical results showed that the former curve corresponds to the Maxwell-model materials, whereas the latter curve corresponds to the Voigt-model materials. The results indicate that the liquid materials with high dispersed-phase content (volumetric ratio $\phi > 0.75$) showed Voigt-model-like behavior, while lower-concentration liquids showed Maxwell-model-like behavior.

(Appendix)

surface tension

1) Derivation of Eq. (2)

The theory of the proposed method is based on the theory for flow through an annulus [7]. The basic equation and boundary conditions are as follows (symbols, see

Nomenclature):

$$d\,(r\,\tau_r)/dr = r\Delta P/L \qquad (A-1)$$

B.C. $u_r = 0$ at $r = R_0$ $\qquad (A-2)$

$\qquad\qquad u_r = V_p$ at $r = R_i$,

The total force, F_v, is the sum of the forces F_s and F_p,

$$F_v = F_s + F_p$$
$$= 2\pi R_i L \tau_i - \pi R_i^2 \Delta P \qquad (A-3)$$

Newton's law of viscosity is as

$$-(d\,u_r/dr) = \tau_r/\mu \qquad (A-4)$$

Both of u_r and τ_r can be derived theoretically from equations (A-1) and (A-2) combined with equation (A-4) as follows:

$$u_r = \{V_p \ln(r/R_0)/\ln \kappa\} + [R_0^2 \Delta P\{1 - (r/R_0)^2$$
$$+ (\kappa^2 - 1) \ln(r/R_0)/\ln \kappa\}/(4\mu L)] \qquad (A-5)$$
$$\tau_r = \{r\Delta P/(2L)\}$$
$$- [\mu V_p + \{R_0^2 \Delta P(\kappa^2 - 1)/4L\}]/(r \ln \kappa) \qquad (A-6)$$

The shear stress at the plunger wall, τ_i, is obtained by substituting $R_i = \kappa R_0$ into r,

$$\tau_i = \{\kappa R_0 \Delta P/(2L)\}$$
$$- [\mu V_p + \{R_0^2 \Delta P(\kappa^2 - 1)/4L\}]/(\kappa R_0 \ln \kappa) \qquad (A-7)$$

The average upward velocity of sample, u_{av}, is calculated from the following equation,

$$u_{av} = [1/\{\pi R_0^2 (1 - \kappa^2)\}] \int_{R_i}^{R_0} 2\pi r u_r\, dr \qquad (A-8)$$

On the other hand, the relationship between u_{av} and V_p is expressed as

$$u_{av} = V_p \kappa^2/(\kappa^2 - 1) \qquad (A-9)$$

Then ΔP can be derived from equations (A-5), (A-8) and (A-9) as follows:

$$\Delta P = 4\mu L V_p/[R_0^2 \{(1 + \kappa^2) \ln \kappa + (1 - \kappa^2)\}] \qquad (A-10)$$

Thus the resulted equation for F_v is simplified as follows:

$$F_v = -2\pi\mu V_p \alpha L$$
$$= -2\pi\mu V_p \alpha [L_0 + \{V_p t/(1 - \kappa^2)\}] \qquad (A-11)$$

where, α is a geometric constant expressed as

$$\alpha = (1 + \kappa^2)/\{(1 + \kappa^2) \ln \kappa + (1 - \kappa^2)\} \qquad (A-12)$$

2) Derivation of Eq. (5)

The force acting on the plunger wall for a perfect elastic body with Young's modulus E ($E = 3G$) is expressed as

$$F_{es} = 2\pi L_0 \tau_r = 2\pi L_0 G\, (dZ/dr) \qquad (A-13)$$

where Z is a relative shear distance for axial direction between the plunger and sample. F_{es} is derived by integrating r for R_i to R_0, and Z for 0 to Z, and combining with $Z = V_p t/(1 - \kappa^2)$ as

$$F_{es} = -[2\pi L_0 V_p t G/\{(1 - \kappa^2) \ln \kappa\}] \qquad (A-14)$$

The compressible force on the bottom area of plunger, F_{ec}, is expressed as following equation by postulating $E = 3G$:

$$F_{ec} = 3\pi (\kappa R_0)^2 V_p t G/L_b. \qquad (A-15)$$

Summation of F_{ec} and F_{es} gives Eq.(5).

Nomenclature

E : Young's modulus, Pa

F_p : viscous force acting on the bottom area of plunger, N

F_s : viscous shear force acting on the side wall of plunger, N

F_v : total viscous force acting on the plunger, N

F_{es} : elastic shear force acting on the side wall of plunger, N

F_{ec} : compressive force acting on the bottom area of plunger, N

F_e : total elastic force acting on the plunger, N

G : Shear modulus, Pa

K : constant shear rate in NRCC method, 1/s

L : dipped distance of plunger in sample liquid during measurement, m

L_b : distance between plunger's bottom and cup bottom, m

L_0 : initial dipped distance of plunger in sample liquid, m

ΔL : moved distance of plunger, m

ΔP : pressure drop for distance L, Pa

R_i : radius of plunger ($= \kappa R_0$), m

R_0 : radius of cup, m

t : moving time of plunger ($= \Delta L/V_p$), s

u_r : flow rate at distance r from the center of coaxial cylinder system, m/s

V_p : moving speed of plunger, m/s

α : geometric constant, -

β : a proportional constant ($= K/V_p$), 1/m

δ : a constant corresponds to $-2\pi\,\alpha/\beta$, 1/m

τ_i : shear stress at plunger side wall ($r = R_i$), Pa

τ_r : shear stress at distance r from the center of coaxial cylinder system, Pa

κ : ratio of R_i to R_0 ($= R_i/R_0$), -

μ : viscosity, Pa·s

ϕ : a constant corresponds to $1/\{\beta(1 - \kappa^2)\}$, m

References

[1] J. Ferguson, Z. Kemblowski; "Applied Fluid Rheology", Essex, England, Elsevier Science Publishers LTD, 1991.

[2] J. F. Steffe; "Rheological Methods in Food Process Engineering", Michigan, USA, Freeman Press, 1992.

[3] M. A. Rao, J. F. Steffe; "Viscoelastic Properties of Foods". Essex, England, Elsevier Science Publishers LTD, 1992.

[4] K. Suzuki; A novel method for evaluating viscosity and viscoelasticity of liquid foods by a non-rotational concentric cylinder setup, Nippon Shokuhin Kagaku Kogaku Kaishi, 46, 657–663 (1999).

[5] K. Suzuki, Y. Hagura; Proceedings of 9th International Conference on Engineering and Food, 468–473 (2004).

[6] N. A. Lange; "Handbook of Chemistry", 10th ed. McGraw-Hill, New York, 1967, p. 1154, p. 1182, p. 1681,

[7] R. B. Bird, W. E. Stewart, E. N. Lightfoot; "Transport Phenomena", John Wiley & Sons, Inc., New York, 1960, pp.51–54.

◇◇◇ 和文要約 ◇◇◇

非回転二重円筒法を用いる液状食品の粘弾性挙動の
2要素モデル解析

鈴木寛一†, 今岡賢一, ソムチャイ キョウカイカ, 羽倉義雄

広島大学大学院生物圏科学研究科

　液体の機械的物性は，おもに粘度または流動挙動で論議されているが，非ニュートン流動性を示す液状食品の多くは，粘弾性体としても挙動する．定形性をもたない液状材料の粘弾性は，これまでは動的測定法で得られる複素弾性率や損失正切（tan δ）などの動的粘弾性パラメータで論議されてきたが，動的粘弾性は周波数などの測定条件によって大きく影響を受けるため，得られる動的粘弾性パラメータの物理的意味が複雑または曖昧となる問題がある．そのため，一般的には限定された線形領域の測定値で粘弾性を評価しているが，液状食品の製造工程管理や品質設計を行うために必要な評価条件にそぐわないことも多い．

　一方，最近著者らが開発した非回転二重円筒型レオメータでは，液状材料の粘度およびずり弾性率（静的粘弾性）を任意のずり速度で同時に直接測定することが可能である．この方法では，カップ（外筒）が定速で軸方向に微小距離（0.1〜0.2 mm）移動する間に試料がプランジャ（内筒）に作用する総合力 F の時間変化曲線から静的粘弾性を測定するが，測定開始直後の F の時間変化曲線が2種類に大別されることを見い出した．1つは，F の瞬間的増加に続いて上に凸の曲線となって F が増加するもの（曲線 I）であり，他の1つは，作用力の瞬間的増加後は，時間に対して直線的に F が増加するもの（曲線 II）である．

　そこで本研究では，非回転二重円筒法で測定される F の変化曲線の形の違いは，液状材料の粘弾性の発現機構の違いに起因するものと推定して，2つの2要素粘弾性モデル，すなわち，粘性要素と弾性要素の直列モデル（Maxwell モデル）および同要素の並列モデル（Voigt モデル）を用いて液状食品の粘弾性挙動の解析を試みた．2要素モデルは，動的粘弾性の挙動を説明する際によく用いられるものであり，非回転二重円筒法で測定される静的粘弾性と動的粘弾性の対応関係を検討する場合にも都合が良い．ここでは，2種類の F の変化曲線と2要素モデルとの対応性および液状食品の性状と2要素モデル適合性を検討した．

　試料には，製造者が異なる2種類のケチャップ（KA，KB）とマヨネーズ（MC, MD）を用いた．マヨネーズの分散相体積分率 ϕ は 0.75 以上である．各試料の初期水分は，KA＝72.6 wt%，KB＝73.8 wt%，MC＝17.5 wt% および MD＝20.0 wt% であり，これらの試料に加水して，水分を 20 〜 32% の範囲で7段階に調整したマヨネーズ試料と 74%，76%，78% に調製したケチャップも用いた．

　測定には，㈱サン科学製のレオメータ（CR-200）を用い，カップ直径は 29.2 mm とし，マヨネーズ試料の測定には直径 25.1 mm のプランジャ，ケチャップ試料には直径 27.1 mm のプランジャを用いた．プランジャの初期液深は 60 mm，カップの移動速度 0.333 mm/s とした．すべての測定は 25℃で行い，粘度と弾性率の値は，1条件で 4 〜 6 回の測定での平均値とした．

　ずり速度一定条件での2要素モデルの解析結果は，曲線 I と曲線 II は，それぞれ直列モデル（Maxwell モデル）と並列モデル（Voigt モデル）に対応することを示した．実験結果は，粘度とずり弾性率はマヨネーズ試料とケチャップ試料のどちらも水分の減少とともに減少することを示した．しかし，マヨネーズ試料は，水分が約 25% 付近で水分に対する減少傾向が変化した．また，水分が 25% 以上のマヨネーズ試料とケチャップ試料（水分は，約 73% 以上）は，プランジャへの作用力 F の瞬間的な増加に続いて上に凸の増加曲線となる曲線 I を示したが，25% 以下のマヨネーズ試料は，曲線 II となった．25% 以下のマヨネーズ試料の分散相体積分率 ϕ は，球状粒子集合体の細密充填濃度（ϕ＝0.7405）以上となっているものと推定される．したがって，分散相または分散固形物の体積分率が細密充填濃度を超える場合（ϕ＞0.75）には，分散相と連続相の変形または移動が相互に干渉しあう挙動，すなわち，粘性要素と弾性要素の並列モデル（Voigt モデル）的な挙動を示すものと考えられる．これに対して，ϕ＜0.75 の液状食品では，分散相の変形または移動に対する連続相の制限が少なくなるか相互が自由に変形できるため，直列モデル（Maxwell モデル）的な挙動となるものと考えられる．まとめとして，液状食品の粘弾性挙動は，2つの2要素モデルのどちらかで近似でき，分散相の体積分率が 0.75 より高い液状食品は並列モデル的な粘弾性挙動，0.75 より低くなると直列モデル的な粘弾性挙動を示すものと推察した．