Experimental Comparison of Static Rheological Properties of Non-Newtonian Food Fluids with Dynamic Viscoelasticity

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Correlations between static rheological properties (G: shear modulus, μ: viscosity, μapp: apparent viscosity) of four food fluids (thickening agent solution, yoghurt, tomato puree and mayonnaise) measured employing a newly developed non-rotational concentric cylinder (NRCC) method and dynamic viscoelastic properties ([G*]: complex modulus, η*: complex viscosity, tanδ: loss tangent, μapp: apparent viscosity) measured by a conventional apparatus (HAAKE MARS III) were studied. μapp and μapph for each sample fluid agreed well. μapp/μapph obeying the Cox–Merz rule was obtained for the thickening agent solution, μapp < η* for mayonnaise and μapp < η* for tomato puree and yoghurt. μ was lower than μapp or μapph for all samples, and reached μapp with an increasing shear rate. Plotting G and [G*] against the shear rate and angular velocity respectively in the same figure revealed G < [G*] for tomato puree, G > [G*] for yoghurt and G > [G*] for mayonnaise and thickening agent solution. The applicability of two-element models in analyzing the viscoelastic behavior of sample fluids was investigated by comparing two characteristic times τK = 1/(ωtanδ) and τs = tanδ/ω, corresponding to Maxwell and Kelvin–Voigt models respectively and evaluated from measurements of tanδ, with τa = μ/G and τapp = μapp/Gapp calculated from rheological properties measured by the NRCC method. Here Gapp (= G(μ/μapp)) is an apparent shear modulus newly defined to evaluate the shear-rate dependency of the elasticity of Non-Newtonian fluids. Results show τs agreed well with τapp, suggesting the possibility of applying the Kelvin–Voigt model to the viscoelastic behavior of sample fluids.

Key Words: Non-Newtonian / Food fluid / Viscoelasticity / Non-rotational concentric cylinder method / Apparent shear modulus

1. INTRODUCTION

Dilute solutions and suspensions in fluid foods such as fruit juice, milk and vegetable oil behave as Newtonian fluids1). However, most fluid foods are Non-Newtonian fluids that have complicated flow properties and commonly behave as viscoelastic materials2). The flow properties of Non-Newtonian fluids are usually studied by examining the shear-rate dependency of apparent viscosity. Meanwhile, the viscoelastic property of Non-Newtonian fluids has been analyzed conventionally employing a dynamic testing method, because a static method of testing viscoelasticity is difficult to apply to fluids owing to their lack of a fixed form. However, the relationship between the flow properties and dynamic viscoelasticity of Non-Newtonian fluids has not yet been clarified. One reason is that the dynamic viscoelastic properties obtained from experimental results in a linear region with small deformation are basically useful for only a very low shear rate, whereas the flow properties are usually measured for a high shear rate with large deformation.

The dynamic viscoelastic behaviors of materials have been explained theoretically using two two-element models. One is the series model (Maxwell model) of the viscosity and shear modulus while the other is the parallel model (Kelvin–Voigt model) of the viscosity and shear modulus2, 3). For Non-Newtonian fluids, however, it is difficult to verify the estimations of viscosity and shear modulus from dynamic viscoelastic properties. Furthermore, it is difficult to estimate the dynamic viscoelastic behavior from flow properties measured employing a static experimental method. The reason is that there is almost no information on the viscosity or shear modulus applicable to the analysis of the dynamic viscoelastic properties of fluids, because no reliable experimental apparatus with which to measure the viscosity (not apparent viscosity) or the shear modulus for fluid materials has yet been developed. The validity of estimations of the viscosity and shear modulus for Non-Newtonian fluids from dynamic viscoelastic measurements made in experiments has therefore not been verified, even if it would be shown that either of
the two-element models for dynamic viscoelasticity is adaptable to the Non-Newtonian fluid studied. Against the background of the rheological study described above, a new experimental method of measuring the static rheological properties of fluid materials, including Non-Newtonian fluids, was proposed recently. The method, called the non-rotational concentric cylinder (NRCC) method, measures static viscoelastic properties (i.e., viscosity, shear modulus and apparent viscosity) of a sample fluid simultaneously during a very short movement of a plunger or cylinder (cup) along the vertical axis at constant speed. The time needed for one measurement including the computer calculation is several seconds. Few methods of measuring the rheological properties of fluids from the change in shear stress on a cylindrical plunger surface during fluid flow through a concentric annular space have been proposed. The penetropviscometer evaluates relative viscosity by comparing the time–shear stress curve of a fluid sample with that of a standard liquid of known viscosity. The back extrusion method measures the viscosity of Newtonian fluids and the apparent viscosity of Non-Newtonian fluids from the change in shear stress on a plunger surface by applying the theory for fluid flow through an annular channel. These methods evaluate viscosity or apparent viscosity by measuring the increase in shear stress on a plunger surface when a fluid is made to flow upward through an annular space by forcing down a plunger a comparatively long distance into the fluid in a cylindrical tube. However, none of these methods estimate the shear modulus of Non-Newtonian fluids. Meanwhile, the NRCC method measures static rheological properties, including the viscosity, shear modulus and apparent viscosity of a sample fluid by analyzing theoretically the response of shear stress on the surface of a plunger when it moves over a short distance at constant speed. For Newtonian fluids, the shear modulus is measured as zero. The plunger is immersed in a sample fluid in a cylinder or cup to the prefixed depth in advance of measurement. The plunger (or cup) usually moves a short distance of about 0.5–1.5 mm that depends on the fluidity of the sample and the speed of the plunger. This distance through which the plunger moves is determined such that there are enough measurement points for analysis of the change in shear stress; the number of measurement points in unit time is inversely proportional to the plunger speed. The NRCC method is thus able to measure the rheological properties consecutively without large deformation of the sample fluid in contrast to other viscometers, such as the rotational viscometer or cone–plate apparatus. The method can also evaluate the shear-rate dependency of the rheological properties of Non-Newtonian fluids by varying the plunger (or cup) speed. Furthermore, it is expected that the method can be used to study the physical properties of complex-component fluids containing solid materials that established dynamic experimental apparatuses have difficulty in measuring. However, the validity or usefulness of measurements of the viscosity and shear modulus of Non-Newtonian fluids made using the NRCC method has not been verified, because no reliable data on the values of viscosity and shear modulus of Non-Newtonian fluids have been obtained for comparison.

The present study investigated the relationship between rheological properties including static viscoelastic values for four Non-Newtonian food fluids (i.e., a thickening agent solution, plain yoghurt, tomato puree and mayonnaise) measured employing the NRCC method and dynamic viscoelastic properties measured by a conventional dynamic experimental apparatus under the same shear-rate conditions. The dynamic viscoelastic properties measured were the complex shear modulus, complex viscosity, storage shear modulus, loss shear modulus and loss tangent. The shear-rate or angular velocity dependency of these values was compared with that of the viscosity, shear modulus and apparent viscosity of the sample fluids. The paper discusses two basic rheological components of the dynamic viscoelastic property (i.e., viscosity and shear modulus) and the applicability of two-element viscoelastic models to the food fluids studied as well as the meaning and usefulness of the viscosity and shear modulus measured with the NRCC method.

2. MATERIALS AND METHODS

2.1 Materials

Three food fluids and a thickening agent were purchased from a local market. The thickening agent (Thickness Yell, Wakodo, Japan) was used to make a Non-Newtonian solution of which the main ingredients were dextrin and polysaccharide thickener. The solution was prepared by dissolving the agent in water at 60 °C at a concentration of 2.5 g/100 g-water with gentle hand stirring using a spatula. Having dissolved adequately, the solution was kept standing at room temperature for 1 day prior to measurement to ensure the stability of rheological properties. Yoghurt (Meiji Bulgaria Yoghurt, Meiji Co., Ltd., Japan) was stored in a refrigerator at 2–3 °C for 1 day before measurement. Tomato puree (Kagome Co., Ltd., Japan) and mayonnaise (Kewpie Co., Japan) were used without treatments. In advance of the rheological experiments on samples, the accuracy of the viscosity measurement for the NRCC method was calibrated using deionized water.
(viscosity: 0.89 × 10⁻³ Pa·s) and six viscosity standard liquids (Brookfield Engineering Lab. Inc., USA) for which the viscosity ranged from 4.7 × 10⁻³ to 1.008 × 10⁻² Pa·s.

2.2 Measurements

Dynamic viscoelastic properties (i.e., complex shear modulus, $|G^*|$, storage shear modulus, $G'$, loss shear modulus, $G''$, complex viscosity, $|\eta^*|$, and loss tangent, tan$\delta$) and apparent viscosity, $\mu_{app}$, were measured using a HAAKE MARS III rheometer (Thermo Fisher Scientific Inc., Germany) with plate/plate geometry ($D = 20$ mm, gap of 0.5 mm). Measurements were conducted two or three times under the same conditions using a new sample for each measurement. The NRCC method (NRCC Visco-Pro, Sun Scientific Co., Ltd. Japan) was used with a CR-3000EX rheometer (Sun Scientific Co., Ltd. Japan) to measure static viscoelastic properties; i.e., viscosity, $\mu$, shear modulus, $G$, and apparent viscosity, $\mu_{app}$. Figure 1(a) is a schematic diagram of the apparatus for the NRCC method. The inner diameter of the outer cylinder (cup) was 50 mm. Three plungers having a diameter of 49 mm (ratio of the plunger diameter to cup diameter $\kappa = 0.98$), 45 mm ($\kappa = 0.90$) and 35 mm ($\kappa = 0.70$) were used in the calibration test of viscosity depending on the viscosity of water and the viscosity standard liquids. The plunger having a diameter of 35 mm was used for the rheological measurement of food fluids, because of the viscous nature of the samples. This meant that the gap between the cup and plunger was 7.5 mm. The initial immersion distance of the plunger in the sample fluids, $L_o$, was 49 mm, and the initial distance between the cup bottom and the plunger bottom, $L_w$, was 16.5 mm. The rheometer used in this study measured the shear stress on the plunger from the sample fluid in a cup while the cup on the stage moved upward a very short distance (instead of the plunger moving downward). The stage returned to the initial position automatically after each run of the measurement at a preset speed. The moving distance of the stage approximately ranged 0.5–1.5 mm according to the measuring speed or shear rate. Average values of rheological properties were obtained from seven measurements for each sample fluid. The values of angular velocity, $\omega$, for the dynamic viscoelastic measurement using the HAAKE MARS III were set in a nearly equal range of the shear rate, $d\gamma/dt$, for the NRCC method. All measurements were made at 25 °C.

3. THEORY AND CHARACTERISTICS OF THE NRCC METHOD

This section outlines the theory and measuring method of the NRCC method. A detailed explanation of the NRCC method was given in the literature[^4]. The plunger (with radius $R_i$) is dipped in advance of each measurement a distance $L_o$ in the sample fluid in a cup (with radius $R_o$) as shown in Fig. 1(b). The initial distance between the plunger bottom and the cup bottom is $L_o$. From this initial spatial arrangement, the plunger is moved downward or the cup is moved upward a short distance $\Delta L$ at constant speed $V_p$. During the period of cup movement, $t = \Delta L/V_p$, the immersion distance of the plunger in the sample fluid increases from $L_o$ to $L$ owing to the upward flow of the fluid due to the cup movement:

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

The NRCC method analyzes the change in the force acting on the plunger during the plunger movement over a short distance.

3.1 Newtonian fluid

The theory of the proposed method is based on the theory for fluid flow through an annulus[^12]. For a Newtonian fluid with no elastic property, the total force, $F_v$, acting on the plunger is the sum of the force $F_s$ acting on the side wall and the force $F_p$ acting on the bottom area:

$$F_v = F_s + F_p = 2\pi R_i L_o - \pi R_i^2 \Delta P.$$  

The basic equation and boundary conditions are (see the Nomenclature list for symbols)

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\[ \frac{d}{dr} \left( r \sigma_r \right) = r \Delta P / L. \quad (3) \]

\[ u_r = 0 \quad \text{at} \quad r = R_o, \quad u_r = V_p \quad \text{at} \quad r = R_i. \quad (4) \]

Newton’s law of viscosity is

\[ - (du_r / dr) = \sigma_r / \mu. \quad (5) \]

\[ u_r \] and \( \sigma_r \) can be derived theoretically from Eqs. (3) and (4) combined with Eq. (5):

\[ u_r = \left\{ V_p \ln(r/R_o) / \ln \kappa \right\} + \left[ R_o^2 \Delta P \{1 - (r/R_o)^2\} \right. \\
+ (\kappa^2 - 1) \ln(r/R_o) / (4\mu L) \right\}, \quad (6) \]

\[ \sigma_r = \{ r\Delta P/(2L) \} \\
- [\mu V_p + \{R_o^2 \Delta P(\kappa^2 - 1) / 4L\}] / (r \ln \kappa). \quad (7) \]

The shear stress at the plunger wall, \( \sigma_r \), is obtained by substituting \( R_i = \kappa R_o \) into \( r \):

\[ \sigma_r = \{ \kappa R_o \Delta P/(2L) \} \\
- [\mu V_p + \{R_o^2 \Delta P(\kappa^2 - 1) / 4L\}] / (\kappa R_o \ln \kappa). \quad (8) \]

The average upward flow rate of the sample, \( u_{av} \), is

\[ u_{av} = \frac{1}{\pi R^2} \int_{R_i}^{R_o} 2\pi r u_r dr. \quad (9) \]

The relationship between \( u_{av} \) and \( V_p \) is expressed as

\[ u_{av} = V_p \kappa^2 / (\kappa^2 - 1). \quad (10) \]

\( \Delta P \) can be derived from equations (6), (9) and (10):

\[ \Delta P = 4\mu LV_p \left( [R_o^2 \{1 + \kappa^2\} \ln \kappa + (1 - \kappa^2)] \right). \quad (11) \]

The resulting equation for \( F_v \) is thus simplified as

\[ F_v = -2\pi \mu V_p aL = -2\pi \mu V_p a[L_o + \{V_p t/(1 - \kappa^2)\}], \quad (12) \]

where \( \alpha \) is a geometric constant of the apparatus expressed as

\[ \alpha = (1 + \kappa^2) / (1 + \kappa^2) \ln \kappa + (1 - \kappa^2). \quad (13) \]

The value of \( \alpha \) depends only on \( \kappa \), and the absolute value of \( \alpha \) increases with increasing \( \kappa \). \( F_v \) changes with time as shown in Fig. 2(a). If it is possible to measure the force at the start of plunger movement (theoretically, \( t = 0 \)), the force \( F_v \) can be simplified to \( F_{vo} \), expressed as

\[ F_{vo} = -2\pi \mu V_p aL_o. \quad (14) \]

The viscosity of the Newtonian fluid can be evaluated from Eq. (14) as well as from Eq. (12). A minute difference in the change in the measured force acting on the plunger from the theoretical curve due to the effect of mechanical motion of the apparatus was corrected by NRCC Visco-Pro analysis software in the present study.

3.2 Elastic material

When the sample is a perfect elastic material with Young’s modulus \( E \) (\( E = 3G \), where \( G \) is the shear modulus), the force acting on the plunger wall is expressed as

\[ F_{es} = 2\pi L_o \sigma = 2\pi L_o G \frac{dZ}{dr}, \quad (15) \]

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

\[ F_{es} = 2\pi L_o \sigma = 2\pi L_o G \frac{dZ}{dr}, \quad (15) \]
The compressible force on the bottom area of the plunger, \( F_{oc} \), is expressed by postulating \( E = 3G \):

\[
F_{oc} = 3\pi(\kappa R)^3 V_p t G/L_0.
\]  

(17)

The total force acting on the plunger, \( F_o \), is thus the sum of \( F_{os} \) and \( F_{ec} \):

\[
F_o = KV_p G t,
\]  

(18)

where \( K \) is a constant that depends on the geometry of the apparatus, expressed as

\[
K = \left\{ \frac{3\pi(\kappa R)^3}{L_o} - 2\pi L_o/(1 - \kappa^2) \right\}. \]  

(19)

The force acting on the plunger in the case of an elastic material is proportional to time as shown in Fig. 2(b). The shear modulus, \( G \), can be obtained from the gradient, \( KV_p G \). The practical applicability of Eq. (19) has been confirmed using agar gels as an elastic model sample.

### 3.3 Non-Newtonian fluid

To estimate the viscosity and shear modulus of a Non-Newtonian or viscoelastic fluid, it is necessary to evaluate the force due to the viscous nature and the force due to the elastic nature of the fluid separately by dividing the total force acting on the plunger into these two forces. The measured force acting on the plunger for a Non-Newtonian fluid is commonly plotted as a curved line owing to the effect of stress relaxation, and reaches a nearly constant value in short time. By postulating that the total force is due to the viscous force only, the NRCC method estimates the apparent viscosity, \( \mu_{app} \), from the total force acting on the plunger at the arbitrary time, \( t_{eq} \), at which the gradient of the tangent reaches a constant value:

\[
F_{in} = -2\pi \mu_{app} V_p [L_o + V_p t_{eq} /(1 - \kappa^2)].
\]  

(21)

The present study evaluates \( \mu_{app} \) from the force acting on the plunger at the end time of plunger movement by assuming the end time satisfies the condition for \( t_{eq} \).

The shear rate at the plunger wall, \( (d\gamma/dt)_{hi} \), is

\[
(\gamma/dt)_{hi} = -(1 - \kappa^2) V_p \alpha/(1 + \kappa^2) R_i.
\]  

(22)

### 3.4 Apparent viscosity of a Non-Newtonian fluid

When the sample is a Non-Newtonian fluid, the gradient of the tangent of the measured force curve decreases sharply immediately after the measurement owing to the effect of stress relaxation, and reaches a nearly constant value in short time. By postulating that the total force is due to the viscous force only, the NRCC method estimates the apparent viscosity, \( \mu_{app} \), from the total force acting on the plunger at the arbitrary time, \( t_{eq} \), at which the gradient of the tangent reaches a constant value:

\[
F_{in} = -2\pi \mu_{app} V_p [L_o + V_p t_{eq} /(1 - \kappa^2)].
\]  

(21)

The present study evaluates \( \mu_{app} \) from the force acting on the plunger at the end time of plunger movement by assuming the end time satisfies the condition for \( t_{eq} \).

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(\gamma/dt)_{hi} = -(1 - \kappa^2) V_p \alpha/(1 + \kappa^2) R_i.
\]  

(22)

### 3.5 Accuracy of the NRCC method for viscosity measurement

Figure 3 shows the calibration results of the viscosity measurement for the NRCC method using Newtonian fluids of known viscosity. The samples were deionized water and six viscosity standard liquids (Brookfield Engineering Lab. Inc., USA). The viscosities of samples at 25 °C ranged from 0.89 × 10⁻³ Pa·s to 1.008 × 10² Pa·s. The largest and smallest root-mean-square errors of measurements were 0.094 and 0.0084, respectively. The results demonstrate that the NRCC method can measure a wide range of viscosities of Newtonian fluids with practical accuracy within the measurement errors given above.
4. RESULTS AND DISCUSSION

4.1 Comparison of the viscosity, \( \mu \), and apparent viscosity, \( \mu_{\text{app}} \), obtained by the NRCC method with the apparent viscosity, \( \mu_{\text{apph}} \), obtained by the HAAKE MARS III

Figure 4 shows two examples of measured force-time curves and analyzed results by the NRCC method for a Newtonian fluid and a Non-Newtonian fluid. Figure 4(a) was the result of a viscosity standard liquid (\( \mu = 1.0 \times 10^{-1} \text{ Pa\cdots} \) at 25 °C, Brookfield Eng. Lab., USA) and Fig. 4(b) was of tomato puree (Kagome Co., Ltd., Japan). Both experimental curves agreed satisfactorily with the theoretically estimated force-time curves shown in Fig. 2(a) and Fig. 2(c). When the shear modulus, \( G \), was measured as zero, the apparent viscosity was not shown in the analyzed results for the reason of that the analysis software classified the sample as a Newtonian fluid.

Experimental results of the viscosity, \( \mu \), and apparent viscosity, \( \mu_{\text{app}} \), of four food fluids measured employing the NRCC method and the apparent viscosity measured using the conventional apparatus, HAAKE MARS III, \( \mu_{\text{apph}} \), are shown in Fig. 5. The results reveal that the NRCC method can measure the apparent viscosity of Non-Newtonian fluids, because almost the same values of \( \mu_{\text{app}} \) and \( \mu_{\text{apph}} \) were measured for each sample fluid. The viscosity was lower than the apparent viscosity for all samples, showing the difference in shear-rate dependencies. The viscosities of mayonnaise and thickening agent solution were considerably low compared with the apparent viscosities in the low-shear-rate region. The shear-rate dependency of viscosities was rather small. However, the difference between the viscosity and apparent viscosity decreased gradually with an increase in the shear rate. The viscosity approached the apparent viscosity in the higher shear-rate region as shown in Fig. 5. The results indicate that the viscosity of a shear-thinning Non-Newtonian fluid is not constant but rather decreases with an increase in the shear rate as does the apparent viscosity, though the shear-rate dependency is weaker than that of the apparent viscosity. It was supposed that the inner structure of mayonnaise or thickening agent solution changed more at a bending point of the shear-rate dependency of the viscosity than in the shear-rate region below the bending point. It is also considered that the shear rate dependency of the viscosity with the bending point might relate to the flow behavior of the sample with a yield stress. But, this supposition should be confirmed by further study. Meanwhile, the viscosities of tomato puree and yoghurt were similar to apparent viscosities, though the shear-rate dependencies of the viscosity were slightly weaker than those of the apparent viscosities. It was assumed from the results that the change in the inner structure of these food fluids occurs gradually, corresponding to the entire range of the shear rate studied.

4.2 Comparison of the apparent viscosity, \( \mu_{\text{app}} \), obtained by the NRCC method with the complex viscosity, \( |\eta^*| \), obtained by the HAAKE MARS III

Figure 6 compares the apparent viscosity, \( \mu_{\text{app}} \), of the sample fluids measured employing the NRCC method with the complex viscosity, \( |\eta^*| \), measured by the HAAKE MARS III. \( \mu_{\text{app}} \) and \( |\eta^*| \) are plotted against the shear rate, \( dy/dt \), and angular velocity, \( \omega = 2 \pi f \), respectively, where \( \gamma \) is the shear strain, \( t \) is time and \( f \) is the frequency. According to the
Cox–Merz rule\textsuperscript{14}, values of $\mu_{\text{app}}$ correspond to $|\eta^*|$ for polymer solutions and dispersions\textsuperscript{15,16}, though the former values are several times lower than the values of $|\eta^*|$ for weak gel systems\textsuperscript{17}. Among the food fluids studied, the values of $\mu_{\text{app}}$ almost agreed with $|\eta^*|$, indicating the Cox–Merz rule could be adopted for the thickening agent solution of which the main ingredients were dextrin and polysaccharide thickener. Values of $\mu_{\text{app}}$ for mayonnaise were slightly lower than $|\eta^*|$. The remaining two fluids showed weak gel-like behavior, because the values of $\mu_{\text{app}}$ were several times lower than the values of $|\eta^*|$. Differences between $|\eta^*|$ and $\mu_{\text{app}}$ for the four sample fluids decreased in the order tomato puree > yoghurt > mayonnaise > thickening agent solution.

4.3 Comparison of the shear modulus, $G$, obtained by the NRCC method with the dynamic shear moduli, $|G^*|$, $G'$, $G''$, obtained by the HAAKE MARS III

The static shear modulus, $G$, measured employing the NRCC method and the dynamic shear moduli ($|G^*|$: complex shear modulus, $G'$: storage shear modulus, $G''$: loss shear modulus) measured by the HAAKE MARS III are plotted in Fig. 7 against the shear rate, $\gamma$, for $G$ and angular frequency, $\omega$, for $|G^*|$, $G'$ and $G''$. In the range of angular frequency studied, the dynamic shear modulus of each fluid increased with $\omega$. The values of $|G^*|$ and $G'$ were almost the same. This result indicates that energy loss in each fluid due to viscous flow was rather small. Meanwhile, the shear
Fig. 6 Experimental results of the apparent viscosity, $\mu_{\text{app}}$, of the sample fluids measured employing the NRCC method and the complex viscosity, $|\eta^*|$, measured by the HAAKE MARS III. Values of $\mu_{\text{app}}$ and $|\eta^*|$ are plotted against the shear rate, $dy/dt$, and angular frequency, $\omega$, respectively.

Fig. 7 Experimental results of the static shear modulus, $G$, measured employing the NRCC method with the dynamic shear moduli ($G^*$: complex shear modulus, $G'$: storage shear modulus, $G''$: loss shear modulus) measured by the HAAKE MARS III. Values of $G$ and the dynamic shear moduli are plotted against the shear rate, $dy/dt$, and angular frequency, $\omega$, respectively.
modulus, $G$, of tomato puree, yoghurt and mayonnaise decreased with an increase in the shear rate. However, the $G$ values of the thickening agent solution were almost unaffected by the shear rate. Figure 7 shows that $G < |G^*|$ for tomato puree, $G \approx |G^*|$ for yoghurt, and $G > |G^*|$ for mayonnaise and thickening agent solution. These results suggest that viscoelastic (Non-Newtonian) fluids for which the Cox–Merz rule can be adopted as for polymer solutions and dispersions might have $G > |G^*|$. However, this inference should be confirmed by further investigation, because the results of the present study are only for four samples.

### 4.4 Proposal of the apparent shear modulus, $G_{app}$, and comparison of $G_{app}$ with the dynamic shear modulus, $|G^*|$, obtained by the HAAKE MARS III

Static rheological properties of Non-Newtonian fluids have been discussed mainly in terms of the measurable apparent viscosity. Several flow models describing the shear-rate dependency of the apparent viscosity and the existence or absence of a yield value have been proposed. For Non-Newtonian fluids, however, the static shear modulus and apparent viscosity might be affected by the shear rate because their inner structures change with the shear rate. The present study thus defines an apparent shear modulus that indicates the shear-rate dependency of the shear modulus of Non-Newtonian (viscoelastic) fluids as

$$G_{app} = \frac{G (\mu / \mu_{app})}{G (\mu / \mu_{app})}.$$  \hspace{1cm} (23)

Changes in $G_{app}$ are then compared with the dynamic shear moduli measured by the HAAKE MARS III. Although the apparent viscosity of a Non-Newtonian fluid is higher than the static viscosity owing to the effect of elasticity, the apparent shear modulus, $G_{app}$, is assumed to be smaller than the static shear modulus, $G$, at a rate of $\mu / \mu_{app}$ because of a viscous effect. When $\mu$ and $\mu_{app}$ are similar, as for tomato puree, $G_{app}$ might be close to $G$. Figure 8 compares the apparent shear modulus, $G_{app}$, and the complex shear modulus, $|G^*|$, of each sample against the shear rate, $d\gamma/dt$, and angular velocity, $\omega$. Among the four samples, there was a large difference between $G_{app}$ and $|G^*|$ for tomato puree but little difference for the other three samples especially in the low shear rate or angular velocity region. $G_{app}$ for mayonnaise and thickening agent solution increased with increasing $d\gamma/dt$ or $\omega$. The present study obtained a relationship between the apparent shear modulus and complex shear modulus that was similar to the relation between the apparent viscosity and the complex viscosity. $G_{app}$ was almost one order of magnitude smaller than $|G^*|$ for tomato puree but close to $|G^*|$ for the other three samples. These results suggest that the static rheological properties, $G$ and $\mu$, measured by the NRCC method and the apparent shear modulus, $G_{app}$, defined in this study are useful to the discussion of the viscoelastic behavior of Non-Newtonian fluids. However, for the limited samples studied,
the present study could not clarify for what kind of Non-Newtonian fluid do $G_{\text{app}}$ and $|G^*|$ coincide.

### 4.5 Application of two-element models to the analysis of the viscoelastic behavior of samples

Dynamic viscoelastic behavior has been analyzed theoretically by postulating that materials to be studied have intrinsic values of viscosity, $\mu$, and shear modulus, $G$. The contributions of $\mu$ and $G$ are usually estimated from the relation of the loss tangent ($\tan \delta$) with angular velocity, $\omega$. As one of the two-element models, the Maxwell model leads theoretically to $\tan \delta = G''/G' = 1/(\omega \tau)$, where $\tau = \mu/G$. In the case of the Kelvin–Voigt model, we might obtain $\tan \delta = G''/G' = \omega \tau_\text{K}^2$. Therefore, if the relaxation time or characteristic time, $\tau$, is a constant, it is expected that $\tan \delta$ will decrease in reverse proportion to $\omega$ for materials of which the viscoelastic behavior follows the Maxwell model. Meanwhile, $\tan \delta$ would increase in proportion to $\omega$ for materials that obey the Kelvin–Voigt model. For solid materials, it might be possible to assume that $\tau$ is a constant, because there is no or extremely little change in the inner structure. For Non-Newtonian fluids, however, it is disputable to postulate that $\tau$ can be a constant, because the inner structure is readily affected by deformation and material flow. The present study found that $\tan \delta$ for all samples measured by the HAAKE MARS III was almost constant or slightly increased with $\omega$ (data not shown). The result indicates that $\tau$ for each sample was not constant, and varied with the shear rate or angular velocity owing to the change in viscosity and elasticity.

The present study thus evaluated two characteristic times, $\tau_\text{M}$ and $\tau_\text{K}$, corresponding to $\tau$ for the Maxwell model and Kelvin–Voigt model respectively, from the dynamic measurements of $\tan \delta$:

$$\tau_\text{M} = 1/(\omega \tan \delta) \text{ for the Maxwell model,}$$

$$\tau_\text{K} = \tan \delta/\omega \text{ for the Kelvin–Voigt model.}$$

$\tau_\text{M}$ and $\tau_\text{K}$ were then compared with the characteristic times $\tau = \mu/G$ and $\tau_\text{app} = \mu_{\text{app}}/G_{\text{app}}$ calculated from the values of $\mu$, $G$ and $G_{\text{app}}$ employing the NRCC method as shown in Fig. 9. $\tau_\text{M}$ and $\tau_\text{K}$ are plotted against angular velocity, $\omega$, while $\tau$ and $\tau_\text{app}$ are plotted against the shear rate, $dy/dt$. Figure 9 clearly shows that $\tau_\text{M}$ was about one order of magnitude larger than $\tau_\text{K}$, though both $\tau_\text{M}$ and $\tau_\text{K}$ decreased exponentially with $\omega$. Meanwhile, for all samples, $\tau_\text{app}$ and its gradient closely match $\tau_\text{K}$ and its gradient in the case of the Kelvin–Voigt model. The result suggests that the viscoelastic behavior of the sample fluids in this study can be expressed by the Kelvin–Voigt model. $\tau$ was shorter than the other three characteristic times, and the decreasing gradient was lower than that of the other three times.
Figure 9 also suggests that it is possible to estimate the dynamic viscoelastic behavior of Non-Newtonian fluids from the static rheological properties measured employing the NRCC method by adopting $\mu_{\text{app}} = \mu_{\text{app}}/G_{\text{app}}$ instead of $\tau = \mu/G$ in the theoretical models. Although these results show the possibility of inferring the viscoelastic behavior of Non-Newtonian fluids using two-element models, it is necessary to accumulate more experimental results for many kinds of viscoelastic fluids and verify the general applicability of the results obtained in this study.

5. CONCLUSION

Correlations between static rheological properties ($G$: shear modulus, $\mu$: viscosity, $\mu_{\text{app}}$: apparent viscosity) of four Non-Newtonian food fluids (thickening agent solution, yoghurt, tomato puree and mayonnaise) measured employing a newly developed NRCC method and dynamic viscoelastic properties ($|G^*|$: complex shear modulus, $G^*$: storage shear modulus, $G'$: loss shear modulus, $|\eta^*|$: complex viscosity, $\tan\delta$: loss tangent, $\mu_{\text{app}}$: apparent viscosity) measured employing a conventional dynamic apparatus (HAAKE MARS III) were investigated. $\mu_{\text{app}}$ and $\mu_{\text{apph}}$ for each sample fluid agreed well with each other. In terms of the relationship between $\mu_{\text{app}}$ and $|\eta^*|$, $\mu_{\text{app}} \geq |\eta^*|$ obeying the Cox–Merz rule was obtained for thickening agent solution, $\mu_{\text{app}} < |\eta^*|$ was obtained for mayonnaise, and $\mu_{\text{app}} < |\eta^*|$ was obtained for tomato puree and yoghurt. $\mu_{\text{app}}$ of mayonnaise was slightly lower than $|\eta^*|$. However, the remaining two fluids showed weak gel-like behavior because $\mu_{\text{app}}$ was several times lower than $|\eta^*|$. $\mu$ was lower than $\mu_{\text{app}}$ or $\mu_{\text{apph}}$ for all samples, and reached $\mu_{\text{app}}$ with an increase in the shear rate. A plot of $G$ and $|G^*|$ against the shear rate, $\text{d}y/\text{d}t$, and angular velocity, $\omega$, respectively in the same figure showed that $G$ was nearly constant or decreased slightly as $\text{d}y/\text{d}t$ increased, though $|G^*|$ increased with $\omega$. A comparison of $G$ with $|G^*|$ showed that $G < |G^*|$ for tomato puree, $G \geq |G^*|$ for yoghurt and $G > |G^*|$ for mayonnaise and thickening agent solution. The present study newly defined an apparent shear modulus as $G_{\text{app}} = G(\mu/\mu_{\text{app}})$ to evaluate the shear-rate dependency of elasticity for Non-Newtonian fluids by following the definition of the apparent viscosity, $\mu_{\text{app}}$, which is an overall indicator of fluidity including the effect of changes in structure and elasticity with the shear rate. Compared with $G$, $G_{\text{app}}$ was nearer to $|G^*|$ for all samples without tomato puree. The applicability of two-element models to the analysis of the viscoelastic behavior of sample fluids was investigated. The loss tangent, $\tan\delta$, is expressed theoretically as $\tan\delta = G''/G' = 1/(\omega\tau)$ for the Maxwell model and as $\tan\delta = \omega\tau$ for the Kelvin–Voigt model, where $\tau = \mu/G$. Therefore, in the case of a constant $\tau$ value, it was expected that $\tan\delta$ increases in reverse proportion to angular velocity, $\omega$, for the Maxwell model behavior and that $\tan\delta$ is proportional to $\omega$ for the Kelvin–Voigt model. However, the experimental results did not agree with the theoretical expectation. Therefore, two relaxation or characteristic times $\tau_M = 1/(\omega\tan\delta)$ and $\tau_V = \tan\delta/\omega$ corresponding to the Maxwell model and Kelvin–Voigt model respectively were evaluated from the measurements of $\tan\delta$. Those values were compared with $\tau = \mu/G$ and $\tau_{\text{app}} = \mu_{\text{app}}/G_{\text{app}}$ calculated from the rheological properties measured employing the NRCC method. The results show that $\tau_V$ was in good agreement with $\tau_{\text{app}}$. The main findings of the study are as follows.

1) It might be possible to apply the Kelvin–Voigt model to the viscoelastic behavior of sample fluids.
2) The characteristic time, $\tau$, for Non-Newtonian fluids can be expressed approximately as $\tau_{\text{app}} = \mu_{\text{app}}/G_{\text{app}}$ instead of $\tau = \mu/G$ because the viscoelastic properties of Non-Newtonian fluids change with the shear rate or angular velocity.
3) The dynamic viscoelastic behaviors of Non-Newtonian fluids are possibly predictable from the static rheological properties measured using the NRCC method and a characteristic time of $\tau_{\text{app}} = \mu_{\text{app}}/G_{\text{app}}$.
4) The results suggest that static values of viscosity, $\mu$, and shear modulus, $G$, measured employing the NRCC method might have meaning for physical properties.

To verify the generality of the results, it is necessary to investigate experimentally and theoretically the relationships of static rheological properties and dynamic viscoelastic behaviors for different Non-Newtonian fluids.

NOMENCLATURE

$E$: Young’s modulus, Pa
$f$: frequency, 1/s
$F_e$: total elastic force acting on the plunger, N
$F_{ec}$: compressive force acting on the bottom area of the plunger, N
$F_{oc}$: elastic shear force acting on the side wall of the plunger, N
$F_{ocg}$: viscous force acting on the bottom area of the plunger, N
$F_{ocg}$: viscous force acting on the side wall of the plunger, N
$F_{ocg}$: tangent of the combined force of $F_e$ and $F_{oc}$ at $t = 0$, N
$F_{ocg}$: tangent of the combined force of $F_e$ and $F_{oc}$ at $t = t_{\text{app}}$, N
$F_{t}$: total viscous force acting on the plunger, N
$F_{toc}$: total viscous force acting on the plunger at $t = 0$, N
$G$: shear modulus, Pa
$G'$: storage shear modulus, Pa
$G''$: loss shear modulus, Pa
$|G^*|$: complex shear modulus, Pa
$G_{\text{app}}$: apparent shear modulus defined in this study, Pa
$K$: constant used in Eq. (19), m
$L$: dipped distance of the plunger in the sample fluid during measurement, m
$L_o$: initial dipped distance of the plunger in the sample fluid, m
$L_b$: distance between the plunger bottom and cup bottom, m
$\Delta L$: moving distance of the plunger, m
$\Delta P$: pressure drop for distance $L$, Pa
$r$: distance from the center of the coaxial cylinder system, m
$R_i$: radius of the plunger ($= \kappa R_o$), m
$R_o$: radius of the cup, m
$t$: moving time of the plunger ($= \Delta L/ V_p$), s
$t_{eq}$: arbitrary time at which the gradient of the tangent reaches a constant value, s
$u_r$: flow rate at distance $r$, m/s
$u_{av}$: average flow rate of the sample, m/s
$V_p$: moving speed of the plunger, m/s
$Z$: relative shear distance in the axial direction between the plunger and sample, m
$\alpha$: geometric constant, –
$\gamma$: shear strain, –
$\delta$: phase shift, rad
$\tan\delta$: loss tangent, –
$\sigma_r$: shear stress at the plunger side wall ($r = R_i$), Pa
$\sigma$: shear stress at distance $r$ from the center of the coaxial cylinder system, Pa
$\kappa$: ratio of $R_i$ to $R_o$ ($= R_i / R_o$), –
$\mu$: viscosity, Pa·s
$\mu_{\text{app}}$: apparent viscosity, Pa·s
$|\eta^*|$: complex viscosity, Pa·s
$\tau$: characteristic time defined as $\tau = \mu / G$, s
$\tau_{eq}$: characteristic time defined as $\tau_{eq} = \mu_{\text{app}} / G_{\text{app}}$, s
$\tau_K$: characteristic time for the Kelvin–Voigt model ($= \tan\delta / \omega$), s
$\tau_M$: characteristic time for the Maxwell model ($= 1 / (\omega \tan\delta)$), s
$\omega$: angular frequency ($= 2 \pi f$), rad/s

REFERENCES