Comparison of the Viscoelastic Properties of Fluid Foods Measured by the Non-rotational Concentric Cylinder Method with Those by the Dynamic Oscillatory Method

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A new method using a non-rotational concentric cylinder (NRCC) rheometer was used to determine the viscoelasticities of selected viscous liquid foods. The results were compared with those of conventional dynamic viscoelastic measurements. Two two-element models, the Maxwell model and the Voigt model, were used to describe the viscoelastic behavior of model foods measured by the NRCC method, which generates force-time curves. Mayonnaises with 28–36 w/w% water content and the 4 w/w% gelatinized potato starch exhibited Maxwell behavior with convex force-time curves. In contrast, mayonnaises with 20–24 w/w% water content and 5–7 w/w% gelatinized potato starches exhibited Voigt behavior with straight force-time curves. These results were in good agreement with the results given by the dynamic viscoelastic method. The $G'$ value of the Maxwell model-like samples showed frequency dependence, while the $G'$ values of the Voigt model-like samples exhibited less pronounced frequency dependence over the observed range.

Key words: viscoelasticity, viscous liquid foods, shear modulus, two-element model, non-rotational concentric cylinder rheometer

1. Introduction

The rheological properties of food materials are not easily measured because of their non-Newtonian flow behavior, which is time and shear rate dependent. In the past few decades, the viscoelastic behavior of many foods has been studied in terms of their dynamic viscoelastic properties. It is a non-destructive technique allowing measurements to be made without inflicting structural damage on the sample if the operation is performed within the linear viscoelastic range. Dynamic viscoelastic measurements have been carried out for many kinds of foods in previous studies [1–4].

Linear viscoelastic properties are useful for clarifying the structural characteristics of food materials, but they are of little value for predicting the viscoelastic properties which emerge during food processing operations [5]. In the food production process (e.g., extrusion, mixing, pumping, chewing), viscoelastic materials are subjected to large deformations, which affect the non-linear viscoelastic behavior of materials [6]. Thus, the dynamic viscoelastic method cannot yield a proper understanding of the viscoelastic behavior emerging in those processes.

Recently, a static method of measuring the viscosity and viscoelasticity of liquid foods using the non-rotational concentric cylinder (NRCC) method has been developed [7]. This simply structured and easily implemented method allows the accurate measurement of the viscosity ($\mu$) and shear modulus ($G$) of liquid foods. In the NRCC method, the sample is placed in a cup and the plunger is partially immersed in the sample before measurement; during measurement, the plunger is moved vertically through the measured sample, and the viscosity is evaluated from the force measured just at the start of plunger movement (theoretically, $t=0$); finally, the shear modulus is calculated from the change in force during the plunger movement. The rheological properties measured by this method are useful for understanding the viscoelasticities of food materials during processing which is encountered large deformation.

A convenient manner of conceptualizing the viscoelastic behavior of foods is in terms of a spring with modulus ($G$) and a dashpot that represents a Newtonian fluid with viscosity ($\mu$). These can be arranged either in series, as in the Maxwell model, or in parallel, as in the Voigt model [8]. Two-element models, which are the simplest models, have been used to explain the dynamic viscoelastic behav-
ior of materials. In our previous work, we have proposed the NRCC method, which measures force-time curves, as a method of measuring the viscoelastic behavior of liquid foods [9]. The NRCC method measures mainly two types of force-time curves that relate to the structure of liquid foods. One is the convex force-time curve, which corresponds to Maxwell model structures, while the other is the linear force-time curve, which relates to Voigt model structures.

In the present study, the viscoelastic properties of mayonnaise and potato starch model foods were investigated by the NRCC method. The Maxwell model and the Voigt model were used to explain the viscoelastic behaviors of the samples measured by this method. Moreover, the results obtained by the NRCC method were compared with those given by the dynamic viscoelastic method (DAR-50, Stresstech rheometer). The mechanism behind the difference in the viscoelastic behaviors of viscous liquid foods was also elucidated.

2. Materials and Methods

2.1 Materials

Mayonnaise and potato starch model foods were prepared to simulate Maxwell model and Voigt model viscoelastic materials.

Commercial mayonnaise was purchased from a local market. The main ingredients of the mayonnaise were vegetable oil, egg yolk, vinegar, salt, and flavoring. The initial water content of the mayonnaise, as measured by the drying method, was 20 w/w%. The water content of the mayonnaise model foods was adjusted to 20, 24, 28, 32 and 36 w/w% by the addition of distilled water. The samples were gently mixed for 10 minutes before rheological measurement.

Chemical reagent grade potato starch and gelatin were purchased from Sigma Aldrich Japan (Tokyo, Japan). Gelatin was added to potato starch solution to enhance the viscoelasticity of the solution and to render the gelatinized potato starches compact. The potato starch model foods (4-7 w/w%) were prepared with 0.3 w/w% gelatin by heating to 90°C for 10 minutes using a hot plate and then cooling to 25°C over a period of approximately 15 minutes. During the cooling process, the samples were covered by a Parafilm until the rheological measurement to prevent water loss.

2.2 Static viscoelastic measurement

The static viscoelasticity was measured by means of a non-rotational concentric cylinder rheometer (NRCC-Visco-PRO, Sun Scientific Co., Japan). Plunger no. 2 \( (\kappa = R / R_o = 0.8928) \) was used; the plunger velocity \( (V_p) \) ranged from 10 mm/min to 80 mm/min and the plunger movement distance \( (\Delta L) \) ranged from 0.1 mm to 0.2 mm. The samples in the measurement cup were cooled to 25°C using a water circulation system. The measurements were performed five times, and the average values were used as the results.

2.3 Dynamic viscoelastic measurement

The viscoelastic properties of the model foods were monitored using a Stresstech rheometer, which performed oscillatory measurement with cone-plate geometry (DAR50, Reologica Instruments, A.B.). The cone was 40 mm in diameter and 4° in cone angle. All measurements were carried out at 25°C. A frequency sweep test for viscoelasticity was performed at an angular frequency of 0.01 Hz to 10 Hz. A stress of 1 Pa and 5 Pa was applied to the mayonnaise and gelatinized potato starch, respectively. Due to the phase difference between the samples, alternate constant stresses were selected for each model food. The dynamic rheological parameters used to evaluate the viscoelastic properties of the samples were storage modulus \( (G') \) and loss modulus \( (G'') \).

2.4 Static measurement of the viscoelastic behavior based on force-time curves

Figure 1 shows a theoretical scheme of the method proposed in this paper. The theoretical derivation of the measurement system has been presented by Suzuki et al. in a previous paper [9]. A plunger (radius: \( R_o \)) is initially dipped at a distance, \( L_o \), in the liquid sample, which is in a

![Fig. 1 Setup of a non-rotational concentric cylinder rheometer.](image-url)
cup (radius: $R_o$). The initial distance between the plunger’s bottom and the cup bottom is $L_h$. The cup is moved upward or the plunger is moved downward at a constant speed, $V_p$.

2.4.1 The Maxwell model

The Maxwell model is commonly visualized as a series combination of a Hookean spring of rigidity $G$, and a Newtonian dashpot of viscosity $\mu$ (Fig. 2a). When the Maxwell model is applied to the force-time curve generated by the NRCC method, the following exponential equation is obtained [9]:

$$ f = \delta K\mu (L_o + \phi K t) + K\mu \left(1 - \exp\left(-\frac{G t}{\mu}\right)\right) $$ (1)

where $f$ is the shear stress (Pa), $K$ is the constant shear rate in the NRCC method (s$^{-1}$), $\mu$ is the viscosity (Pa · s), $t$ is the time of plunger movement (s), $G$ is the shear modulus (Pa), $\delta$ is a constant which corresponds to $-2\pi a/\beta$, and $\phi$ is a constant which corresponds to $1/(1/\beta(1-\kappa^2))$. $\beta$ is obtained when the constant shear rate, $K$, is assumed to be proportional to $V_p$, i.e. $K = \beta V_p$. $a$ is a geometric constant of the apparatus defined as follows:

$$ a = \frac{(1 + \kappa^2)}{(1 + \kappa^2) \ln \kappa + (1 - \kappa^2)} $$ (2)

where $\kappa = R_i/R_o$. The force-time curve of the Maxwell model shows a convexly increasing shear stress as a function of time.

2.4.2 The Voigt model

The Voigt model is described by the parallel connection of a Hookean spring and a Newtonian dashpot. When the Voigt model is applied to the force–time curve generated by the NRCC method, the resulting linear equation can be written as follows [9]:

$$ f = \delta K\mu (L_o + \phi K t) + K\mu + K G t $$ (3)

Eq. (3) indicates that the shear stress increases linearly with increasing time, as shown in Figure 2(b).

3. Results and Discussion

3.1 Viscosity and static shear modulus

Figures 3 and 4 show the viscosities and shear moduli ($G$) of the mayonnaise and gelatinized potato starch, as measured by the NRCC method. The viscosity of the mayonnaise gradually decreased with the addition of distilled water (water content: 20, 24, 28, 32 and 36 w/w%; dispersed phase content: 80, 76, 72, 68 and 64 w/w%). The
same results were found for the gelatinized potato starches, whose viscosity increased with increasing starch concentration. Both model food systems exhibited shear-thinning (pseudoplastic behavior), where the viscosity decreased with increasing shear rate. This pseudoplastic behavior of the mayonnaises was in agreement with the result of a previous study [10]; Ma and Barbosa-Canovas [11] have reported pseudoplastic behavior in mayonnaises whose oil concentrations ranged from 75–85 w/w%. It can be deduced from these facts that high oil content correlates with high viscoelasticity in emulsions. At higher oil concentrations, a more compact three-dimensional network is formed between the egg protein molecules and the absorbed oil droplets, which causes an increase in the viscoelasticity of mayonnaise [12, 13]. The increase in the viscosity and shear modulus of gelatinized potato starch may be attributed to the degree of granular swelling, which tends to fill the entire available volume of the system [14, 15], and the intergranule contact, which might lead to the formation of a three-dimensional network of swollen granules [16].

Indeed, at low concentrations, the starch particles are completely swollen [17]. As the swollen particles continue to fill the available space, the viscoelasticity of the system increases, which could be explained by the increase in the volume fraction of the dispersed system. At higher concentrations, the starch granules cannot fully swell to their equilibrium volume due to the lack of water. The starch granules fill the limited space and form a compact structure, which causes an increase in viscosity and shear modulus.

The results for the shear modulus were similar, in that the G value increased in the gelatinized potato starches as the concentration of the potato starch increased, and decreased in the mayonnaises with the addition of water (Figs. 3(b) and 4(b)). However, it should be noted that the shear moduli of both sample types showed shear rate independence over the observed ranged.

3.2 Determination of viscoelastic behavior

According to the background described above, a sample will behave in a Maxwell model way when the NRCC rheometer detects a convex force-time curve. On the other hand, a straight force-time line will be observed for Voigt materials. Figures 5(a) and 5(b) present the force-time curves of model mayonnaises and gelatinized potato starches, respectively, as measured by the NRCC method. The viscoelastic behavior of mayonnaises with 20–24 w/w% water content (or 80–76 w/w% dispersed phase content) and 5–7 w/w% gelatinized potato starch fall into the category of Voigt behavior, for which straight lines were observed a short period after the start of cup movement. In contrast, convex force-time curves were detected for mayonnaises with 28–36 w/w% water content (or 72–64 w/w% dispersed phase content) and the 4 w/w% gelatinized potato starch. These results are consistent with Maxwell behavior, as described above.

The results of small amplitude oscillatory shear tests are expressed in terms of storage modulus (G') and loss modulus (G''). When G' is greater than G'', the material will exhibit the behavior of a solid (i.e. deformation in the linear range will be recoverable), which with the phase angle lower than 45 degrees. On the other hand, if G'' is greater than G', the material will behave like a liquid (i.e. the energy used to deform the material will be dissipated), with the phase shift factor higher than 45 degrees [18].

Figure 6 shows the effect of frequency on G' and G'' for mayonnaise and gelatinized potato starch. For mayonnais-
Static and dynamic viscoelasticities of liquid foods

Fig. 5 Force-time curves for mayonnaises (a) and gelatinized potato starches (b), as measured by NRCC-ViscoPRO.

Fig. 6 Frequency dependence of the dynamic viscoelasticity: (a) $G'$ of mayonnaises, (b) $G$ of gelatinized potato starches, (c) $G'$ of mayonnaises, (d) $G''$ of gelatinized potato starches (the symbols are the same as in Figs. 3 and 4).

On the contrary, mayonnaises with 28–36 w/w% water content and the 4 w/w% gelatinized potato starch showed a more pronounced frequency dependence, which suggests liquid-like behavior. The Maxwell model describes a progressive transition of the liquid from viscous to elastic, where the storage modulus increases with increasing frequency. In addition, the Maxwell model-like samples showed liquid behavior, with phase angles higher than 45 degrees (i.e. the $G''$ exceed the $G'$), except for the mayon-
naise with 28 w/w% water content.

The results shown above suggest that the viscoelastic behavior of viscous liquid foods can be determined by means of the NRCC method, and that viscoelastic behaviors can be simply divided into two categories corresponding to the Maxwell model and the Voigt model. However, it is difficult to find viscoelastic materials which display both ideal Voigt model and ideal Maxwell model characteristics. Most viscoelastic materials behave in either a Voigt model-like or a Maxwell model-like manner. As shown in Figure 5(b), the 5 w/w% gelatinized potato starch had a straight force–time line at the beginning of measurement; nevertheless, the line began to curve as time passed. This indicates that the sample underwent stress relaxation due to Voigt model-like (not ideal Voigt model) viscoelastic behavior.

The transition from Maxwell behavior (4 w/w% gelatinized potato starch) to Voigt behavior (5–7 w/w% gelatinized potato starches) may be explained by the difference in the concentration regimes of the swellable (starch) particles [17]. At low concentration (4 w/w%), the gel particles are completely swollen (Fig. 7(a)). The rheological properties are mainly determined by the volume fraction of the particles and to a lesser extent by the soluble fraction [19]. Therefore, in this concentration regime, the rigid parts represented by the swollen starch granules and the viscous part represented by water can freely move, which leads to Maxwell behavior. At higher concentrations, the swollen starch granules just fill up the free space, a process referred to as "close packing" (Fig. 7(b)). Our data from gelatinized potato starch images taken after centrifugation were used to determine the close packing concentration of the samples (data not shown). The close packing concentration was between 4 and 5 w/w% potato starch after the centrifugation of a 4 w/w% potato starch suspension (which means that water remained in the sample after centrifugation), while water availability was limited in the 5–7 w/w% potato starch suspensions. At high concentration, the granules cannot fully swell owing to the lack of available water (Fig. 7(c)).

The system is a compact structure formed by swollen starch granules, and the viscoelastic properties of the system are predominantly affected by the rigidity of the swollen starch granules. Due to the compact structure and high rigidity, the particles hardly flow past each other. Therefore, the complex structure of such materials can be expected to correspond to the Voigt materials.

In the case of mayonnaise model foods, the transition from Maxwell behavior to Voigt behavior should also be explained by the close packing concentration principle. Mayonnaise is a semi-solid oil-in-water emulsion which contains high amounts of oil (about 80%). The theoretical limit of the close packing concentration of oil in the emulsion, which contains spherical oil particles of equal size, is about 74 v/v% [20]. Stauffer [21] stated that the concentration limit is 72 v/v%. Langton et al. [20] have used confocal laser scanning microscopy (CLSM) and transmission electron microscopy (TEM) to study the structure of mayonnaises and have reported that, at 80 v/v% emulsion, the oil concentration exceeded the concentration limit and dispersed into smaller droplets. Those smaller droplets filled the spaces between the large droplets to form a more compact structure, which probably exhibited Voigt behavior, as elucidated in this study. The density of most liquid foods is nearly the same as that of water, whose weight concentration is assumed to be roughly equal to the volumetric concentration [9]. Therefore, samples with 76–80 w/w% dispersed phase content show Voigt behavior, with the dispersed phase concentration higher than the close packing concentration (72–74%).
4. Conclusions

In this study, the static shear modulus and viscosity of semi-solid foods were determined by means of the novel non-rotational concentric cylinder rheometer method. The viscosity of the samples showed shear rate dependence, according to the type of non-Newtonian fluid. The viscoelastic properties can be determined based on the force-time curves generated by the proposed method, and the viscoelastic properties of semi-solid foods can be simply divided into 2 types: straight force-time lines correspond to the compact structure of a Voigt material, while convex force-time curves correspond to a Maxwell material. These results, which were obtained using the proposed method, were confirmed by those given by the conventional dynamic viscoelastic method, with which there was a good agreement.

Knowledge of static viscoelasticity is useful for understanding the viscoelastic behavior of foods, which are subjected to large deformations during most stages of processing. Moreover, such knowledge could facilitate process quality control, the creation of new food products, and the design of new food-processing equipment, such as pumps, extruders and mixers.

Nomenclature

\[ \dot{\gamma} : \text{shear stress, Pa} \]
\[ G : \text{shear modulus, Pa} \]
\[ K : \text{constant shear rate in NRCC method, 1/s} \]
\[ L_b : \text{distance between plunger's bottom and cup bottom, m} \]
\[ L_i : \text{initial dipped distance of plunger in sample liquid, m} \]
\[ R_p : \text{radius of plunger, m} \]
\[ R_c : \text{radius of cup, m} \]
\[ t : \text{moving time of plunger, s} \]
\[ V_p : \text{moving speed of plunger, m/s} \]
\[ a : \text{geometric constant, \text{-}} \]
\[ \beta : \text{a proportional constant (=K/V_p), 1/m} \]
\[ \delta : \text{a constant corresponds to } -2\pi \cdot a/\beta \quad \text{, 1/m} \]
\[ \kappa : \text{ratio of } R_1 \text{ to } R_0 \quad (=R/R_0), \text{-} \]
\[ \mu : \text{viscosity, Pa \cdot s} \]
\[ \phi : \text{a constant corresponds to } 1/(\beta(1-\kappa^2)), \text{m} \]

References


動的測定法と非回転二重円筒法との比較による
液状食品の粘弾性挙動の検討

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液状食品にはニュートン流動性を示すものが多く、これからの粘弾性体としても動すると、定形性をもたない流体の粘弹性は、これまで動的な粘弾性測定法では測定できなかった。動的粘弾性値は、静的な粘弹性率μと弾性率Gおよび周波数の関数であるが、測定条件が定数であるだけでなく、測定値から静的な粘弾性値を求めることは難しい。

これに対して、最近、液状材料の静的粘弾性を直接測定することが可能な測定法（非回転二重円筒法）が開発された。静的粘弹性が測定できれば、粘弾性モデルを用いて、粘弾性および粘弹性の発現状況の解析や動的粘弾性とその周波数依存性の推定などが可能となる。さらに、非回転二重円筒法では、測定開始直後の荷重値（F）の時間変化曲線が2種類に大別され、2要素モデル、すなわち、粘性要素と弾性要素の直線モデル（Maxwellモデル）と並列モデル（Voigtモデル）に対応することがわかった。

そこで本研究では、非回転二重円筒法を用い、測定されるFの変化曲線の形から、2つ2の要素粘弾性モデル（MaxwellモデルおよびVoigtモデル）を用いて液状食品の粘弾性および粘弹性を測定する。併せて、非回転二重円筒法で測定される静的粘弾性（μ、G）と動的粘弾性（G'、G''、tan δ）およびその周波数依存性などの対応関係を検討した。

試料には、市販マヨネーズおよびベリシジョンブン糊を用いた。マヨネーズモデル食品は、初期値20 w/w%のマヨネーズに加水して、水分を20、24、28、32、36 w/w%に調整した。ベリシジョンブンモデル食品はベリシジョンブン(4~7 w/w%)にゼラチン（0.3 w/w%）を加え、80℃、10分間加熱したものを用いた。

測定条件は、(株)サン科学製のレオメーター（CR-200）を用い、カップ直径は50.07 mmとし、直径45.07 mmのブランジャー（R1/R2=0.8928）を用いた。カップの移動距離（ΔL）は0.1~0.2 mm、すり速度1.74~12.18 1/sとした。粘度と弾性値の値は、全て1条件で5回の測定での平均値とした。動的粘弾性測定はDAR-50（Reologica Instrument, A.B.）のcone-plate型（R=2 cm, φ=4°）を用いた。周波数依存性測定は周波数0.01~10 Hzとし、マヨネーズモデル食品には一定ずり応力1 Pa、ベリシジョンブンモデル食品には一定ずり応力5 Paで測定した。液状食品の動的粘弾性値は貯蔵弾性率（G'）および損失弾性率（G''）を用いた。すべての粘弾性測定は25℃で行った。

水分が20~24 w/w%マヨネーズおよび5~7 w/w%ベリシジョンブン糊の場合は、測定値が直線的な変化を示し、粘弾性は、Voigtモデルで近似できる挙動を示すことがわかった。これに対して、水分が28~36 w/w%マヨネーズおよび4 w/w%ベリシジョンブン糊の場合は、特に凸の曲線を示し、Maxwellモデルで近似できる粘弾性挙動を示すことが示唆された。

一方、動的粘弾性試験の周波数依存性試験では、水分が20~24 w/w%マヨネーズおよび5~7 w/w%ベリシジョンブン糊、G'の周波数依存性がほとんどなく、Voigtモデル的な挙動を示した。一方、水分が28~36 w/w%マヨネーズおよび4 w/w%ベリシジョンブン糊の場合は、G'が大きく周波数依存性を示し、Maxwellモデル的な変化を示し、静的測定法によるレオロジー挙動の推定を支持した。

以上の結果から、液状食品の粘弾性挙動の違いは分散相の密度差（体積分率φ=0.74）の原理で説明された。分散相体積濃度が密度差の密度で大きい（φ>0.74）、すなわち、水分が20~24 w/w%マヨネーズおよび5~7 w/w%ベリシジョンブン糊の場合は分散相と連続相の形状または移動は相互に誤まった挙動となり、粘性要素と弾性要素が自由に移動できないVoigtモデル的な挙動を示すものと考えられた。一方、分散相体積濃度が密度差の密度で小さい（φ<0.74）水分が28~36 w/w%マヨネーズおよび4 w/w%ベリシジョンブン糊の場合は、分散相と連続相の形態は移動は可能かつ分散相が自由に移動できるMaxwellモデル的な挙動を示すものと考えられた。