Attempt of the quantitative evaluation of flow properties of agar microgel suspensions using a weak-gel model

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Abstract It is important to quantitatively evaluate the flow behaviour of complex fluids such as paste-like foods. In this study, we investigated the flow properties of a paste-like food model using a weak-gel model. As a model of paste-like food, agar microgel suspensions were prepared using a water-in-oil (W/O) emulsion system. Because the microgels prepared by this method have a spherical shape, their flow properties can be evaluated quantitatively. The steady state viscosity and dynamic modulus of the suspensions were measured with the volume fraction of the microgel particles ranging from 0.68 to 0.80. Because the flow curves showed a pseudo-plastic flow, they were analysed using the Herschel-Bulkley equation to obtain characteristic flow parameters, namely, the viscosity coefficient \( k \), apparent yield stress \( \sigma_y \), and the Herschel-Bulkley index \( n \). The frequency dependence of the complex modulus was analysed using the weak-gel model to obtain two parameters, namely the coordination number \( z \), which relates to the relaxation behaviour, and gel strength \( A_f \). A sudden increase in both \( \sigma_y \) and \( z \) was observed when the volume fraction was close to 0.77. Moreover, \( k \) and \( A_f \) were also found to undergo a sudden increase at the same volume fraction. This value is expected to be the critical volume fraction at which the microgel particles reach a random close packing state. The results showed that we can make quantitative evaluation of the flow behaviour of a complex fluid under a small deformation by using the weak-gel model.

Keywords cooperative flow theory, flow properties, microgel suspension.

Introduction

Quantitatively evaluating the rheological properties of food is important in different areas such as food production and processing, as well as chewing and deglutition of the food. However, food is generally considered a “complex fluid”, and it is difficult to describe its rheological properties in the form of a unique parameter, such as equilibrium modulus, zero-shear viscosity, or relaxation time, etc. The rheological characteristics of food are often analysed using various empirical laws. Although such methods can quantify flow properties under certain conditions, it is difficult to interpret its mechanism at the molecular level.

It is often observed that the rheological properties of a soft food obey the scaling law. The flow behaviour for such food exhibits non-Newtonian characteristics, e.g., it follows the empirical scaling law [1].

\[
\sigma \propto \dot{\gamma}^n
\]  

(1)

In addition, the frequency dependence of the dynamic modulus often obeys.

\[
G^*(\omega) = A\omega^n
\]  

(2)

In Eq.2, \( n \) is the scaling number and the pre-factor \( A \) is a parameter indicating the strength of the gel [2]. According to the sol-gel transition theory of Winter, the mechanical spectrum of Eq.2 is observed in the vicinity of the sol-gel transition point. They called this state the “critical gel” or “weak gel”.

It is clear that an internal stress occurs as a response to deformation in weak gels. However, it is difficult to determine the characteristic size or time constant of the weak gel uniquely, as discussed previously. Winter and his co-workers discovered a concept called “critical gel” or “weak gel”. 

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gelation of dimethyl siloxane, but a weak gel is observed as well as linear high polymer gel in various instances. Moreover, such a concept also addressed in the viewpoint of hydrocolloids rheology [3].

The cooperative flow theory by Bohlin is one of the theoretical models for analysing the rheological properties of weak gel quantitatively [4]. This theory is the statistical mechanics theory adopted by the Ising model. In this model, the real structure of the complex fluid is substituted by a cooperative arrangement of flow units, which can take two states, namely the “stressed state” and “relaxed state”. Energy between the flow units needed to bring them into closest contact is calculated, and a parameter called coordination number \( z \) is derived. This coordination number \( z \) quantitatively expresses the degree of stressed state (relaxed state). If we assume that weak-gel contains topological connections, the number of topological connecting points would be related to coordination number \( z \).

Finally the time dependence of the relaxation modulus is described as

\[
G(t) \propto t^{-1/2z}
\]

(3)

From Eq.3, we can obtain

\[
G'(\omega) \propto \omega^{1/2z}
\]

(4)

Gabriele et al. [5] suggested a new model for analysis of weak gels from Eq.2 and Eq.4.

\[
G'(\omega) = A_f \omega^{1/2z}
\]

(5)

where \( A_f \) is a parameter indicating the strength of the gel. Gabriele et al. analysed the rheological properties of soft foods such as yogurt and jam.

In this study, we prepared samples with varying volume fractions of agar microgel, and measured their rheological properties. First, we analysed a flow curve with the Herschel-Bulkley equation, and estimated an apparent yield stress and confirmed the volume fraction dependence. In the next step, we analysed the frequency dependence of the dynamic modulus successively in a weak gel model (Eq.5) and estimated the coordination number \( z \) and gel strength \( A_f \). By comparing with the results of the apparent yield stress mentioned previously, we confirmed the validity of the modified Bohlin theory.

**Materials and Methods**

**Materials**

Agar (UP-16, Ina Food Ind., Japan) and liquid paraffin (Wako Pure Chemicals, Japan) were used without further purification. Sucrose erucic fatty acid esters ER-190 (Mitsubishi-Kagaku Foods; Tokyo, Japan) were used as emulsifiers and distilled water was used as the aqueous solvent.

**Preparation of microgel suspensions**

Agar microgel (AMG) samples were prepared according to a method reported previously [6]. The procedure is described briefly as follows. A heated aqueous solution of agar was added to the liquid paraffin, which dissolved the emulsifier. The mixed system was then irradiated by supersonic waves to obtain water-in-oil (W/O) emulsion. This W/O emulsion was cooled to 10°C to create AMG particles in the liquid paraffin. To determine the volume fraction of AMG, the density of the emulsion was measured with a density meter (DMA 600; Anton Paar) at 25°C. The volume fraction of the aqueous phase was calculated using Eq. (6):

\[
\rho_{em} = \phi \rho_{w} + (1-\phi) \rho_{oil}
\]

(6)

where \( \phi, \rho_{em}, \rho_{w} \) and \( \rho_{oil} \) are the volume fraction of the aqueous phase, the density of the emulsion, the density of the aqueous phase and the density of the liquid paraffin, respectively.

To obtain concentrated AMG suspensions, the prepared suspension was condensed by centrifugation for 6 h at 12000 rpm using a high-speed centrifuge (SCR20B; Hitachi, Japan).

The samples having various volume fractions were obtained by adding liquid paraffin to the condensed suspension. The final volume fractions were adjusted in the range of 0.68 to 0.8.

**Rheological measurements**

A strain controlled rheometer (ARES; TA instruments) was employed for rheological measurement. A cone-plate fixture was used, and the steady state viscosities were measured at shear rates between 1 to 100 s\(^{-1}\). The frequency dependence of the dynamic modulus was measured at angular velocities ranging from 1 to 100 rad/s. The applied strain was within a linear viscoelastic region. All measurements were performed at 30°C.

**Optical microscope observation**

The shape and size of AMG particles were observed with an optical microscope (BA210E; SHIMADZU, Kyoto, Japan) equipped with a digital camera system (Moticam 1080 BMH; Shimadzu). The diameter of the microgel particles were measured using an image analyzer (Image-J). The size distribution and the average diameter were estimated using the image data.
Results and discussion

The greatest advantage of the analysis of rheological properties using the AMG suspension prepared in W/O emulsification system is that the AMG particles are spherical, which makes it easier to analyse the rheological behaviour using a theoretical or empirical model. An optical microscope image of the AMG is shown in Fig. 1(a). The diameters of all the AMG particles appear in the frame were measured and the size distribution plot was obtained (Fig. 1(b)). Although there is a distribution of particle diameters, it is evident that AMG is completely spherical.

First, the shear rate dependency of the steady state viscosity of the various volume fraction AMG suspensions is shown in Fig. 2. The apparent viscosity seems to scale with shear rate for all the samples. To estimate the flow behaviour, generally we tried to determine a characteristic parameter such as the zero-shear rate viscosity, if there are Newtonian plateaus in the flow curve. However, as you can see in Fig. 2, it is difficult to determine a characteristic parameter from these curves. Therefore, we attempted to analyse the flow curve using Herschel Bulkley equation.

\[ \sigma = k\gamma^n + \sigma_y \]  \hspace{1cm} (7)

where \( k \), \( n \), and \( \sigma_y \) denote the viscosity coefficient, Herschel Bulkley index, and apparent yield stress, respectively. Although the equation is empirical, it is useful for estimating the flow characteristic parameters of non-Newtonian fluid [7–10]. The flow curves are shown in Fig. 3. It is clear that all the flow curves show typical pseudo-plastic flow behaviour. The measurement data were applied to Eq.7 to obtain these unknown parameters. The solid lines in Fig. 3 indicate the fitting results. As shown in Fig. 3, the calculation
agrees closely with the experimental result. The estimated parameters are listed in Table 1.

It is considered that there are not any special attractive interaction between AMG particles, because enough amount of emulsifier absorbed to the interface of AMG. However, when the particles close packed each other, repulsive force due to steric hindrance may occur. It is considered that such repulsive force would be a source of apparent yield stress. Therefore, it is expected that the apparent yield stress strongly depends on the packing status of the AMG particles. Therefore, the apparent yield stress is a good index of the packing. The volume fraction dependency of the apparent yield stress is shown in Fig. 4. The apparent yield stress gently increases at approximately $\phi = 0.7$ and suddenly rises beyond $\phi = 0.77$. This result shows that this AMG suspension experiences random close packing at approximately $\phi = 0.77$. The value $0.77$ is somewhat higher than the theoretical value of random close packing for uniform hard particles; however, it is believed that this value is correct, because of the particle size distribution. As shown in Fig. 1(b), this AMG suspension is having size distribution. It is considered that if small size particles were contained in the suspension, such small particles filled into the void of the packing structure of the regular size particles. It results the particles able to reach higher volume fraction.

The volume fraction dependency of the viscosity coefficient ($k$) is also shown in Fig. 5. It shows a similar tendency to that of Fig. 4. However, the Herschel-Bulkley indices also depend on the volume fraction (see Table 1). The problem is that the physical meaning of $k$ is unclear. Although the value $k$ strongly depends on the value “$n$”, namely the physical unit of $k$ is “Pa s$^n$”, the physical meaning of “$n$” is unclear. Therefore, value $k$ is not suitable for quantitatively estimating the flow behaviour of the samples.

Although the analysis of the flow curve using an empirical equation is useful for evaluation of such complex fluids, we can obtain more useful information from the measurement under a small deformation that never destroys the microscopic structure. In the next step, we analysed the dynamic modulus using weak-gel model (Eq.5) to obtain the coordination number ($z$), which is a characteristic parameter for weak gel.

The frequency dependence of the dynamic modulus of the low volume fraction sample ($\phi = 0.68$) and the high volume fraction sample ($\phi = 0.80$) is shown in Fig. 6. It is apparent that both plots scale with $\omega$ and we can see that the modulus of the AMG suspension depends on volume fraction. Because the modulus depends on the frequency, it is impossible to obtain either the plateau modulus (equilibrium modulus), or a characteristic time constant. Therefore, we attempted to determine $z$ and $A_f$ of the weak-gel model. The frequency dependence of the complex modulus for the samples is shown in Fig. 7. The measured complex modulus data was applied to Eq.5 to obtain the coordination number ($z$) and gel strength ($A_f$) for all the samples. The lines in Fig. 7 show the fitting results using Eq.5. It is clear that the weak-gel model worked well for these samples. The actual results are listed in Table 2.

The AMG volume fraction dependence on the coordination number ($z$) is shown in Fig. 8. The coordination number ($z$) was approximately 2 for lower volume fraction; however, it abruptly increased to over 6 at $\phi = 0.8$. This behaviour is similar to that of Fig. 4 which is a result of the apparent yield stress analysed with the Herschel-Bulkley equation.

### Table 1: Herschel-Bulkley parameters obtained from the flow curves

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$k$ [Pas$^n$]</th>
<th>$n$ [-]</th>
<th>$\sigma_y$ [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>0.932 ± 0.0448</td>
<td>0.723 ± 0.00666</td>
<td>0.806 ± 0.0185</td>
</tr>
<tr>
<td>0.71</td>
<td>1.45 ± 0.118</td>
<td>0.696 ± 0.00604</td>
<td>0.960 ± 0.0410</td>
</tr>
<tr>
<td>0.74</td>
<td>2.78 ± 0.241</td>
<td>0.653 ± 0.00861</td>
<td>1.37 ± 0.0576</td>
</tr>
<tr>
<td>0.77</td>
<td>4.26 ± 0.131</td>
<td>0.621 ± 0.00403</td>
<td>2.33 ± 0.0592</td>
</tr>
<tr>
<td>0.80</td>
<td>12.7 ± 1.14</td>
<td>0.520 ± 0.00643</td>
<td>7.83 ± 0.525</td>
</tr>
</tbody>
</table>

![Fig. 4](image-url) Volume fraction dependence of the apparent yield stress estimated using Eq.7.

![Fig. 5](image-url) Volume fraction dependence of the viscosity coefficient estimated using Eq.7.
This result is not surprising if the background of the Bohlin theory is checked. The value of $z$ indicates how many neighbouring flow units are "stressed". It means that the value of $z$ shows a packing state of the microgel particles quantitatively. In another words, the value $z$ indicates how many flow units mechanically interacts each other. If we consider the topological interaction of spherical particle in two dimensions, any one particle (microgel) may contacts six particles in the close packed status. Therefore, it is reasonable that a $z$ of approximately at $\phi = 0.8$ means the AMG particles started to be close packed at approximatley $\phi = 0.77$.

The volume fraction dependence on the gel strength ($A_f$) is also shown in Fig. 9. This figure is similar to the results of the viscosity coefficient ($k$) in Fig. 5. We strongly insist that an important meaning is included in this result. Although the viscosity coefficient ($k$) in the Hershel- Bulkley equation is useful to estimate apparent viscosity of a non-Newtonian fluid, its physical meaning is unclear. Moreover, the value may vary depending on the measurement condition, because the steady state viscosity measurement is essentially a non-linear measurement. On the other hand, gel strength ($A_f$) can be obtained from the small deformation measurement, that is, we can obtain the parameter with a non-destructive measurement. It is expected that we can obtain reproducible data using this method. Although the physical unit of $A_f$ includes the scaling number ($z$), in this case, the physical meaning of $z$ is clear as described above. Therefore, $A_f$ is quite different from $k$ in the view point of physics.

**Table 2** Weak-gel model parameters obtained from the dynamic modulus

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$A_f$ [Pas$^1$]</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.68</td>
<td>12.9 ± 2.19</td>
<td>2.28 ± 0.0809</td>
</tr>
<tr>
<td>0.71</td>
<td>23.7 ± 1.84</td>
<td>2.64 ± 0.0804</td>
</tr>
<tr>
<td>0.74</td>
<td>28.6 ± 1.54</td>
<td>2.60 ± 0.630</td>
</tr>
<tr>
<td>0.77</td>
<td>47.5 ± 4.82</td>
<td>3.11 ± 0.194</td>
</tr>
<tr>
<td>0.80</td>
<td>244 ± 23.0</td>
<td>6.87 ± 0.275</td>
</tr>
</tbody>
</table>

*Fig. 6* Dynamic modulus of $\phi = 0.68$ (circles) and $\phi = 0.80$ (squares). The open and closed symbols denote the storage modulus and loss modulus, respectively.

*Fig. 7* Frequency dependence of the complex modulus for the various volume fraction samples. The squares, circles, triangles, inverse triangles, and diamonds denote the measured results of $\phi = 0.68$, 0.71, 0.74, 0.77, and 0.80, respectively. The lines denote fitting results by using Eq.5.

*Fig. 8* Volume fraction dependence of the coordination number ($z$) estimated using Eq.5.
The combination of these two parameters, $z$ and $A_f$, is quite useful for investigating the structure of soft foods. The value $z$ includes the information of the “structure topology” and the value $A_f$ includes the “intensity of the interaction.” It is considered that we can depict the expectation of such a weak-gel structure at the molecular level by using the weak-gel model.

**Conclusion**

We found that the weak-gel model works well for analysis of agar microgel suspension as a soft food model. It is expected that this model for the analysis of the rheological characteristics works not only for spherical solid suspensions but also various soft and fluid foods.

We are currently working on the development of a low-fat food where oils and fats can be replaced with an agar microgel. It is expected that the flow properties of such emulsions will change greatly. In other words, the texture of the food may change greatly, but it is expected that this theoretical model will be useful in adjusting to the texture of soft foods.

**Acknowledgements**

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**References**