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The Effects of Emulsifiers on Flow Properties of Cocoa Butter/ Silica Dispersion as Model Chocolates

Isamu KANEDA, Hajime MIYAZAWA and Momo ITO

ココアバター/シリカ微粒子分散系から成るモデルチョコレートによる溶融チョコレートの流動特性に対する乳化剤の影響に関する研究

金　田　　勇・宮　澤　　元・伊　藤　　桃
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1. Introduction

Chocolate comprises dispersions of fine solid particles of sugar and cocoa mass, approximately 70% in total, in a continuous cocoa butter phase. As chocolate melts in the mouth, the lipids and fine solid particles coat the oral epithelial surfaces and affect taste perception. Therefore, the rheological properties of chocolate have a strong influence on the sensation of smoothness left in the taster's mouth. In addition, the rheological properties of molten chocolate are important in the manufacturing and processing of chocolate, particularly during enrobing, molding, and panning. Because chocolate is a relatively high-cost product, it is necessary to reduce process loss during manufacturing.

The rheology of molten chocolate, mainly their flow property, has been studied in the viewpoint of the quality control. The International Office of Cocoa, Chocolate and Sugar Confectionery (IOCCC) has established a standard protocol for the estimation of molten chocolate. The viscosity of the molten chocolate should be measured under a cretin range of the shear rate (for example, 5~40 s^{-1}), and the measured data should be analyzed with Casson equation or a power low equation. Since the ingredient of chocolate is expensive, it is quite important issue to precisely control the rheological property of the molten chocolate in the processing of the confectionery. One of the important factors affecting the rheology of the molten chocolate is the size distribution of the solid dispersant in chocolate; namely sugar or cocoa nib. The solid particle size in chocolate is quite important with respect to its flow properties [1]. Particle-size distribution is also a key factor in determining the flow properties of chocolate [2, 3]. We can control the rheology of the molten chocolate by changing the content or size of sugar, however there is a limit changing the sugar content. Another method to control the rheology of the molten chocolate is adding emulsifiers. If small amounts of certain emulsifiers are added to chocolate, they change the rheological properties. For example, lecithin is widely used in modern chocolate confectionery. Adding lecithin dramatically changes the rheological properties of chocolate by reducing its viscosity [5, 6]. Polyglycerol polyricinoleate (PGPR) is another ingredient that is used; it does not have a large effect on viscosity, but it reduces yield stress [5, 6]. These previous studies have shown that adding a surfactant to either real or modified chocolate affects its rheological properties. Moreover, the rheological properties of molten chocolate were estimated using the Casson equation, which is an orthodox style for studying chocolate rheology mentioned above. Such an orthodox method is quite useful to pre-

酪農学園大学農食環境学群食と健康学類食品物性学研究室
Food Physical Chemistry Lab, Department of Food Science and Wellness, College of Agriculture, Food, and Environment Science, Rakuno Gakuen University, Bunkyodai Midorimachi, Ebetsu, Hokkaido, 069-8501, Japan
Correspondance　E-mail: kaneda-i@rakuno.ac.jp　Tel/Fax: +81-11-388-4701

cisely estimate the flow property of the chocolate, however, to our regret; it can only show phenomenological result. In other words, it is impossible to understand the mechanism of changing viscosity by adding emulcifiers. Therefore, we attempted to construct a novel chocolate model system for the rheology study.

A serious problem in studying the rheology of chocolate is its complexity. Because the dispersants of chocolate have complex shapes and physicochemical surface properties, it is difficult to study the precise effects of the surfactants added during chocolate manufacturing. First of all, we attempt to simplify the chocolate. The main component of the solid dispersant (fine sugar particles) was replaced with spherical silica particles. Silica particles were chosen to represent sugar particles because spherical silica particles are easy to obtain and have similar surface properties (both surfaces have many hydroxyl groups). We expected that the rheological measurement data using such a simplified model chocolate can be analyzed by using a theoretical model for the viscosity of spherical hard colloid dispersion.

In addition, we studied the effect of an emulsifier on the flow property of the molten chocolate. We focused on sucrose fatty acid ester, which is a popular edible emulsifier. Since the HLB value of the emulsifier can be tuned in wide range, it is quite useful in food industry. Although the effect of lecithin or PGPR on the chocolate rheology is well understood, there are just few reports on sucrose fatty acid ester. Since the polar residue of the emulsifiers is sucrose, it is expected that the emulsifiers well absorb to the surface of sugar crystal in chocolate. Therefore, it is expected that the emulsifiers show a special effect on the flow property of molten chocolate. Moreover, we expected that a precise study by using the novel chocolate model, which is added an emulsifier, would help for well understanding the mechanism of alternation for flow property by adding an emulsifier. We studied the effect of a sucrose erucic acid ester in the model chocolate system, as adding agent for molten chocolate, confirmed the validity of the model chocolate by studying the effects of emulsifiers on the flow properties of the model chocolate.

2. Materials and Methods

2.1 Materials

Cocoa butter (Nisshin Kako Co. Ltd., Osaka, Japan), soy lecithin (SLP-Paste; TSUJI SEIYU Co. Ltd., Mie, Japan), PGPR (CR-500; SAKAMOTO YAKUHIN KOGYO Co. Ltd., Osaka, Japan) and sucrose erucic acid ester (ER-290; Mitsubishi Kagaku Foods Co. Ltd., Tokyo, Japan) were purchased and used without further purification. For fine silica particles, EXCELICA (Tokuyama Co. Ltd., Yamaguchi, Japan) was used. The average diameter and specific surface area of the silica particles were 10.6 μm and 1.9 m^2/g, respectively.

2.2 Model chocolate

The model chocolate was prepared as follows: cocoa butter and silica particles were mixed with a hand mixer at 50 ℃. The volume fraction of the silica particles in the model chocolate was calculated according to Eq. 1:

$$\phi = \frac{w_s(1/\rho_s)}{w_{cb}(1/\rho_{cb}) + w_s(1/\rho_s)}, \tag{1}$$

where w_s and ρ_s are the weight and density of silica particles, and w_{cb} and ρ_{cb} are the weight and density of cocoa butter, respectively. The density of cocoa butter was measured using a pycnometer at 50 ℃. In the case of silica particle, the density was determined by dispersion in methanol. Since the density of methanol is easily obtained, we can calculate the density of silica particles from the result of the dispersion. The density values were as follows: cocoa butter, 820 kg/m^3 and silica particles, 8120 kg/m^3. The model chocolate was prepared and contained various amounts of silica particles ranging from $\phi = 0.3$ to 0.55. The model chocolate was also prepared using an emulsifier to study its effect. The emulsifier was added to molten cocoa butter, followed by the addition of silica particles. The concentration of each emulsifier was 0.5 wt%. Since this value was relatively low, the change in density by the addition of the emulsifier was neglected.

2.3 Rheology measurement

The steady-state viscosity was measured using an ARES rheometer (TA instruments, USA) equipped with a water bath temperature control system. A parallel plate fixture was used (diameter: 25 mm, gap: 1 mm). The measurement was performed at 50 ℃. The time development of the shear stress under constant shear flow, from 0.05 to 200 s^{-1}, was measured and followed by the preshear procedure (at 100 s^{-1}, 30 s). Then, the steady-state viscosity was obtained using a steady value of shear stress.

2.4 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to check the sharpness of the silica particles. The specimen for SEM observation was prepared using the following method. A carbon sticky tape was placed on the specimen stage. Then a small amount of EXCELICA was applied. The excess material on the carbon sticky tape was blown off, and then the sample was coated with a Pt-Pb thin layer. The specimen was then observed by SEM (S-2460; Hitachi, Tokyo, Japan).

3. Results and Discussion

3.1 Flow properties of model chocolate

The SEM image of the silica particles used in the model chocolate is shown in Fig. 1. Although particle-size distribution is recognized, the particles appear to be spherical.

The flow curves of the molten cocoa butter and silica/cocoa butter dispersions are shown in Fig. 2. The flow curves of the dispersions follow flow behavior typically seen for condensed colloid dispersions; namely, viscosity increases with the volume fraction, and two plateaus appear at the low and high shear rate regions. On the contrary, the molten cocoa butter appears to have an almost Newtonian flow.

Since spherical particles were used instead of sugar particles, the flow properties can be analyzed using a suitable theoretical model. In general, the viscosity of a colloid dispersion is governed by Einstein's law:

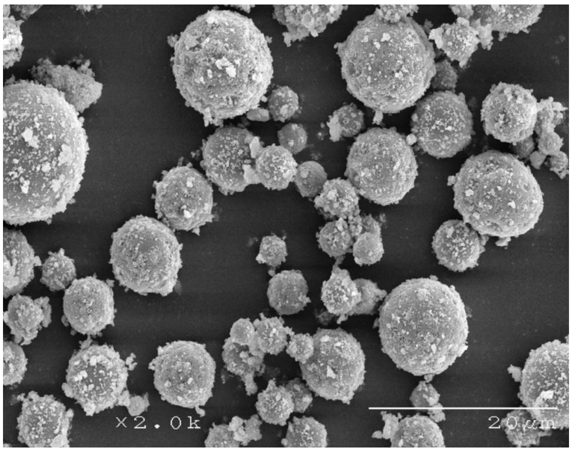

Fig. 1 Scanning electron microscopic image of silica particles used in the model chocolate.

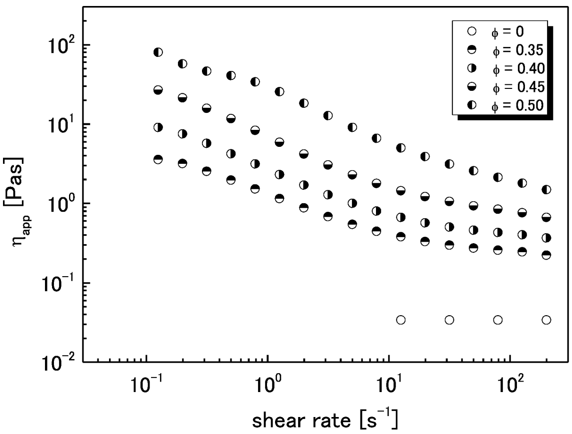

Fig. 2 Flow curves of the model chocolate with various volume fractions of silica particles at 50 ℃. ϕ denotes the volume fraction of silica particles in the system, where $\phi = 0$ denotes molten cocoa butter.

$$\frac{\eta}{\eta_s} = 1 + k\phi \quad (2)$$

where η is viscosity of the suspension, η_s is the viscosity of the continuous phase, ϕ is the volume fraction of the colloid particles, and k is the Einstein coefficient, which equals 2.5 for non-interacting particles of spherical shape. The volume fraction dependence of the low and high shear rate limiting relative viscosities is well described by Krieger-Dougherty.

$$\frac{\eta}{\eta_r} = \left(1 + \frac{\phi}{\phi_m}\right)^{-k\phi_m}, \quad (3)$$

where ϕ_m is the maximum packing volume fraction, depends on the physical characteristics of the particles, the particles size distribution, and the suspension structure. In particular, the most important factor affecting the ϕ_m of highly concentrated suspensions is particles size distribution. Because smaller particles can fit into the voids of bigger ones, ϕ_m increases gradually from mono-dispersed particle system to poly-dispersed particles systems. In this study, since we used spherical silica particle instead of sugar particle, we can assume that the Einstein coefficient, which is the shape factor of the particle would show the information of the aggregation behavior for the particles under the shear flow. Therefore, if we make the value of k fitting parameter, we can understand the situation of the dispersity of the particle system, which would be a hint for the thinking of the effects of emulsifiers on the molten model chocolate flow properties in the micro-scopic aspect.

To analyze the flow data using Eq. 3, the characteristic viscosity value has to be obtained. As shown in Fig. 2, the flow curve of the model chocolate follows a non-Newtonian behavior. In general, the flow curve of a colloid dispersion exhibits the first Newtonian plateau at a low shear rate. This is followed by the power-law shear-thinning region, which then flattens into the second Newtonian plateau [8]. If we analyze the flow curves using Eq. 3, we have to obtain the Newtonian viscosity at the low or high shear rate. As you can see in Fig. 2, it was difficult to precisely detect the plateau region in the experimental results. In particular, it is quite difficult to determine the Newtonian viscosity at low shear rate region due to pseudo plastic flow like behavior. Therefore, we assume that the apparent viscosity at $125\ s^{-1}$ is considered to be the Newtonian viscosity at the high shear rate in this study. Then the relative viscosity was obtained by normalizing the viscosity of the medium, molten cocoa butter.

Fig. 3 shows the volume fraction dependency of the relative viscosity at a high shear rate. The line in Fig. 3 shows the analysis results using Eq. 3. Since ϕ_m and k are unknown parameters in Eq. 3, they were estimated by the nonlinear least squares method using experimental data. The experimental data agreed with the fitting line (square of the correlation coefficient, $R^2 = 0.992$). The fitting parameters, ϕ_m and k, were 0.672 and 4.26, respectively. The value of ϕ_m exceeded the limit for random close packing (ca. 0.63–0.64) [9]. Since the silica particles used in this study have a relatively wide size distribution (Fig. 1), the particles can be more compactly packed than the ideal limit.

3.2 Effect of emulsifiers on the flow properties of the model chocolate

As previously mentioned, the tuning of molten chocolate is an important issue in chocolate con-

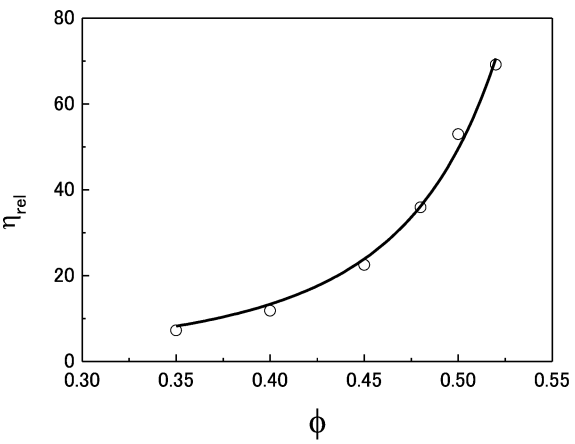

Fig. 3 Volume fraction dependence of relative viscosity of the model chocolate without emulsifier at a high shear rate ($125\ s^{-1}$). The line denotes the prediction based on the Krieger-Dougherty equation (Eq. 3)

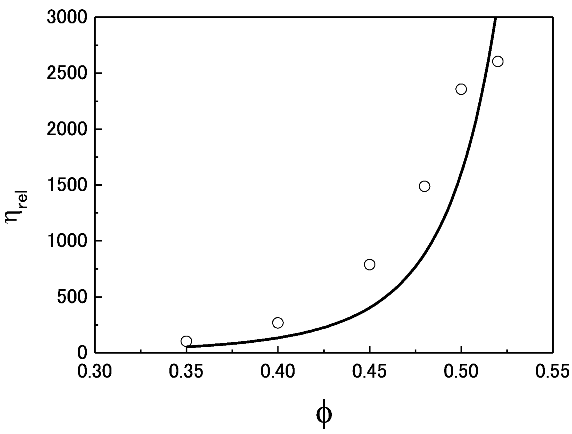

Fig. 4 Volume fraction dependence of relative viscosity for the model chocolate without emulsifier at a low shear rate ($1.25\ s^{-1}$). The line denotes the prediction based on the Krieger-Dougherty equation (Eq. 3)

fectionary. Although there is significant empirical knowledge in this field, the detailed mechanism of an emulsifier's influence when added to molten chocolate is not well understood because of the chocolate complexity. This study attempts to determine the mechanism using a model chocolate. First, the viscosity reduction effects of lecithin and PGPR were studied.

Fig. 5 shows the flow curves of the model chocolate, which had a silica-particle volume fraction of 0.5 and contained an emulsifier. The flow curve of the sample containing lecithin (triangles in Fig. 5) had a pattern similar to the control curve without emulsifier (circles in Fig. 5). However, the viscosity decreased over the range of the shear rate. On the contrary, the flow curve of the sample containing PGPR (squares in Fig. 5) has Newtonian-like behavior. The effect of

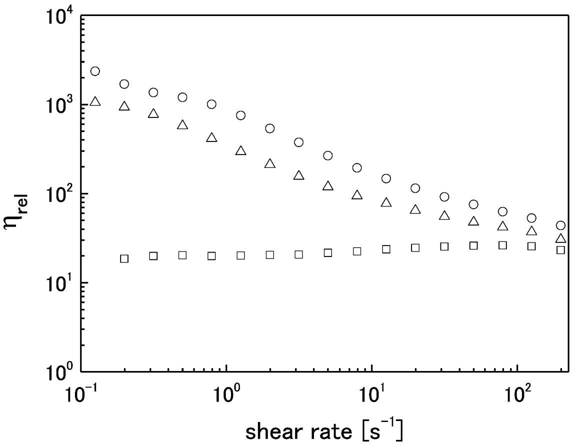

Fig. 5 Flow curves of the model chocolate ($\phi=0.5$). Circles denote the results of the control (no emulsifier), triangles and squares denote the results of samples containing lecithin and PGPR, respectively. The concentrations of lecithin and PGPR were 0.5 wt%.

emulsifiers at low and high shear rate is quantitatively shown in Figs. 6a and 6b. As mentioned above, both lecithin and PGPR have been reported to reduce molten chocolate viscosity; in particular, PGPR also reduces the yield value. The experimental results obtained using the model chocolate successfully reproduced the phenomenon observed in real chocolate.

The effect of emulsifiers on k in the model chocolate was also studied. As discussed in Section 3.1, the main focus was on the viscosity at a high shear rate (125 s^{-1}).

Figs. 7 and 8 show the volume fraction dependence of the relative viscosity at a high shear rate for the sample containing 0.5 wt% lecithin and PGPR, respectively. The lines in Figs. 7 and 8 show the analysis results using Eq. 3. In this case, ϕ_m was fixed at 0.672, which was obtained from the control sample results without emulsifier, since it was expected that adding a small amount of emulsifier would not influence the maximum close packing limit. Moreover, the effect of emulsifiers on k can be directly compared. The values of k and R^2 are listed in Table 1. The values of k are reduced upon the addition of emulsifiers. The apparent viscosity of the model chocolate was also reduced when the emulsifier was added. The apparent viscosity, particularly under high shear rate flow, was obviously influenced by k. The reduction of k may mean that the aspect ratio of the dispersant approached, but did not reach, 1. Such an effect may be caused by the improvisation of dispersibility upon the addition of emulsifiers.

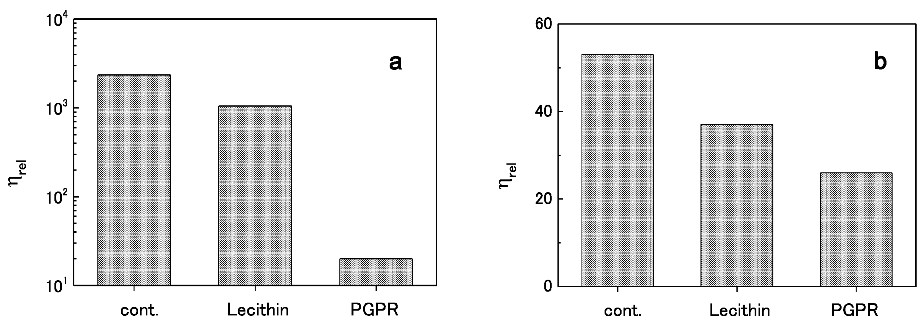

Fig. 6 Effect of emulsifiers on relative viscosity at 0.125 s^{-1} (a) and 125 s^{-1} (b) for the model chocolate. The concentration of both lecithin and PGPR was 0.5 wt%.

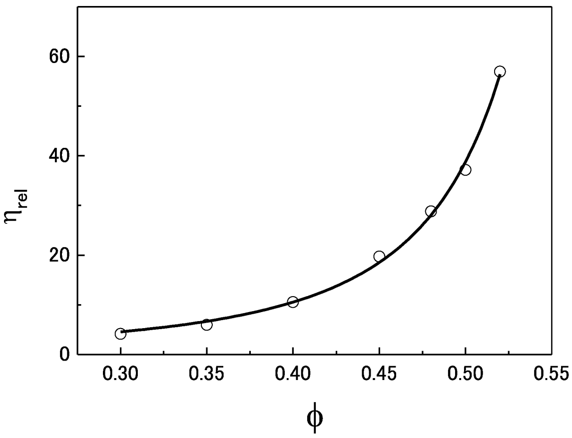

Fig. 7 Volume fraction dependence of relative viscosity for the model chocolate containing lecithin (0.5 wt%) at a high shear rate (125 s^{-1}). The line denotes the prediction of the Krieger-Dougherty equation (Eq. 3).

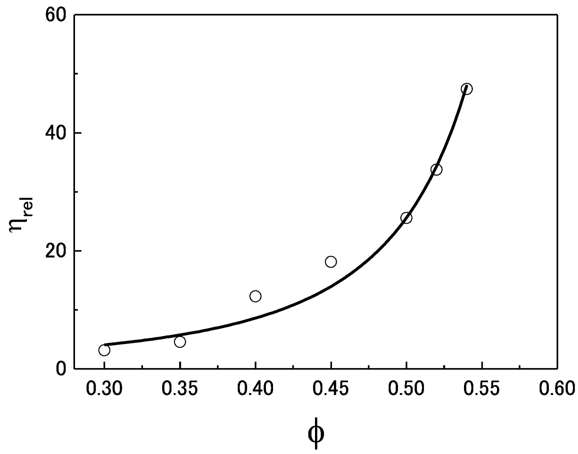

Fig. 8 Volume fraction dependence of relative viscosity for the model chocolate containing PGPR (0.5 wt%) at a high shear rate (125 s^{-1}). The line denotes the prediction of the Krieger-Dougherty equation (Eq. 3)

Table 1 Values predicted by the Krieger-Dougherty equation (Eq. 5)

sample		$^{*}\phi_m$	k	R^2
Cont.	Low shear	0.672	8.06	0.754
	High shear	0.672	4.26	0.992
	**lecithin	0.672	4.01	0.994
	**PGPR	0.672	3.97	0.978

* The value of the maximum packing volume fraction was fixed at 0.672, a value obtained from the analysis of the control sample (at high shear rate, 125 s^{-1})
**The emulsifier concentrations were 0.5 wt%.

3.3 Effect of sugar ester on the flow properties of the model chocolate

Since we have confirmed the effect of lecithin and PGRP, which are quite popular additives for chocolate confectionary, we attempted to study the effect of sucrose fatty acid esters (SEs). SEs are also quite popular emulsifiers in food industry, however they has never often applied in the chocolate confectionary. It is quite useful to obtain the experimental data of SE on the molten chocolate. We used a sucrose ercaic acid ester (ER-290) since this type of ester has low HLB value. The viscosity reduction effect of ER-290 for the samples containing the silica particles in various volume fractions is shown in Fig. 9. The viscosity reduction effect was more significant in the high volume fraction sample. These results suggest that the viscosity reduction effect of ER-290 is due to the change in the surface property of the silica particles, because the mechanical friction between the particles may influence the bulk viscosity of the high volume fraction samples. On the basis of these results, we would expect ER-290 to be absorbed on the surfaces of the silica particles.

To check the dispersibility of the silica particles in the model chocolate, we estimated the intrinsic viscosity of the silica particles. Changing the concentration of ER-290 in the model chocolate (Fig. 10) clearly showed that intrinsic viscosity reduced with increasing surfactant concentration. In particular, the concentration dependency of the intrinsic viscosity reduction effect is quite interesting. As shown in Fig. 9, the apparent viscosity reduction effect was saturated at around 1 wt% of ER-290. On the other hand, the intrinsic viscosity reduction effect was also saturated at the same concentration region. These results mean that the dispersibility of the dispersant is strongly links to the bulk rheology for the molten chocolate.

4. Conclusion

In this study, we proposed a novel model chocolate system. Although the reorganization of the flow properties of molten chocolate is an important issue, it has been difficult to analyze because of the complexity of real chocolate. We considered chocolate to be a condensed solid/liquid dispersion and attempted to substitute the sugar

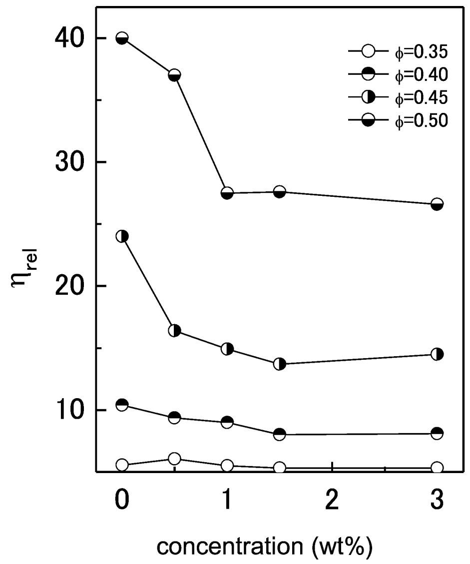

Fig. 9 The relative viscosity for the model chocolate with various volume fractions of silica particles containing ER-290. ϕ denotes the volume fraction of silica particles in the system. The viscosities were measured at 125 s^{-1} and 50 ℃.

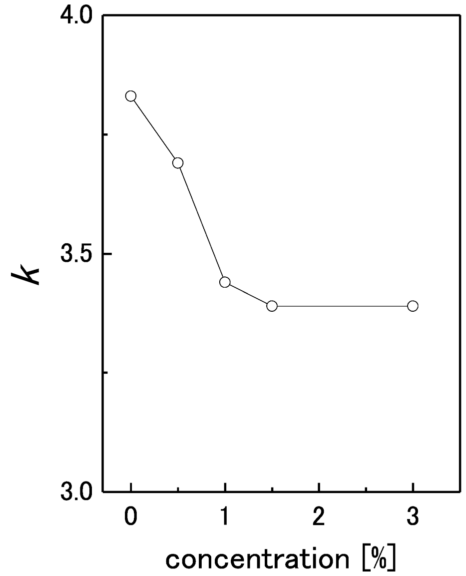

Fig. 10 The Einstein coefficient for the model chocolate containing various concentrations of ER-290.

particles, which is main dispersant in real chocolate, with the spherical silica particles. The surface of the silica particles appeared like sugar in terms of physical chemistry because there are plenty hydroxyl groups on both surfaces. Moreover, it is rather easy to obtain spherical silica particles. Here the dispersant shape is quite essential because several theories concerning the flow properties of colloid dispersions can be utilized and quantitative estimations can be made using spheres. The Einstein coefficient of silica particles in the model chocolate was successfully estimated using the Krieger-Dougherty equation. The effect of emulsifiers, generally used for chocolate confectionery, was studied using k. Moreover, we also studied the effect of sugar fatty acid ester (ER-290) on the flow property and k. Finally, we revealed that k was strongly linked to the bulk rheology for the molten chocolate. This novel model chocolate is expected to be useful for quantitative estimation of food additives for the modification of molten chocolate flow properties.

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Abstract

In this study, we constructed a model chocolate, comprising fine spherical silica particles and cocoa butter, to study the rheological properties of molten chocolate. By using spherical silica dispersants to represent sugar, the flow properties of the model chocolate were quantitatively analyzed using a theoretical model. The Einstein coefficient, which is a shape factor for colloid particle, of silica particles in the model chocolate was successfully estimated by the Krieger-Dougherty equation. The effects of typical food emulsifiers, namely soy lecithin, polyglycerol polyricinoleate, and sucrose erucic acid which are used in chocolate confectionery, were studied. The effects of these emulsifiers have been previously confirmed in studies with real chocolate. The results showed that the model chocolate is a useful tool to study molten chocolate rheology for application in the chocolate manufacturing process.

Keywords: chocolate, flow property, emulsifier, silica particle

要　　約

球状のシリカ微粒子をココアバターからなるモデルチョコレートを構築し，それを用いて溶融状態の流動特性を詳細に研究した。不定形な砂糖微粒子を球状シリカ微粒子に置換することで流動特性を理論式で解析することが可能になった。具体的には濃厚コロイド分散液の流動挙動を記述する *Krieger-Dougherty* 式を用いて粒子の形状因子であるアインシュタイン係数を実験的に決定し，シリカ微粒子の分散状態を考察した。チョコレート加工に汎用される大豆レシチン，ポリグリセリン脂肪酸エステルおよびショ糖脂肪酸エステルをこのモデルチョコレートに配合し，これらの流動特性に対する影響を調べた。大豆レシチンは溶融チョコレートの降伏応力には影響を及ぼさず，高ずり速度下の粘度を低下させること，またポリグリセリン脂肪酸エステルは降伏応力を低下させる効果があることが知られているが，本モデルチョコレートでもこれらの効果が再現され，球状シリカ微粒子を配合したモデルチョコレートが溶融チョコレートの流動特性に関する研究に適用可能であることが確認された。また従来あまりチョコレートには配合されていなかったショ糖脂肪酸エステルは大豆レシチンと類似した効果があることが確認された。溶融チョコレートの流動特性の解析は工業的にもきわめて重要な課題であるが，実際のチョコレートが複雑な混合物であるために経験的あるいは現象論的な理解に留まっていたが，本研究で構築されたモデルチョコレートはチョコレート加工において重要な添加物である乳化剤の効果を定量的に評価するための強力なツールになると期待される。