Particle layer formation of gelled clay particle dispersions during drying

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Introduction

Particle dispersions are frequently used in the coating and drying processes. In the case of low particle concentration or weakly interacted particles, the effect of particles on the rheological properties of suspension is small and just increases viscosity. If the dispersing medium has a constant viscosity, the suspension will be still Newtonian. However, highly concentrated suspension frequently shows non-Newtonian rheological behavior including shear-thinning, yielding or jamming, and sometimes viscoelasticity. Since such complex behaviors are related to particle aggregation or particle networking, the internal structure of particles generated will change depending on the shear history the suspension experienced.

The conversion process from highly concentrated suspension becomes popular in the coating industries, such as battery electrode and conductive film. The internal structure of particles after drying is required to be controlled, and is considered to be largely determined by drying conditions. However, since particle will just form aggregates in the drying process, the initial status of particle aggregates must be controlled by coating process, which is the last process where shear applied to suspension. In this study, we have chosen shear-sensitive material as a coating suspension and investigated the effect of shear strain in the coating process on the drying or particle layer formation process. We have also proposed experimental procedures for elucidating the status of particle packing and ordering during drying.

Experiment

Materials

The suspension we have investigated in the present study is composed of clay particles (organically modified bentonite particles), activator (Polyether-modified silicones), and volatile silicone oil (Decamethylcyclopentasiloxane). The clay particles are frequently used as an organogelator in order to control rheological properties of cosmetics, because they form loosely-connected networks [1, 2, 3]. Clay particle has a plate-like shape with equivalent diameter of approximately 0.5 μm and formed aggregates with the size of 5 μm in the dispersing medium. The rheological behavior is significantly depends on the composition. The concentration of activator is required to be almost the same with clay particle in order to show viscoelastic behavior.

The elasticity of clay suspension can be controlled by particle concentration. Dilute suspension shows too less viscous to keep suspension as a coating, and concentrated suspension is rarely spread over the substrate when coating. The composition thus used in this study is 6wt% of clay particles, 6wt% of activator and 88wt% of silicone oil. The volume fraction of clay particles is 3.6vol%. Since only silicone oil evaporates with the latent heat of evaporation: 57.8 kJ/kg, the film obtained after drying is composed of clay particles, activator and, in some case, pore.

The rheological behavior of the clay suspension has been measured using a stress-controlled rheometer. Fig.1 shows viscoelastic behavior of the suspension. The storage modulus *G*' is sufficiently larger than loss modulus *G*'' and shows little effect of frequency, which are characteristic behavior of gel-like materials. Drastic decrease in *G*' with the increase in strain applied indicates the destruction of internal structure. Fig.2 shows the stress response of the clay suspension with an exponential increase in shear strain. In a smaller strain regime, shear stress increases in proportional to applied strain, showing an elastic or a solid-like response of gel-like material. As increasing shear strain, shear stress is deviates from the elastic response and then shows notable decrease. This suggests the first yielding behavior or the start of internal structure deformation. As increasing strain further, the stress shows second gradual decrease, probably corresponding to the complete destruction of gelled network structure of clay particles.

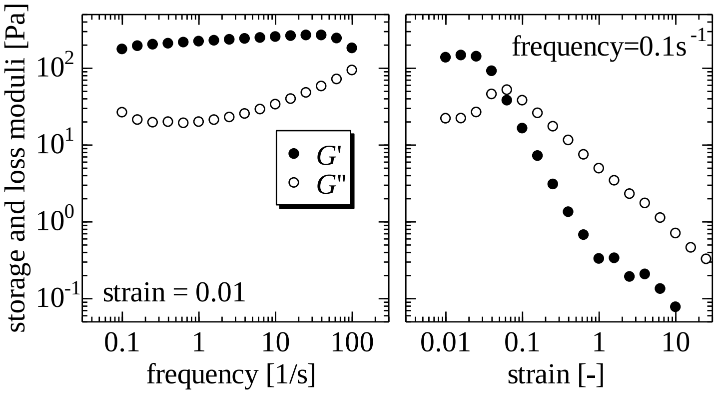


Fig.1 Viscoelastic behavior of gelled clay particle dispersion

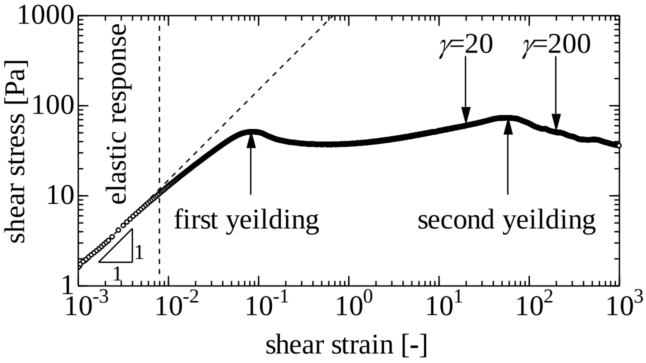


Fig.2 Yielding behavior of gelled clay dispersion with exponential increase in strain

Experimental setup

Experimental setup for coating, drying and evaluating the drying process of clay suspension is shown in Fig.3. The experimental setup is composed of moving stage, heating plate and laser displacement sensor. A glass plate (100mm x 200mm) is fixed onto the heating plate and heated from the bottom at 40ºC. A doctor blade is placed onto the glass plate and is slid over the plate by moving the electrical controlled stage below. Therefore, suspension placed onto the glass plate and in front of the doctor blade is spread over the plate. In the present study, we have used two doctor blade having different coating length of 2 and 20 mm and a constant coating gap of 100 μm. Therefore, the shear strain applied is 20 and 200 in this experiment. The shear rate applied is $100s^{-1}$ because the electrical controlled stage moved at the speed of 10 mm/s. All experiment and measurements have been carried out in the chamber where temperature and humidity controlled air was supplied.

During drying, we have performed two measurements. One is the thickness variation of suspension coating[4)], and the other is the observation of scattering pattern[5, 6)] at the surface of the coating. With the help of the electrical controlled stage, both measurement have carried out at the exactly same position in the coating. Thickness decrease was measured using a laser displacement sensor with the spatial resolution of 10 nm, and the final thickness was evaluated by the comparison of surface profiles of the glass plate and the dried coatings. From the thickness decrease change and final film thickness, we obtained thickness variation during drying. A red semiconductor laser beam was irradiated on to the suspension coating at the angle of 45º and scattered ray was projected on a while paper aligned normal to the coating. The projected image of scattering pattern was observed and recorded using USB camera.

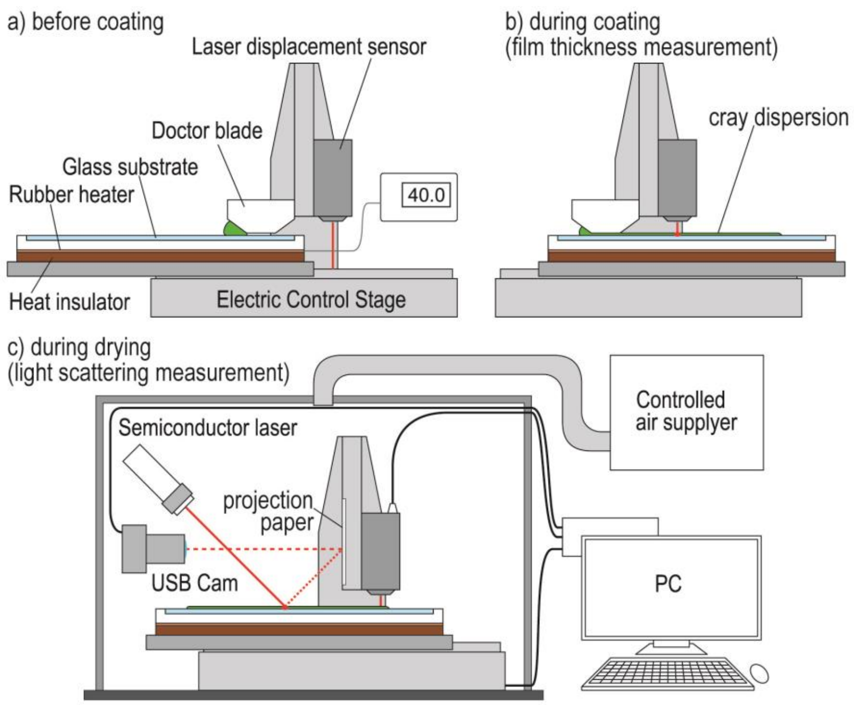


Fig.3 Experimental setup for coating and drying of clay dispersion

We have also demonstrated simultaneous measurement of film thickness decrease and film weight loss. Owing to the capacity of the electrical balance, we have prepared another light-weight heating plate placed. We also have prepared a smaller glass plate (50mm x 70mm), and then coated suspension all over the glass plate using a commercial desktop coater. The assembly of the suspension coated glass plate and the light-weight plate heater (40ºC) was placed onto an electrical balance below the displacement sensor. Weight loss and thickness decrease are measured continuously during drying in the temperature and humidity controlled chamber.

Results and Discussion

Effect of liquid phase composition on drying rate

First of all, we have measured the thickness decrease of the mixture of silicone oil and activator in order to confirm the effect of activator on the drying rate of silicone oil. A couple of mixtures with different initial composition is poured into a shallow bath on the glass plate heated at 40ºC and the position of the liquid surface was measured continuously. In spite of the increase in activator concentration with drying, the thickness decreased at a constant rate. Therefore, we have concluded silicone oil will dry at a constant rate with no effect of activator.

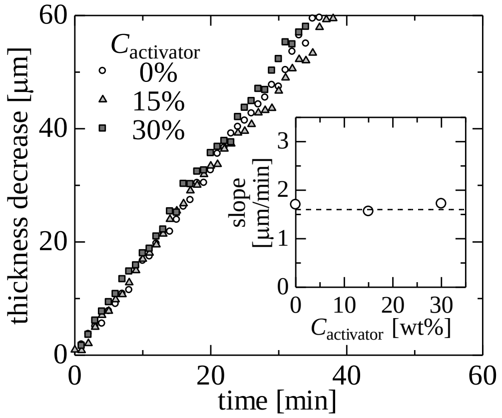


Fig.4 Effect of activator concentration on drying rate of silicone oil

Thickness decrease and weight loss

Gravimetric analysis is a popular measurement for characterizing the drying process of coating. However, in the case of drying process of coating of highly aggregated or concentrated particle suspension, the coating thickness frequently attains constant even though coating weight is still in decreasing or solvent keeps evaporating. The different behavior between thickness decrease and weight loss suggests the formation of porous structure within a particle packed layer. Although surface temperature change is useful for detecting drying rate change or calculating drying rate, the clay suspension coating showed roughly constant temperature throughout drying probably because of small latent heat of evaporation of silicone oil and relatively slow drying rate.

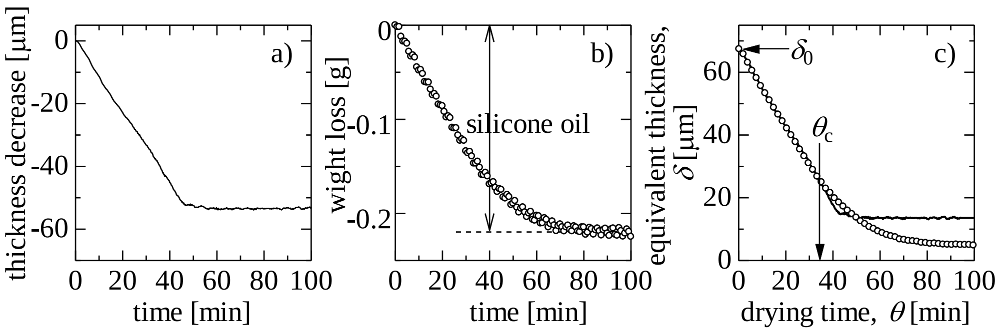


Fig.5 Weight loss and thickness decrease of coated clay dispersion during drying

The result of simultaneous measurements of weight loss and film thickness is shown in Fig.5. As described above, coating thickness was not decreased anymore after 40min, though coating weight continue decreasing until 80min. Constant weight loss after 80min indicates the end of evaporation and corresponds to the amount of silicone oil evaporated. Then, initial weight and thickness of clay suspension coating on the small glass plate can be estimated from the amount of evaporated silicone oil and the initial composition. Finally, we have obtained the variation of actual film thickness and equivalent film thickness with no pore as shown in Fig.5c. In the early stage of drying, both equivalent film thickness show good agreement with a constant slope, suggesting clay suspension was dried uniformly at a constant drying rate. After a while, the film thickness continues decreasing keeping the constant drying rate and shortly attains constant value, although the decreasing rate of the equivalent thickness became gradually small. The slope change in equivalent thickness indicates the transition from a constant drying rate period to a falling drying rate period, denoted by the drying time $\theta = \theta_c$. Initial film thickness was denoted by δ_0 as well.

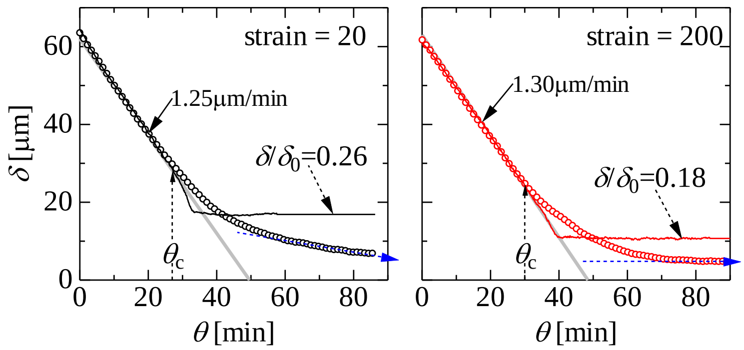


Fig.6 Effect of strain on the variation of equivalent film thickness

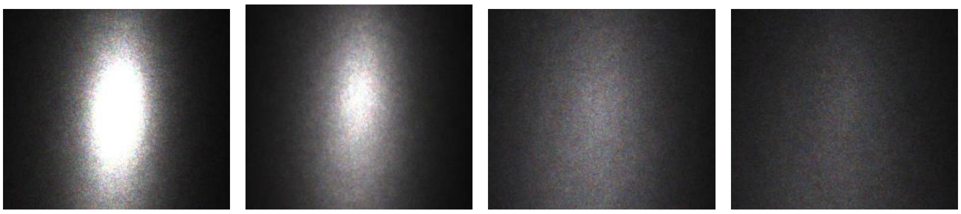
Fig.6 shows the effect of applied shear strain on the drying process of clay suspension. The slope in the constant drying rate period was almost the same regardless of applied shear strain. This result is reasonable because clay particles are suspended in a sufficient amount of liquid phase and have small effect on evaporation of silicone oil. Thus, the slope is also roughly same with that in Fig.4. Two significant difference can be seen in a falling drying rate period. One is the terminated film thickness and the other is the slope of equivalent film thickness decrease.

Considering the initial composition, clay suspension can shrink by more than 90vol% accompanied by the evaporation of silicone oil, but actually shrunk by roughly 80vol%. This fact supports the formation of porous clay particle layer at the end of drying and a portion of void space is filled with activator. Therefore, smaller δ/δ_0 at the large strain condition indicates the formation of more tightly packed particle layer. At the smaller strain condition, loosely packed particle layer contains much amount of silicone oil and has small effect on drying rate reduction. As a result, the falling drying rate period lasted long if loosely connected networks remains before drying.

<u>Scattering pattern analysis</u>

A laser beam irradiated to a suspension coating is scattered and makes scattering pattern on the projected paper. Since the intensity of laser beam sharply distributed as Gaussian function, the scattering pattern becomes a bright spot with sharp decay of brightness as long as sufficiently flat surface (reflection). However, the laser beam scattered on a rough surface generates broad distribution in brightness (scattering). In actual case, we will observed the superposition image of reflection and scattering, and the ratio of these component will change as drying proceed as are shown in Fig.7a. That is to say, in the early stage of drying, the brightness distribution is dominated by reflection because the coating surface is largely occupied by liquid phase and clay particles lie over the liquid surface. However, as drying proceeds, the bright spot disappear and smaller brightness distributes broadly because of scattering at the surface of randomly packed particle layer. Then, we have calculated span-wise distribution of brightness by averaging brightness distribution in each pixel row. If the maximum brightness in a pixel row is saturated or more than 250 in 8bit grayscale, the row is omitted in averaging brightness.

a) Projection image of scattering pattern



b) Brightness distribution and Gaussian fitting

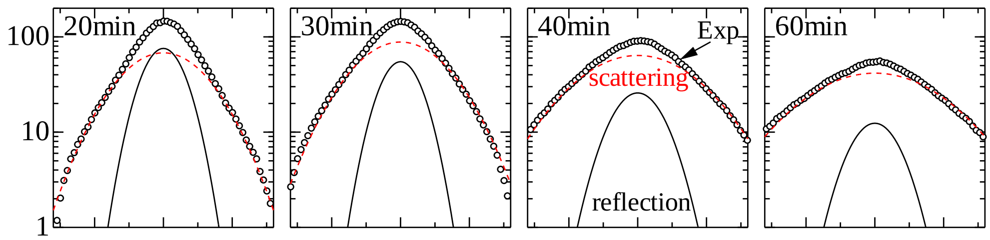


Fig.7 Projection image of scattered laser beam and brightness distribution fitted by the superposition of two Gausian functions (strain = 200)

As can be seen in Fig.7b, the brightness distributions were reasonably fitted by the superposition of two Gaussian functions having different intensity I and standard deviation σ expressed by Eq. (1). The Gaussian function with smaller standard deviation corresponds to reflection component, and that with larger standard deviation to scattering component. It was found reflection component shows relatively small change in distribution after 20min and scattering component becomes more widely distributed as drying proceeds.

$$I = I_{\mathrm{refl}} \exp\left(-\frac{x^2}{\sigma_{\mathrm{refl}}{}^2}\right) + I_{\mathrm{scat}} \exp\left(-\frac{x^2}{\sigma_{\mathrm{scat}}{}^2}\right) \quad (1)$$

Fig.8 shows the effect of strain on the variations of characteristic parameters of reflection and scattering components during drying. Since too bright pixel rows are omitted in calculating brightness distribution, intensity apparently increase with drying. Additionally, the brightness of the image is also affected by camera and light configurations. However, the relative intensity of scattering component to reflection one must not change by calculating procedure and exposure conditions, and plays sufficient role on discussing the dominant component of scattering pattern. On the contrary, scattering is caused by surface roughness or packing status of clay particles. That is to say, standard deviation of scattering component keep small when plate-like clay particles are placed flattened, and random packing particle layer will give widely distributed scattering component with large standard deviation. The standard deviation of reflection component also increased gradually, but the mechanism have not yet been clearly specified.

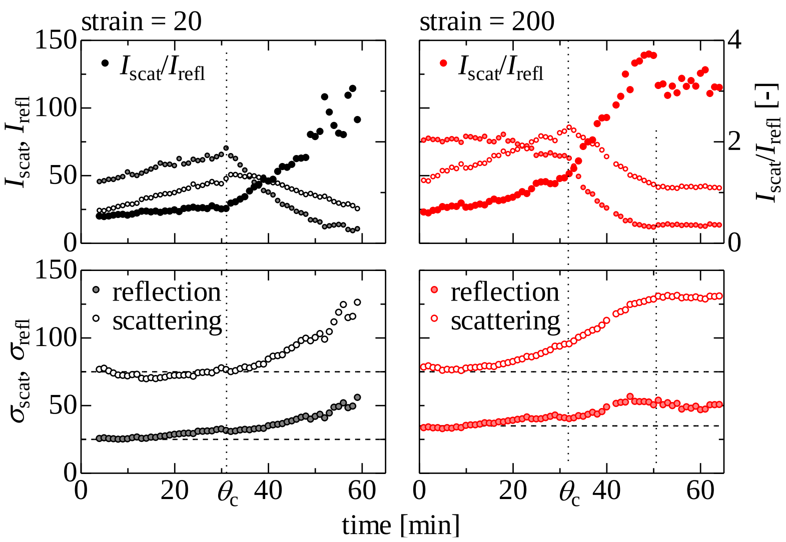


Fig.8 Variations of intensity and standard deviation of reflection and scattering components.

We thus discuss the variation of intensity ratio and standard deviation of scattering component in Fig.8. Sufficiently dispersed clay suspension with a larger strain coating process showed gradual increase in both intensity ratio and standard deviation of scattering component even in the constant drying rate period. Although both parameters continued increasing in the falling drying rate period, they each attained steady in a short time. Therefore, the packing process of well dispersed particles has already been started in the constant drying rate period and scattering intensity became dominant factor suggested from intensity ratio larger than unity. On the contrary, in the case of smaller strain, both intensity ratio and standard deviation were not increased in the constant drying rate period, and then increased rapidly in the following falling drying rate period even though the coating thickness was not decreased anymore. Therefore, in the constant drying rate period, no significant structural formation have taken place at least at the surface of coating, probably because of the existence of loosely connected particle networks. During this period, clay particles are gradually packed keeping the loosely connected network and the intensity ratio smaller than unity indicates reflection is still dominant in the scattering pattern. In the falling drying rate period, structural change lasted long similar to the variation of weight loss. Remember that the morphological changes have occurred with no change in coating thickness. In other words, after the formation of loosely packed particle layer with relatively flat surface, the ordering of clay particles changed depending on the status of particle network before drying.

Conclusion

In the present study, we have investigated the effect of strain applied in the coating process on the particle layer formation process during drying. For this purpose, we have chosen gelled clay dispersion as a coating material because loosely connected network structure is broken up depending on the strain applied. At a large strain condition or clay particles are dispersed before drying, it was found particles are randomly assigned even in a constant drying rate period and finally produced tightly packed layer. On the other hand, since loosely connected network structure of clay particles is remained with a smaller strain applied, no significant structural change was observed in the constant drying rate period and drastic change in the status of particle packing without film shrinkage, resulting in a highly porous particle layer.

Reference

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