

Self-Assembly of Surface-Active Powder at the Interfaces of Selective Liquids. 2: Behavior of an Organic-Crystalline Powder

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Received August 18, 2003. In Final Form: September 17, 2003

A ternary system consisting of a surface-active organic-crystalline powder (fluorinated calcium *N*-lauroyl taurate powder), fluorinated oil (perfluoropolymethylisopropyl ether, PFPE), and silicone oil (dimethylpolysiloxane, DMS) has been studied to examine the self-assembling behavior of the powder. Mixed states of the ternary system were classified into eight regions: (i) network-structured state, (ii) O/F emulsion state (O/F emulsion means DMS-in-PFPE type emulsion), (iii) O/F emulsion state with excess PFPE and DMS phases, (iv) separated state, (v) powdery state, (vi) granular state, (vii) powder dispersion state with excess PFPE and DMS phases, and (viii) dispersion state of powder and PFPE. The separated state, in which a transparent DMS phase was separated from a milky white phase containing the powder and PFPE, was observed first in this system. The O/F emulsion was able to contain a larger amount of DMS oil than the ternary system having a spherical surface-active resin powder reported in our previous paper [*Langmuir* 2002, 18, 10163]. Shear-stress curve and contact angle measurements as well as theoretical analysis indicated that these interesting observations originated from the plate-type shape of the organic-crystalline powder and its characteristic network in the fluorinated oil.

Introduction

Amphiphilic molecules and polymers form stable supramolecular assemblies, such as micelles, microemulsions, and liquid crystals, in which their structure is dependent on thermodynamic or kinetic parameters.^{1,2} However, there are a few reports on surface-active powders producing self-assembling states. Pickering reported an emulsion stabilized with powder particles in 1907.³ Since then, some other solid-stabilized emulsion systems have been found.^{4–6} Some surface-active powders adsorb, align at a liquid–liquid interface, and form self-assembled structures in multicomponent systems. Because this type of emulsion is stable due to the adsorption of the particles on the interface, it has been applied to food or cosmetic products.^{5,7} In recent years, some scientists have focused on this type of emulsion as a template of functional composite materials. A microstructured hollow sphere and a ribosome-like nanocapsule were obtained through the

emulsion state.^{8–11} A “liquid marble”, being an aqueous liquid droplet covered with a hydrophobic powder, was prepared and behaved like a soft solid in air.¹²

Some organic-crystalline powders behave as a surface-active powder. The crystalline powders of triglyceride and fatty acid affect the taste and the quality of emulsion-type foods, that is, whipped cream and margarine, through the dispersed state of the inner phases of the emulsions.⁵ On the other hand, the powders are useful to stabilize emulsion-type cosmetics and to control the viscosity and the lubricity.¹³ However, the governing factors to control the behavior of these products are not well-known.

In our previous work, we studied the behavior of a spherical surface-active resin powder.¹⁴ In a mixture of the powder and two liquids, multiple structures such as O/F emulsion state (where O/F denotes an emulsion of silicone oil in fluorinated oil), network-structured state, and granular state were observed. The wettability of the powders with the fluorinated and silicone oils is the governing factor in the structure formation. However, these results for the resin powder should not be applied to the system having the organic-crystalline powder, because the shape and the surface composition of the powder are quite different from those of the spherical resin powder. Many organic-crystalline powders, such as zinc

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stearate and *N*-lauroyl-L-lysine, are plate-shaped since these molecules contain alkyl chains and assemble to form lamellar crystals.^{15–18} Moreover, they change the rheology of some nonaqueous liquids. The powders increase the viscosity of the suspensions, since the crystalline powders form network aggregates in the nonaqueous liquids.¹³

In the present study, we have focused on the fluorinated calcium *N*-lauroyl taurate powder, PF-5 CaLT, to characterize the self-assembled structure of the organic-crystalline powder (the nomenclature PF-5 denotes a powder treated with a 5 wt % solution of the fluorinated agent, diethanolamine salt of perfluoroalkyl phosphate). CaLT is a lamellar molecular-crystal with laminated layers of linear molecules.^{17,18} This powder is suitable for our purpose, because such a layered structure is typical for the organic-crystalline powders. This powder is expected to be useful as an ingredient of cosmetics or lubricants because of its high lubricity and high stability for thermolysis. The mixed state and the physicochemical properties of the ternary system consisting of PF-5 CaLT, fluorinated oil (perfluoropolymethylisopropyl ether, PFPE), and silicone oil (dimethylpolysiloxane, DMS) have been investigated. The characteristic behaviors and their mechanisms are studied by a shear-stress curve, contact angle measurements, and theoretical analysis.

Experimental Section

Materials. CaLT was synthesized by a method described in the literature.¹⁷ CaLT has a molecular structure of $C_{11}H_{23}CONH(CH_2)_2SO_3 \cdot 0.5Ca$, a specific gravity of 1.25 g cm^{-3} , and an average particle diameter of $8 \mu\text{m}$.¹⁷ PFPE and DMS were commercially available and were used as received. PFPE (FOMBLIN HC/04, Ausimont Co.) has a molecular structure of $CF_3-[(OCF(CF_3)-CF_2)_n-(OCF_2)_m]-OCF_3$ ($n/m=20/40$), a molecular weight of 1500, and a specific gravity of 1.79 g cm^{-3} . DMS (KF96A(6CS), Shin-estu Chemical Co., Ltd.) has a molecular structure of $(CH_3)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3$, a molecular weight of 900, and a specific gravity of 0.93 g cm^{-3} . A fluorinated powder treated with a fluorinated agent, diethanolamine salt of perfluoroalkyl phosphate, was purchased from Daito Kasei Co. The degree of surface modification was analyzed by contact angle measurements, an electron probe microanalyzer, and an X-ray photoelectron spectroscopy technique. The contact angle was measured for powder tablets with water, PFPE, and DMS.

Preparation and Characterization of the Ternary Mixtures. The powder and PFPE were mixed using a conditioning mixer (Thinky MX-201) at 2000 rpm for 3 min. After adding DMS, the mixture was restirred under the same conditions. The ternary mixtures thus obtained were transferred into screw-capped test tubes and placed in a thermostatic water bath at $298 \pm 1 \text{ K}$. The mixed states of the samples were observed with a Nikon OPTIPHOTO-2 optical microscope. Determination of the continuous and discrete phases of the mixtures was accomplished by observing the dispersibility of the mixture drop in either PFPE or DMS. PFPE-continuous (DMS-continuous) mixtures are easily dispersed in PFPE (DMS) and remain as drops in DMS (PFPE).

Separations of PFPE and/or DMS were observed within a few hours after preparation of the mixtures. The mixed states were rechecked 12 h after the preparation to produce the state diagram of the PF-5 CaLT/PFPE/DMS ternary system.

Measurements. The contact angle was measured by a CA-X contact angle measurement apparatus (Kyowa Interface Science Co.) 30 s after putting a DMS droplet on the powder/PFPE mixture. Viscosity measurements were carried out by an A & D vibro viscometer CVJ5000 at $298 \pm 1 \text{ K}$. The shear-stress curve, that is, strain–stress relations under constant shear rates, was measured with an RFS-II viscoelastic measuring apparatus

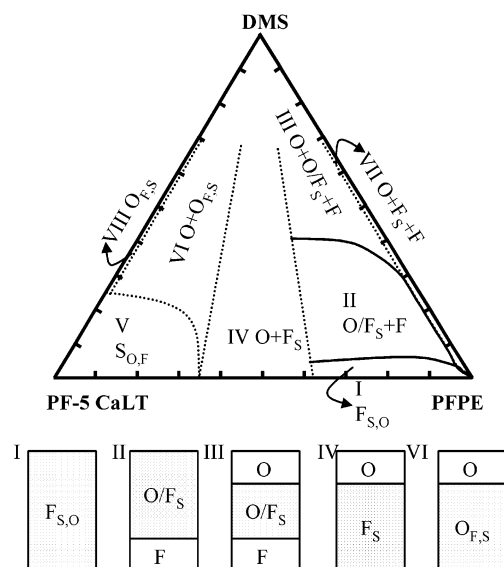


Figure 1. A mixed state diagram of the PF-5 CaLT powder/PFPE/DMS mixtures: region I, network-structured state; region II, O/F emulsion 1 state; region III, O/F emulsion 2 state; region IV, separated state; region V, powdery state; region VI, granular state; region VII, O + F_S + F; region VIII, O_{F,S}.

(Rheometrics Co.) using a cone–plate rotator (diameter, 25 mm; angle, 0.04 rad). The shear rate was in the range of $0.01–20 \text{ s}^{-1}$. Samples were allowed to stand for 30 min before each run of the measurements. The shear stress of Bingham plastics can be written as $\tau = \tau_B + \eta_B \dot{\gamma}$; where τ_B is the yield stress, η_B is the plastic viscosity, and $\dot{\gamma}$ is the shear rate. The yield stress τ_B is adopted as an index of strength of the network aggregate and is obtained by the extrapolation of the shear-stress curves.

Interpretation of Symbolism. In the diagram, S, F, and O denote the powder, PFPE, and DMS, respectively. F_S (O_S) indicates a state in which the powder particles were dispersed in PFPE (DMS). F_{S,O} (O_{F,S}) means that the powder and DMS (PFPE) were dispersed in PFPE (DMS). S_{O,F} means that the powder component absorbs PFPE and DMS oils in the spaces between the particles. O/F indicates a DMS-in-PFPE type emulsion. O/F_S + F indicates an emulsion with a separated phase of PFPE, and O + O/F_S + F an emulsion with two separated phases of DMS and PFPE. O + F_S indicates a dispersion with a separated phase of DMS, and O + F_S + F a dispersion with two separated phases of DMS and PFPE. O + O_{F,S} indicates a dispersion with a separated phase of DMS. The average volume fraction of DMS in the system is denoted as α ($\alpha = \text{DMS}/(\text{DMS} + \text{PFPE} + \text{powder})$). The volume fraction of the powder in the PFPE/powder mixture is denoted as β ($\beta = \text{powder}/(\text{PFPE} + \text{powder})$).

Results

The mixed states were mainly governed by the composition ratio of the powder and PFPE, β . The continuous phase was PFPE when $\beta < 0.4$ (Figure 1, I–III and VII), while that was DMS when $\beta > 0.65$ (Figure 1, VI and VIII). In the powdery state, the continuous phase was unclear, because the powder component contained both PFPE and DMS oils in the inside spaces among the particles (Figure 1, V). The separated state consisting of a milky PFPE phase (containing PF-5 CaLT particles) and a transparent DMS phase was observed for $\beta = 0.4–0.65$ (Figure 1, IV). The details of the mixed states are as follows:

(i) *Network-Structured State.* When $\alpha < 0.07$ and $\beta < 0.4$, the mixture was in the “network-structured state” (F_{S,O}) (Figure 1, I; Figure 2a). The effect of DMS content on the viscosity of the PF-5 CaLT/PFPE/DMS ternary system at $\beta = 0.26$ is shown in Figure 3. When β was

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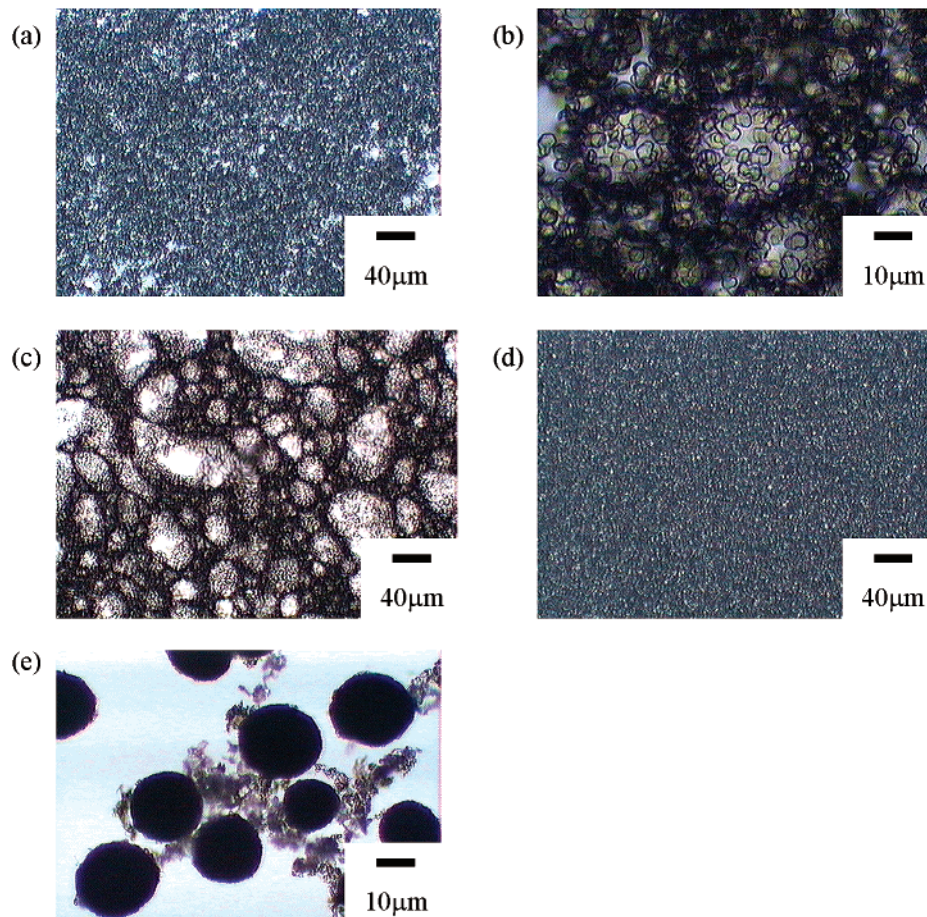


Figure 2. Optical microscopic photographs of the PF-5 CaLT powder/PFPE/DMS mixtures: (a) 26/72/2 (v/v/v), network-structured state ($F_{S,O}$, region I in Figure 1); (b) 19/54/27 (v/v/v), O/F emulsion 1 state ($O/F_S + F$, region II); (c) 10/27/63 (v/v/v), O/F emulsion 2 state ($O + O/F_S + F$, region III); (d) 42/44/14 (v/v/v), separated state (F_S phase in $O + F_S$, region IV); (e) 9/2/89, granular state ($O + O_{F,S}$, region VI).

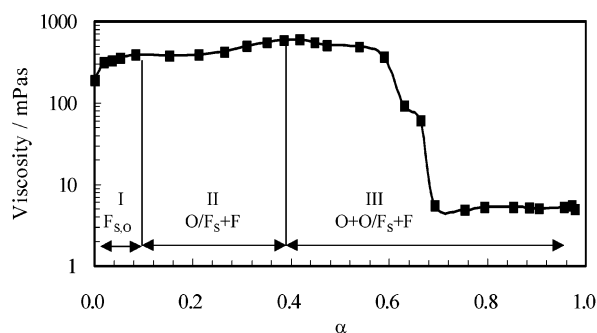


Figure 3. Viscosity of the PF-5 CaLT powder/PFPE/DMS mixtures plotted against DMS composition α when $\beta = 0.26$.

0–0.07, the viscosity increased with the DMS content because the powder particles were bound to each other by the addition of DMS to form a network structure.

(ii) *O/F Emulsion 1 State.* When α was 0.07–0.40, the mixture was in the “O/F emulsion 1 state” ($O/F_S + F$), which was a milky DMS-in-PFPE type emulsion (Figure 1, II; Figure 2b). The emulsion was fluid, and the size of DMS droplets with the adsorbed powder particles was about several tens of micrometers. Flocculation and creaming of the DMS droplets and separation of the excess PFPE phase at the bottom were observed. When β was constant, the viscosity remained almost constant and independent of the DMS composition. For example, the viscosity was 400–600 (mPa s) when β was 0.26 (Figure

3). The maximum amount of DMS contained as stable emulsion droplets was about 40 vol %. This amount of upper limit was about 1.3 times larger than that for the spherical surface-active resin powder reported in our previous paper.¹⁴ The reason will be described in the discussion section.

(iii) *O/F Emulsion 2 State.* When the DMS content exceeds the limit value of the O/F emulsion 1 state ($\alpha > 0.4$), the mixture becomes the “O/F emulsion 2 state” ($O + O/F_S + F$) (Figure 1, III; Figure 2c). The DMS oil phase separated out by coalescence, and the PFPE phase by creaming. The size of DMS droplets was larger and more widely distributed compared with that in the O/F emulsion 1 state. Some emulsion droplets were distorted from the spherical shape.

(iv) *Separated State.* When $\beta = 0.4–0.65$, self-assembled structures such as solid-stabilized emulsions or granules were not observed. The system consisted of two separated phases: the white PFPE phase in which the powder was dispersed and a transparent DMS phase (“separated state” ($O + F_S$), Figure 1, IV; Figure 2d). These two phases were separated regardless of the composition ratio of DMS. This region was not observed in the system of the spherical surface-active resin powder.¹⁴ To our knowledge, this is the first finding of such an unusual region in the ternary system consisting of the powder and two immiscible liquids.

(v) *Powdery State.* When the PFPE content was less than the limiting amount of oil absorption to the powder

($\beta > 0.65$) and α was also below a certain volume, the mixture was in the “powdery state” ($S_{O,F}$; Figure 1, V). In this state, the powder component contained both PFPE and DMS oils in the inside spaces among the particles.

(vi) *Granular State*. When more DMS oil was added to the powdery state, the mixture entered into the “granular state” ($O + O_{F,S}$) (Figure 1, VI; Figure 2e). The powder particles were granulated in the DMS medium. PFPE was absorbed among the particles and acted as a binding material. A clear DMS phase was separated from the mixture by creaming after standing for a couple of hours and attained a stationary state after approximately 10 days.

(vii) *Powder Dispersion State with Excess PFPE and DMS Phases*. When the powder content was small (<0.5 vol %), neither emulsion nor granules were obtained (Figure 1, VII; $O + F_S + F$). The powder particles were dispersed in one PFPE phase, while another clear PFPE phase and a DMS phase were separated.

(viii) *Powder/PFPE Dispersion State*. When the PFPE content was small (<0.5 vol %), the powder particles and PFPE were dispersed in DMS (Figure 1, VIII; $O_{F,S}$).

Discussion

The surface-active organic-crystalline powder, PF-5 CaLT, shows some characteristics of the self-assembling behavior resulting from its shape, the chemical composition, and the aggregation of the particles. These characteristics become clear by comparison with the behavior of the spherical surface-active resin powder, that is, PF-5 silicone resin powder.¹⁴

(a) Higher Capacity of the O/F Emulsion with the Organic-Crystalline Powder for the DMS Droplets Than with the Spherical Resin Powder. A simple theoretical analysis can be given, taking into account the effect of the platelike shape of PF-5 CaLT on the maximum amount of DMS contained as stable emulsion droplets. A geometrical consideration has been made on the adsorption of the plate-shaped and the spherical particles at the liquid–liquid interfaces. The plate-shaped powders cover a larger interface than the spherical ones, if the volume and the number of powder particles are the same. The volume of emulsion droplets *per unit volume* ϕ is described by eq 1:

$$\phi = \frac{4}{3}\pi R^3 N \quad (1)$$

where R and N are the radius and the number of emulsion droplets *per unit volume* (number density), respectively. If all the powder particles are adsorbed on the liquid–liquid interface in a hexagonal close-packed arrangement, N can be written as eqs 2:²¹

$$N = \frac{\sqrt{3}}{2\pi} \frac{r_p^2}{R^2} n_p \quad \text{plate-shaped powder} \quad (2)$$

$$N = \frac{\sqrt{3}}{2\pi} \frac{r_s^2}{R^2} n_s \quad \text{spherical powder}$$

where the plate-shaped powder is assumed to be a cylindrical shape whose radius is r_p , while the radius of a spherical powder is r_s (Figure 4). In eq 2, n_p and n_s are the number of plate-shaped powder particles and spherical

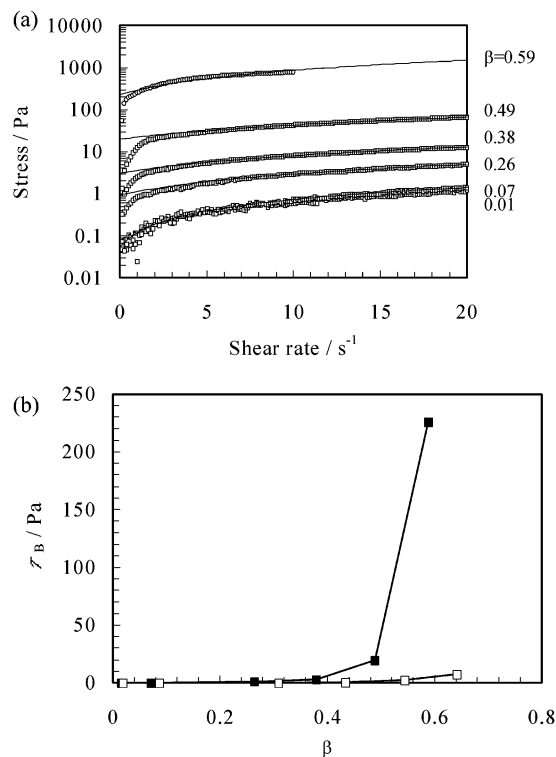


Figure 4. The effect of β on the shear-stress curve (a) and the yield stress τ_B of the powder/PFPE mixture (b). Panel b: (■) platelike PF-5 CaLT powder; (□) spherical PF-5 silicone resin powder.

powder particles *per unit volume*, respectively. Equations 3 can be obtained by substituting eqs 2 into eq 1:

$$\phi = \frac{2}{\sqrt{3}} R r_p^2 n_p \quad \text{plate-shaped powder} \quad (3)$$

$$\phi = \frac{2}{\sqrt{3}} R r_s^2 n_s \quad \text{spherical powder}$$

Equations 3 imply that the upper-limit amount of emulsion droplets is proportional to the quadratic power of r_p or r_s , when R is constant and $n_p = n_s$. According to this result, the plate-shaped powder can stabilize more volume of the emulsion droplets than the spherical powder because r_p is usually larger than r_s , if the volumes of both the powder particles are the same, as shown in eq 4:

$$r_p = \frac{2}{\sqrt{3}} \left(\frac{r_s}{d} \right)^{1/2} r_s \quad (4)$$

where d is the thickness of the plate-shaped powder and is much less than r_p and r_s . For example, the plate-shaped powder whose r_p and d are 4.0 and 0.9 μm , respectively, can stabilize 3 times more volume of emulsion droplets than can the spherical powder whose r_s is 2.2 μm . The predicted difference of the plate-shaped powder from the spherical powder is much larger than our experimental result.

The reason for the discrepancy between the theoretical and experimental values is as follows. Although both PF-5 CaLT and the PF-5 spherical silicone resin powder are surface-active, their chemical compositions are quite different. The different wettability of these two powders with PFPE and DMS might account for the above discrepancy. The adsorption energy E_s for the spherical

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powder particle adsorbed on an interface between liquid A and liquid B can be written as^{21,22}

$$E_s = \pi r_s^2 \frac{(\gamma_{AB} - \gamma_{AS} + \gamma_{BS})^2}{\gamma_{AB}} \quad (5)$$

where γ_{AB} and γ_{AS} (γ_{BS}) are interfacial tensions between liquid A and B and between the powder surface and liquid A (liquid B). Alternatively, the adsorption energy for the plate-shaped powder, E_p , can be described by eq 6, if the effect of the contact between the edge of the powder and the two liquids is neglected.

$$E_p = \pi r_p^2 (\gamma_{AB} - \gamma_{AS} + \gamma_{BS}) \quad (6)$$

Equations 5 and 6 indicate that not only the size of the powder particle but also the interfacial tensions are important factors to determine the adsorption energy. When these interfacial tensions are balanced, most of the powder particles adsorb on the liquid–liquid interface. But if the affinity of PF-5 CaLT with PFPE is higher than the balanced value, some powder particles might be dispersed in the PFPE phase and not contribute to the emulsification. This may be the reason the experimental upper limit of the DMS content is less than the theoretical value.

(b) Mechanism of Formation of the Separated State. The effects of increasing β on the shear-stress curve and yield stress of the powder/PFPE mixture, τ_B , are shown in Figure 4. The shear stress of these dispersions increased with increasing shear rate and β (Figure 4a). The profile of the shear-stress curves indicates that these dispersions are thixotropic. The yield stress τ_B as a function of β is shown in Figure 4b. The τ_B of the PF-5 CaLT/PFPE mixture increased abruptly when $\beta > 0.4$ and was higher than that of the spherical surface-active resin powder dispersions. These higher τ_B values indicate a stronger interaction between powder particles in the network aggregates.²²

The contact angle of the PF-5 CaLT/PFPE mixture with DMS droplets increased sharply with the fraction of the powder when $\beta > 0.4$, while it decreased continuously for the PF-5 spherical silicone resin powder/PFPE mixture (Figure 5). These results indicate that the addition of PF-5 CaLT reduces the affinity of the powder/PFPE mixture with DMS. This reduction of the affinity should prevent the DMS oil from being emulsified into the powder/PFPE mixture. Although the reason for these unusual behaviors is not clear at present, the β value at the onset of increasing τ_B and contact angle in the PF-5 CaLT/PFPE mixture

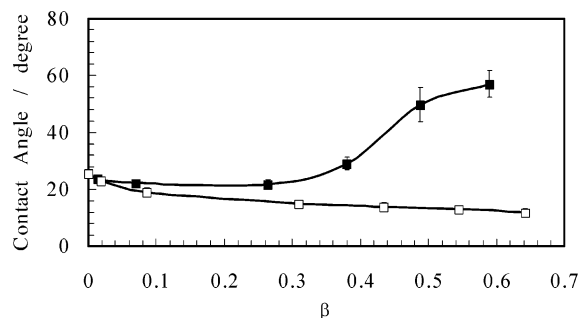


Figure 5. The effect of β on the contact angle of the powder/PFPE mixtures with the DMS oil: (■) plate-like PF-5 CaLT powder; (□) spherical PF-5 silicone resin powder.

interestingly coincides with the composition at which the separated state starts to appear (Figures 4 and 5). The effect of the dispersed state and the affinity between two phases of the powder on the emulsion stability will be studied in the future.

Conclusions

We have studied the ternary system consisting of the plate-shaped fluorinated CaLT powder, PFPE, and DMS to characterize the self-assembled structure of the organic-crystalline powder. The maximum content of DMS was approximately 40 vol % in the O/F emulsion 1 state and was larger than the value observed for spherical surface-active powder. According to the simple theoretical analysis, the difference is mainly due to the geometrical and/or thermodynamic characteristics of the plate-shaped powder. The separated state, in which the transparent DMS phase was separated from the milky white phase consisting of the powder and PFPE, was observed. The results of the shear-stress curve and the contact angle measurements suggest that this characteristic state seems to appear due to the network aggregate of the powder particles and the low affinity of the powder/PFPE mixture with DMS.

In industrial applications, organic-crystalline powders with various shapes and sizes are applied as functional materials. Our results are useful in the efforts to improve the properties of many industrial products, such as foodstuffs, pharmaceuticals, cosmetics, or chemical products. The results are important not only for their potential industrial applications but also from a fundamental scientific viewpoint. The appearance of the separated state is not a common phenomenon in colloid and surface science and may be characteristic of the plate-shaped powder particles.

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