

Particles at Oil–Air Surfaces: Powdered Oil, Liquid Oil Marbles, and Oil Foam

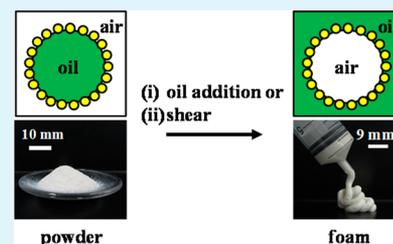
Bernard P. Binks,^{*,†} Shaun K. Johnston,[†] Tomoko Sekine,[‡] and Andrew T. Tyowua[†]

[†]Surfactant and Colloid Group, Department of Chemistry, University of Hull, Hull HU6 7RX, U.K.

[‡]Shiseido Research Center, Shin-Yokohama, 2-2-1 Hayabuchi, Tsuzuki-Ku, Yokohama 224-8558, Japan

ABSTRACT: The type of material stabilized by four kinds of fluorinated particles (sericite and bentonite platelet clays and spherical zinc oxide) in air–oil mixtures has been investigated. It depends on the particle wettability and the degree of shear. Upon vigorous agitation, oil dispersions are formed in all the oils containing relatively large bentonite particles and in oils of relatively low surface tension ($\gamma_{la} < 26 \text{ mN m}^{-1}$) like dodecane, 20 cS silicone, and cyclomethicone containing the other fluorinated particles. Particle-stabilized oil foams were obtained in oils having $\gamma_{la} > 26 \text{ mN m}^{-1}$ where the advancing air–oil–solid contact angle θ lies between ca. 90° and 120° . Gentle shaking, however, gives oil-in-air liquid marbles with all the oil–particle systems except for cases where θ is $< 60^\circ$. For oils of tension $> 24 \text{ mN m}^{-1}$ with omniphobic zinc oxide and sericite particles for which advancing $\theta \geq 90^\circ$, dry oil powders consisting of oil drops in air which do not leak oil could be made upon gentle agitation up to a critical oil:particle ratio (COPR). Above the COPR, catastrophic phase inversion of the dry oil powders to air-in-oil foams was observed. When sheared on a substrate, the dry oil powders containing at least 60 wt % of oil release the encapsulated oil, making these materials attractive formulations in the cosmetic and food industries.

KEYWORDS: dry oil, oil foam, liquid oil marbles, surface energy, omniphobicity



INTRODUCTION

Colloidal particles of suitable wettability are surface-active adsorbing on liquid droplet or gas bubble surfaces, preventing them from coalescing and ultimately giving rise to kinetically stable oil–water emulsions¹ and aqueous^{2,3} and nonaqueous (oil) foams.^{4,5} Particle wettability, quantified by the three-phase contact angle θ , dictates the type of the final product. For instance, in systems containing oil (o), water (w), and spherical solid particles, oil-in-water (o/w) emulsions are stabilized if the particles are relatively hydrophilic ($\theta < 90^\circ$) but water-in-oil (w/o) emulsions are stabilized if the particles are relatively hydrophobic ($\theta > 90^\circ$).⁶ In contrast, in systems containing air (a) and water (w) and partially hydrophobic (very hydrophobic) particles, aqueous foams⁷ (aqueous liquid marbles)^{8,9} are preferentially stabilized. In the case of oil, air, and particle mixtures, oil foams and oil liquid marbles are prepared by using oleophilic ($\theta < 90^\circ$) and oleophobic ($\theta > 90^\circ$) particles, respectively.¹⁰ Omniphilic particles are wet by both oil and water and tend to stabilize both oil and aqueous foams. By contrast, omniphobic particles are only slightly wet by oil and water and tend to stabilize both oil and aqueous liquid marbles. Preparation of oleophobic and omniphobic surfaces usually involves surface chemical modification of the hydrophilic precursors using suitable fluorocarbons of low surface energy.^{11–13} The type of final product obtained in liquid–air systems is also dictated by the type of liquid and the speed of mixing.¹⁴ Binks and Tyowua⁵ have studied these variables in oil–air systems. They reported that, with appropriate shear, a mixture of a relatively low surface tension liquid and relatively high surface energy oleophilic particles yield a particle

dispersion. However, a mixture of a liquid of intermediate (high) tension and oleophobic particles of intermediate (low) surface energy give oil foams (oil liquid marbles).

Liquid marbles⁸ are now widely studied^{15–18} and can be considered as an element of dry liquid (water or oil) powdered materials. Dry water¹⁹ (dry oil^{20,21}) is a free-flowing powder composed of small (diameter 50–400 μm) water (oil) droplets coated with solid particles of low surface energy. The encapsulated liquid may be released on application of mechanical stress or by evaporation, a property which makes them potential candidates in drug delivery and cosmetics. The particles protect the liquid droplets against coalescence and allow them to move with minimum adhesion to a substrate. This principle is also evident in nature, for example, in the self-cleaning of plant leaves²² and in the excretion of honeydew globules from aphids.²³ Despite the potential applications of both dry water and dry oil powders in the cosmetic and pharmaceutical industries, few reports exist, particularly for the latter. This is mainly due to the relatively low surface tension of many oils and the relatively high surface energy of many solid particles. Reports on oil liquid marbles are also limited for the same reason. Using a thermodynamic analysis,²⁴ it was shown that this prevents particle adsorption and hence stabilization of the relevant materials.⁵ Dry water has been studied by a number of groups.^{19,25–30} Phase inversion of particle-stabilized aqueous foams to dry water was shown in ref 19, by either a progressive

Received: April 2, 2015

Accepted: June 12, 2015

Published: June 24, 2015

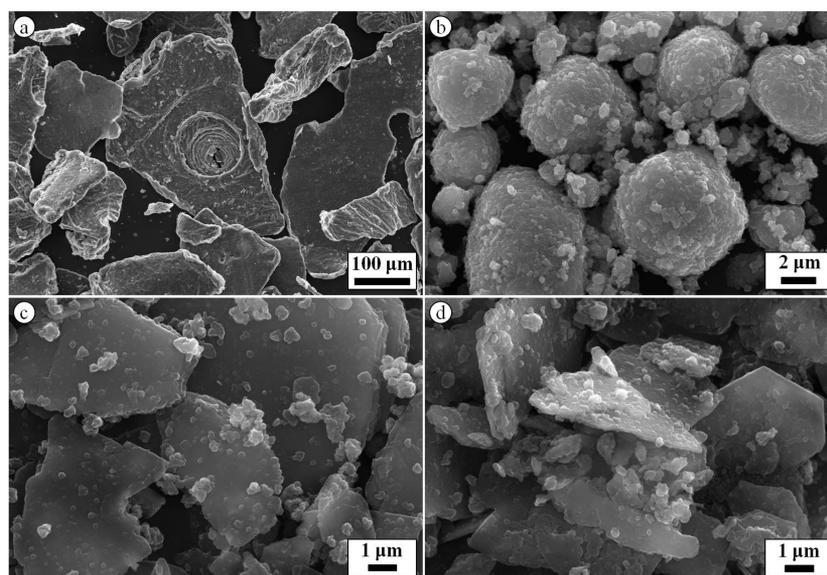


Figure 1. SEM images of powdered (a) PFX-10 Kunipia F, (b) PFX-10 ZnO (TP), (c) PF-10 Eight Pearl 300S-Al, and (d) PF-10 FSE-Al particles.

change in particle hydrophobicity (constant air:water ratio) or by changing the air:water ratio (fixed particle wettability). Dry water containing up to 98 wt % of water by mass has been used to store water,²⁷ to enhance the kinetics of heterogeneous catalytic hydrogenation,²⁹ and to enhance gas uptake rates in gas hydrates.³⁰

In the case of dry oil powders, Murakami and Bismarck²⁰ prepared these from oleophobic agglomerated oligomeric tetrafluoroethylene particles and contained 10–15 wt % of oil relative to the total mass. In other examples, protein³¹ or particle-stabilized o/w emulsions³² were dried to yield oil powders containing about 90 wt % of oil and showed no sign of oil leakage over several months. This process however requires energy input and the drying stage is time-consuming. Oil-in-water-in-air (o/w/a) materials, also known as powdered emulsion³³ or a dry water emulsion,³⁴ were prepared from o/w emulsions without the need to evaporate the aqueous phase. For powdered emulsions,³³ the particle-stabilized emulsion was aerated with very hydrophobic solid particles using high shear. The hydrophobic particles adsorb around the newly created water globules in air which encase the original oil droplets in water. Similarly, the dry water emulsion was prepared from a polymeric surfactant-stabilized emulsion after aeration in the presence of hydrophobic silica particles.³⁴ Dry oil powders containing up to 80 wt % of oil (relative to the total mass) were prepared very recently using fluorinated clay platelet particles by gentle hand shaking of an oil–particle mixture.²¹ The degree of particle fluorination was systematically varied and the dry oil powders were shown to undergo catastrophic phase inversion to stable oil foams at a critical oil:particle ratio (COPR). As an extension to this work, we discuss here the behavior of other fluorinated solid particles of varying surface energy with polar oils and *n*-alkanes of varying surface tension and show that dry oil powders containing up to around 80 wt % of oil can be prepared by simply hand shaking a mixture of the particles and oil. We show that the dry oil powders undergo catastrophic phase inversion to ultrastable oil foams at high COPR. Liquid oil marbles, an element of dry oil powder, can also be successfully prepared.

EXPERIMENTAL SECTION

Materials. Four types of fluorinated solid particles, namely, PFX-10 Kunipia F, PF-10 FSE-Al, PF-10 Eight Pearl 300S-Al, and PFX-10 ZnO (TP), were used. The particles were modified from their omniphilic precursors by Daito Kasei Kogyo Company Ltd., Japan, using a known amount of C₉–C₁₅ perfluoroalkyl phosphate diethanolamine salt, [F₃C-(CF₂)_{*n*}(CH₂)₂O]_{*m*}POO[(ONH₂(CH₂CH₂OH))₂]₂ (where *n* = 6–18 and 2 > *m* > 1). The details of the surface chemical modification reaction can be found elsewhere.²¹ All the particle types are omniphobic toward water and most oils. These particles are used in cosmetics to prepare long lasting makeup resilient to perspiration and sebum. The precursor of the PF-10 FSE-Al and PF-10 Eight Pearl 300 S-Al particles is omniphilic sericite (clay) particles, while that of the PFX-10 Kunipia F and PFX-10 ZnO (TP) particles is omniphilic bentonite and zinc oxide particles, respectively. Sericite is a white, monoclinic, powdered mica mineral composed mainly of SiO₂ (~54%), Al₂O₃ (~31%), and K₂O (~7%). The particles are platelike of average size around 5 μm. They have a three-layer unit cell consisting of a SiO₂ tetrahedron, an Al₂O₃ octahedron, and a SiO₂ tetrahedron held together by potassium ionic bonds.³⁵ Bentonite (a montmorillonite clay) however is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. The substitution of Mg²⁺ for Al³⁺ in the octahedral layer and Al³⁺ for Si⁴⁺ in the tetrahedral layer results in a net negative surface charge on the clay. This is offset by cations (Na⁺, Ca²⁺) at the clay surface.³⁶

Most of the oils used were received from Shiseido, Japan. They were of different types and include mineral, silicone, ester, and vegetable oils. Their structure and density are given in ref 21. For the sake of comparison, *n*-alkanes (C₅–C₁₆) were also used. These include *n*-pentane (Aldrich, 98%), *n*-hexane (Fisher Scientific, 95%), *n*-heptane (Sigma-Aldrich, 99%), *n*-octane (Sigma-Aldrich, >98%), *n*-decane (Avocado, 99%), *n*-dodecane (Sigma, ≥99%), *n*-tetradecane (Aldrich, >99%), and general purpose grade *n*-hexadecane from Fisher Scientific. Water was passed through an Elga Prima reverse osmosis unit and then a Milli-Q reagent water system. The treated water has a surface tension of 72.1 mN m⁻¹ and a resistivity of 18 MΩ cm

at 25 °C. Five other liquids (in addition to *n*-hexadecane and water) from Sigma-Aldrich were used as probe liquids to estimate the surface energies of the particles from contact angle data. They include ethylene glycol (>99%), diiodomethane (99%), α -bromonaphthalene (97%), glycerol (99%), and formamide (>99%).

Methods. *a. Particle Characterization.* Scanning electron microscopy (SEM) was used to probe the morphology and elemental content of the particles. SEM micrographs showing the particle morphology were obtained from the powdered particles while their energy dispersive X-ray elemental maps showing their elemental composition was obtained from compressed disks of the particles. To obtain an SEM micrograph from the dry particles, a sample mount (carbon sticky disk) containing a self-adhesive was pressed into a powdered bed of the particles. A thin layer (ca. 15 nm) of carbon was then applied using an Edwards high vacuum coating unit and examined with a Zeiss EVO 60 SEM at a beam current of 40 μ A and probe current of 101 pA. Similarly, particle disks were stuck to the SEM sample mount and probed for elemental content. The SEM micrographs (Figure 1) show that the PFX-10 Kunipia F, PF-10 Eight Pearl 300S-Al, and PF-10 FSE-Al particles are made up of textured discrete platelet primary particles while the PFX-10 ZnO (TP) particles are made up of textured relatively spherical particle agglomerates (size >3 μ m). The textured nature (\approx 200 nm) of the surfaces of these particles was imparted by Al(OH)₃ crystals which were used to augment the fluorination reaction. The primary particles of the PFX-10 Kunipia F particles are several times larger than those of PF-10 Eight Pearl 300S-Al and PF-10 FSE-Al which are only several micrometers long and a few nanometers thick. The elemental composition of the particles is shown quantitatively in Table 1. Al, Si, and O are predominant in PFX-10 Kunipia F, PF-10 Eight Pearl 300S-Al, and PF-10 FSE-Al particles while Zn and O are predominant in PFX-10 ZnO (TP) particles as expected.

Table 1. Elementary Composition (wt %) of Particles Used

wt %	PFX-10 Kunipia F	PFX-10 ZnO (TP)	PF-10 Eight Pearl 300S-Al	PF-10 FSE-Al
C	7.08	3.87	0.00	2.56
O	40.5	20.2	49.7	45.7
F	17.1	8.56	5.23	9.79
Na	1.97	0.00	0.16	0.16
Mg	1.52	0.00	0.16	0.15
Al	8.42	0.00	17.7	16.9
Si	21.6	0.00	19.4	17.3
P	0.31	0.34	0.42	0.35
S	0.14	0.00	0.24	0.39
K	0.00	0.00	6.40	6.20
Ca	0.28	0.00	0.00	0.00
Ti	0.06	0.00	0.10	0.00
Fe	1.04	0.00	0.54	0.47
Cl	0.00	0.21	0.00	0.00
Zn	0.00	66.8	0.00	0.00

b. Estimation of Particle Surface Energy from Contact Angle Data. The apparent surface energy γ_{sa} of the various solid particles was estimated using the equilibrium advancing contact angle (θ) values of several probe liquids in air. For irregular and polydisperse particles, difficulties exist in directly measuring the contact angle at a liquid surface so disks of the

particles (diameter, 13 mm; thickness, \approx 1 mm) were used using the sessile drop technique. Disks were made by compressing ca. 400 mg of dry particles in a 13 mm diameter steel die with a hydraulic press (Research & Industrial Instrument Co., U.K.) under a pressure of approximately 9.0×10^8 N m⁻². For all the liquids, the advancing and receding contact angles were measured using drops of 0.1 cm³. The contact angle was measured using a Krüss DSA Mk 10 apparatus. An average of four separate measurements was taken.

c. Particle Immersion. Fifty milligrams of particles was placed on the surface of 3 cm³ of liquid in a screw cap glass vessel (inside diameter, 1.8 cm; height, 7.2 cm). We observed whether the particles were wetted by the liquid and entered it or not. Two hours later, the mixture was hand shaken vigorously for 30 s. Particle dispersions, oil foams, or climbing films, which were not seen in the absence of the particles prior to the experiment, were observed. The glass vessels were photographed using a 4.3 V Power Shot SX220 HS Canon digital camera.

d. Preparation of Oil Marbles and Dry Oil Powders. Oil marbles were prepared by allowing a 10 μ L droplet of oil to touch a dry bed (100 mg) of the particles placed on a Teflon substrate (4 cm \times 4 cm \times 3 mm, Radio Spares, U.K.). The drop was then rolled on the particle bed to and fro. The Teflon substrate was cleaned prior to the experiment. The cleaning process consisted of washing with a warm aqueous solution of liquid soap, rinsing with clean water, and then wiping with a clean soft tissue.

Dry oil powder formation should be possible with the oil–particle combinations which form liquid oil marbles. However, it is vital to know the amount of particles required to cover a given mass of oil to give it a dry oil powder appearance. To that effect, the critical oil:particle ratio (COPR), defined as grams of oil per gram of particles, was determined by sequential addition of \leq 0.25 g of oil to 0.5 g of particles in a screw cap glass vessel followed by 3 min of gentle hand shaking.²¹ Foams formed above the COPR for all the particle types except those of PFX-10 Kunipia F, which forms a paste at any oil content. Keeping the COPR in mind, four different protocols were used to prepare dry oils with the PFX-10 ZnO (TP), PF-10 Eight Pearl 300S-Al, and PF-10 FSE-Al particles. The first protocol described above yielded dry oil powders with many of the oil–particle combinations that formed oil marbles previously. The other protocols were used for squalane and sunflower oil only. The second method involves addition of the total amount of oil at the COPR at once to the particles followed by gentle hand shaking. This method gave oil foams with the PF-10 Eight Pearl 300S-Al and PF-10 FSE-Al particles and dry oil powders with the PFX-10 ZnO (TP) particles. The third method involved adding 0.2 g of oil below and above the COPR in a nonsequential way (i.e., the required mass of oil was added at once to 0.5 g of particles) followed by 10 min of gentle hand shaking. Finally, dry oil powder formation was attempted using an IKA T25 Ultra-Turrax homogenizer (i.e., high shear) at 4000 rpm for 3 min below and above the COPR. A given mass of oil (0.2 g below or above COPR) was placed in a glass vessel, followed by addition of 0.5 g of particles, and then sheared. In another experiment, the particles were placed in the glass vessel before oil addition and then sheared. Both approaches yielded oil foams. Dry oil powders were thus prepared mainly using the first method as it gives powders with relatively high oil content for many of the oil–particle combinations. Properties of dry oil

Table 2. γ_{la} and Corresponding γ_{la}^d and γ_{la}^p of Probe Liquids at 25 °C (from ref 41) as well as Apparent Equilibrium Advancing θ of the Liquids Measured on Compressed Disks of Particles in Air

liquid	tension (mN m ⁻¹)			θ ($\pm 2^\circ$)			
	γ_{la}	γ_{la}^d	γ_{la}^p	PFX-10 Kunipia F	PFX-10 ZnO (TP)	PF-10 Eight Pearl 300 S-Al	PF-10 FSE-Al
water	72.1	21.6	50.5	<5	116	130	139
glycerol	64.0	34.0	30.0	94	136	145	148
formamide	58.0	39.0	19.0	88	113	106	133
ethylene glycol	48.0	29.0	19.0	70	94	114	112
diiodomethane	50.8	58.0	0.0	88	106	94	123
α -bromonaphthalene	44.4	44.4	0.0	76	83	104	111
<i>n</i> -hexadecane	27.8	27.8	0.0	67	77	93	95

powders described hereafter are those at the COPR, unless stated otherwise.

e. Characterization of Dry Oil Powders and Oil Foams. In addition to visual observation, the dry oil powders and the oil foams were distinguished from each other by using the dispersion test. A dry oil powder and an oil foam of known mass (~ 0.7 g) from a given oil was placed on the surface of the neat oil (~ 30 cm³) in a beaker and stirred vigorously. It was noted whether they dispersed or not. The oil foams dispersed while the dry oil powders did not. Also, small samples of the powdered oils and oil foams were placed on a dimple glass slide (Fisher Scientific) and imaged with an Olympus BX-51 optical microscope fitted with a DP50 digital camera using Image-Pro Plus 5.1 software (Media Cybernetics). Cryo-SEM was done in one case. The dry oil powder was placed on a perforated aluminum stub and plunged into liquid nitrogen slush (-210 °C). The frozen powder was transferred to a cryo system (Quorum Technologies PP3010T) and sputter-coated with platinum without fracturing. It was then transferred to the SEM cold stage and studied at -140 °C at a beam voltage of 15 kV and probe current of 20–35 pA. To verify whether the dry oil powders leak or not, they were placed on a Sartorius Stedim filter paper (diameter, 70 mm) or a clean Pyrex watch glass (diameter, 50 mm) for 1 min. After removal of the dry oil powders, the filter paper and watch glass were observed for evidence of oil staining. The effect of shear on the dry oil powders was investigated by shearing them (8.5 mg) on the back of a hand (surface area, ca. 13 cm²) with an index finger. Dry oil powders (0.5 g) of liquid paraffin, squalane, and jojoba oil stabilized by PFX-10 ZnO (TP) and PF-10 Eight Pearl 300S-Al particles were also shaken vigorously (10 s) in a screw cap glass vessel to verify the effect of shear on the powdered oils. Most experiments were conducted at room temperature (21 ± 2 °C).

RESULTS AND DISCUSSION

With use of the contact angle data of the probe liquids on particle disks, determination of the apparent surface energy of the particles is first described. Then the results of the particle immersion test (at rest and with agitation) are presented. This is followed by a description of the characteristics of the oil liquid marbles and the powdered oils and how the latter undergo phase inversion to oil foams at relatively high COPR. Lastly, the correlation between the type of material (oil foam, liquid marble, and dry oil powder) and the apparent contact angle is discussed.

Apparent Particle Surface Energies. The surface energy of a solid or liquid material contains contributions from the polar γ^p and dispersion γ^d components and they are additive.^{37,38}

$$\gamma = \gamma^d + \gamma^p \quad (1)$$

The polar component comes from dipolar interactions, while the dispersion component is due to van der Waals forces between the molecules of the material.³⁹ The interfacial tension γ_{AB} between two phases A and B is expressed in terms of the two components for each phase according to eq 2:

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\left(\sqrt{\gamma_A^d \gamma_B^d} + \sqrt{\gamma_A^p \gamma_B^p}\right) \quad (2)$$

Young's equation⁴⁰ developed for perfectly smooth and chemically homogeneous surfaces relates the contact angle θ of a liquid droplet (l) in air (a) on a substrate (s) to γ_{sa} , γ_{sl} and the solid–liquid interfacial tension γ_{sl} as shown in eq 3:

$$\cos \theta = \frac{\gamma_{sa} - \gamma_{sl}}{\gamma_{la}} \quad (3)$$

Equation 3 can be combined with eq 4, which is the appropriate form of eq 2 for the solid–liquid interface, to give eq 5 as illustrated in refs 5 and 41:

$$\gamma_{sl} = \gamma_{sa} + \gamma_{la} - 2\left(\sqrt{\gamma_{sa}^d \gamma_{la}^d} + \sqrt{\gamma_{sa}^p \gamma_{la}^p}\right) \quad (4)$$

$$\frac{1}{2}\gamma_{la}(1 + \cos \theta) = \sqrt{\gamma_{sa}^d \gamma_{la}^d} + \sqrt{\gamma_{sa}^p \gamma_{la}^p} \quad (5)$$

Equation 4 contains two unknowns, γ_{sa}^d and γ_{sa}^p , being the components of the solid surface energy as the other terms can be found from the literature for the probe liquids. Since simultaneous versions of eq 4 must be solved for the unknowns, θ from at least two liquids of different polarity is required. It has been shown previously⁴¹ that it is more beneficial to use more than two probe liquids (water, glycerol, formamide, ethylene glycol, diiodomethane, α -bromonaphthalene, and *n*-hexadecane) and to perform a least-squares calculation to determine the best combination of γ_{sa}^d and γ_{sa}^p that fits all the data simultaneously. Assuming Young's equation applies, the apparent equilibrium advancing θ of the probe liquids on the compressed particle disks in air are given in Table 2. The 3-D plots in Figure 2 contain the goodness of fit to θ (=inverse of sum of square of variances) against a matrix of possible values of γ_{sa}^d and γ_{sa}^p . The coordinates of the peak represent the best fit to all θ and are given in Table 3. This gives $\gamma_{sa}^d = 18$ mN m⁻¹ and $\gamma_{sa}^p = 4$ mN m⁻¹ for PFX-10 Kunipia F particles. The value of γ_{sa}^p is 0 mN m⁻¹ for the rest of the particles, but γ_{sa}^d varies across the particles. The γ_{sa} of the particles decreases in the order PFX-10 Kunipia F > PFX-10 ZnO (TP) > PF-10 Eight Pearl 300S-Al > PF-10 FSE-Al, but does not correlate with the fluorine content of the particles. As such, PFX-10 Kunipia F

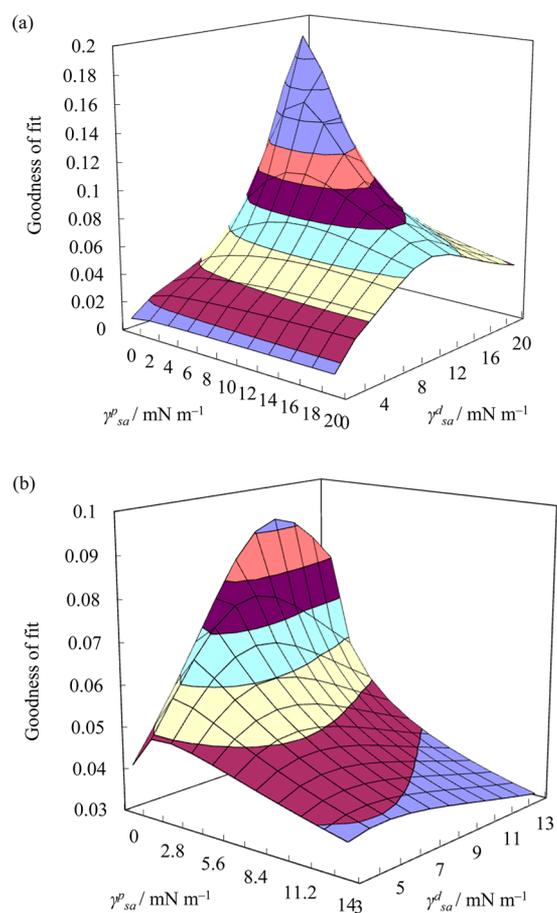


Figure 2. 3-D surface energy chart for (a) PFX-10 Kunipia F and (b) PFX-10 ZnO (TP) particles as a function of possible values of γ_{sa}^d and γ_{sa}^p . The ordinate represents the goodness of fit which is 1/sum of square of variances.

Table 3. Apparent Values of γ_{sa} of Fluorinated Clay and Zinc Oxide Particles along with Their Polar and Dispersion Components^a

particle	γ_{sa} (mN m ⁻¹)	γ_{sa}^p (mN m ⁻¹)	γ_{sa}^d (mN m ⁻¹)
PFX-10 Kunipia F	18.0	4.0	14.0
PFX-10 ZnO (TP)	10.0	0.0	10.0
PF-10 Eight Pearl 300S-Al	6.5	0.0	6.5
PF-10 FSE-Al	3.9	0.0	3.9

^aAll values are ± 0.3 mN m⁻¹.

and PF-10 FSE-Al are expected to be the least omniphobic and most omniphobic particles, respectively.

Particle Behavior on Oil Surfaces with Agitation. The results of the particle immersion experiment are summarized in Figure 3. It can be seen that PFX-10 Kunipia F was completely wetted by cyclomethicone and *n*-octane and was partially wetted by poly(dimethylsiloxane) (PDMS), 6 and 20 cS, but was not wetted by the rest of the liquids. In the case of water, we noticed that some water was imbibed into the particle layer on the surface, resulting in swelling. We extended the range of liquids to include those with surface tension between that of octane and that of water. These particles were not wetted at rest by α -bromonaphthalene (44.4 mN/m), ethylene glycol (48.0 mN/m), or glycerol (64.0 mN/m). A cloudy dispersion forms in all the liquids on shaking. The PFX-10 ZnO (TP) particles were completely or partially wetted only by liquids

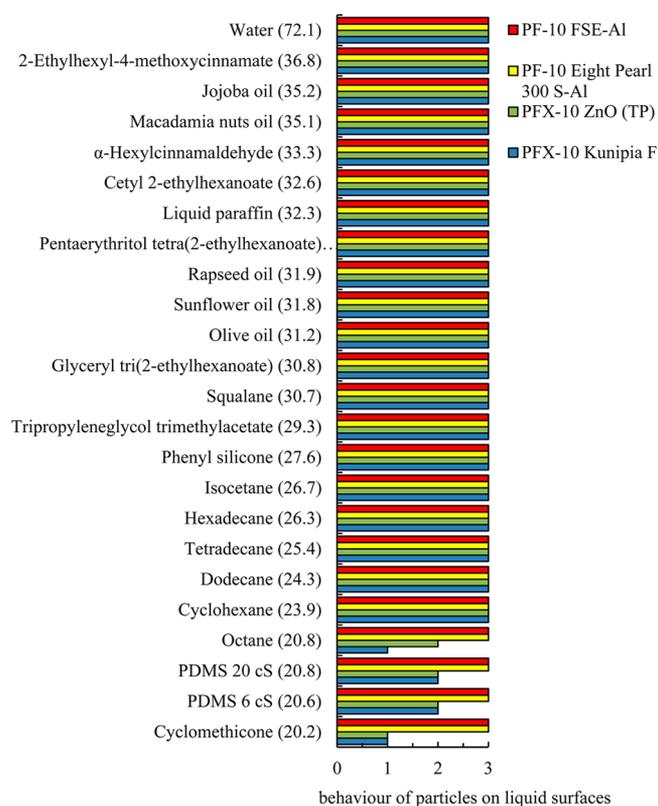


Figure 3. Behavior of fluorinated clay platelet and fluorinated spherical ZnO particles (50 mg) on liquid surfaces at rest. Abscissa: 1, particles were wetted by the liquid; 2, particles were partially wetted by the liquid; 3, particles were not wetted by the liquid. Ordinate: number in brackets is liquid surface tension (± 0.1 mN m⁻¹) at 25 °C.

having γ_{la} below 21 mN m⁻¹. When agitated, a cloudy dispersion forms in these liquids and in those of higher γ_{la} up to 25 mN m⁻¹, which did not wet them previously. Foams formed in liquids having $\gamma_{la} > 25$ mN m⁻¹, for example, *n*-hexadecane and glyceryl tri(2-ethylhexanoate) and water gives climbing films. The PF-10 Eight Pearl 300S-Al and PF-10 FSE-Al particles were not wetted by any of the liquids at rest. Upon agitation, cloudy dispersions were seen in liquids of γ_{la} below 26 mN m⁻¹, foams in liquids of higher tensions, and climbing films in water of highest tension. Climbing films are formed when bubbles sparsely coated with particles coalesce with the planar liquid–air surface.⁴² The reduction in surface area leads to an increase in the concentration of adsorbed particles, resulting in an increase in the surface pressure of the planar interface causing the film to climb. Examples of the materials formed by the particles with the various oils are given in Figure 4. The progression from oil dispersions to oil foams and ultimately climbing films as γ_{la} of the liquid increases is consistent with earlier findings in fluorinated particle–oil systems.^{5,21}

Liquid Oil Marbles and Dry Oil Powders Stabilized by Fluorinated Solid Particles. It has been shown previously^{5,21} that fluorinated solid particles of relatively low γ_{sa} are required to stabilize liquid oil marbles and dry oil powders. As such, one would expect the four types of particles here exhibiting relatively low γ_{sa} to stabilize marbles and dry oil powders also. We could make liquid marbles with all the oil–particle combinations except four, as shown in Table 4. Apart from the PFX-10 ZnO (TP) particle-stabilized marbles which were all quasi-spherical as expected (considering their capillary length

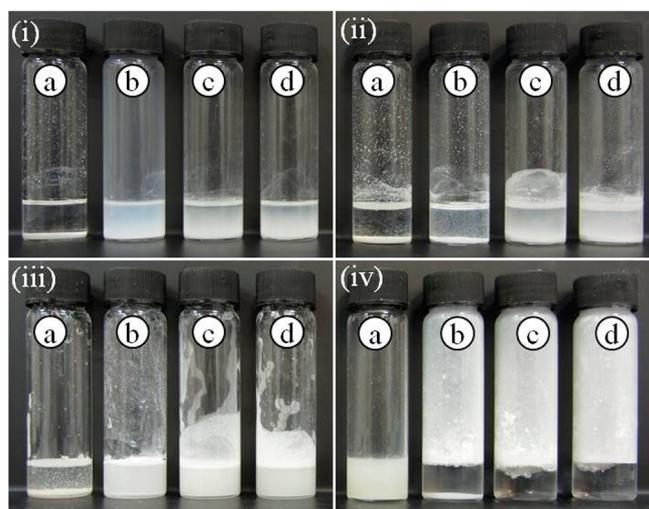


Figure 4. Photos of vessels containing 50 mg of (a) PFX-10 Kunipia F, (b) PFX-10 ZnO (TP), (c) PF-10 Eight Pearl 300S-Al, and (d) PF-10 FSE-Al and 3 cm³ of (i) cyclomethicone, (ii) *n*-dodecane, (iii) 2-ethylhexyl-4-methoxycinnamate, and (iv) water after agitation showing dispersions, foams, or climbing films.

κ^{-1} and radius R), many of the other marbles were cylindrical in shape, especially if the oil droplet was rolled on the particle bed in only one direction. This observation deviates from the general rule which says the effect of γ_{la} dominates that of gravity for relatively small ($\leq 10 \mu\text{L}$) liquid marbles having $R \ll \kappa^{-1}$ and are quasi-spherical and vice versa for relatively large ones ($\geq 50 \mu\text{L}$, $R \gg \kappa^{-1}$) which are puddle-shaped.^{15,43} The reason for this deviation is not clear, but might be due to the shape of the particles in that the PFX-10 ZnO (TP) particles are spherical while the rest of the particle types are platelets.

Attempts were made to prepare dry oil powders from the particle–oil combinations yielding oil liquid marbles. The best method was the sequential approach whose results are discussed here. We succeeded in making dry oil powders with the majority of the PFX-10 ZnO (TP), PF-10 Eight Pearl 300S-Al, and PF-10 FSE-Al particle–oil combinations that formed oil marbles. The PFX-10 Kunipia F particles did not stabilize any dry oil powders and this could be due to their large particle size ($>100 \mu\text{m}$) compared with the rest of the particles. For the rest of the particle types, the COPR increases as the γ_{la} of the liquids increases as shown in Figure 5. The PFX-10 ZnO (TP) particle-stabilized dry oil powders appear to be composed of fine oil droplets and are free-flowing. The encapsulated oil varies from ca. 30 wt % (dry cyclohexane powder stabilized by PFX-10 ZnO (TP) particles) to ca. 80 wt % (rapeseed oil powder stabilized by PF-10 Eight Pearl 300S-Al particles), both exceeding that reported earlier²⁰ by at least a factor of 2, but comparable with that reported recently.²¹ Dry water could not be prepared since the high γ_{la} of water did not allow its disruption into small droplets by shaking which is crucial for dry powder formation, unlike the case with low surface tension oils. Photographs and optical micrographs of some dry oil powders as well as photographs of some liquid marbles are given in Figures 6 and 7. The cryo-SEM image from an oil powder included in Figure 7 allows the visualization of frozen oil droplets coated with particles. Some nonspherical oil droplets exist within the powders. This deviation from spherical shape is common for particle-coated drops due to the jamming

Table 4. Advancing (First Entry) and Receding (Second Entry) θ in Degrees Measured into the Liquid of 0.1 cm³ (Advancing) and 0.05 cm³ (Receding) of a Selected Drop of Liquid in Air on Compressed Particle Disks at Ambient Conditions.^a The materials obtained after agitating the systems described in Figure 4 are also shown: ○, dispersion; ●, foam; †, climbing film. For liquid marbles: ×, not formed; √, formed.

liquid	Particle			
	PFX-10 Kunipia F	PFX-10 ZnO (TP)	PF-10 Eight Pearl 300S-Al	PF-10 FSE-Al
cyclomethicone	58, 35: ×, ○	54, 39: ×, ○	61, 49: √, ○	49, 35: √, ○
silicone, 6 cS	76, 57: √, ○	56, 35: ×, ○	69, 48: √, ○	69, 44: √, ○
silicone, 20 cS	72, 41: √, ○	60, 33: √, ○	72, 47: √, ○	73, 47: √, ○
<i>n</i> -octane	72, 45: √, ○	71, 32: √, ○	75, 39: √, ○	68, 38: √, ○
cyclohexane	71, 46: √, ○	87, 44: √, ○	92, 59: √, ○	79, 36: √, ○
<i>n</i> -dodecane	√, ○	√, ○	√, ○	√, ○
<i>n</i> -tetradecane	√, ○	√, ○	√, ●	√, ●
<i>n</i> -hexadecane	67, 45: √, ○	77, 47: √, ○	93, 67: √, ●	95, 54: √, ●
isocetane	√, ○	√, ●	√, ●	√, ●
phenyl silicone	88, 53: √, ○	92, 63: √, ●	105, 75: √, ●	109, 75: √, ●
tripropylene glycol trimethyl acetate	√, ○	√, ●	√, ●	√, ●
squalane	100, 68: √, ○	123, 90: √, ●	114, 83: √, ●	106, 82: √, ●
glyceryl tri(2-ethylhexanoate)	√, ○	√, ●	√, ●	√, ●
olive oil	√, ○	√, ●	√, ●	√, ●
sunflower oil	101, 67: √, ○	120, 82: √, ●	124, 89: √, ●	121, 82: √, ●
rapeseed oil	√, ○	√, ●	√, ●	√, ●
pentaerythritol tetra(2-ethyl hexanoate)	101, 66: √, ○	105, 76: √, ●	122, 93: √, ●	115, 79: √, ●
liquid paraffin	√, ○	√, ●	√, ●	√, ●
cetyl 2-ethylhexanoate	√, ○	√, ●	√, ●	√, ●
α -hexylcinnamaldehyde	96, 68: √, ○	117, 81: √, ●	111, 75: √, ●	117, 80: √, ●
macadamia nuts oil	98, 77: √, ○	111, 81: √, ●	122, 89: √, ●	115, 83: √, ●
jojoba oil	√, ○	√, ●	√, ●	√, ●
2-ethylhexyl-4-methoxy cinnamate	104, 76: √, ○	117, 89: √, ●	122, 90: √, ●	111, 79: √, ●
water	<5, <5: ×, ○	127, 88: √, †	127, 101: √, †	132, 94: √, †

^aAll angles quoted are $\pm 2^\circ$.

of interfacial particles which prevents relaxation to a spherical geometry.⁴⁴

The oil droplets in the dry oil powders are stable to oil leakage as evidenced by the lack of oil staining upon placing the powders on a filter paper or watch glass. Apart from the release of some of the encapsulated oil after 1 week in the case of some *n*-alkanes, the dry oil powders do not leak oil for over 2 years. When sheared on the skin or a surface, however, they liquefy and release oil except in cases where the oil content is <60 wt %, which form a paste. Importantly, the dry oil powders can be phase-inverted to oil foams at least at the COPR following vigorous shaking as verified with liquid paraffin, squalane, and jojoba oil stabilized by PFX-10 ZnO (TP) particles. The dry oil

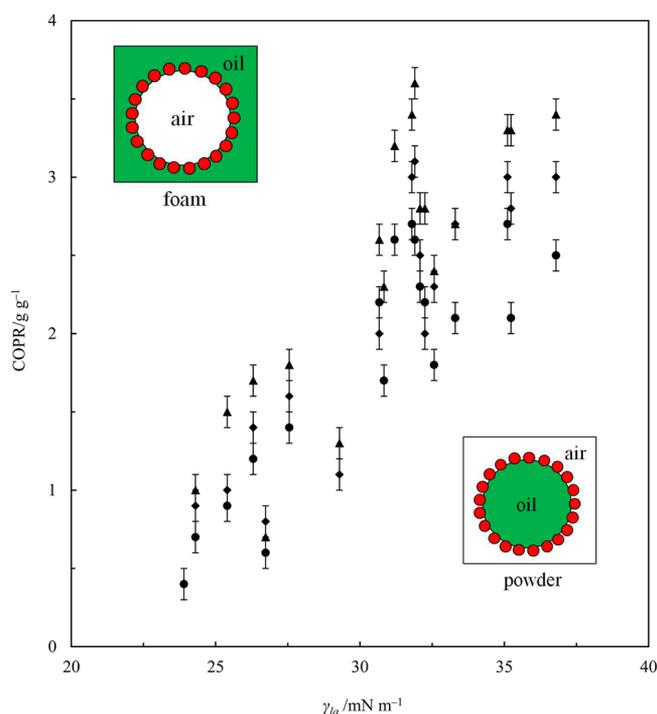


Figure 5. Variation of COPR with γ_{la} of the oils for PFX-10 ZnO (TP) (●), PF-10 Eight Pearl 300S-Al (▲), and PF-10 FSE-Al (◆). Inset: schematic illustration of dry oil powder below COPR and air-in-oil foam above COPR. For simplicity, the particles, oil droplets, and air bubbles are spherical.

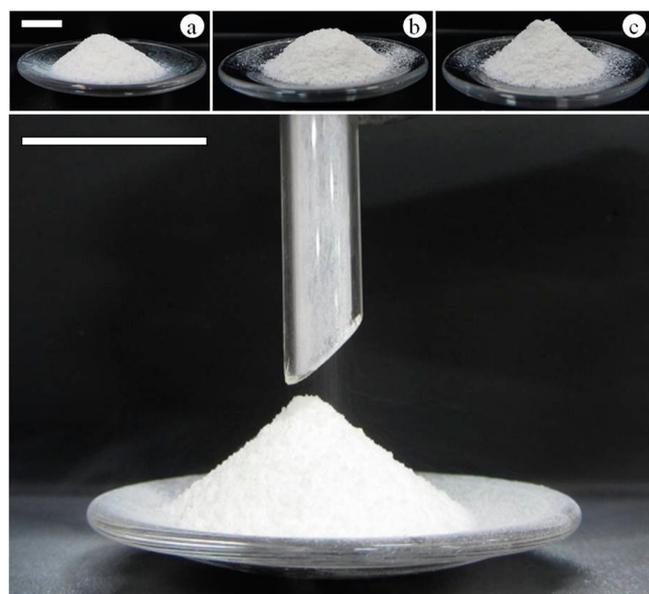


Figure 6. (upper) Photos of watch glasses containing dry oil powders (1 year after formation) for (a) squalane stabilized by PFX-10 ZnO (TP) particles, (b) olive oil stabilized by PF-10 FSE-Al particles, and (c) macadamia nuts oil stabilized by PF-10 Eight Pearl 300S-Al particles. (lower) Photo of dry squalane powder flowing freely through a glass funnel onto a Pyrex watch glass. Scale bar = 10 mm.

powders are thus metastable with the oil foam being the stable state.

Catastrophic Phase Inversion of Dry Oil Powders to Oil Foams. The conversion of a dry oil powder to an oil foam upon increasing the oil content is an example of catastrophic

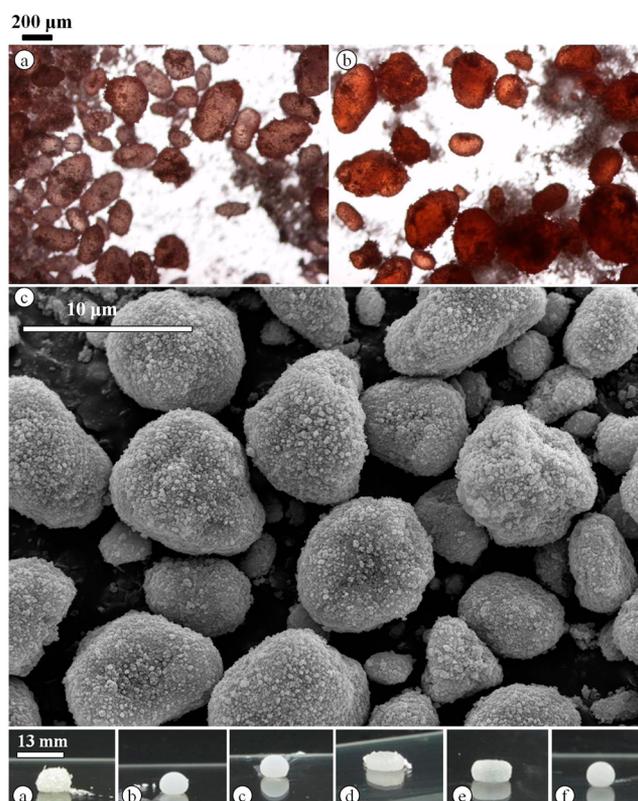


Figure 7. (upper) Optical micrographs of dry oil powders of (a) squalane and (b) sunflower oil stabilized by PFX-10 ZnO (TP) particles prepared from 5 cm³ of the oils containing 4 mg of Sudan Red dye and (c) cryo-SEM image of dry squalane powder stabilized by PFX-10 ZnO (TP) particles. (lower) Photos of liquid marbles (10 μ L) resting on a hydrophilic glass slide soon after preparation. The liquid-particle combinations are (a) olive oil–PFX-10 Kunipia F, (b) olive oil–PFX-10 ZnO (TP), (c) sunflower oil–PFX-10 ZnO (TP), (d) macadamia nuts oil–PF-10 Eight Pearl 300S-Al, (e) rapeseed oil–PF-10 FSE-Al, and (f) water–PF-10 FSE-Al.

phase inversion. It was observed for all the particle-stabilized dry oil powders above the COPR. The foams contain spherical and nonspherical air bubbles coated with particles whose size is smaller than the oil droplets in dry oil powders. The inversion was confirmed by the drop test in that foams dispersed in the neat oil whereas dry oil powders did not. This phase inversion can be likened to that in emulsions⁴⁵ and is driven by the high oil:particle ratio. Phase inversion driven in this way has been reported for dry water¹⁹ and for dry oil powders stabilized by fluorinated platelet particles.²¹ The latter was said to be driven by the increasing size of oil droplets at a fixed mass of particles which increases the total area of oil surfaces particles can coat in the dry oil powder compared to that of the air surfaces within the vessel, making the oil-in-air powders metastable. Most of the oil foams showed signs of liquid drainage and coalescence upon storage; however, some of them were very stable to both drainage and coalescence for over 2 years (see Table 5). Coalescence is presumably due to the progressive wetting of the particles by the oils. In systems where coalescence was observed, the particles entered the oils and the air bubbles were lost. Examples of some of the foams are given in Figure 8 where the fluid nature of the PFX-10 ZnO (TP) squalane foam is evident. The viscoelastic nature of the other particle-stabilized foams is also illustrated in Figure 8 for the PF-10 Eight Pearl 300S-Al squalane foam.

Table 5. Stability of Oil Foams for Different Systems

particle	drainage	coalescence	ultrastable
PFX-10 ZnO (TP)	all oils except those listed under the other headings	olive oil, sunflower oil, α -hexylcinnamaldehyde, and glyceryl tri(2-ethylhexanoate)	<i>n</i> -dodecane and phenyl silicone
PF-10 Eight Pearl 300S-Al	all oils except those listed under the other headings	olive oil, rapeseed oil, and α -hexylcinnamaldehyde	<i>n</i> -dodecane, <i>n</i> -tetradecane isocetane, phenyl silicone, and tripropylene glycol trimethyl acetate
PF-10 FSE-Al	all oils except those listed under the other headings	tripropylene glycol trimethyl acetate, sunflower oil, rapeseed oil, and α -hexyl- cinnamaldehyde	<i>n</i> -dodecane, <i>n</i> -tetradecane, silicone 20 cS, isocetane, and phenyl silicone

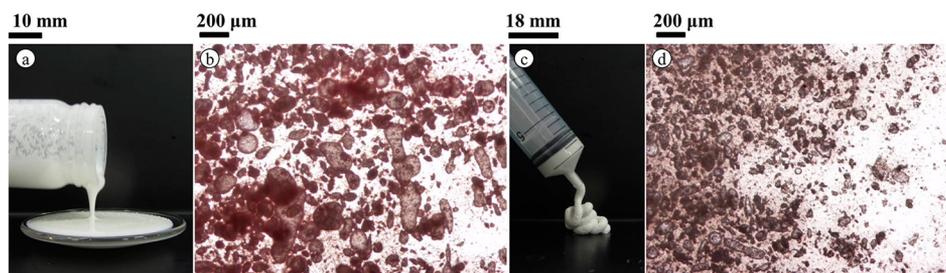


Figure 8. (a) Photo of squalane foam stabilized by PFX-10 ZnO (TP) particles being poured onto a Pyrex watch glass, (b) optical micrograph of foam in (a), (c) photo of squalane foam stabilized by PF-10 Eight Pearl 300S-Al particles being forced from a plastic syringe onto a black aluminum substrate and (d) optical micrograph of foam in (c). The foams were obtained by inverting the corresponding dry oil powders and viewed soon after formation.

Correlation between Type of Material Formed and Air–Liquid–Solid Contact Angle. It has been shown^{4,5,10,21} that the type of material preferred from a mixture of air, liquid, and solid particles depends *inter alia* on the contact angle that the particles exhibit with the liquid. For $\theta = 0^\circ$ (180°), the liquid wets (does not wet) the particles completely with no particle adsorption occurring. For values of θ between these extremes, particles are more wetted by the air ($\theta > 90^\circ$) or liquid ($\theta < 90^\circ$) phase and liquid marbles/dry liquid powders or foams are stabilized, respectively, at least in the case of water and certain spherical particles.^{2,19} However, the contact angles we measure do not refer to the particles themselves but on disks composed of many particles. The possibility exists that certain surface groups are buried during compression of the particles which may influence the values of θ measured. In addition, for the platelike particles, it may be that the fluoro-coating differs on the faces compared with the edges. The configuration of these asymmetric particles at the liquid interface within oil foams and oil powders is unknown at present, although the likely configuration at an air–water surface has been discussed by Garrett who shows that it depends on the particle geometry.⁴⁶ As a result, establishing a clear correlation between θ and the type of material presents a challenge. Despite this, we list both the advancing and receding contact angle values along with the type of material obtained from selected oil and particle combinations in Table 4. The liquids are arranged in order of increasing surface tension. For the PFX-10 Kunipia F particles, which were completely or partially wetted by a few oils at rest, the advancing θ ranges from 0° (water) to 104° (2-ethylhexyl-4-methoxycinnamate) with hysteresis of $>20^\circ$ in many cases. The wetting by water is complicated due to the imbibition of water into the particle disk. Upon vigorous agitation, the liquid–particle combinations all form a particle dispersion, but marbles were obtained with all the combinations except cyclomethicone and water. For the PFX-10 ZnO (TP), PF-10 Eight Pearl 300S-Al, and PF-10 FSE-Al particles, values of advancing θ were between 54° (cyclomethicone) and 127° (water), 61° (cyclomethicone) and 127° (water), and 49° (cyclomethicone) and 132° (water),

respectively, with high ($>25^\circ$) hysteresis in many cases. Relatively smooth surfaces are known to have high contact angle hysteresis¹³ compared to rough ones.⁴⁷ Unlike the PFX-10 Kunipia F particle–liquid combinations, foams were obtained with the other particle–liquid combinations upon vigorous agitation provided the γ_{la} of the liquid is above 26 mN m^{-1} ; otherwise, a particle dispersion results, and climbing films form in water (highest tension). Also, the particles were able to stabilize marbles of all the liquids except PFX-10 ZnO (TP)–cyclomethicone or PDMS 6 cS combination. It is clear that, for these particles, the stabilization of foams and marbles can be achieved in one and the same system depending on the mixing conditions.

The cosine of both the advancing and receding θ on particle disks is plotted as a function of γ_{la} in Figure 9. An example of a typical disk is seen in the inset. It can be seen that the magnitude of $\cos \theta$ decreases with increasing γ_{la} . Such plots are often linear of negative gradient for certain smooth substrates, for example, poly(tetrafluoroethylene) (PTFE).⁴⁸ When the data for all particle types are extrapolated to $\cos \theta = 1$, the estimated critical surface tension is around $12\text{--}15 \text{ mN/m}$, similar to that of PTFE of 18 mN/m . The areas on the graphs are divided into different regions depending on whether dispersions, foams, or climbing films appear after vigorous agitation or whether dry oil powders form after gentle mixing. The boundaries between the different regions depend on which angle is taken, as the receding θ is always less than the advancing one. During the mixing of particles and liquid, it is unknown which angle is operative. For oil–water systems, the type of emulsion was seen to depend on which liquid first makes contact with the particles and the observation was argued⁴⁹ in terms of the hysteresis in the contact angle. Apart from the PFX-10 Kunipia F particles that form a particle dispersion with all the liquids, it can be seen that a particle dispersion forms when $\cos \theta$ is between 0.05 and 0.7 (advancing) or between 0.4 and 0.85 (receding), whereas a foam and dry oil powder form when $\cos \theta$ is <0.05 (advancing) or <0.4 (receding) for the other particles. Similar findings have

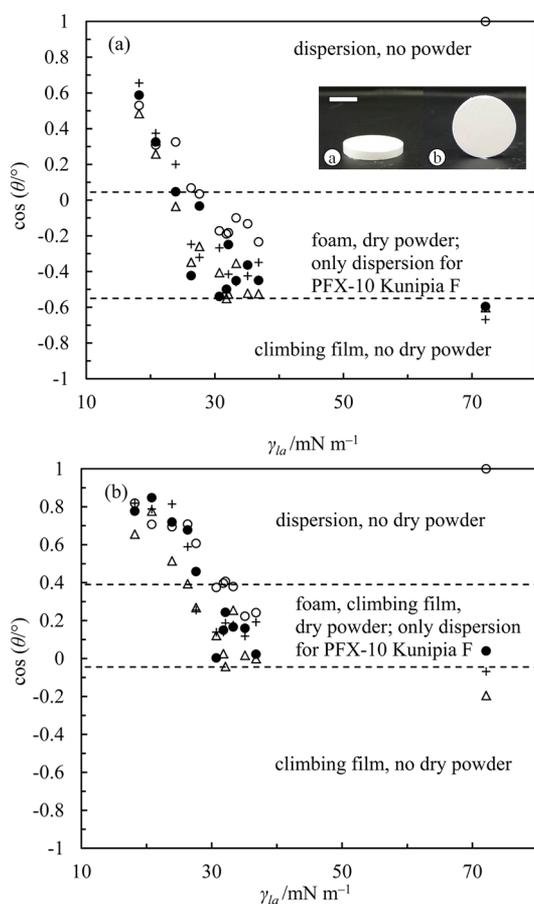


Figure 9. Cosine of (a) advancing and (b) receding θ of a liquid droplet in air on compressed particle disks of PFX-10 Kunipia F (○), PFX-10 ZnO (TP) (●), PF-10 Eight Pearl 300S-Al (Δ), and PF-10 FSE-Al (+) particles versus γ_{la} at 25 °C. Inset: photograph of (a) side and (b) top view of an PF-10 Eight Pearl 300S-Al disk made by compressing 500 mg of the powdered particles (scale bar = 6 mm). The type of material formed upon vigorous agitation or gentle mixing is also given, respectively.

been reported previously on PTFE,⁴ fluorinated silica,⁵ and fluorinated clay platelet²¹ particles.

CONCLUSIONS

Different kinds of materials can be stabilized in mixtures of fluorinated particles, oil, and air. They depend on the surface energy of the particles, the surface tension of the oil, and the energy input. These include liquid oil marbles, powdered dry oil, and oil foam. Vigorous agitation produces either oil dispersions in all the liquids containing relatively large bentonite particles and in liquids of relatively low γ_{la} like *n*-dodecane and cyclomethicone containing the other particles, or particle-stabilized air-in-oil foams in liquids having $\gamma_{la} > 26 \text{ mN m}^{-1}$ where the advancing θ lies between ca. 90° and 120° . However, oil-in-air marbles were obtained with all the oil-particle combinations upon gentle agitation, except in cases where the advancing θ is $< 60^\circ$. For oils of tension $> 24 \text{ mN m}^{-1}$ and omniphobic sericite and zinc oxide particles for which advancing $\theta \geq 90^\circ$, dry oil powders which do not leak oil for over 2 years were also stabilized by gentle agitation up to a COPR. The dry oil powders invert to air-in-oil foams above COPR. The dry oil powders with $\geq 60 \text{ wt } \%$ of oil release oil

when sheared on a substrate while the oil foams disappear, leaving an oily surface once sheared.

AUTHOR INFORMATION

Corresponding Author

*E-mail: b.p.binks@hull.ac.uk

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the Tertiary Education Trust Fund of Nigeria and the University of Hull for a scholarship award to A.T.T., Mr. A. Sinclair (University of Hull) for the SEM images, and Shiseido (Japan) for partial financial support.

REFERENCES

- (1) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 503–546.
- (2) Binks, B. P.; Horozov, T. S. Aqueous Foams Stabilized Solely by Silica Nanoparticles. *Angew. Chem., Int. Ed.* **2005**, *44*, 3722–3725.
- (3) Gonzenbach, U. T.; Studart, A. R.; Tervoort, E.; Gauckler, L. J. Stabilization of Foams with Inorganic Colloidal Particles. *Langmuir* **2006**, *22*, 10983–10988.
- (4) Binks, B. P.; Rocher, A.; Kirkland, M. Oil foams stabilised solely by particles. *Soft Matter* **2011**, *7*, 1800–1808.
- (5) Binks, B. P.; Tyowua, A. T. Influence of the degree of fluorination on the behaviour of silica particles at air-oil surfaces. *Soft Matter* **2013**, *9*, 834–845.
- (6) Schulman, J. H.; Leja, J. Control of contact angles at the oil-water-solid interfaces. *Trans. Faraday Soc.* **1954**, *50*, 598–605.
- (7) Stocco, A.; Rio, E.; Binks, B. P.; Langevin, D. Aqueous foams stabilized solely by particles. *Soft Matter* **2011**, *7*, 1260–1267.
- (8) Aussillous, P.; Quéré, D. Liquid marbles. *Nature* **2001**, *411*, 924–927.
- (9) McEleney, P.; Walker, G. M.; Larmour, I. A.; Bell, S. E. J. Liquid marble formation using hydrophobic powders. *Chem. Eng. J.* **2009**, *147*, 373–382.
- (10) Binks, B. P.; Rocher, A. Stabilisation of liquid-air surfaces by particles of low surface energy. *Phys. Chem. Chem. Phys.* **2010**, *12*, 9169–9171.
- (11) Sheen, Y.-C.; Huang, Y.-C.; Liao, C.-S.; Chou, H.-Y.; Chang, F.-C. New approach to fabricate an extremely super-amphiphobic surface based on fluorinated silica nanoparticles. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46*, 1984–1990.
- (12) Campos, R.; Guenther, A. J.; Haddad, T. S.; Mabry, J. M. Fluoroalkyl-Functionalized Silica Particles: Synthesis, Characterization, and Wetting Characteristics. *Langmuir* **2011**, *27*, 10206–10215.
- (13) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. Robust omniphobic surfaces. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 18200–18205.
- (14) Eshtiaghi, N.; Hapgood, K. P. A quantitative framework for the formation of liquid marbles and hollow granules from hydrophobic powders. *Powder Technol.* **2012**, *223*, 65–76.
- (15) Aussillous, P.; Quéré, D. Properties of liquid marbles. *Proc. R. Soc. Chem. London A* **2006**, *462*, 973–999.
- (16) Bormashenko, E. Liquid marbles: Properties and applications. *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 266–271.
- (17) Bormashenko, E.; Musin, A. Revealing of water surface pollution by liquid marbles. *Appl. Surf. Sci.* **2009**, *255*, 6429–6431.
- (18) Tian, J.; Arbatan, T.; Li, X.; Shen, W. Liquid marble for gas sensing. *Chem. Commun.* **2010**, *46*, 4734–4736.
- (19) Binks, B. P.; Murakami, R. Phase inversion of particle-stabilized materials from foams to dry water. *Nat. Mater.* **2006**, *5*, 865–869.
- (20) Murakami, R.; Bismarck, A. Particle-Stabilized Materials: Dry Oils and (Polymerized) Non-Aqueous Foams. *Adv. Funct. Mater.* **2010**, *20*, 732–737.

- (21) Binks, B. P.; Sekine, T.; Tyowua, A. T. Dry oil powders and oil foams stabilised by fluorinated clay platelet particles. *Soft Matter* **2014**, *10*, 578–589.
- (22) Barthlott, W.; Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**, *202*, 1–8.
- (23) Pike, N.; Richard, D.; Foster, R.; Mahadevan, L. How aphids lose their marbles. *Proc. R. Soc. London B* **2002**, *269*, 1211–1215.
- (24) Kralchevsky, P. A.; Nagayama, K., Eds. Capillary interactions between particles bound to interfaces, liquid films and biomembranes. *Adv. Colloid Interface Sci.* **2000**, *85*, 145–192.
- (25) Binks, B. P.; Johnson, A. J.; Rodrigues, J. A. Inversion of 'dry water' to aqueous foam on addition of surfactant. *Soft Matter* **2010**, *6*, 126–135.
- (26) Binks, B. P.; Duncumb, B.; Murakami, R. Effect of pH and Salt Concentration on the Phase Inversion of Particle-Stabilized Foams. *Langmuir* **2007**, *23*, 9143–9146.
- (27) Forny, L.; Pezron, I.; Saleh, K.; Guigon, P.; Komunjer, L. Storing water in powder form by self-assembling hydrophobic silica nanoparticles. *Powder Technol.* **2007**, *171*, 15–24.
- (28) Forny, L.; Saleh, K.; Denoyel, R.; Pezron, I. Contact Angle Assessment of Hydrophobic Silica Nanoparticles Related to the Mechanisms of Dry Water Formation. *Langmuir* **2009**, *26*, 2333–2338.
- (29) Carter, B. O.; Adams, D. J.; Cooper, A. I. Pausing a stir: heterogeneous catalysis in "dry water". *Green Chem.* **2010**, *12*, 783–785.
- (30) Carter, B. O.; Wang, W.; Adams, D. J.; Cooper, A. I. Gas Storage in "Dry Water" and "Dry Gel" Clathrates. *Langmuir* **2009**, *26*, 3186–3193.
- (31) Mezzenga, R.; Ulrich, S. Spray-Dried Oil Powder with Ultrahigh Oil Content. *Langmuir* **2010**, *26*, 16658–16661.
- (32) Adelman, H.; Binks, B. P.; Mezzenga, R. Oil Powders and Gels from Particle-Stabilized Emulsions. *Langmuir* **2012**, *28*, 1694–1697.
- (33) Murakami, R.; Moriyama, H.; Yamamoto, M.; Binks, B. P.; Rocher, A. Particle Stabilization of Oil-in-Water-in-Air Materials: Powdered Emulsions. *Adv. Mater.* **2012**, *24*, 767–771.
- (34) Carter, B. O.; Weaver, J. V. M.; Wang, W.; Spiller, D. G.; Adams, D. J.; Cooper, A. I. Microencapsulation using an oil-in-water-in-air 'dry water emulsion'. *Chem. Commun.* **2011**, *47*, 8253–8255.
- (35) Perng, Y.-S.; Wang, E.I.-C.; Lu, C.-C.; Kuo, L.-S. Application of sericite to WLC coatings. *TAPPI J.* **2008**, *3*, 21–31.
- (36) Shen, Y.-H. Preparations of organobentonite using nonionic surfactants. *Chemosphere* **2001**, *44*, 989–995.
- (37) Owens, D. K.; Wendt, R. C. Estimation of the surface free energy of polymers. *J. Appl. Polym. Sci.* **1969**, *13*, 1741–1747.
- (38) Fowkes, F. M. Additivity of intermolecular forces at interfaces. I. Determination of the contribution to surface and interfacial tensions of dispersion forces in various liquids 1. *J. Phys. Chem.* **1963**, *67*, 2538–2541.
- (39) Van Oss, C. J. *Interfacial Forces in Aqueous Media*; Marcel Dekker: New York, 1994.
- (40) Young, T. An essay on the cohesion of fluids. *Philos. Trans. R. Soc. London* **1805**, *95*, 65.
- (41) Clint, J. H.; Wicks, A. C. Adhesion under water: surface energy considerations. *Int. J. Adhes. Adhes.* **2001**, *21*, 267–273.
- (42) Binks, B. P.; Clint, J. H.; Fletcher, P. D. I.; Lees, T. J. G.; Taylor, P. Particle film growth driven by foam bubble coalescence. *Chem. Commun.* **2006**, 3531–3533.
- (43) Bormashenko, E.; Progreb, R.; Whyman, G.; Musin, A. Surface tension of liquid marbles. *Colloids Surf., A* **2009**, *351*, 78–82.
- (44) Subramaniam, A. B.; Abkarian, M.; Mahadevan, L.; Stone, H. A. Mechanics of Interfacial Composite Materials. *Langmuir* **2006**, *22*, 10204–10208.
- (45) Binks, B. P.; Isa, L.; Tyowua, A. T. Direct Measurement of Contact Angles of Silica Particles in Relation to Double Inversion of Pickering Emulsions. *Langmuir* **2013**, *29*, 4923–4927.
- (46) Garrett, P. R. *Defoaming: Theory and Industrial Applications*, Garrett, P. R. Ed.; Surfactant Science Series; Marcel Dekker: New York, 1993; p 1.
- (47) Quéré, D. Wetting and Roughness. *Annu. Rev. Mater. Res.* **2008**, *38*, 71–99.
- (48) Fox, H. W.; Zisman, W. A. The spreading of liquids on low-energy surfaces. III. Hydrocarbon surfaces. *J. Colloid Sci.* **1952**, *7*, 428–442.
- (49) Binks, B. P.; Rodrigues, J. A. Types of Phase Inversion of Silica Particle Stabilized Emulsions Containing Triglyceride Oil. *Langmuir* **2003**, *19*, 4905–4912.