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Patterning of a Drying Emulsion Film

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ABSTRACT: Stabilizing layers of colloidal dispersions or emulsions to obtain homogeneous films is a real challenge. We describe here a new kind of instability in drying films of emulsions: during evaporation of the internal phase, cracks appear between the droplets that create aggregates according to a regular pattern. We show that this pattern only appears if the emulsion is adhesive, i.e., if droplets stick together. The pattern exhibits a characteristic length which depends on the adhesion strength and film thickness. These experimental results support a model where this instability is due to the gel structure and elastic properties of adhesive emulsions. Understanding this phenomenon will allow us to get a homogeneous film or to control it to get structured materials.



Article

■ INTRODUCTION

Studying films is important for many different industrial domains such as coatings,¹ cosmetics,² and microelectronics.³ Deposited materials are usually particle dispersions as in paints or emulsions as in cosmetics, enabling them to meet requirements such as anticorrosion,⁴ color,⁵ and sensoriality.⁶ In addition, volatile phases are essential so that the material is fluid enough to be spread but solid when dry. Evaporation, most of the time part of the external phase, may provoke instability.⁷ For example, dewetting may appear due to differential evaporation of the solvents.^{8–11} Other capillary phenomena may cause convection that structures the film.¹²⁻¹⁴ Boundary conditions strongly affect evaporation,¹⁵ as discussed notably for evaporation of droplets.^{16,17} Furthermore, in deposited films of colloidal dispersions cracks have been regularly observed.^{18,19} The crack mechanism has been studied for thin films of coatings,²⁰ old paintings,²¹ and even blood.²² These processes lead to heterogeneities and may alter the properties of the material over time,²³ so they need to be limited. Some solutions already exist for these described instabilities. $^{24-26}$

We have discovered a new kind of instability for water-in-oil emulsion drying films deposited on a polyester plastic sheet at thicknesses from 20 to 150 μ m. During water droplets evaporation, cracks appear and separate droplets into aggregates. These aggregates have a regular pattern. We experimentally show that this pattern is exhibited only if the emulsion is adhesive, according to a characteristic length which increases with the film thickness but does not depend on the volume fraction of the droplets. These experimental results led us to a phenomenological explanation.

MATERIALS AND METHODS

The studied emulsion is a water-in-oil emulsion. The internal phase consists of a MgSO₄ solution (2% wt MgSO₄ (Sigma-Aldrich) in deionized water). The external phase is a mixture of dodecane

(Sigma-Aldrich) and silicone oil (1000 cSt, Aldrich), the relative proportions of which can be varied. Water droplets are stabilized with Span 80 (sorbitan monooleate, Sigma) at 0.9% wt regarding the oily phase. A primary concentrated emulsion is formulated with a large quantity of surfactant (15% wt) and silicone oil (8% wt) and a small amount of dodecane (2% wt), adding progressively 75% wt of salted water mixed manually with a mortar. To reduce the surfactant concentration to 0.9% wt and eventually adjust the ratio of dodecane to silicone oil, this primary emulsion is diluted and centrifuged at 200g. Water droplets are concentrated as a pellet at the bottom of the centrifuge tube, where they have a volume fraction of about 75% vol, which corresponds to 80% wt. We get a monodisperse emulsion with small droplets. The diameter has been measured to be about 600 nm using static light scattering (Mastersizer 3000, Malvern). To enhance contrast and improve observation, tracers (iron oxide particles, diameter 300 nm, Sensient) may be added afterward, about 0.1% wt. We have checked that they follow the droplets organization without disturbing the phenomenon.

The surface tension between the two phases of the emulsion is measured using the pendant drop method (Drop Shape Analyzer, Krüss). The contact angle between droplets is estimated by observing big droplets (about 30 μ m diameter) of the studied emulsions under an inverted microscope (Eclipse Ti, Nikon).27 Rheological characterization is done using a stress-controlled rheometer (Discovery AR-G2, TA-Instruments) with stress = 6 mPa, oscillatory frequency = 1.5 rad/ s, and strain = 2%.

Emulsions are spread using an automatic film applicator (bykodrive, BYK) and a bar applicator (PA-5355, BYK) on a transparent polyester film (PA-2870, BYK). This substrate has been chosen because it is convenient to spread the sample and to observe the sample with a transmission microscope. Moreover, it is used in the cosmetics industry because the wetting properties are close to those of

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the skin. The initial film thickness is measured just after application using a wet film thickness gauge (Erichsen). The uncertainty is estimated to be 50 \pm 5 μ m considering the standard deviation for an emulsion applied on 5 different films at a given thickness. The film is observed under a transmission microscope (Eclipse Ti, Nikon) over time. Image data is processed using Fourier transform radially averaged to quantify the patterning. Images are recorded with 4× magnification to get at least 10 iterations of the pattern. The analysis is limited by the size of the image $L_{\text{image}} = 3240 \ \mu\text{m}$ and the size of a pixel $L_{\text{pixel}} = 1.62 \ \mu\text{m}$. A dark reference—with an opaque sample—is subtracted, and the images are normalized by illumination of the background, which corresponds to the bare substrate. If the spatial frequency f stands out in the Fourier analysis of normalized images, the patterning describes a characteristic length $L_{car} = 1/f$. Evaporation of the emulsion layers is measured thanks to mass measurement. The system {film + substrate} is weighed over time. The mass is deduced from the initial mass and then normalized by the effective radius of the film. This enables one to compare samples of different surfaces.²

RESULTS AND DISCUSSION

Water Evaporation Leads to Film Patterning. For a 50 μ m thick film of an emulsion containing 19.1% wt silicone oil, 80% wt of dodecane, and 0.9% wt of surfactant in the external phase, 80% wt water, and 0.1% wt tracers, the film is homogeneous just after deposition; concentrated droplets are in contact. As shown in Figure 1, cracks appear after a few



Figure 1. (a) Zoom of transmission microscope images for a 50 μ m thick film of emulsion containing 19.1% wt silicone oil, 0.9% wt surfactant, and 80% wt dodecane in the external phase, 80% wt water, and 0.1% wt tracers just after application, 4 min after application, and 8 min after application, when all water has evaporated. Regular pattern appears over time. (b) Scheme of the observed instability: during drying, water droplets evaporate, their size decreases, and they create aggregates separated by oil. (c) Radially averaged Fourier transform of the microscope images: pattern appears according to a characteristic length that remains constant over time.

minutes between the droplets that become separated with oil (see Movie 1). Droplets scatter light and appear dark, whereas the bright surface corresponds to oil. Droplet aggregates draw a pattern and then retract. Tracking the mass of the film over time shows that it is essentially water that evaporates from the film, while the amount of oil remains almost constant (see Figure S1). As we never observe coalescence events between the drops, their radius must then decrease over time. Tracers follow and emphasize droplet organization that remains even after evaporation. At the initial time, the Fourier transform spectrum shows a uniform picture. Over time, a characteristic length of typically 100 μ m, corresponding to the distance between two aggregates, is exhibited. This length remains constant over time from apparition of the aggregates until complete evaporation of the internal phase (see Figure 1c).

During the whole process, the interface is glossy, so no surface rugosity has appeared; the interface remains flat.

Role of Adhesion between Droplets. To understand this phenomenon, we considered the physicochemical properties of emulsions, in particular, droplet interaction. Previous works have shown that this kind of inverse emulsion may be adhesive,²⁷ which means there is a strong attraction between the droplets. Once in contact, they are distorted according to a contact angle θ as illustrated in the inset of Figure 2. The



Figure 2. Characteristic length (blue circles) is measured for a 50 μ m thick film of emulsions containing various concentrations of silicone oil and dodecane in the external phase, 80% wt water, and 0.1% wt tracers, after drying. Uncertainty is estimated to be 6 μ m thanks to the standard deviation on a given emulsion applied on five different films. Elastic modulus (orange crosses) is measured for emulsions containing various concentrations of silicone oil, 63% wt of water, and 0.1% wt tracers with oscillating shear at 1.5 rad/s, stress at 6 mPa, and strain at 2%. Error bars are estimated to be 30% according a variation coefficient of 5 repetitions of the measurement on a given emulsion (19.1% wt silicone oil, 80% wt dodecane, and 0.9% wt surfactant in the external phase, 63% wt water, and 0.1% wt tracers). Adhesion increases with the concentration of silicone oil in the external phase. Patterning appears when the emulsion is adhesive. (Inset) Schematic of two adhesive droplets.

adhesion depends on different parameters²⁹ including surfactant solubility: the less soluble the surfactant in the external phase, the more adhesive the emulsion.²⁷ Indeed, the surfactant is localized at the surface of the droplets. When its hydrophobic tail is in poor solvent, it tends to interact with the surfactant molecules on neighboring droplets and form a bilayer between the droplets. In our case, Span 80 is very soluble in dodecane but not in silicone oil, so adhesion increases with the quantity of silicone oil in the external phase.²⁷ A range of emulsions more or less adhesive is formulated by changing the ratio of dodecane/silicone oil in the external phase but keeping the same concentration of surfactant. They all come from the same primary emulsion; only dilution is adjusted. We thus consider that they are identical, including the droplet size, except for the adhesion. These emulsions are applied in thin films and observed during drying. For low amounts of silicone oil (<1% wt), no patterning is observed and no characteristic length is measured. For larger amounts of silicone oil (>1% wt), a pattern appears with a characteristic length that increases with the quantity of silicone oil, as shown in Figure 2.

To determine whether the studied emulsions are adhesive or not, the elastic modulus is measured for each of them, slightly diluted at 63% wt, corresponding to 56% vol of water. Indeed, it has been shown that adhesive emulsions exhibit an elastic modulus even below random close packing ($\sim 64\%$ vol): for an adhesive emulsion, the bonds between droplets leads to the formation of a cohesive connected network of aggregates and create a gel³⁰ that can support a shear stress.³¹ As shown in Figure 2, emulsions containing less than 1% wt of silicone oil in the external phase exhibit no elasticity, so they are not adhesive. On the contrary, those containing more than 1% wt of silicone oil demonstrate significant elasticity, so they are adhesive. These results are consistent with microscopic observation when emulsions are diluted: for nonadhesive emulsions, droplets are separated and present a clear Brownian motion whereas as the amount of silicon oil increases above 1% wt droplets aggregate. We conclude that patterning occurs only for adhesive emulsions, and the characteristic length increases with silicone oil amount, which means with adhesion.

Patterning Depends on Film Thickness. The behavior of an adhesive emulsion (19.1% wt silicone oil and 80% wt dodecane in external phase, 80% wt water, and 0.1% wt tracers) has been investigated at different film thicknesses and volume fractions of water. A pattern appears whatever the thickness in the studied range, from 20 to 150 μ m, and concentration of water droplets, from 25% to 80% wt corresponding to volume fractions from 20% to 75% vol. The characteristic length increases linearly with the initial thickness, as shown on Figure 3. However, we show that it does not depend on the volume fraction of droplets (see Figure S2). This result is surprising because the volume fraction of droplets influences the rheological properties of the emulsion, and we expect that rheology has a strong impact on a kinetic phenomenon like this one.

The kinetics of the cracks can be followed binarizing the images and quantifying the bright surface, that is the surface where there are no droplets. Just after deposition, the image is mainly dark because the scattering droplets are concentrated and all connected. When cracks appear, a bright surface increases according to the shrinkage speed. When all of the water has evaporated, almost the entire picture is bright and only tracers remain. We can extract the time of crack, shown in Figure 3 for different initial thicknesses, with a relative uncertainty of a few minutes depending on the binarization threshold. Evaporation measurements show that in the first minutes evaporation does not depend on the thickness of the film and corresponds to evaporation of bulk water (see Figure S1). Considering the time of crack and the evaporation rate, we compute that cracks appear when the droplet volume has



Figure 3. Characteristic length increases with the initial thickness. (a) Zoom of transmission microscope images for an adhesive emulsion (19.1% wt silicone oil and 80% wt dodecane in the external phase) with 80% wt water and 0.1% wt tracers applied on a plastic sheet at different initial thicknesses after drying. (b) Characteristic length measured after drying (black dots) and time of crack (blue squares) according to the initial thickness for this adhesive emulsion. $L_{\rm car}$ data corresponds to the mean value \pm standard deviation calculated based on measurements on 5 different locations of each film. Dotted line corresponds to a linear fit.

decreased $\delta \approx 10\%$, whatever the initial thickness is. The rupture seems to be due to geometrical constrains on the droplets: they have retracted a given volume at crack time.

Proposed Model for Drying Emulsion Patterning. Numerous instabilities have been observed in drying films: changes in composition may induce dewetting,⁹ convection,¹³ phase transition,³² etc. In our case, the instability takes place on oleophilic (polyester) or hydrophilic (glass, data not shown) solid surfaces, which seems to exclude dewetting phenomena. The air–liquid interface remains flat throughout water evaporation, which is not compatible with the appearance of Marangoni-type instability coupled to hydrodynamics. Finally, the composition of the continuous phase remains essentially unchanged during the experiment, and the phenomenon is independent of the volume fraction of the water drops, which presumably rules out a phase transition in the oil or of the emulsion as a whole.

The observed patterns may also be due to mechanical instabilities when mechanical stress is released through cracks or delamination. The crack mechanism has been studied for thin films of coatings,²⁰ paints,²¹ or miscellaneous colloidal dispersions.³³ Upon solvent evaporation, films bonded to the substrate often develop tensile stresses. Opening cracks are considered when the elastic energy stored in the material becomes greater than the interfacial energy needed to create new surfaces.

One key observation in our case is that the instability appears only for adhesive emulsions, i.e., for samples with a nonzero elastic modulus. We will therefore consider here a mechanical model of the instability. For an adhesive emulsion, the bonds between droplets lead to the formation of a connected network of aggregates and create a gel³⁰ that can support a shear stress.³¹ We will assume that this gel is also connected to the plastic film underneath. Indeed, in the case of adhesive inverse emulsions, at the surface of the droplets, the hydrophobic part of the surfactant being in poor solvent, it generally prefers to adhere to hydrophobic substrates (or to form bilayers between the droplets or between droplets and hydrophilic substrates). Shrinkage of water droplets during water evaporation creates elastic stress among the gel that cannot be relaxed due to the adhesion to the substrate. At some point it has to be released through a crack. In accordance with this hypothesis, no significant movement is observed before the appearance of fractures (Figure 1 and Movie in SI).

More precisely, we will model the emulsion as an isotropic elastic film bonded to a rigid substrate. The film is uniformly stressed prior to cracking. A simplified two-dimensional model has been proposed for such cases, which accounts for multiple experimental observations.^{34,35} When a linear fracture appears, the stress will relax transversally on each side of the fracture over a distance on the order of the thickness *h* with an exponential decay.³⁴ At larger distances, adhesion to the rigid substrate prevents stress–relaxation, so new fractures may appear. In the case of parallel cracks, the distance between the fractures L_{car} should be then around 2*h*. A more rigorous calculation shows indeed that the characteristic length L_{car} between two parallel fractures is proportional to the thickness *h* with a numerical prefactor that depends on the elastic response of the material.³⁵

We can see that this simple mechanical model accounts for our two major experimental observations: on one hand, instability does not appear for nonadhesive emulsions (Figure 2) because there can be no tension stress in the emulsion. On the other hand, the characteristic length of the instability is proportional to the thickness (Figure 3). It is interesting to note that this model, originally used for rigid materials (elastic modulus > MPa), applies equally well to these soft materials (elastic modulus of a few tens of Pa).

If we compare it to mechanical instability with a suspension of solid particles, we note several differences. The origin of the instability is different in that case; it is related to the capillary action. The meniscus between particles at the interface with air reduces the pressure inside the film and thus induces the tensile stress. The properties of the dispersed phase will strongly influence the process (initial volume fraction of particles, their deformability).²¹ In our case, it is rather the properties of the continuous phase that are important (solubility of the surfactant). These findings are important because they imply very different solutions if we want to avoid fracture formation.

CONCLUSION

We describe a new instability in drying emulsion films occurring during evaporation of the internal phase: cracks appear between adhesive droplets, creating aggregates according to a regular pattern. We determined that this phenomenon is generic for different adhesive emulsions on different substrates. Considering previous works on painting cracks, we suggest that this phenomenon is due to the gel structure of this kind of emulsion and the elastic properties.

Previous works have mainly focused on the effect of evaporation of the external phase. We believe that it is relevant to deepen our results since inverse emulsions are usually adhesive and widely used in industry. Furthermore, industrial systems are often even more complex, containing colloidal particles also. It will be interesting to understand the coupling effects of adhesive emulsions and colloidal dispersions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.1c00246.

Complementary experimental results about evaporation and impact of the volume fraction on characteristic length (PDF)

Transmission microscope images for a 50 μ m thick film of emulsion containing 19.1% wt silicone oil, 0.9% wt surfactant, and 80% wt dodecane in the external phase, 80% wt water, and 0.1% wt tracers after application on a polyester sheet (MP4)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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