In-situ Characterization of Drying Particulate Coatings

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Abstract

Film thin drying is a process to create functional interfaces in solidifying liquids, rather than to separate volatile components from solutions or suspensions. Indeed, recent developments in coating technologies have shed light on self-organization in evaporating complex thin fluids. In particulate coatings, final properties of dried film depend not only on initial liquid compositions but also the imposed drying conditions, which significantly influence local particle distributions, contact area of rigid and/or deformable particles, anisotropic particle orientation, and amounts of adsorbed molecules on particle surfaces. It is of importance to understand how a directional film shrinkage and spontaneous solidification constrain the particle motions, and how they induce particular film structures in a non-equilibrium state. Recently, there has been a great deal of progress in measurement techniques and numerical approaches for analyzing transient structures in evaporating thin liquid films. This article presents an overview of current research activities on local, in-situ determination of (i) fluid properties at air-liquid and liquid-liquid interfaces, and (ii) distributions of particles or solutes in the thickness direction in shrinking films.

Keywords: coating, drying, suspension, interfaces, modeling

1. Introduction

Drastic changes in local structures and physical properties emerge when thin liquid film suspension or solution coatings dry or solidify. Typical examples include molecular adsorptions at interfaces, reductions in solvent diffusivity due to polymer-chain entanglements, phase separation, crystallization, and bubble nucleation in concentration solutions, the electrostatic ordering and/or disordering of particles, air invasion in pore spaces, stress developments due to capillary forces and/or an anisotropic film shrinkage, buckling, cracking and other deformations of interfaces to release the stress, and even chemical reactions by irradiations of ultraviolet lights or electron beams. The major difficulty stems from the fact that these local phenomena can co-exist in the liquid with different time scales, and significantly influence the bulk fluid properties, which, in turn, alter the local dynamic events in the fluids in a complicated manner. Because of complexity of the system, the physics of drying of thin films is still far from complete understanding, and what determines the characteristics of final film products often remains unresolved.

Despite formidable difficulties inherent in film drying, there has been a great deal of progress in experimental and numerical analyses of evaporating thin films. In this short review, we attempt to provide a brief guide to the recent in-situ monitoring techniques (Table 1) and some modeling approaches on micro-structuring of suspension and solution films. In order to access how the drying operation impacts the fluid structures, we restrict ourselves on a simple case of a non-reactive, initially homogeneous, single liquid film coated on an impermeable, smooth solid surface. Drying of multi-layer liquid coating would receive extensive practical interests, but it is beyond the scope of this review. Section 2 emphasizes variations in local fluid properties at air-liquid and liquid-liquid interfaces for evaporating liquid films. Some new, non-contact measurement techniques...
are introduced for determining local surface viscosities and surface tensions. Section 3 assesses how the unidirectional film shrinkage competes against motions of particles or solutes to give particular concentration profiles in the film. Some advanced optical techniques for determining the local distributions are introduced and compared with other methods. The applications of the techniques to mono-dispersed particles, bimodal particles, surfactant solutions, polymer solutions, and combinations of these systems are discussed, and comparisons with numerical models are also addressed. Brief summaries and concluding remarks are shown in Section 4.

2. Local fluid Properties at air-liquid Interface

Monitoring of local viscosities and interfacial tensions at air-liquid and liquid-liquid interfaces is the key to understand how the solvent dries from a liquid surface. Indeed, a driving force for the solvent diffusion is provided by a partial pressure difference between the liquid-gas interface and the gas far from the interface. Furthermore, a significant drop in evaporation rate arises when a decrease in the solvent concentration causes diffusion coefficients of solvents to be decreased by orders of magnitude due to complex molecular interactions. However, conventional techniques based on mechanical contacts are hopeless to capture the time-dependent variations in interfacial properties without disturbing concentration and/or temperature profiles in the fluid. Recently, some attempts have been reported to use (i) thermally excited capillary waves called “ripplons” on a fluid surface, and (ii) fluid surface deformations imposed by a sudden laser irradiation, for non-contact measurement of surface viscosities and interfacial tensions.

2.1 Surface Wave (SW) methods

The liquid surface is, even macroscopically uniform, covered by capillary waves with amplitudes of the order of nanometers and the wavelengths of ~ 100 nm. When a laser light is irradiated on a fluid surface with propagating surface waves, the waves act as a diffraction grating and induce Doppler-shifted scattered components in response to the propagation speed. The scattered light signals include information on frequencies $\omega$ and attenuation rates $\Gamma$ of the surface waves. For Newtonian fluids of constant density $\rho$, these two quantities are the function of fluid viscosity $\mu$ and surface tension $\sigma$ for a given wave-number $k$ as:

$$\omega^2 = \left(\frac{\sigma}{\rho}\right) k^3,$$

$$\Gamma = 2 \left(\frac{\sigma}{\rho}\right) k^2.$$

Thus we can determine these two fluid properties by analyzing the scattered light signals. An example of the schematic experimental setup is shown in Fig. 1. The linearly S-polarized laser light was first divided into P-waves (incident beam) and S-waves (reference beam) by using a beam splitter, and then the frequencies of the split lights were shifted using acousto-optic modulators (AOM) to eliminate the influence of undesired external oscillations of the system. The scattered light, showing a heterodyne interference with the reference light, was received by a photomultiplier tube and processed by a high-speed fast Fourier transform (FFT) analyzer. This method has advantages over conventional methods as

(1) Non-contact technique applicable on fluids with micro/nano structures or even at high temperatures

(2) Suitable for real-time observation

Table 1. In-situ measurement techniques for drying films

| Properties                     | Methods                                 | Ref. |
|-------------------------------|-----------------------------------------|------|
| Surface viscosity &           | Ripplon surface wave                    | 1-3  |
| Interfacial tension           | Laser-induced surface deformation       | 4-7  |
| Concentration profiles        | Confocal Raman spectroscopy             | 17-20|
|                               | Infrared microscopy                     | 27   |
|                               | Magnetic resonance                      | 21   |
|                               | Cryogenic scanning electron microscopy  | 22-26|
| Tensile Stress                | Cantilever beam deflection              | 35-55|
|                               | Distortion of flexible reflective        | 56   |
|                               | membrane                                |      |
| Drying rate                   | Confocal Raman spectroscopy             | 17-20|
|                               | Infrared spectroscopy                   | 27-57|
|                               | Mass loss                               | 58   |
|                               | Temperature variation                   | 59   |
|                               | Heat flux variation                     | 60   |
|                               | Gas Chromatography                      | 61   |
| Reaction rate                 | Infrared spectroscopy                   | 54-55|
| Domain size                   | Light scattering                        | 62-63|

![Schematic setup of SW method](image-url)
local properties can be determined within orders of nanometers in thickness.

2.1.1 Pure liquids

Oki and Nagasaka applied the SW method to measure viscosities and surface tensions of pure Newtonian liquids (water, tetrahydrofuran, methyl ethyl ketone, methyl alcohol). They used 20 mW Nd:YAG laser with a wavelength of 532 nm as a light source in order to monitor the traveling surface waves, and the diffraction grating was chosen to be approximately 100 μm within a beam diameter of 750 μm. The determined kinematic viscosities ranged between 0.5 and 2 mm²/s, and showed a good agreement with those determined by the conventional falling ball methods. In addition, the static surface tension using Ripplon technique well reproduced the data measured by the Wilhelmy method, showing the validity of the SW method in a quantitative sense.

2.1.2 Polymeric liquid

The SW method was also applied to polymeric solutions of cellulose acetate butyrate (CAB) dissolved in methyl ethyl ketone (MEK). The polymer can adsorb onto the liquid surface to reduce the surface tension. When the adsorption and desorption of polymers are too slow compared with the surface wave modulation, the adsorption layer behaves like an insoluble molecular film, and thus shows different interfacial kinetics from pure liquids. The surface tension measurements revealed that, the measured surface tensions using the SW method monotonically decreased with increasing CAB concentrations, while no variations was observed by the Wilhelmy plate method, indicating that the former method can capture the variations in interfacial properties due to the existence of adsorption film in a molecular scale.

2.1.3 Photo-responsive liquid

The SW technique was successfully extended to monitor anisotropic variations in surface tensions of solutions containing photo-responsive azobenzene derivatives. When an ultraviolet light is irradiated onto the solution, an intra-molecular rotation around the double bond N=N gives rise to a transition from its trans to its cis form. The molecules then tend to align perpendicular to the polarized direction of light when the cis form re-converts to trans form. Interestingly, the measured static surface tension revealed a particular anisotropic feature under a UV light irradiation: the surface tension along X-direction was kept constant, but that along the perpendicular direction increased with time. This is, to the best of the author’s knowledge, the first experimental evidence that the light-induced molecular orientations at the air-liquid interface can be directly monitored during drying. Furthermore, the alternate exposure to UV light (365 nm) and visible light (435 nm) showed a particular increase and decrease in surface tension, indicating that the photo-induced transition between trans and cis forms allows us to switch the interfacial property in a sequential manner.

However, the application of the SW technique is currently limited to pure fluids or solutions, and no data is currently available for particle dispersion systems. Furthermore, the validity of the measured surface properties has not yet been verified when the characteristic size of particles or solutes exceeds the amplitude of surface waves. Nevertheless, this technique suggests some directions for understanding the drying kinetics in a molecular scale on the evaporating thin films.

2.2 Laser-induced surface deformation (LISD) method

The alternative non-contact approach to determine fluid viscosity at air-liquid interface has been proposed by imposing a surface deformation by light. When a laser light is irradiated into a planar surface of a liquid, the difference in refractive index induces a force to deform the air-liquid interface against the surface tension. A simple estimation showed that an irradiation of 300 mW laser with a Gaussian profile of 100 μm in width gives the absolute surface displacement of 2 nm for water. When the irradiation stops, the capillary pressure in the liquid promotes a viscous flow to level the surface. The surface liquid viscosity can be determined by using a relaxation behavior of the surface deformation with a characteristic delay time. This non-contact measurement technique is often called laser interface manipulation (LIM) or laser induced surface deformation (LISD) method.

2.2.1 Pure liquid

Yoshitake et al. successfully determine the kinematic viscosities of pure liquids using the LISD method. They used 0.6 W Nd–yttrium–aluminum–garnet laser light as a source to excite the surface deformation and another probe laser to monitor its relaxation. They demonstrated that the LISD method is applicable to measure viscosities of homogenous Newtonian liquids for the wide range from 1 to 10^6 cSt, which is much higher than those determined by the surface...
wave method. The artificial excitation of light-induced surface deformation allows us to promote the surface flow even in high viscosity fluids, and thus provides a great advantage of the LISD technique over the other methods. This technique also seems to be promising to determine the fluid properties of gelling, evaporating, and cross-linking fluids, which can exhibit time-dependent drastic changes in interfacial properties.

2.2.2 Stratified two immiscible liquids

Mitani and Sakai\(^7\) have successfully extended this technique to measure ultralow interfacial tension of liquid-liquid interfaces with a surfactant and an electrolyte. They demonstrated that static interfacial tensions for heptane-water-sodium di(2-ethylhexyl) sulfosuccinate system drastically decreased as increasing the electrolyte concentration and showed the lowest tension below 1 mN/m at a certain electrolyte content. The significant reduction in interfacial tension by orders of magnitude can be attributed to the suppressed ionization of surfactant molecules by the electrolyte counter-ions.

It is worth noting that their analysis is essentially based on the motion of bulk Newtonian fluids by simply assuming that the adsorption and desorption of surfactant molecules are so fast that they play a negligible role in the leveling of the surface deformation. As described in 2-1-2, this assumption may break when the adsorbed molecules at the air-liquid interface act as a distinct insoluble layer, usually referred to as “elastic layer”, and impact the local fluid motions. More detailed studies would be needed to understand how the surface relaxation behavior observed by the LISD method is influenced by the local events at liquid-liquid interfaces.

2.3 Numerical modeling of periodic variations in surface properties\(^8\)-\(^9\)

In continuous coating processes, a liquid film on a moving substrate is often subject to air blowing from slit and/or round nozzles. The resulting periodic variations in heat and mass transfers across the gas-liquid interface strongly impact the viscosity and surface tension through its coupling with the local temperature and concentration. However, no direct experimental evidence is currently available for describing the periodic variations in fluid surface properties in industrial dryers, because of difficulties in measurements under high speed, high temperature, and fast airflow conditions. Indeed, most previous drying studies have simply assumed constant mass/heat transfer coefficients, and hence uniform interfacial properties\(^10\)-\(^16\).

One of the successful computational approaches for predicting the drying behavior on a moving substrate is to numerically move the profiles in heat/mass transfer coefficients at the same speed as, but in the opposite direction to, the substrate motion\(^8\). Such a conceptually simple procedure enables us to determine the periodic variations in surface properties. Fig. 2 presents one of the extreme cases when a polymeric liquid film is introduced at a constant speed into an impingement dryer, in which 10 m/s hot air is vertically impinged from regularly-spaced slit nozzles onto the coating surface\(^8\). The spatial concentration variation results in sequential spikes in the surface tension and the fluid viscosity (Fig. 2). The former tends to induce interfacial Marangoni stress to drive surface flows, whereas the latter resists the liquid motion. The previous drying models using spatially-uniform mass/heat transfer coefficients hardly predict such a periodic growth and relaxation in interfacial fluid properties.

However, no physical models are currently available for describing the dynamics of evaporating nanoparticle suspensions under periodic air blowing conditions. Though the aforementioned SW and LISD methods would be suitable for the local in-situ monitoring at a given spot of laser irradiation, a precise, in-plane scanning of the measuring point is required to obtain the two-dimensional profiles of interfacial fluid properties. The development of non-contact, two-dimensional imaging techniques would provide us a new direction for understanding how the fluid on moving coatings responds to the spatial variations in evaporative conditions.

![Fig. 2 Periodic variations in viscosity and surface tension in air drier\(^9\).](image-url)
3. Local Concentration Profiles in Shrinking Films

Fluid properties in drying films in a thickness direction are equal to that at the air-liquid interface only in the case when the shrinking rate is sufficiently slow compared to diffusion rates of solutes or particles. The ratio between the shrinkage and diffusion rates is usually referred to as Peclet number $Pe = E_0 H_0 / D_0$ where $E_0$ is the characteristic shrinkage rate of the film, $H_0$ the film height, and $D_0$ the diffusion coefficient of solute or particles in the fluid. In suspension systems in which the density of dispersing particles are larger than that of the solvent, the sedimentation number can be similarly defined as the ratio between the sedimentation rate and the diffusion rate as $Ns = U_0 / E_0$ where $U_0$ is the rate of gravity-driven particle sedimentation. The composition profiles become uniform across the film when $Pe << 1$ and $Ns << 1$. The solutes or particles are accumulated at the evaporating surface for $Pe >> 1$, and dense particles can settle down by gravity for $Ns >> 1$. In the intermediate cases, the solutes or particles are enriched at the top or bottom surface, or even at both interfaces, depending on the fluid properties and the drying conditions. Indeed, the enriched polymer distribution at the film-substrate interface is required in some industrial coating applications to improve adhesion of films to the substrate. Because the shrinkage, diffusion and sedimentation rates can change during drying, the initial values of these rates are often taken as the characteristic rates for the simplicity.

Well-designed, in-situ experimental techniques to determine the depth profiles of particle or solute concentrations have been reported in the literatures, which include (1) confocal micro Raman spectroscopy (RMS), (2) Infrared microscopy (IRM), (3) Magnetic resonance (MR), and (4) Cryogenic scanning electron microscopy (Cryo-SEM). Here some experimental examples as well as numerical modeling results are introduced in particular fluid systems to access how they can capture dynamic drying behavior in polymeric and/or suspension films.

3.1 Confocal Micro Raman spectroscopy (RMS)

A confocal microscope combined with Raman spectroscopy has been developed to measure concentration profiles in thin polymeric solvent coatings with a spatial resolution of 1-2 μm. A typical experimental setup proposed by Schabel et al. is shown in Fig. 3. A laser beam with a wavelength of 514 nm or 633 nm enters from below and is focused at a spot in a liquid sample drying in an airflow channel. The laser spot moves in the sample by means of a piezo nano-positioning system. The backscattered light is directed through a pinhole in order to obtain light from a certain spatial region in the film. After a calibration by taking Raman spectra of fluids with given concentrations, the local concentration can be determined by calculating the ratio of the light intensities of the characteristic Raman peaks.

3.1.1 Polymer-solvent system

The concentration profiles in 75 μm thick polyvinyl acetate (PVAc)-toluene films have been successfully measured by choosing the characteristic Raman wavelength of 2941 cm$^{-1}$ for PVAc and 3062 nm$^{-1}$ for toluene. The measured concentration profile of toluene after 30 s drying revealed a particular concentration gradient in the vicinity of the evaporating surface, showing non-uniform solvent distributions in the coating. Note that the final polymer concentration profile becomes uniform when all solvent completely evaporates. The non-uniform solute distribution can remain in the coating in a particular case when a thin surface layer with low solvent concentrations, and hence low solvent diffusivities, can trap the solvent inside the film, usually referred to as skinning. Because of the limited spatial resolution of the local measurements, no experimental data are currently available to directly determine local concentrations inside a skin layer.

3.1.2 Polymer-solvent-solvent system

One of the major advantages of the RMS is a straightforward extension to multi-component systems. Krenn et al. used the RMS method to measure the residual solvents in polyvinyl acetate (PVAc)-toluene films evaporating in methanol vapor. The methanol can penetrate into the liquid film during the
evaporation of toluene to give a ternary solution. In the airflow without the preloaded methanol, the toluene content in the liquid film decreased in the early evaporation stage but soon reaches a constant value, showing that a surface skinning due to a drop in the diffusion coefficient traps toluene inside the film. When the methanol vapor is loaded in the airflow, on the contrary, the RMS measurements revealed that the evaporation of toluene was significantly enhanced by the introduction of methanol vapor. Both the toluene and methanol contents finally decrease with time after the gas loading ends, resulting in dried films with less residual solvents. Such a gas loading of a secondary solvent provides a useful route to promote a preferential solvent diffusion from multi-component thin liquid films.

3.1.3 Particle-solvent system

The RMS method has also been successfully applied to measure local particle distributions in drying water films. Ludwig et al.\(^{19}\) carefully considered a decrease in Raman signals due to a light scattering from particle surfaces, and provided the first experimental evidence that the particle concentration profile at Pe = 0.04 is uniform across the film when acrylic latex particles with 100 nm in diameter were dispersed in water. This is consistent with the aforementioned discussion that the particles neither accumulate at the air-liquid interface nor settle down at the substrate-liquid interface when the Brownian motion of particles are sufficiently fast compared to the film shrinkage and the particle sedimentation. Their optical configurations allowed to scan the 75 μm thick film in 30 s with a spatial resolution of 2-3 μm.

3.1.4 Particle-solvent-surfactant system

In electrostatic repulsive particle systems, the local particle ordering significantly influences the surfactant distribution. Arnold et al.\(^{20}\) have successfully applied the RMS method to measure surfactant distributions in aqueous dispersions of charged, deformable latex particles. They prepared suspensions of acrylic latex particles with 110 nm or 30 nm in diameter, and determined the concentration profiles of sodium dodecyl sulfate (SDS) added as an anionic surfactant. Surprisingly, the surfactant concentration profiles under low pH conditions are heterogeneous and vary in the thickness direction to show a particular “zigzag” profiles, whereas those at high pH are homogeneous throughout the film. The arising questions are (i) why does the transition from a homogeneous to a heterogeneous surfactant distribution happen, and (ii) how does the non-uniform surfactant distribution relax during drying. A possible explanation for the former is that, a homogeneous compaction of particles in repulsive systems at high pH tends to trap free surfactant molecules in narrow inter-particle spaces, resulting in a drastic decrease in surfactant mobility to give the uniform distributions. In less stable systems at low pH, on the contrary, possible particle flocculation gives a more open structure, in which surfactants diffuse to form micrometer-sized aggregates in inter-particle spaces\(^{20}\). However, such aggregates were not visible in their optical configuration because of a spatial resolution limit. In addition, the effect of drying conditions on time-dependent surfactant distributions across the film has not yet well explored.

3.2 Magnetic resonance

Alternatively, Gorce et al.\(^{21}\) obtained water concentration profiles in 255-420 μm thick aqueous dispersion systems of spherical alkyd particles by Magnetic Resonance (MR) method with a pixel resolution better than 10 μm. \(^1\)H NMR signals averaged over 256 scans revealed a uniform water concentration distribution for Pe = 0.2, showing qualitative agreement with the RMS results\(^{19}\). At higher Peclet number of Pe = 16, on the other hand, a linear gradient in the water profile was observed after 7 min drying, indicating that the particles are accumulated near the air-liquid interface because of the fast film shrinkage. Interestingly, the measured local volume fraction of water near the evaporating surface was below the value corresponding to a face-centered cubic (FCC) particle packing, indicating that particles at the top surface reached a closed-packing structure and started to deform from their spherical shape.

3.3 Cryogenic scanning electron microscopy\(^{22)\)-26)\)

In a visualization of particle distributions using cryoSEM, samples dried for various amounts of time are plunged into liquid ethane to vitrify. Then the samples are fractured under liquid nitrogen to expose the coating cross-section, sublimed for a few minutes to reveal the particles, and imaged in a SEM at low temperatures.

3.3.1 Hard particle-solvent system

Recently, Cardinal et al.\(^{23}\) successfully visualized the particle distributions in early evaporation stages for different Peclet (Pe) and sedimentation numbers (Ns). They prepared aqueous suspensions of monodisperse, non-deformable silica particles with diam-
3.3.2 Soft particle-solvent system

The drying of deformable latex particle suspensions generally involves three stages of (i) consolidation, (ii) compaction, and (iii) coalescence\(^{23}\). In the consolidation stage, the solvent evaporation concentrates the suspension as would in hard-particle systems, and gives rise to the particle accumulation on the top surface for high Peclet numbers. In the second stage after particles reach a critical volume fraction for closed packing, capillary forces tend to compact the neighboring particles as the air begins to invade the pore space to form pendular rings hanging between the particles. In the last stage, polymer chains can diffuse through partially-flattened particle surfaces, leading to a homogeneous polymer film after the polymer migration completes. Ma et al.\(^{24}\) used monodisperse polystyrene and polymethylmethacrylate-co-n-butyl acrylate latexes suspended in water to observe these three stages of latex film formation by cryoSEM. Furthermore, they demonstrated a well-refined imaging technique by carefully considering the artifacts in freezing, fracturing, and sublimation procedures. However, the effect of drying condition on particle distributions has not been fully described.

3.3.3 Bimodal hard particle-solvent system

As mentioned in 3-1-1, a final distribution of solids in binary systems is uniform through a film after the complete evaporation of volatile components. However, this is not the case in ternary systems containing the third component in suspensions, because a preferential segregation of particles during drying significantly influences the distribution of other components. Typical example includes bimodal particle dispersions, in which one particulate component can be accumulated at the air-liquid interface for high Pe but not so is the other. Recently, CryoSEM technique has been applied to observe the particle distributions in a bimodal silica dispersion containing particles of 1 \(\mu\)m in diameter and 200 nm in diameter\(^{23}\). The microscope observation revealed a top layer composed of smaller particles and a bottom layer of small particles dispersed between large particles, indicating that the small particles were accumulated at the evaporating surface, whereas the larger particles settled down toward the substrate-liquid interface. A simple extension of drying regime map (shown below in 3-5-1) to the bimodal system showed that the small particles are in a evaporation-dominated regime, whereas the larger particles are in sedimentation regime, suggesting that their cryoSEM observations well reproduce the predicted drying map.

3.3.4 Bimodal soft particle-solvent system

On the contrary, no preferential segregation of smaller particles has been observed for a bimodal aqueous suspension containing hollow polystyrene latex of 0.5 \(\mu\)m in diameter and polyyvinyl acetate latex of 0.1 \(\mu\)m in diameter\(^{23}\). CryoSEM observations revealed that hollow PS particles showed a homogeneous distribution across the film, and surrounded by smaller particles coalescing each other. As the film dried further, the voids filled with water was replaced by air, and the particles eventually collapsed due to strong capillary forces. Because of the complexity of the system, the dynamics of the particle segregation in such deformable, bimodal particular systems is still an ongoing debate.

3.3.5 Particle-polymer-solvent system

An addition of soluble polymeric binder in a particle suspension is common in many industrial coating applications such as paper coatings, optical films, paints, conductive films, fuel cells, capacitors etc. Binders provide adhesion to a substrate to improve a mechanical strength of film, reduce pore spaces between particles, adsorb on particle surfaces to alter interfacial forces, and sometimes acts as a surfactant. As expected from 3-1-1 and 3-1-3, both the particle and the binder can segregate in shrinking coatings, depending on Pe and Ns of each component. The local distribution of binder significantly impacts that of particles though the coupling with an increase in bulk liquid viscosity, and thus a decrease in particle diffusivity, as well as a drop in film shrinkage rate due to polymer chain entanglements in the vicinity of the evaporating interfaces. The former tends to reduce Pe and Ns, whereas the latter promotes lower Pe but higher Ns, giving rise to a complex variation in concentration distributions due to the existence of binders.

In order to verify the suppressed particle sedimentation at higher binder concentrations, cryoSEM ob-
3.4 Infrared microscopy (IRM)

Guigner et al. measured the water distribution in drying O/W emulsion films by means of infrared microscopy (IRM). The polydimethylsiloxane/water emulsion was prepared by adding a surfactant with a linear alkyl group with 13 carbon atoms as a hydrophobic part and with eight ethoxy groups as a hydrophilic part. The IR analysis was performed in transmission mode by irradiating the beam through the cross section of the liquid sandwiched between two CaF2 crystal plates. The 50 μm beam spot moved along the vertical direction of samples in 10 mm thick, and time-dependent concentration profiles of the surfactant was obtained for 16 days drying. The validity of the IR measurement was confirmed by comparing the water fraction cumulated over the whole sample height with the total mass loss of the film. The local distribution measurements showed that a strong concentration gradient of water first developed at the air-liquid interface but it became more heterogeneous after 20 h drying. The simultaneous attenuated total reflection (ATR) spectroscopy revealed that the water content in the vicinity of emulsion-substrate interface first decreased, and then increased in a certain drying time, and eventually decreased again as the water further dried. This peculiar increase in the local water concentration was attributed to the possible coalescence events of neighboring emulsions in the concentrating fluids. However, the spatial resolution of the concentration measurements was orders of magnitude larger than the characteristic emulsion size of 0.3 μm. No direct experimental evidence for the emulsion coalescence was currently provided, and the detailed drying mechanism is still an ongoing debate. A novel in-situ monitoring with a finer resolution would allow us to capture local dynamic events on each emulsion surfaces, and give a new physical insight in the drying systems involving liquid-liquid interfaces.

3.5 Numerical modeling

3.5.1 Particle-solvent system - continuous model -

The Pe-dependent variations in the particle distribution have been predicted by the one-dimensional continuous model under no bulk flow. Routh and Zimmerman first proposed a physical model for spherical particles by considering the competition between the film shrinkage and the particle diffusion. They solved the time-dependent conservation equation for the volume fraction of particles under a constant film shrinkage rate but at different Peclet numbers. In their computations, the compressibility of the dispersion was given to diverge at the maximum particle volume fraction in close packing limit. The computational results for Pe=10 showed a sharp discontinuity in volume fraction between a close packed region and the region still at the initial condition, showing the same trends observed in experiments. However, their computations have been limited to the Peclet numbers below 10. For Pe>10, the volume fraction in the packed region tends to exceed the close packing limit, resulting in an unphysical situation due to numerical instabilities.

The model has been recently extended to higher Pe, including the particle sedimentation by gravity. The examples of numerically predicted particle distributions are shown in Fig. 4. At low Ns, the evaporation and diffusion compete, and the sedimentation plays a minor role. The particle distribution becomes uniform for low Pe (a), while the fast evaporation for high Pe accumulates particles at the air-liquid interface to give a skinning (c). At high Ns and low Pe, on the other hand, the evaporation is unimportant and the sedimentation and diffusion compete (b). The effects of sedimentation and evaporation coexist for higher Ns and Pe, and the particle can be accumulated both at the top and the bottom surfaces (d).

The characteristic particle distributions are summarized in a universal drying region map for a given initial particle volume fraction of 0.1 (Fig. 5). The curves in the figure represent the conditions where the coating reaches 90 % of the maximum packing fraction in less than half the time needed for the entire coating to reach the fraction limit. Cardinal et al. demonstrated that the predicted three drying regimes agree well with cross-sectional observations of particle distributions by cryoSEM. It is worth noting that the drying regime map strongly depends on the initial particle concentration in the liquid. Indeed, the numerical results revealed that the diffusion regime shrinks, but the evaporation regime expands, at higher particle contents because the resulting increase
in bulk fluid viscosity resists the particle motion, and hence, more particles can be trapped at the receding air-liquid interface.

Although these drying models are useful to predict the drying behavior in suspension, the continuous models simply neglected interfacial contributions of each particle. Supposing particles floating on an air-liquid interface, concave menisci between the particles create a low pressure in the liquid, which promotes a driving force for liquid motion toward the evaporating interface, depending on the meniscus curvature, and thus liquid contact angles on the particle surface. In non-spherical particles, the capillary forces would strongly influence the orientation of particles, which, in turn, give rise to a complex deformation of the free surface.

3.5.2 Particle-solvent system - discrete model

In order to access how the local alignment of particles impacts the drying behavior, some numerical attempts have been proposed to solve motions of each particle in shrinking films\(^\text{29,30}\). Ohta et al.\(^\text{30}\) recently showed drying-induced structural transitions in suspensions of rod-like nanoparticles by using a connected-sphere model. The rod-like particle was simply represented by the serial connection of spherical segments, and the Langevin equation for each segment was numerically solved under a constant film shrinkage rate of 0.01 m/s. Ordered and disordered particle domains coexisted in dried films when the computation started with a random particle configuration, whereas a well-ordered particular film was obtained with a aligned initial particle configuration under a high zeta potential condition. However, the effects of \(\text{Pe}\) and \(\text{Ns}\) on the particle orientation have not yet well explored. Further systematic studies would be required to compare such a “discrete” suspension model with the previous bulk models as well as the experimental observations by RMS, MR, and cryoSEM described above.

3.5.3 Particle-solvent-surfactant system

The particle segregation can impact a surfactant distribution, especially in the case when they adsorb on particle surfaces. Gundabala et al.\(^\text{31}\) numerically solved the 1D conservation equation for surfactant in the limit of high particle Peclet number. For simplicity, they assumed that surfactant molecules partly adsorbed onto the particles and partly remained in the bulk solution. The particle distribution was assumed to show a sharp profile given by a Heaviside step function at high \(\text{Pe}\). Furthermore, they assumed that the particle layer involved the close packed particle volume fraction and linearly grew with time. The computed surfactant concentration showed a particular discontinuous profile: surfactant distributions showed local peaks both at the bottom surface of the particle layer and the evaporating surface (Fig. 6). The discontinuity arises because the low void fraction in the particle layer gives slower surfactant diffusion toward the air-liquid interface. The sharp concentration profiles then relax as the drying proceeds, and eventually the surfactant was enriched at the top and bottom surfaces of the film, indicating a drying-induced segregation of surfactants in particulate coatings. The enriched surfactant concentration at the bottom surface showed a good agreement with experimental observations by attenuated total reflection (ATR). Their computations also demonstrated
that the surfactant concentration at the evaporating surface increased, whereas that at the bottom surface decreased, as increasing the maximum surface adsorption onto the particle. This fact suggests that the surfactant distribution in the shrinking suspension film is tunable by properly choosing adsorption isotherms of the surfactant as well as the evaporation conditions. However, no experimental data is currently available to validate the predicted discontinuous surfactant distribution inside the film. The RMS or IRM may be useful tool to verify the computations in detail.

3.5.4 Particle-polymer-solvent system

Recently, Buss et al. developed a 1D isothermal model that combines two conservation equations for particle and polymeric binder. For simplicity, they neglect (i) polymer adsorption onto the particles, (ii) capillary forces between particles at the free surface, (iii) drying in lateral direction, (iv) temperature variations due to solvent evaporation, and (v) the cross- and non-Fickian terms for the multi-component diffusion. Their model is a straightforward extension of previous models for particle-solvent systems as mentioned in 3-5-1. The variations in fluid viscosity and solvent evaporation rate were taken into account by using empirical poly-nominal function of viscosity with respect to polymer volume fraction, and the concentration-dependent solvent activity given by Flory-Huggins theory. The numerical computations show that the evaporation regime, in which particles tend to be accumulated at the top surface, expands as increasing polymer content since both the diffusion and sedimentation of particles are slowed down in the presence of the soluble binders, showing a qualitative agreement with cryoSEM observations.

Here we should note that their computations were limited to the dimensionless drying time of 0.35, above which the particle concentration reaches the maximum packing fraction. The resultant binder concentration remained so low that the computed partial pressure of solvent, and thus the film shrinkage rate, was almost independent on the polymer contents. Thus the raise in liquid viscosity, rather than a reduced evaporation rate, plays a major role in the predicted particle distributions during time. A rigorous model that can overcome the computational limit at high particle packing fractions would be required to obtain final concentration distributions of binders in dried coatings. Furthermore, the effect of binder adsorption at the particle-liquid and air-liquid interfaces should be taken into account because it would significantly alter the local distributions as described in 3-5-3. Nevertheless, to the best of the author’s knowledge, their work is the first to predict the particle segregation behavior in ternary coating systems of practical interest.

4. Concluding Remarks

This paper reviews the recent progress in in-situ measurement techniques and numerical approaches for determining local distributions of particles or solutes in evaporating thin liquid films. The ripplon surface wave (SW) and laser-induced surface deformation (LISD) methods are suitable to measure local surface properties at the air-liquid and liquid-liquid interfaces by detecting a motion of interfacial waves with the amplitude of orders of nanometers. However, two-dimensional imaging along the interface is usually required in practical coating applications to determine heterogeneous in-plane distributions of physical properties. A high-speed 2D scanning or a direct 2D imaging may be required in the future applications of these techniques.

The concentration distributions in the thickness direction have been successfully measured by confocal micro Raman spectroscopy (RMS), Infrared microscopy (IRM), and Magnetic resonance (MR), and summarized by using non-dimensional numbers of Pe and Ns. Despite the formidable consistency with the computational results for hard particle-solvent and polymer-solvent systems, the spatial resolutions of these techniques are currently not sufficient to elucidate the detailed drying kinetics in suspensions of deformable particles, those containing surfactants, suspensions on a moving substrate.
under practical high speed operating conditions, and even phase-separating fluid systems involving three-dimensional, interconnected domain structures. Furthermore, these spectroscopics require an optical transparency of the sample at the wavelength of interest, and thus might not be suitable for measurements of thick, opaque samples with amounts of absorption and/or scattering of irradiated light. Cryogenic scanning electron microscopy (Cryo-SEM) involves the higher spatial resolution compared with those methods, yet the sampling rate of the images is limited to relatively low speeds because of careful procedures required for the sample freezing.

These local property measurements provide complementary information for averaged physical quantities obtained by other techniques. The UV-VIS or infrared spectroscopy\(^\text{54-55}\) and the laser scattering (LS)\(^\text{62-63}\) respectively give information on reaction rates and characteristic domain sizes in the evaporating coatings, but these properties are averaged in the thickness direction as a laser beam passes through the film to give integrated signals. In the drying rate measurements by the mass loss\(^\text{58}\), the heat-flux variation\(^\text{60}\), and the gas chromatography\(^\text{61}\), the measurable evaporation rates of solvent are in principal averaged in-plane along the evaporating surface, whereas the tensile stress measurement by the cantilever beam deflection (CBD)\(^\text{35-51}\) method detects forces averaged both in the thickness and span-wise directions. Fig. 7 schematically depicts possible combinations of these techniques with the aforementioned local property measurements. Indeed, some previous studies\(^\text{54-55}\) have successfully demonstrated the simultaneous measurements of averaged stresses and reaction rates during the solvent evaporation. Other proper combinations for local and averaged measurement techniques will results in a better understanding of microstructure formation in evaporating thin liquid films.

Acknowledgements

The author acknowledges the financial support of Japan Society for the Promotion of Science (JSPS) KAKENHI (23560912) Grant-in-Aid for Scientific Research C.

References

1) Nishio T., and Nagasaka Y. ((1995)): Simultaneous Measurement of surface tension and kinematic viscosity using thermal fluctuations, International Journal of Thermophysics, 16, pp.1087-1097.
2) Oki, K., and Nagasaka, Y. (2008): Dynamic Observation of the Behavior of the Surface of Liquid Films of Polymer–Organic Solvent System by Ripple Surface Laser-Light Scattering Method, Kagaku Kogaku Ronbunshu, 34, pp.587-593.
3) Oki, K. and Nagasaka, Y. (2009)): Measurements of
4) Sakai K., Mizuno D., and Takagi K. (2001): Measurement of liquid surface properties by laser-induced surface deformation spectroscopy, Physical Review E, 63, 046302.

5) Yoshitake, Y., Mitani, S., Sakai, K., and Takagi, K. (2005): Measurement of high viscosity with laser induced surface deformation technique, Journal of Applied Physics, 97, 024901-1-024901-6.

6) Sakai K., Tachibana, K., Mitani, S., Takagi K. (2003): Laser excitation of high-frequency capillary waves, Journal of Colloid and Interface Science, 264 pp.446-451.

7) Mitani, S., and Sakai K. (2002): Measurement of ultralow interfacial tension with a laser interface manipulation technique, Physical Review E, 66, 031604.

8) Yamamura M., Uchinomiya, T., Mawatari, Y., and Kage, H. (2007): Asymmetric surface roughness formation on moving non-isothermal liquid coatings, International Polymer Processing, 22, pp.22-26.

9) Yamamura M. Uchinomiya, T., Mawatari Y., and Kage H. (2009): Drying-induced Surface Roughening of Polymeric Coating under Periodic Air Blowing, AIChE Journal, 55, pp.1648-1658.

10) Cairncross R.A, Jeyadev S, Dunham R.F, Evans K, Francis L.F. and Scriven L.E. (1995): Modeling and design of an industrial dryer with convective and radiant heating. Journal of Applied Polymer Science, 58, pp.1279-1290.

11) Price PE Jr, and Cairncross, R.A. (1999): Optimization of single-zone drying of polymer solution coatings to avoid blister defects, Drying Technology, 17, pp.1303-1311.

12) Wong, S.S, Altinkaya, SA. and Mallapragada, S.K. (2004): Drying of semicrystalline polymers: mathematical modeling and experimental characterization of poly(vinyl alcohol) films, Polymer, 45, pp.5151-5161.

13) Cairncross, R.A, Francis, L.F and Scriven, L.E. (1996): Predicting drying in coatings that react and gel—drying regime maps, AIChE Journal, 42, pp.55-67.

14) Alsøy, S. and Duda, J.L. (2002): Influence of swelling and diffusion-induced convection on polymer sorption processes, AIChE Journal, 48, pp.1849-1855.

15) Vinjamur, M. and Cairncross, R.A. (2002): Non-Fickian nonisothermal model for drying of polymer coatings, AIChE Journal, 48, pp.2444-2458.

16) Okuzono, T. Ozawa, K. and Doi, M. (2006): Simple model of skin formation caused by solvent evaporation in polymer solutions, Physical Review Letters, 97, 136103-1-136103-4.

17) Schabel, W., Ludwig, I. and Kind, M. (2004): Measurements of concentration profiles in polymeric solvent coatings by means of an inverse confocal micro Raman spectrometer-initial results, Drying Technology, 22, pp.285-294.

18) Krenn, J., Scharfer, P., Kind, M., and Schabel, W. (2009): Drying of solvent-borne coatings with pre-loaded drying gas, Eur. Phys. J., 166, pp.45-48.

19) Ludwig, I., Schabel, W., Kind, M., Castaing, J.C., and Ferlin, P. (2007): Drying and Film Formation of Industrial Waterborne Latices, AIChE Journal, 53, pp.549-560.

20) Arnold, C., Thalmann, F., Marques, C., Marie, P. and Holl, Y. (2010): Surfactant distribution in waterborne acrylic films. 1. Bulk Investigation, Journal of Physical Chemistry B, 114, pp.9135-9147.

21) Gorce, J.P., Bovey, D., McDonald, P. J., Palasz, P., Taylor, D. and Keddie, J.L. (2002): Vertical water distribution during the drying of polymer films cast from aqueous emulsions, European Physical Journal E, 8, pp.421-429.

22) Cardinal, C.M., Jung, Y.D., Ahn, K.H. and Francis, L. F. (2010): Drying regime maps for particulate coatings, AIChE Journal, 56, pp.2769-2780.

23) Sutanto, E., Ma, Y., Davis, H.T. and Scriven, L.E. (2001): Cryogenic Scanning Electron Microscopy of early stages of film formation in drying latex coatings, ACS Symposium Series, 790, pp.174-192.

24) Ma, Y., Davis, H.T. and Scriven, L.E. (2005): Microstructure development in drying latex coatings, Progress in Organic Coatings, 52, pp.46-62.

25) Cardinal, C.M., Francis, L.E., Scriven, L.E. (2009): Drying and collapse of hollow latex, Journal of Coatings Technology and Research, 6, pp.457-469.

26) Buss, F, Roberts, C.C., Crawford, K.S., Peters, K. and Francis, L. (2011): Effect of soluble polymer binder on particle distribution in a drying particulate coating, Journal of Colloid and Interface Science, 359 pp.112-120.

27) Guigner, D., Fischer, C. and Holl, Y. (2001): Film formation from concentrated reactive silicone emulsions. 1. Drying mechanism, Langmuir, 17, pp.3598-3606.

28) Routh, A.F., Zimmerman, W.B. (2004): Distribution of Particles during Solvent Evaporation from Films, Chemical Engineering Science, 59, pp.2961-2968.

29) Fujita, M. and Yamaguchi, Y. (2007): Simulation of 3D Crystallization of Colloidal Nanoparticles on a Substrate during Drying, International Polymer Processing, 22, pp.16-21.

30) Ohta, S., Inasawa, S., Koike, O., Fujita, M. and Yamaguchi, Y. (2009): Formation of well-aligned thin films of rod-like nanoparticles via solvent evaporation: a simulation study, Applied Physics Express, 2, 065002-1-065002-3.

31) Gundahala, V.W.B., Zimmerman, A.F and Routh, (2004): A model for surfactant distribution in latex coatings, Langmuir, 20, 8721.

32) Zielinski, J.M. and Hanley, R.F. (1999): Practical friction-based approach to modeling multicomponent diffusion, AIChE Journal, 45, pp.1-12.

33) Price, Jr. P.E. and Romdhane, I.H. (2003): Multicomponent diffusion theory and its application to polymer-solvent systems, AIChE Journal, 49, pp.309-322.

34) Yamamura, M., Kajiwara, T. and Kage, H. (2003): Multispectral surface properties of liquid films of azobenzene derivatives, Colloids and Surfaces A: Physicochem. Eng. Aspects, 333, pp.182-186.
isocomponent diffusion in phase separating polymer blends with different frictional interactions: a mean-friction model, Chemical Engineering Science, 58, pp.3891-3899.

35) Corcoran, E.M. (1969): Determining Stresses in Organic Coatings using Plate Beam Deflection, Journal of Paint Technology, 41, pp.635-640.

36) Perera, D.Y. and Eynde, D.V. (1981): Considerations on a Cantilever (Beam) Method for Measuring the Internal Stress in Organic Coatings, Journal of Coating Technology, 53, pp.39-44.

37) Chiu, R.C. and Cima, M. J. (1993): Drying of Granular Ceramic Films; II, Drying Stress and Saturation Uniformity, Journal of American Ceramic Society, 76, pp.2769-2777.

38) Lewis, J.A., Blackman, K.A., Ogden, A. L., Payne, J.A. and Francis, L.F. (1996): Rheological Property and Stress Development during Drying of Tape-Cast Ceramic Layers, Journal of American Ceramic Society, 79, pp.3225-3234.

39) Payne, J.A., McCormick, A.V. and Francis, L.F. (1997): In situ stress measurement apparatus for liquid applied coatings, Rev. Sci. Instrum., 68, pp.4564-4568.

40) Payne, J.A., Francis, L.F. and McCormick, A.V. (1997): The effects of Processing Variables on Stress Development in Ultraviolet-Cured Coatings, Journal of Applied Polymer Science, 66, pp.1267-1277.

41) Petersen, C., Heldmann, C. and Johannsmann, D. (1999): Internal Stresses during Film Formation of Polymer Latices, Langmuir, 15, pp.7745-7751.

42) Lei, H., Payne, J.A., McCormick, A.V., Francis, L.F., Gerberich, W.W. and Scriven, L.E. (2001): Stress development in drying coatings, Journal of Applied Polymer Science, 81, pp.1000-1013.

43) Lei, H., Francis, L.F., Gerberich, W.W. and Scriven, L.E. (2002): Stress development in drying coatings after solidification, AIChE Journal, 48(9), pp.437-451.

44) Francis, L.F., McCormick, A.V. and Vaessen, D.M. (2002): Development and Measurement of Stress in Polymer Coatings, Journal of Materials Science, 37, pp.4717-4731.

45) Martínez, C.J. and Lewis, J.A. (2002): Shape Evolution and Stress Development during Latex-Silica Film Formation, Langmuir, 18, pp.4689-4698.

46) Tirumkudulu, M.S. and Russel, W.B. (2004): Role of Capillary Stresses in Film Formation, Langmuir, 20, pp.2947-2961.

47) Wedin, P., Martínez, C.J., Lewis, J.A., Daicic, J. and Bergstrom, L. (2004): Stress Development during Drying of Calcium Carbonate Suspensions Containing Carboxymethylcellulose and Latex Particles, Journal of Colloid and Interface Science, 272, pp.1-9.

48) Wedin, P., Lewis, J.A. and Bergstrom, L. (2005): Soluble Organic Additive Effects on Stress Development during Drying of Calcium Carbonate Suspensions, Journal of Colloid and Interface Science, 290, pp.134-144.

49) Kiennemann, J., Chartier, T., Pagnoux, C., Baumard, J.F., Huger, M., and Lamerant, J.M. (2005): Drying Mechanisms and Stress Development in Aqueous Alumina Tape Casting, Journal of European Ceramic Society, 25, pp.1551-1564.

50) Lan, W. and Xiao, P. (2007): Drying Stress of Yttria-Stabilized-Zirconia Slurry on a Metal Substrate, Journal of the European Ceramic Society, 27, pp.3117-3125.

51) Kim, S., Sung, J.H., Ahn, K.H. and Lee, S.J. (2009): Drying of the silica/PVA suspension: effect of suspension microstructure, Langmuir, 25, pp.6155-6161.

52) Shiga, T., Narita, T., Tachi, K., Okada, A., Takahashi, H. and Kurauchi, T. (1997): Measurement of Internal Stresses in Coatings Using Time Resolved Fluorescence, Polymer Engineering and Science, 37, pp.24-30.

53) Shiga, T., Narita, T., Ikawa, T. and Okada, A. (1998): Stress Monitoring in Thin Polymer Coatings Using Time Resolved Fluorescence, Polymer Engineering and Science, 38, pp.693-698.

54) Stolov, A.A., Xie, T., Penelle, J. and Hsu, S.L. (2001): An Analysis of Photopolymerization Kinetics and Stress Development in Multifunctional Acrylate Coatings, Polymer Engineering and Science, 41, pp.314-328.

55) Stolov, A.A., Xie, T., Penelle, J. and Hsu, S.L. (2000): Simultaneous Measurement of Polymerization Kinetics and Stress Development in Radiation-Cured Coatings: A New Experimental Approach and Relationship between the Degree of Conversion and Stress, Macromolecules, 33, pp.6970-6976.

56) Koenig, A.M., Bourgeat-Lami, E., Mellon V., von der Ehe, K., Routh, A.F. and Johannsmann, D. (2010): Ditional lateral stress in drying latex films, Langmuir, 26, pp.3815-3820.

57) Suzuki, I., Yasui, Y., Udagawa, A. and Kawate, K. (2004): Drying process monitoring by rapid scanning FT-IR spectrometer, Industrial Coating Research, 5, pp.107-123.

58) Yamamura, M., Horiuchi, K., Kajiwara, T., and Adachi, K. (2002): Decrease in solvent evaporation rate due to phase separation in polymer films, AIChE Journal, 48, pp.2711-2714.

59) Imakoma, H., Nagaoka, S., and Takigawa, T. (2007): Measurement of drying rate of water-based coat by temperature change method, Kagaku Kogaku Ronbunshu, 26, pp.358-359.

60) Yamamura, M. Ohara, K., Mawatari, Y., and Kage, H. (2009): Measuring the drying rate of liquid film coatings using heat-flux method, Drying Technology, 27, pp.817-820.

61) Vinjamur, M., and Cairncross, R. (2001): A high airflow drying experimental set-up to study drying behavior of polymer solvent coatings, Drying Technology, 19, pp.1591-1612.

62) Miyake, Y., Sekiguchi, Y., and Kohjiya, S. (1993): Formation of percolated structure during solvent casting of polymer blend-solvent systems, Kagaku Kogaku Ronbunshu, 26, pp.543-550.

63) Ermi, B.D., Nisato, G., Douglas, J.F., Rogers, J.A. and...
Karim, A. (1998): Coupling between phase separation and surface deformation modes in self-organizing polymer blend films, Physical Review Letters, 81, pp.3900-3903.

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