Two-step particle segregation in drying latex coatings

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INTRODUCTION

Functional particulate coatings are fabricated sometimes in favor of the self-stratification of particles, and sometimes against. Under particular fast drying conditions, for instance, smaller particles in bimodal colloidal suspensions preferentially segregate on evaporating surface. A gravity-driven settling (Cardinal et al. 2010), or selective electrostatic repulsions of larger particles (Nikiforow et al. 2010, Atmuri et al., 2012) can partially explain underlying physics of the particle segregation. However, these hypotheses fail to understand the particle migration in a practical case when both large/small particles are equally charged, and do not settle down in a finite drying time because of high viscosity of the suspension medium (Lim et al., 2013).

Luo et al. (2008) have proposed an alternative stratification mechanism by considering a capillary-pressure-driven transport of smaller particles through a pore space between large particles. A consolidation layer of particles first form in the vicinity of the receding air-liquid interface, and then smaller particles preferentially move toward the surface via the capillary action as the interface invades into the consolidation layer (Fig. 1). Strictly, however, no direct experimental evidence has been shown to prove the validity of this hypothesis. Despite the extensive studies to characterize particle concentration distributions by utilizing NMR imaging (Trueman et al. 2012), cryogenic scanning electron microscopy

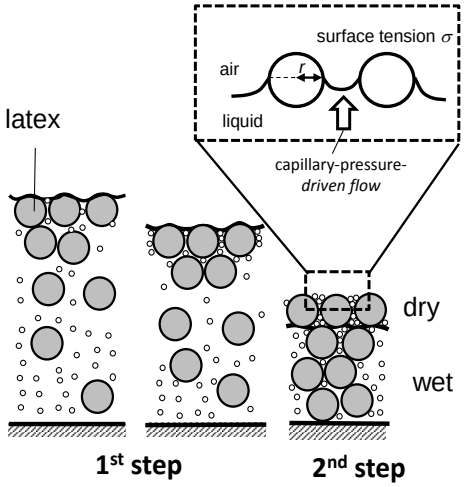

Fig.1 Schematic co-consolidation of large and small latex particles during drying. Adapted from Luo et al. (2008)

(Cryo-SEM) (Cardinal et al. 2010, Buss et al., 2012), Raman spectroscopy (Hagiwara et al., 2014), and ellipsometry (Tzitzinou and Keddie, 2000), it is still challenging to directly capture the flow-driven motion of particles because of limited sampling rates, relatively low imaging resolutions, or undesirable light scattering in sample suspensions. Despite the practical utility of particulate coatings, rigorous migration mechanism is a subject of ongoing debate.

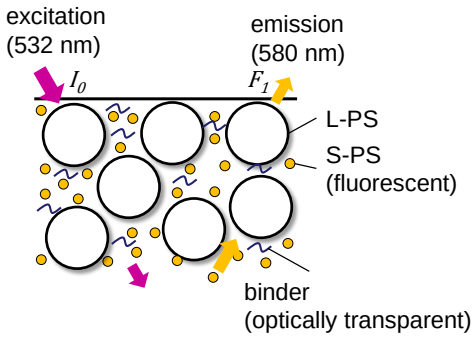

Fig.2 Fluorescence imaging in bimodal suspension of small emissive (S-PS) and large, non-emissive (L-PS) particles

In this study, we newly used real-time photoluminescence microscopy (PLM) to investigate preferential migration of small fluorescence latex particles co-dispersing with non-emissive large latex particles. The small latex particles emit photo-luminescence light in liquids when an excitation laser beam is irradiated through the whole coating (Fig. 2). The time-evolution of photoluminescence light intensity was detected and analyzed to estimate the vertical distributions of particles.

EXPERIMENTALS

Fluorescence polystyrene (S-PS) latex (micromer-redF, micromod, Germany; diameter = 100 nm; zeta potential in water = - 40 ± 5 mV) and non-emissive PS latex (L-PS, micromer, micromod, Germany; diameter = 200 nm or 8 μm) particles were used in this study. The maximum excitation and emission wavelengths of the fluorescence particles (S-PS) were 552 and 580 nm, respectively. Sodium carboxymethyl cellulose (CMC; Mn = 180,000 – 190,000 g/mol, Dai-ichi Kogyo Seiyaku, Japan) was used as a water-soluble polymer. The preliminary UV-vis spectroscopy showed that light absorption coefficients of the aqueous CMC solutions were negligible small at the excitation/emission wavelengths of interest. The aqueous polymer solution was added to the bimodal latex suspensions and stirred for 12 h. A micropipette was used to coat the specified volume of suspension onto the glass substrate. The glass surface was cleaned using a plasma etching device (Meiwafosis, SEDE-GE) for 15 min in vacuum before coating. The initial height of the coating ranged between 500 and 1000 μm, and the coated area was specified to be 25 cm^2 by gluing a 1.0-mm-thick duralumin shim on the substrate. The drying temperature of the film was adjusted using a micro warm plate (MD-10DMFH, Kitazato, Japan) located beneath the coating at interspaces of 250 μm to uniformly heat the bottom of the coating. Solvent loss was measured using an electronic balance (Cubis

MSE-3203S-0-00-DE, Sartorius, Japan) at a sampling rate of 1.0 Hz. The Peclet numbers (Pe), defined as the rate of film shrinkage rate divided by the rate of Brownian diffusion of particles (Cardinal et al. 2010), were chosen to be Pe $>10^3$ in order to ensure that both large/small particles can form a consolidation layer in early evaporation stages.

To excite the fluorescence particles, a TEM00-mode laser (LasirisTM Green, Coherent, USA; wavelength = 532 ± 1 nm) whose beam intensity obeyed a single Gaussian distribution was held in position at a 45° incidence to the coating. The laser intensity was adjusted using a neutral density (ND) filter to avoid a saturation of photoluminescence images. A charge-coupled device (CCD) color camera system (VB-7010, Keyence, Japan) with a band-pass filter (580 ± 5 nm) was used to capture the emission signals from the S-PS particles. The maximum intensity of the Gaussian distribution with respect to the background value was analyzed using software and was used as the characteristic intensity of the photoluminescence light. A CCD beam profiler (Beam On, Duma Optronics, Ltd., Israel) was located on the opposite side of the laser at a 45° reflection, and it was used to capture the size and shape of the laser beam reflected from the coating. The captured image was analyzed using software (Beam On USB 2.0 measurement system, Duma Optronics, Ltd., Israel). All equipment was set up on a vibration isolator and was covered with a black curtain to prevent outside light from interfering with the measurements. The dried specimen was fractured after 20 s immersion into liquid nitrogen to obtain the cross-sectional images using a field-emission scanning electron microscopy (FE-SEM, JSM-7000, JEOL, Japan). The detailed experimental procedure has been shown elsewhere (Lim et al., 2013).

RESULTS AND DISCUSSION

Fig. 3 shows a typical example of the time-evolutions of photo-luminescence light intensity (F) normalized by that of the initial value (F_0) just after coating. The PL intensity gradually increased in the early evaporation stage, indicating a consolidation of small particles in the vicinity of evaporating surface. As drying proceeds, the PL intensity exhibited a step-wise increase at a certain drying time in the late drying stage, indicating a secondary migration of fluorescence small latex particles toward the evaporating surface. The transition from the first to the second migration corresponds to the decrease in the slope of mass-loss curve (solid

curve in Fig. 3). The image analysis of laser beam reflected from the fluid surface also revealed that the drying time at the onset of the second migration agreed with the onset time of light scattering from the coating surface (not shown). These facts imply that the secondary migration of small particles emerges when the air-liquid interface invades into the consolidation layer of particles, strongly supporting the Luo's hypothesis.

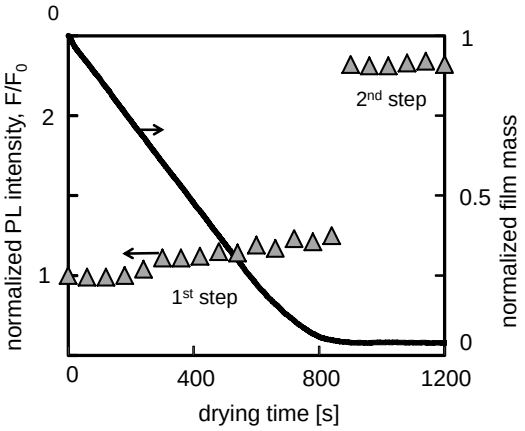

Fig.3 Time evolutions of PL intensity and film mass. The emission shows a two-step increase in intensity.

CONCLUSIONS

We report real-time photoluminescence (PL) microscopy to investigate the segregation of fluorescence small latex particles dispersing with non-emissive large latex particles in aqueous polymer solution. The results revealed that the fluorescence particles segregated in two-steps: the primary segregation proceeded in the early evaporation stage, whereas the secondary, stepwise segregation emerged when the air-liquid interface invaded into the particle consolidation layer. The drying time at the onset of secondary segregation agreed with the onset time of light scattering from the coating surface. These facts imply that the secondary segregation is attributed to a flow-induced motion of small particles that move though interstitial spaces between large particles, providing a direct evidence to support previously-proposed drying models.

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