



Regular Article

Stratification during evaporative assembly of multicomponent nanoparticle films



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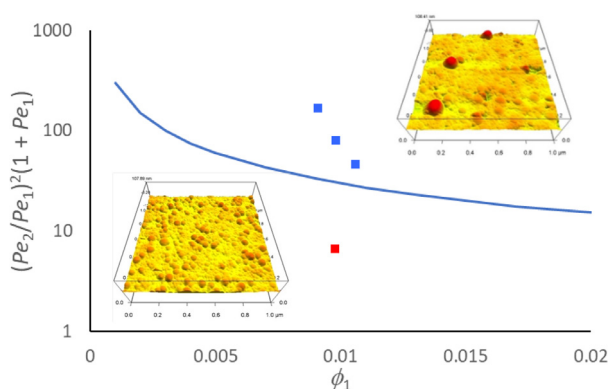
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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 October 2017

Revised 31 December 2017

Accepted 2 January 2018

Available online 3 January 2018

Keywords:

Film formation

Evaporative assembly

Multilayer

Coating

Paint

ABSTRACT

Hypothesis: Multicomponent coatings with layers comprising different functionalities are of interest for a variety of applications, including electronic devices, energy storage, and biomaterials. Rather than creating such a film using multiple deposition steps, we explore a single-step method to create such films by varying the particle Peclet numbers, Pe . Our hypothesis, based on recent theoretical descriptions of the stratification process, is that by varying particle size and evaporation rate such that Pe of large and small particles are above and below unity, we can create stratified films of polymeric and inorganic particles. **Experiments:** We present AFM on the surface composition of films comprising poly(styrene) nanoparticles (diameter 25–90 nm) and silica nanoparticles (diameter 8–14 nm). Previous studies on films containing both inorganic and polymeric particles correspond to large Pe values (e.g., 120–460), while we utilize $Pe \sim 0.3$ –4, enabling us to test theories that have been developed for different regimes of Pe .

Findings: We demonstrate evidence of stratification and effect of the Pe ratio, although our results agree only qualitatively with theory. Our results also provide validation of recent theoretical descriptions of the film drying process that predict different regimes for large-on-top and small-on-top stratification.

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1. Introduction

Multicomponent films based on colloidal dispersions have a wide range of applications, including antimicrobial coatings for medical instruments [1], conductive textiles for flexible electronics [2], anti-reflective coatings for optical devices [3], paints for humid environments that are resistant to mold growth [4], and drug-loaded coatings for medical implants [5]. Often, there is a need to spatially control location of certain components in the film. For example, silver nanoparticles can be used to impart antimicrobial activity to coatings [1], but this component is expensive and may only be needed in the top few layers of the coating, not throughout the entire film. Another example, relevant to the system presented in this study, are anti-reflective coatings described by the Velev group [6] and Sunkara and coworkers [3], where the desired optical properties arise from controlling the concentration profile of silica nanoparticles, either in films containing silica particles of different sizes [6] or in multilayer polymer-silica coatings [3].

The traditional way to achieve such coatings involves a multi-step deposition process, resulting in vertically structured films with the film layers having different composition. Alternatively, to reduce production time and cost, stratification of different components in the film during the drying process can produce multifunctional films through a single-step process [7]. In creating a film through evaporative drying, a colloidal suspension is first applied to a substrate, which results in close-packed layers of particles upon evaporation of the solvent. In the polymeric films typically encountered in paints and varnishes, the colloids are typically latex particles, and the above steps are followed by slow interdiffusion of polymer chains among neighboring particles to form a homogenous film [8]. The distribution of particles during the drying process is greatly determined by the Peclet number, Pe , which relates the rate of evaporation to the rate of particle diffusion, and is given as [8,9].

$$Pe = \frac{6\pi\eta RHE}{kT} \quad (1)$$

where η is the solvent viscosity, R is the particle radius, H is the initial film thickness, E is the rate of evaporation, k is Boltzmann's constant, and T is the temperature. The Peclet numbers of constituent particles determine the final profile of dried films. When $Pe \ll 1$, diffusion is fast and the particles are able to move quickly as the film dries; when $Pe \gg 1$, diffusion is slow as compared to the evaporation rate, and the particles can get trapped at the interface as evaporation occurs. In a binary mixture containing small (1) and large (2) particles, if conditions are such that $Pe_2 > 1$ and $Pe_1 < 1$, the dominant mechanism for particle motion differs for the two particles. In principle, this can lead to a final coating that is stratified, where there is a concentration gradient of each particle throughout the thickness of the film. A theoretical model for self-stratification based on this phenomenon has been presented by Routh and coworkers [9], which predicts that for binary mixtures, the top surface will be enriched with large particles when the Pe of the two particles are on either side of unity. Under conditions of maximum segregation, this model predicts a 25–30% increase in the volume fraction of large particles in the top layers of the film, and the concentration profile throughout the film is more gradual rather than having well-defined layers [9]; however, as discussed further below, more recent simulation studies suggest stronger segregation within the film, with more defined layers and a greater enhancement of one particle at the top surface.

Some experimental studies on films containing polymeric particles of different sizes (e.g., films of large and small polymer particles) qualitatively agree with predictions of the Routh model and show an increase in the number of large particles at the surface

when the Pe numbers are in the correct range [10]. Grillet et al. also report stratification of large particles at the top layer in films formed from small silica particles and large poly(butyl methacrylate) particles where the size ratio of large to small particles is 20 [11]. However, interpretation of these results is complicated by aggregation of silica particles in their system, and it appears that the stratification they observed is due to formation of large silica aggregates which undergo sedimentation during the film formation process. Overall, agreement between experiments and the theory of Routh and coworkers has been qualitative, suggesting that there are other phenomena that are important to consider in the stratification process.

More recent theoretical work on stratification includes the effect of interparticle interactions [12–14]. Results based on the Routh model with a very simple pairwise interaction term predict that an attraction between large particles will enhance stratification of large particles at the top surface [12]. Experiments of Nikiforow and coworkers [7] on films formed from charged particles and neutral particles seem to agree qualitatively with these predictions, as do studies of films based on polymeric particles where the interparticle potentials are controlled by pH variation [12]. However, while the above-mentioned modeling work predicts that the top surface will be enriched with large particles, some simulations and models find the opposite effect, with small particles being enriched at the top of the film. This effect is typically seen in a very different drying regime than that described by Routh and coworkers. Fortini et al. performed simulations on drying films of binary mixtures where $Pe \gg 1$ for both particles [13]. They predict that an osmotic pressure gradient will be set up that will drive large particles to move downward faster than small particles, despite hydrodynamic effects. Simulations were performed for systems with $Pe_1 = 75$, $Pe_2 = 525$. It is difficult to quantify the expected degree of segregation in the final films, as their simulations were not run until the final stages of drying. However, from their simulation results on partially dried films, it is very clear that separate well-defined layers of large and small particles are expected to form during the drying process. Their predictions were found to be in agreement with experiments on films with $Pe_1 = 14$, $Pe_2 = 100$ [13]. Zhou and coworkers also predict conditions under which the top surface will be enriched with small particles [14]. They attribute this behavior to an asymmetric cross interaction between large and small colloids. Their model leads to a state diagram showing regions with no stratification, large-on-top stratification, and small-on-top stratification. The boundary between large-on-top and small-on-top stratification is predicted to be $(Pe_2/Pe_1)^2(1 + Pe_1)\phi_1 = C$, where ϕ_1 is the initial volume fraction of small particles and C is a constant. They also find that the boundary condition for this stratification to occur does not depend on the initial volume fraction of large particles. Generally, a large size difference and high volume fraction of small particles were found to enhance the degree of stratification, with small particles favored to be at the surface [14]. Makepeace et al. [15] recently performed the first experimental test of the state diagram proposed by Zhou et al. They present experimental studies and simulations for systems with $Pe_2/Pe_1 = 2$ and $Pe_2/Pe_1 = 7$ and find regimes of no stratification and small-on-top stratification that are in qualitative agreement with predictions from Zhou et al.

Panagiotopoulos and coworkers [16] also observed small-on-top stratification in implicit-solvent molecular dynamics simulations of small polymers and larger particles, performed under similar conditions of the study of Fortini et al. [13]. Their simulations account for Brownian motion of particles and drag from the solvent, but neglect local density-dependent contributions to the particle friction coefficients. In this model, the particle velocities are dependent on the chemical potential gradient and the friction

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