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Tuning crack pattern by phase separation in the drying of binary colloid–polymer suspension

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ABSTRACT

Drying the colloidal suspension leads to the versatile crack patterns, where the microstructure formed during the drying process determines crack patterns. Here, the polymer is introduced into a silica suspension to tune the crack arrangement in the drying deposit. Five dominated types of crack patterns are defined by varying the ratio of nanoparticles to polymer. Two phase separation processes are proposed to explain the spatial characteristics of the crack patterns: the depletion-induced phase separation of particles and polymer in their mixture; and the separation of water and particle (or polymer) clusters by the water drainage.

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1. Introduction

Cracks in the deposition film resulting from drying colloidal suspension have obtained extensive attention in recent decades, due to the vital significance in nature and industrial applications for the uniform film production [1–3] and the fundamental mechanism [1,4–11]. The spatial arrangements of cracks display various complex patterns, for example, the patterns of spiral [12,13], hierarchy [5,14,15], network [16], array [17], wavy and curve [3,18]. Meanwhile, the influences of the concentration, qualities of colloid and the substrate nature, and the evaporating rate (affected by humidity and temperature) on the crack formation have been experimentally investigated [15,19,20]. Interestingly, for drying dilute suspension, the dried structures display diverse dendrite patterns in the microstructure of deposition rather than the crack pattern formation, as indicated in the experiments by Darwich et al. [21].

For the practical usage, a variety of methods have been proposed to restrain cracks arising in industrial applications [22], including optimizing procedures for the deposition [23], selecting

the material with matched elasticity, controlling the evaporation rate [19], adding particles or nanofibers [19,24,25], and adjusting the chemical feature of the suspension by using polymer as the additive [26]. For the method of adding the polymer, the flexible polymer chains make the film present desirable resistance against the higher stress induced from the coating process. On the other hand, the additive of polymer to the suspension has been employed as the model system for binary mixture to understand the dynamics of the phase separation [27–36].

Flaws in the microstructure are believed important to initiate the cracks formation. The flaws could be developed from the suspension by flocculation or aggregation. The phase separation process is essential to the flaw formation. For phase separation occurring in the mixture of colloid–colloid or colloid–polymer suspension, extensive attentions have been paid experimentally and theoretically, firstly proposed by the idea of depletion-induced phase separation from Asakura and Oosawa [37], then advanced by Vrij [38], Gast and Lekkerkerker [39,40] and others [41,42]. Although the dynamics of phase separation in mixed solution of colloidal particles and polymer could be deduced by the optical and other apparatus [24,29,43,44], crack originating from the flaws produced from phase separation remains missing.

In our recent study [4], the circular crack results from a preexisting trajectory — a flaw loop, which could be formed by a phase separation process of the nanoparticles from the solvent. Then an analytical model was proposed in the later work [20].

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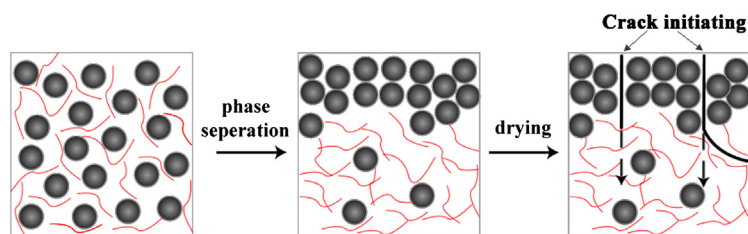
Fig. 1. Illustrative diagram for the phase separation in the mixture of nanoparticles (gray spheres) and polymer chains (red chains), and the crack inhabitation or redirection during drying. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The wavelength (crack spacing) was introduced to define the periodicity of the cracks. This is the phase separation of the particle clusters and solvent resulting from the drainage produced by the capillary force, at the last stage of the drying process. Moreover, the other phase separation also occurs during the drying process. The polymer introduced into the silica suspension acts as the depletant, inducing the phase separation at a critical polymer/particle concentration during the evaporation, which plays a main role on the formation of crack patterns.

Here we investigate the crack pattern formation in the deposit produced from the mixture of silica suspension and polyacrylamide (PAAm). The variation of patterns is tuned by varying the concentration ratio between the polymer and silica. The two phase separation processes occurring during the drying process are: the segregation of silica nanoparticles resulting from the depletion force acted by the polymer molecules during the drying process; the water drainage from the clusters of silica particles and polymer molecules due to the capillary force near the end of the drying. The pattern composed of polymer rich and colloid rich areas is theoretically discussed to address the diversity of crack patterns. This phase separation behavior accounting for the unique crack pattern is also examined by different experimental tools including the optical microscopy, atomic force microscopy (AFM) and X-ray spectra. This suggests whether the PAAm can confine or even restrain the cracks formation during the evaporation.

2. Materials and methods

2.1. Materials

Colloidal suspension here is the silica aqueous (Ludox AS-40, Sigma), and the polyacrylamide (PAAm, Mw $\sim$10k, Sigma) is selected as the polymer additive in the drying experiments. The SiO_2 particles are used as received, with the negative charge (Zeta potential of $\sim$$-50$ mV by our measurement using Zetasizer Nano-ZS, Malvern, UK), and without coating layers. The approximate size of silica nanoparticle is calculated as 22 nm in diameter according to the data of surface area and the density of bulk silica. In addition, microspheres of silica (Sil-N-11011, Sphere Scientific Co. Ltd., China, diameter $\sim$1.5 μm) are also used to examine the phase separation between polymer and silica spheres for the observation under the optical microscopy, considering the limit imaging resolution. Note that the solvent is the deionized water (18.2 MΩ cm, UP water system, China) in all the drying experiments and cleaning process. A set of mixtures with different ratios between the silica nanoparticles and the PAAm are prepared. The SiO_2 nanoparticles are negatively charged for the reason of stabilization by repulsive force. On the other hand, the PAAm in the mixture exhibits very weak negative charge properties (i.e. -4.2 mV of Zeta potential by the measurement). It is expected that the weak repelling interaction between the SiO_2 nanoparticles and the PAAm occurs, which implies that the attractive force by depletion interaction is achieved by the entropy effect of the mixture. The mixture suspension is treated by ultrasound facility for 15 minutes to alleviate the adsorption of polymer on nanoparticles. And the PH of the mix suspension is about 9.

All the suspensions are assured to be uniform dispersions in a shaker for about 12 hours and ultrasonic treating for about 30 minutes before using for drying experiments.

2.2. Setup

A clean microscopic glass slide used as the substrate is placed horizontally to support the sessile drops drying under the ambient condition (temperature of 25 °C and relative humidity of 20%). Two CCD cameras (Marlin AVT F201B and Marlin AVT F131B) with lens of AF Micro Nikkor 60 mm f/2.8D are used for top-view and side-view observing, respectively. It is important to note that the glass slides are all treated into the hydrophilic substrates. The procedures of the Piranha method are as follows: (a) the glass slides were put in the hot mixture of 40% hydrogen peroxide and 98% sulfuric acid with the volume ratio of 3/7 for 15 minutes ($\sim$150 °C), then (b) rinsed with deionized water for at least three times and (c) dried with dry nitrogen flow.

An optical microscopy (LV100, Nikon) is used to observe the distributions of polymer and silica microspheres in the dried film. The film of pure PAAm is recognized by the color gradient due to the variation of the deposition thickness. AFM (Dimension Icon, Veeco) is employed to examine the morphology of the film surface. Energy Dispersive X-ray spectroscopy (EDX) equipped in the Scanning Electron Microscope (SEM, Quanta 400 FEG, FEI) is utilized to characterize the PAAm distribution thanks to representative element of the nitrogen differentiated from the silica nanoparticles with high spatial resolution.

3. Results and discussion

The process of the drying of the mixture suspension can be schematically described into three stages shown in Fig. 1. When the polymer molecules are mixed into the silica suspension by ultrasonic and shaking procedures, the molecules and the silica nanoparticles are uniformly distributed at the initial stage (the left panel in Fig. 1). A depletion layer near the particle surface results from the loss of configuration entropy of polymer chain [31]. Thus the mixture of particles and polymer is unstable since the depletion force leads to the segregation of hard silica nanoparticles. This depletion force pushes the silica particles into the clusters and collects the polymer into molecular mesh, as shown in the middle panel of Fig. 1. The distribution of the polymer develops a net-like texture, which forms the two kinds of structure phases: polymer poor and rich regions.

During the evaporation process, the suspension of silica and polymer was gradually concentrated into a film of particle deposit, in which polymer chains were embedded non-uniformly. At the end of the evaporation process, a meniscus forms between adjacent silica clusters on the air–water interface. Water passes through silica/polymer clusters due to the capillary pressure on the meniscus. The further drying produces the internal stress resulting from the shrinkage of the deposition film, accordingly forming the cracks under a critical stress (the right panel of Fig. 1). Without the polymer addition, the cracks originate in order to release the accumulated stress and propagate towards the deposit to form multiple