Abstract: We performed microscopic, in situ visualizations of spontaneous cracking in drying silica-poly(vinyl alcohol) aqueous suspension coatings. The cracking event was quantified by measuring numbers of nucleation points per unit area from acquired time-lapse video images. Direct imaging revealed that the primary nucleation rate decreases obeying a power law, whereas the secondary nucleation rate first increases and then decreases with increases in the particle-to-polymer weight ratio. The resultant cross-over between two nucleation rates leads to a drastic morphology transition from isolated star-like cracks to interconnected ladder-like cracks. The maximum crack surface density was obtained at a critical cross-over particle loading.
Multiple crack nucleation in drying nanoparticle-polymer coatings

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ABSTRACT

We performed microscopic, in situ visualizations of spontaneous cracking in drying silica-poly(vinyl alcohol) aqueous suspension coatings. The cracking event was quantified by measuring numbers of nucleation points per unit area from acquired time-lapse video images. Direct imaging revealed that the primary nucleation rate decreases obeying a power law, whereas the secondary nucleation rate first increases and then decreases with increases in the particle-to-polymer weight ratio. The resultant cross-over between two nucleation rates leads to a drastic morphology transition from isolated star-like cracks to interconnected ladder-like cracks. The maximum crack surface density was obtained at a critical cross-over particle loading.

Keywords: colloidal suspension, coating, drying, crack, thin film
1. INTRODUCTION

Colloidal suspensions containing soluble organic binders are commonly used in coating industries. In particular, a nanoparticle-filled polymer matrix with regulated porosity plays a key role in a high resolution ink-jet printing as an ink-absorption layer. However, such particle-polymer suspension coatings often crack under drying to release growing tensile stresses. Despite numerous studies on drying suspensions, the mechanisms responsible for the crack nucleation are not yet fully understood.

During suspension drying, three distinct regions - supersaturated, saturated, and dry- can be identified [1] (Figure 1). The first region, in which particles are freely suspended, shrinks in the transverse direction and leaves the second region behind, supplying liquids to the coating edge. A curved liquid meniscus between neighboring particles recedes to promote a lower liquid pressure than atmospheric, which draws in and concentrates more particles toward the evaporating interface. In the subsequent saturated region, the particles are packed together but the liquid still fills the space between particles. In the final dry region, air begins to invade the pores and remaining liquid-rings at inter-particle contacts promote strong capillary forces to compress the particles. This transient drying behavior instantaneously yields local tensile stress distributions in coatings that are binding to a
substrate. The stress promotes spontaneous crack nucleation when it exceeds a critical value, as determined by the subtle balance between the released elastic energy and the surface energy required for the creation of new surfaces. Furthermore, a drying-induced polymer diffusion significantly impacts the stress development through its coupling with complex rheological changes in solidifying phases [2-5].

There has been a great deal of work on stress measurements [1, 6-9], direct visualizations [8-13], and theoretical modeling [14-15] for colloidal suspensions. However, most previous studies have focused on a regularly spaced cracking in binder-free suspensions and thus give only limited insight into cracking behavior in particle-polymer suspensions. Moreover, the stress once released via cracking would re-grow during drying due to continuous stress development in the solidifying polymeric phase, giving rise to sequential, multiple cracking on the coating surface. Few physical models are currently available to describe the multiple crack nucleation in particle-polymer suspensions, and what determines the nucleation rates still remains unresolved. In this article, we performed microscopic visualizations of drying silica-poly(vinyl alcohol) aqueous suspension coatings to newly quantify the crack nucleation rates from the direct imaging.
2. EXPERIMENTAL

2.1 Suspension preparation

Silica particles with an average diameter of 45nm and a negative zeta potential of -38.1 mV were stabilized in distilled water without the aid of surfactants. The organic binder used was 98.0-99.0 mol% hydrolyzed poly(vinyl alcohol)(PVA, Kurary Co.) with a 1,700 degree of polymerization. The PVA powders were dissolved in distilled water and stirred for 4h above 333 K to obtain a homogenous polymer solution. The PVA solution was then slowly added to the silica suspension, filtered though a nylon mesh, and continuously stirred maintaining a constant temperature of 318 K. The solid weight fraction, i.e., the amounts of particle and binder in the solutions, was fixed at 8 wt %. The particle-to-binder weight ratio, hereafter referred to as \( r \), ranged between 1.5 and 7.

2.2 Visualization

The suspension was cast on a clean glass substrate at 298K using a blade coater (model-411, Erichsen) to obtain films 8cm wide (Figure 2). The initial film thickness was measured using a con-focal laser displacement meter (LT8110, Keyence), and ranged between 40 and 60 \( \mu \)m with an uncertainty of 2 \( \mu \)m. The coating was then mounted on a transparent, conductive glass heater (MP-10DMH, Kitazato) pre-heated at 333 K by
regulating the current through the glass. The center of the drying coating was directly visualized from underneath the transparent heater using an upright CCD microscope (VH5000, Keyence) at varying magnifications and captured in real time using a digital video recorder (DMR-E500H, Panasonic). The corresponding visualization area was 380 μm × 280 μm or 1.46mm × 1.09mm. The use of a transparent heating plate enabled us to monitor the cracking behavior without disturbing vapor transports in the upper gas phase. A substantial LED light source was set on the coating surface with an air clearance of 10cm in order to enhance the image contrast. The experiments were conducted in pre-filtered air at a constant temperature of 298K and at a relative humidity ranging between 20% and 45%. The visualization system was shielded to minimize disturbances by air currents.

2.3 Crack surface density

The crack nucleation event was quantified by measuring the number of cracking points per unit visualization area, i.e., the crack surface density. Three distinct crack densities, PN, SN, and CN, are respectively defined as the number of points at which an isolated primary crack nucleates (Figure 3a), that at which a secondary crack nucleates from an existing crack (Figure 3b), and that at which a propagating crack connects or merges with a neighboring one (Figure 3c). The crack passing through the visualization area without
involving any new nucleation or connection points is not taken into account in the surface-density measurement (Figure 3d). Note that $\sqrt{1/PN}$ gives the characteristic mean spacing of isolated cracks nucleated on a surface.

3. RESULTS AND DISCUSSION

Figure 4 is a typical example of time-lapse image sequences showing crack nucleation during the suspension drying. The initial film thickness was 40 $\mu$m and the particle-to-binder weight ratio was $r = 3$. An isolated crack first nucleates at a spot, and then starts to propagate in different directions, but almost at the same speed, in the evaporating film to form a “star-like” crack (Figure 4a-c). Subsequently, the secondary nucleation follows the propagation of primary cracks to give a particular branched pattern. No visible air-bubbles or other contaminants were observed at the nucleation points. The direct imaging also showed that an opaque dry region, easily distinguished by gradients in the image contrast, passed through the visualization area just after the termination of crack propagation, implying that the crack nucleated in the saturated regime. Indeed, this finding is consistent with the recent laser-speckle measurements on the drying coating surface [13].

Figure 5 shows the time-variations in the crack surface-densities and the corresponding final morphologies of the dried films for three different particle-to-binder weight ratios. The
initial film thickness was 40 μm. At the low particle ratio of \( r = 2 \), distinct star-like cracks developed in the coating (Figure 5a). The number of primary nucleation points first increased and then reached a constant value of \( PN=50 \) mm\(^2\) before the suspension completely dried. Few secondary nucleations or crack-interconnections were observed, and thus \( SN=CN=0 \). In contrast, apparent secondary nucleation at the higher particle loading of \( r = 5 \) leads to a particular "ladder-like" pattern (Figure 5c). The surface density of the secondary nucleation was found to be equal to that of the crack-interconnection, i.e., \( SN\sim CN \), indicating that most branched, secondary cracks continuously propagate until they merge to a neighboring primary crack. Few isolated cracks were observed in the high particle loadings. In the intermediate case of \( r = 3 \), the rapid primary crack nucleation was readily followed by secondary nucleation from existing cracks (Figure 5b). The secondary cracks then propagated and merged with neighbors, giving rise to a transient surface pattern, in which the distinct star-like and highly branched cracks co-exist. Interestingly, the cracks exhibit an intermittent motion that lead to a stepwise increase in the crack surface density for the primary and the secondary nucleation. The crack nucleation ceased at a certain drying and then re-started, showing a particular multiple crack nucleation due to the sequential stress growth and release.
The effects of the particle-to-binder weight ratio on the total crack surface-density, $PN + SN + CN$, are summarized in Figure 6. Crack-free films were obtained below the minimum particle content of $r_{\text{min}} = 1.8$. At higher particle loadings, the total crack density first increased, exhibited a maximum, and then decreased with increases in particle loadings. The critical particle weight ratio at the peak shifted to higher particle-to-binder weight ratios as the drying progressed, eventually converging to $r_c \sim 3$.

In order to clarify the cracking behavior in detail, we first calculated the primary nucleation rate from the average slope of the $PN$ curves for different particle-to-binder weight ratios. As depicted in Figure 7, the primary nucleation rate exhibits a particular power-law decay with respect to the particle weight ratio as $\frac{dPN}{dt} \sim r^n$, where the exponent $n=6$ is independent of the initial film thickness. The slower nucleation in the thicker film results in a wider crack spacing of $\sqrt{1/PN} \sim 200 \mu m$ at a given particle loading.

We next compared the measured primary and secondary nucleation rates as a function of particle contents in Figure 8. In contrast to the power-law decay in the primary nucleation, the secondary nucleation rate first increases and then decreases with the particle-to-binder weight ratio. Consequently, the two nucleation rates show a cross-over at a particular
particle-to-binder weight ratio of $r \sim 3$, showing a good agreement with $r_c$, at which the total crack density reaches a peak (see Figure 6). These results ambiguously suggest that the suspension exhibits two distinct cracking regimes: the primary nucleation is dominant at low particle contents below $r_c$ (Regime A) to give star-like cracking, while the secondary nucleation plays a key role at higher particle loadings (Regime B) to promote branched ladder-like crack formation. The transition between these two regimes gives rise to a complex combination of star- and ladder-like crack patterns, leading to show a maximum nucleation density.

In order to gain better insight into the power-law rate decay shown in Figure 7, let us consider a sequential series of stress development and the subsequent relaxation. Previous experimental study [8] has shown that the critical stress at cracking obeys the scaling law $\sigma_c \sim (G/h^2)^{1/3}$ derived from the Griffith’s criterion, where $G$ is the shear modulus and $h$ is the film thickness at cracking. Replacing $G$ with an effective modulus in a polymer-particle suspension, $G_e$, and assuming the time scale required for the drying being proportional to the thickness, i.e. $t \sim h$, we obtain the stress growth rate scaled as $\sigma_c/t \sim (G_e/h^5)^{1/3}$. Thus the stress once released via spontaneous cracking requires a characteristic time $\tau_e = \Delta \sigma / (G_e/h^5)^{1/3}$ to re-grow to the critical cracking stress, where $\Delta \sigma$ denotes the stress
released via a single crack nucleation. When the time required for stress release is much shorter than $\tau$, a coating can involve $\tau/\tau$ nucleation events within a drying time $\tau$, and thus we obtain the averaged nucleation rate in a power-law form as $v=1/\tau \sim ((1-\phi^n/h)^{3/2}/\Delta \sigma$ where the effective modulus is assumed to be given by the empirical expression with respect to the particle volume fraction $\phi$ [16 and references therein]. The derived equation indicates that the crack nucleation rate is significantly reduced in thicker films as well as at high particle loadings, showing a good qualitative consistency with the present measurements.

We here note that the nucleation rate predicted from the simplest scaling shows much weaker thickness-dependence than our measurements. An increase in initial thickness from 40$\mu$m to 60$\mu$m led to a drastic reduction in crack-nucleation rates by two orders of magnitude, whereas the equation above only predicts a 50% decrease in nucleation rate, indicating that the present theory is not quantitatively satisfactory. The invariance possibly stems from the fact that ladder-like cracking in a thicker film significantly relaxes more tensile stress than predicted. Indeed, our microscopic observations show that some ladder cracks delaminate from the substrate and shrink in the transverse direction just after the completion of crack propagation. Further studies are necessary to clarify the detailed
physical mechanism of spontaneous cracking by taking into account the sequential stress growth and relaxation in a rather short time scale, accompanied by viscoelastic deformation of solidifying polymer phases confined between compressing particles.

4. CONCLUSIONS

We measured the nucleation rates of primary and secondary cracks in drying silica-poly(vinyl alcohol) suspension coatings from in situ visualizations. The use of a transparent heating plate enabled us to monitor the cracking behavior without disturbing vapor transports in the upper gas phase. The direct imaging reveals that the nucleation rates show a particular cross-over at the critical particle-to-polymer weight ratio, at which the maximum crack surface density was obtained. The final crack morphology shows a transition from distinct star-like cracks to ladder-like patterns.

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