Cracking in Drying Colloidal Films

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(Received 22 November 2006; published 25 May 2007)

It has long been known that thick films of colloidal dispersions such as wet clays, paints, and coatings crack under drying. Although capillary stresses generated during drying have been recently identified as the cause for cracking, the existence of a maximum crack-free film thickness that depends on particle size, rigidity, and packing has not been understood. Here, we identify two distinct regimes for crack-free films based on the magnitude of compressive strain at the maximum attainable capillary pressure and show remarkable agreement of measurements with our theory. We anticipate our results to not only form the basis for design of coating formulations for the paints, coatings, and ceramics industry but also assist in the production of crack-free photonic band gap crystals.

DOI: 10.1103/PhysRevLett.98.218302 PACS numbers: 82.70.Dd

When a thin film of wet paint or coating containing suspended submicron sized colloidal particles is dried on a substrate, evaporation of the solvent concentrates the particles into a closed packed array. Further evaporation causes the liquid menisci at the top layer of the particle network to exert compressive capillary force on the particle network [1,2]. The film generally binds to the substrate and resists deformation in the transverse direction giving rise to transverse tensile stresses [3]. If the particles are soft, they deform to close the pores but in the case of hard particles the film cracks to release the stresses. Though cracking in drying systems has been investigated on diverse systems such as wet clays [4–7], ceramic films [8,9], latex, and model colloidal dispersions [10,11], it is only recently that a fundamental understanding of the cracking mechanism is beginning to emerge [3,12–14]. For instance, it has long been observed that irrespective of the particle size and hardness, cracks nucleate spontaneously only above a critical film thickness. Chiu *et al.* [8,9] measured the maximum crack-free thickness for films cast on glass substrates and prepared from aqueous dispersions of alumina, polystyrene, and zirconia. The thickness was independent of the drying rate and increased with particle size suggesting that films containing large particles were less likely to crack, though crack-free films of polystyrene spheres of similar size were considerably thinner than those obtained with alumina and zirconia. The measured critical tensile stress at cracking scaled with the capillary pressure (based on particle size). On the theoretical front, Meakin [10,11] and others [14] adopted the statistical description where, starting from a uniformly stressed film, bonds (or springs) between the particles are broken at random and the system relaxes to a new equilibrium. When this process is repeated a number of times, crack patterns emerge that resemble those observed in experiments. Alternatively, the continuum approach that will be adopted here assumes a macroscopic stress versus strain relation along with energy balances to predict crack dynamics. To this end, we adopt the nonlinear stress strain relation proposed by Routh and Russel [2] for drying films composed of a homogeneous packing of deformable particles. The constitutive relation was derived by accounting for the viscoelastic deformation of a pair of particles due to both interfacial tension and external forces such as those exerted by contacting neighbors. Tirumkudulu and Russel [3] measured the stress evolution and the crack spacing for drying films of dispersions containing polymer spheres of varying diameters and shear moduli. They employed the Griffith's criterion for equilibrium crack propagation [15] along with the aforementioned constitutive relation for a network of identical elastic spheres to predict the critical stress (σ_c) for nucleation of an isolated crack,

$$\frac{\sigma_c R}{2\gamma} = 0.1877\left(\frac{2R}{h}\right)^{2/3}\left(\frac{GM\phi_{\mathrm{rcp}}R}{2\gamma}\right)^{1/3}. \tag{1}$$

Here, R is the particle radius, γ is the solvent-air interfacial tension, h is the film thickness at cracking, G is the shear modulus of the particles, M is the coordination number, and ϕ_{rcp} is the particle volume fraction at random close packing. The model assumed no slip between the substrate and the particle layer in contact with it, with the former assumed to be rigid. Consequently, the film consolidates in the direction perpendicular to its plane. For particles and substrate of comparable modulus, the multiplying constant in Eq. (1) reduces by a factor of 0.7. Thus Eq. (1) predicts thinner films to be tougher as they crack at higher stresses. The predicted scaling agrees with experiments though the measured values were about twice the predictions. Next, the biaxial stress, $\sigma = (3/35)MG\phi_{\mathrm{rcp}}(\varepsilon)^2$ in the crack-free state at the maximum compressive strain, $\varepsilon_{\max} = 1 - \phi_{\mathrm{rcp}}$, was set equal to the critical stress for cracking to obtain the critical thickness [3,16],

$$h_{\max} = \frac{37\gamma}{GM\phi_{\mathrm{rcp}}(1-\phi_{\mathrm{rcp}})^3}. \tag{2}$$

This regime, henceforth referred to as the *strain-limited* regime, predicts the critical thickness to be independent of particle size and increases with decrease in modulus, both in variance with experiments [8]. These discrepancies led to the current investigation where we show the existence of a second regime for crack-free films which is applicable for films containing hard particles.

Our experiments were performed with various stable aqueous dispersions containing particles over a wide range of sizes and shear moduli. Colloidal silica dispersion of particle volume fraction 0.03 and particle size 330 nm was obtained from Colloidal Dynamics (CD 350 NM®) and concentrated to 0.14 via centrifugation. Colloidal silica dispersion (LUDOX® TM-50) of particle size 22 nm was procured from Sigma-Aldrich and diluted to 0.03 volume fraction by adding deionized water. Acrylic dispersions with product codes BX 261, BX 269, BX 273, and Standard were obtained from ICI, Inc. and diluted to particle volume fraction of 0.13 by adding deionized water. Further, styrene-butadiene dispersion (Styronal™ ND 811) was obtained from BASF and diluted to 0.06 particle volume fraction by adding deionized water.

Thin circular films of approximately 10 mm diameter were cast on clean glass substrates using a spin coater. The experiments were conducted at temperatures ranging from 26 to 29 °C and relative humidity from 50% to 60%. The thickness of the final dried film could be varied by controlling the initial amount of dispersion disbursed on to the substrate. On complete drying, the film was examined for cracks under an upright optical microscope (Olympus, BX-60) at varying magnifications. Most films exhibited cracks at the rim and close to the center (relatively thick regions) with the remaining area devoid of cracks. The thickness profile of the film was measured using a surface profilometer (Sloan Dektak-II). The critical thickness corresponds to the maximum thickness of the film in the crack-free region. Figure 1 shows a typical thickness profile for one such film with the region between S and T being crack-free. Films whose thicknesses were everywhere less than the critical thickness were completely devoid of cracks. Not only were the measured critical thicknesses larger than that predicted by Eq. (2) by over two orders, but scanning electron microscopy images [Fig. 1(b) and 1(c)] of the top and interior of the crack-free domains showed negligible particle deformation even for films containing polymer spheres. These observations suggest a maximum capillary pressure ($P_{\max}$) beyond which the liquid menisci recede into the porous film, limiting the deformation of the film (Fig. 2). Thus, we predict a *stress-limited* regime, where the critical thickness is set by the balance of the biaxial stress [17] at the maximum attainable capillary pressure ($P_{\max}$) and the critical stress for cracking, Eq. (1) [16],

$$h_{\max} = 0.64\left[\frac{GM\phi_{\mathrm{rcp}}R^3}{2\gamma}\right]^{1/2}\left[\frac{2\gamma}{(-P_{\max})R}\right]^{3/2}. \qquad (3)$$

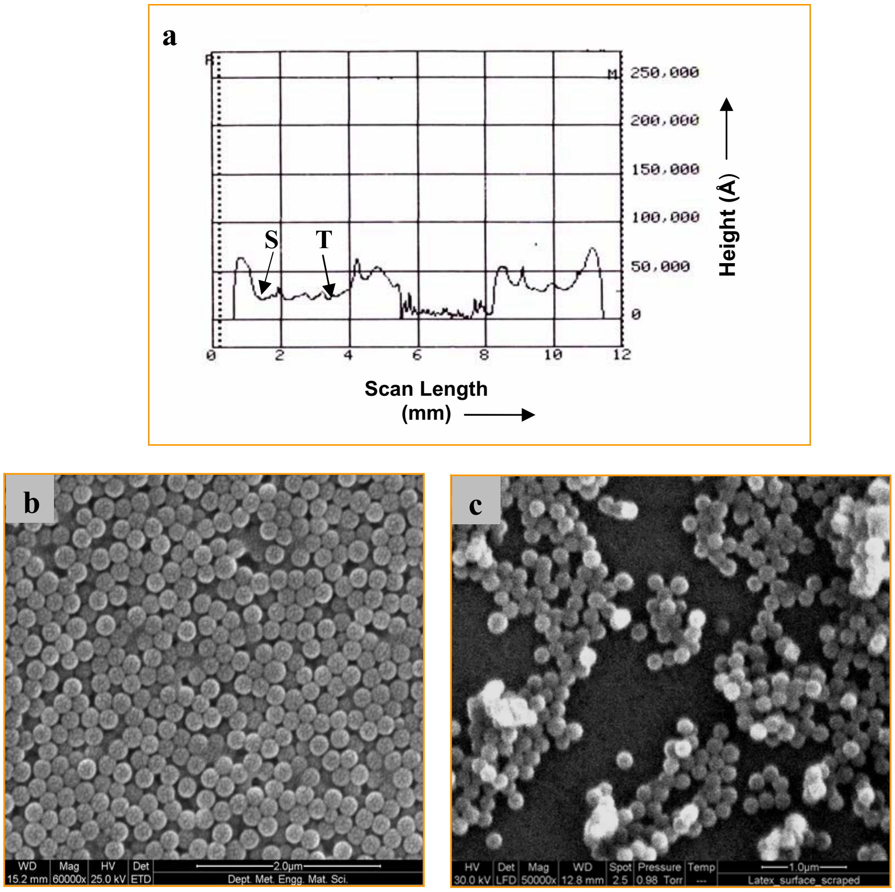

FIG. 1 (color online). Thickness profile of a dried film. (a) Thickness profile measured along the diameter of a dry styrene-butadiene film. (b) SEM of the film surface in the crack-free region. (c) SEM of the film interior in the crack-free region. The region between S and T was crack-free.

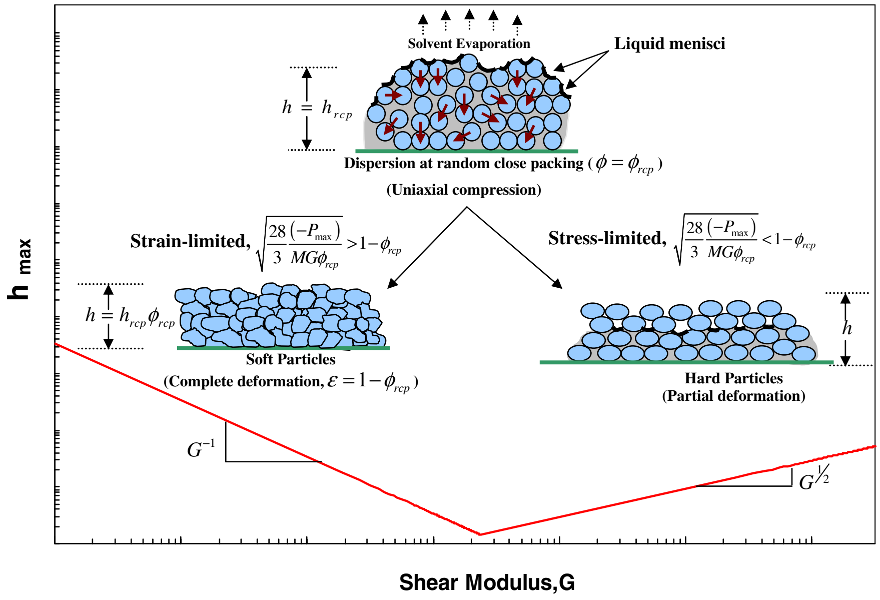

FIG. 2 (color online). Critical thickness variations as a function of the shear modulus. At random close packing, the menisci at the top particle layer exert a compressive force on the particle network. For very soft particles, the particles deform completely to close the voids for capillary pressure less than the maximum so that the uniaxial compressive strain is $\varepsilon \equiv \frac{(h_{\text{rcp}}-h)}{h_{\text{rcp}}} = 1 - \phi_{\text{rcp}}$. In case of hard particles, the menisci adjust their curvature till the maximum capillary pressure (P_{max}) is reached, beyond which they recede into the network resulting in partial deformation.

Since the final crack-free film is porous, the strain at the maximum attainable capillary pressure, $\sqrt{(28/3)(-P_{\text{max}})/MG\phi_{\text{rcp}}}$, is less than $(1-\phi_{\text{rcp}})$. Interestingly, while the critical thickness decreases with shear modulus for the first regime, the trend is exactly opposite for the *stress-limited* regime. This is because for a given maximum capillary pressure, the stored elastic energy density decreases with increasing shear modulus, thereby allowing thicker crack-free porous films.

A better insight into the above theoretical results can be gained by a simple scaling analysis. According to the nonlinear constitutive relation for a drying colloidal film containing monodisperse elastic spheres [2], the transverse tensile stress scales with the square of the compressive strain, $\sigma \sim G\varepsilon^2$. When an isolated crack nucleates spontaneously in the film, portions of the film over a length that scales with the film thickness (h) relax, so that elastic energy recovery per unit length of the crack scales as $E_{\text{elastic}} \sim h^2\sigma\varepsilon$. On setting this equal to the increased surface energy per unit length ($E_S \sim \gamma h$) gives (1), $\sigma_c \sim G^{1/3}(\gamma/h)^{2/3}$. The strain-limited regime is obtained when the capillary pressure is able to completely deform the particles without inducing a crack. This is possible only when the tensile stress at maximum deformation ($\varepsilon_{\text{max}} = 1 - \phi_{\text{rcp}}$) is less than the critical stress. Thus the critical film thickness (h_{max}) for this regime scales as $G^{1/3}(\gamma/h_{\text{max}})^{2/3} \sim G(1-\phi_{\text{rcp}})^2$ giving (2), $h_{\text{max}} \sim \gamma/G(1-\phi_{\text{rcp}})^3$. On the other hand, if the particles are so hard that even the maximum capillary pressure is not able to completely deform them, then the critical cracking thickness is obtained by equating the critical stress to the tensile stress at the maximum capillary pressure, $G^{1/3}(\gamma/h_{\text{max}})^{2/3} \sim (-P_{\text{max}})$, giving (3), i.e., $h_{\text{max}} \sim \gamma G^{1/2}/(-P_{\text{max}})^{3/2}$.

Figure 3 plots the measured critical thickness over a wide range of sizes and shear moduli against the characteristic scale for the stress-limited regime. Here, the particle volume fraction was measured by drying the dispersion in a capillary tube and noting the initial and the final length of the dispersion plug. The measured values of ϕ_{rcp} varied from 0.60 to 0.68 while that for Chiu *et al.* [8] were from 0.59 to 0.62. While the measured values of ϕ_{rcp} were used for our experiments, we chose $\phi_{\text{rcp}} = 0.6$ for that of Chiu *et al.* [8]. The observed scaling is in remarkable agreement with the predictions over five orders of the characteristic scale. Interestingly, though both alumina and zirconia particles had a narrow size distribution, the particles were not spherical [8] suggesting that in the present case, the asphericity of the particles does not significantly affect the critical thickness. The coefficient of the best fit (solid line) when compared with Eq. (3) gives the maximum attainable dimensionless capillary pressure, $(-P_{\text{max}})R/2\gamma = 1.4$. We also measured the vapor pressure at equilibrium for a saturated dispersion of styrene-butadiene particles at close packing ($\phi_{\text{rcp}} = 0.64$) using a dew point potential meter (WP4®, Decagon Devices). The dimensionless capillary pressure was determined using Kelvin equation [18] to be 1.2 ± 0.08 which is close to the predicted value of 1.4. Energetic arguments [19] for a packing of identical spheres show that the maximum capillary pressure depends on the wetting characteristics of the solvent and is given by $(-P_{\text{max}})R/2\gamma = 3\cos\theta\phi_{\text{rcp}}/2(1-\phi_{\text{rcp}})$, where θ is the wetting angle. At complete wetting and for $\phi_{\text{rcp}} = 0.64$, we obtain a value of 2.7. Given that the wetting angle will depend on the nature of particles, the predicted value of the maximum capillary pressure from the power law fit and that measured using the dew point potential meter is within the expected range. Further, substituting the maximum capillary pressure in Eq. (3) results in the critical thick-

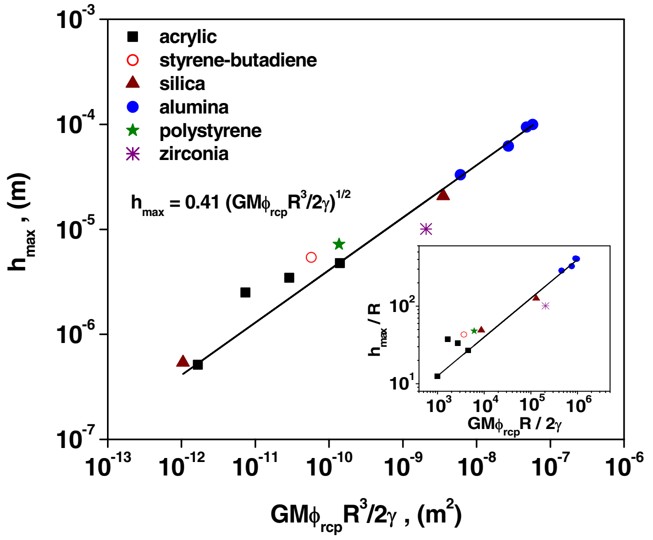

FIG. 3 (color online). The measured critical thickness vs the characteristic scale, $\frac{GM\phi_{\rm rcp}R^3}{2\gamma}$. The data points are for films of acrylic [■, $G = 0.8$ GPa, $2R = 82$, 133, 206, and 353 nm, and $\phi_{\rm rcp}(M) = 0.65(6.7)$, 0.66(6.8), 0.68(7.0), and 0.67(6.9), respectively], styrene-butadiene [○, $G = 1$ GPa, $2R = 250$ nm, and $\phi_{\rm rcp}(M) = 0.64(6.6)$], silica [▲, $G = 31$ GPa, $2R = 330$, and 22 nm, and $\phi_{\rm rcp}(M) = 0.60(6.1)$ for both], alumina [8] [●, $G =$ 156 GPa, $2R = 230$, 379, 458, and 489 nm, and $\phi_{\rm rcp}(M) =$ 0.60(6.1) for all], polystyrene [8] [★, $G = 1.6$ GPa, $2R =$ 300 nm, and $\phi_{\rm rcp}(M) = 0.60(6.1)$], and zirconia [8] [∗, $G =$ 81 GPa, $2R = 200$ nm, and $\phi_{\rm rcp}(M) = 0.60(6.1)$]. Here the value of surface tension, γ, is taken as 0.072 N/m for all the cases. The solid line is a power law with an exponent 1/2 and the multiplying coefficient is obtained via regression. The inset plots the same data in the nondimensional form.

ness being proportional to $\sqrt{M(1-\phi_{\rm rcp})^3/\phi_{\rm rcp}{}^2}$. Consequently, the close packing concentration/coordination number could be varied to control the critical thickness. Experiments [8] show that the critical thickness increased by about a factor of 2 when the addition of electrolyte flocculated the dispersion and reduced the packing fraction of the final film from 0.62 to 0.53. Interestingly, with $M =$ 6.5 for $\phi_{\rm rcp} = 0.62$ and $M = 5$ for $\phi_{\rm rcp} = 0.53$ [20], our model predicts an increase by a factor of 1.4, in line with the observations.

Our study identifies a new regime for obtaining crack-free films and thereby elucidates the fundamental mechanism responsible for cracking in drying dispersions. Since a control on the crack-free film thickness is critical to several industrial coating processes, the results presented here could form the basis for efficient design of coating formulations. These results also have implications for the synthesis of photonic band gap crystals via the colloidal crystallization route where capillary forces induced during drying of colloidal dispersions pack particles into an ordered 3D array [21,22]. Our analysis sets an upper limit on the thickness of large single domain band gap crystals possible via this synthesis route.

The present work was financially supported by the Department of Science and Technology, India under Project No. 04DS026. The experimental support of Dr. S. L. Kamath and Professor N. Venkataramani of Department of Metallurgical Engineering and Materials Science, IIT-Bombay and Professor D. N. Singh of Department of Civil Engineering, IIT-Bombay is acknowledged. The authors thank Dr. Martin Murray of ICI and Dr. Richard Buscall of MSACT Consulting for stimulating discussions and for generous donation of dispersions. Dr. K. Takamura of BASF is also acknowledged for providing the styrene-butadiene dispersion.

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