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Langmuir, 2009, 25 (8), 4284-4287 • DOI: 10.1021/la804331c • Publication Date (Web): 26 March 2009

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**Cracking in Drying Colloidal Films of Flocculated Dispersions**

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Received December 31, 2008. Revised Manuscript Received March 13, 2009

Understanding the mechanism of cracking during the drying of aqueous colloidal dispersions is important to preventing film failure. While most of the reported work has dealt with stable aqueous dispersions, a few studies have focused on flocculated systems. The latter especially assumes importance because the role of particle packing in the mechanism of cracking is not completely understood. In this work, we study the cracking of colloidal films cast from flocculated aqueous dispersions of α-alumina. Here, the extent of flocculation is controlled by varying the pH of the dispersion and characterized in terms of the final packing volume fraction of the dried film. The influence of varying the close-packed volume fraction on the critical cracking thickness and critical cracking stress is measured. The measurements are compared with the model predictions based on Griffith’s energy balance, and good agreement is found between theory and experiments, suggesting that the model is universal and applies equally well to stable as well as flocculated systems.

**Introduction**

The cracking of colloidal films has received considerable attention because of its importance in many important applications such as paints, wet clays, ceramics, and so forth. When a thin film of an aqueous colloidal dispersion is applied on an impermeable substrate, water evaporates, resulting in an increase in the solid concentration. In stable dispersions, the strong interparticle repulsive forces disperse the particles against the tendency of the attractive forces to bring them together. Further evaporation causes particles to concentrate into a closed-packed array, accompanied by capillary stresses that either deform them to close the pores (soft particles) or result in the nucleation and propagation of cracks (hard particles). The experiments of Chiu et al. show that irrespective of particle size and rigidity there exists a critical cracking thickness (CCT) below which films do not crack. On the theoretical end, Tirumkudulu and Russel proposed a model based on the Griffith’s criterion wherein a balance between elastic energy released during crack propagation and the increased surface energy accompanies capillary stresses that either completely deform the film of an aqueous colloidal dispersion is applied on an impermeable substrate, water evaporates, resulting in an increase in the film thickness of the film. The network has a yield stress, and the film cracks under the final packing volume fraction, φ_{rcp} is the random close-packed volume fraction, γ is the solubility–air interface tension, M is the coordination number, N ≡ (h/2R) is the dimensionless film thickness with h being the film thickness, and G is the shear modulus of the particles. Singh and Tirumkudulu report CCTs for a large number of stable aqueous dispersions and identify two regimes for obtaining crack-free films.

For dispersions containing hard particles (stress-limited regime), particle deformation is negligible, and the CCT increases with particle size as well as particle rigidity whereas for soft particles where the particles completely deform to close the pores (strain-limited regime) the CCT decreases with increasing particle rigidity but is independent of particle size. The CCT \( h_{\text{max}} \) for the stress-limited regime is obtained by equating the tensile transverse stress at the maximum attainable capillary pressure \( P_{\text{max}} \) to \( \sigma_c \),

\[
\frac{\sigma_c R}{2\gamma} = 0.1877 \left( \frac{M \phi_{\text{rcp}}}{N^2} \right)^{1/3} \left( \frac{GR}{2\gamma} \right)^{1/3}
\]

Here, \( \sigma_c \) is the critical cracking stress, \( R \) is the particle radius, \( \phi_{\text{rcp}} \) is the random close-packed volume fraction, \( \gamma \) is the solubility–air interface tension, \( M \) is the coordination number, \( N \equiv (h/2R) \) is the dimensionless film thickness with \( h \) being the film thickness, and \( G \) is the shear modulus of the particles. Singh and Tirumkudulu report CCTs for a large number of stable aqueous dispersions and identify two regimes for obtaining crack-free films.

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

and it agrees well with measurements over a wide range of particle properties. Furthermore, the model also suggests that the cracking behavior is influenced by the final packing volume fraction, a prediction yet to be completely verified.

We study the effect of flocculation on both the critical stress and the critical cracking thickness in drying films. Here, the weaker stabilizing interparticle forces are overcome by the attractive van der Waals forces causing the particles to come into contact with one another well before they reach random close packing. An electrostatically stabilized dispersion can be flocculated either by the addition of electrolytes or by altering the pH of the dispersion. In general, the particles agglomerate to form flocs (open fractal structures (Figure 1)). With further evaporation, the flocs connect to form a percolating network that spans the entire thickness of the film. The network has a yield stress, and the film consolidates when the capillary pressure exerted by the fluid interface at the top of the film exceeds the network strength. As the film consolidates and the particles rearrange to form stronger networks, the liquid either recedes into the porous packing when the capillary pressure reaches a maximum while still below the yield stress of the network or the film cracks under transverse tensile stresses generated as a result of the constraint imposed by the substrate on lateral shrinkage. The final packing volume fraction (\( \phi_f \)) of the dried film is less than the random close-packing fraction. Recent experiments on lattices containing soft...
polymer particles and flocculated by the addition of salt indicate skin formation on top of drying films leading to a significant reduction in evaporation rates.\textsuperscript{10,11} Chiu et al.\textsuperscript{8} varied the degree of flocculation of alumina dispersion by adding salt (NaCl) and found that the CCT initially increases with salt concentration, passes through a maximum, and then starts to decrease. The increase in CCT was attributed to the decrease in stabilizing electrostatic double layer forces. However, Carreras et al.\textsuperscript{12} have recently shown that the measured CCTs for alumina dispersions (pH $\sim$1.75) were 3 times higher than that obtained from flocculated suspensions (pH $\sim$9), in apparent contradiction to the earlier work of Chiu et al.\textsuperscript{8} Here, the higher CCT at low pH is attributed to the superior mechanical properties due to the higher packing fraction.

While the above experiments do suggest a clear influence of flocculation on cracking, the observed trends are contradictory. More importantly, it is not clear what mechanism controls cracking in flocculated systems. Furthermore, if the Griffith criterion\textsuperscript{13} is applicable to flocculated systems, how does one account for the network strength? We address these questions by varying the degree of flocculation of aqueous $\alpha$-alumina dispersions over a wide range of pH and measuring the final packing volume fraction, the critical stress at cracking for varying film thicknesses, and the CCT. We show that the model for stable dispersions predicts the measurements for flocculated dispersions equally well if $\phi_{cp}$ is replaced by $\phi_f$ while correcting for the number of neighbors in contact with one another.

### Experimental Section

Dilute dispersions (10–20\% by volume) of high-purity $\alpha$-alumina (AKP-30) (average particle size of 335 nm) were prepared by dispersing AKP-30 in deionized water. The pH of these dispersions was adjusted using analytical-grade HNO$_3$ and KOH. The final packing volume fraction ($\phi_f$) was determined by drying the dispersions in glass capillaries with an inner diameter of 500–1000 $\mu$m. Here, the original dispersion with different initial lengths ($l_0$) was allowed to dry from one end of the capillary tube, and the final length ($l_f$) of the dried dispersion plug was measured. The final packing volume fraction ($\phi_f$) was obtained from volume balance, $l_0\phi_f = l_f\phi_0$. The reported value of $\phi_f$ for each pH was averaged over 12 independent experiments with different initial lengths. Note that the diameter of the capillary ($D \approx$ 500–1000 $\mu$m) was at least 3 orders of magnitude larger than the particle size.

For CCT measurements, thin films of the dispersions were cast on glass substrates by dispersing the liquid using a spin coater (slow rotation rate of $\sim$20 rpm). In the case of highly flocculated dispersions that had very large critical thicknesses, the films were dried in open vials with a square cross section (1.3 cm $\times$ 1.3 cm). Finally, the thickness profile of the dry film was obtained using a surface profilometer (Dektak-150). The classical cantilever

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic of a drying colloidal film of (i) a stable and (ii) a flocculated dispersion.}
\end{figure}

Results and Discussion

The zeta potentials for AKP-30 dispersions as reported by Johnson et al.\textsuperscript{15} are reproduced on the secondary y axis of Figure 2. The potential is high and positive at low pH and decreases with increasing pH. At pH $\sim$9.6, the potential passes through the isoelectric point (iep) and decreases further with pH to become large and negative. We quantify the extent of flocculation in terms of the final packing volume fraction ($\phi_f$). The variations of final packing volume fraction with pH are plotted on the primary y axis of Figure 2. The measured $\phi_f$ shows direct correspondence with the reported zeta potential measurement in that, at low pH, the final packing volume fraction is highest because of the higher surface charge. As the pH is increased, the surface charge decreases, which results in a weaker stabilizing force and leads to particle flocculation. This is evident from lower values of the final packing volume fraction. At the iep, the charges at the surface are completely neutralized, and there are no stabilizing forces. Consequently, the final packing volume fraction is the lowest at pH $\sim$9.6. With further increase in pH, the particle surface acquires negative charge, leading to a greater stability of the dispersion that results in higher $\phi_f$. The low values of $\phi_f$ close to the iep suggest that the system transforms into a gel-like structure with a loose network of particles. The gelation volume fraction (i.e., the volume fraction at the liquid—solid transition) at the iep is approximately\textsuperscript{16,17} 0.14, which is lower than the measured $\phi_f$. We also include for comparison the final volume fraction at pH 4, 7, and 9 implied by the compressive yield stress ($P_y$) measurements.\textsuperscript{16,17} While our measured values of $\phi_f$ are in broad agreement with the yield stress data away from the iep, there is a large discrepancy close to the iep. To resolve this, we computed the total network strength ($P_y + 4T_s/D$) where $T_s$ is the shear yield stress at $\phi_f$ measured using the capillary and found it to be 2 orders of magnitude lower than the capillary pressure (eq 3) compressing the network. Although we are unable to explain this discrepancy, drying experiments performed with the same system but on hydrophobic capillaries also resulted in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Variation of the final packing volume fraction ($\phi_f$) measured using the capillary tube and that implied by compressive yield stress and zeta potential as a function of pH for the AKP-30 dispersion (26.1 °C and 43% RH). The zeta potential data is taken from Johnson et al.\textsuperscript{15} The solid lines are provided as a guide to the eye.}
\end{figure}

\begin{thebibliography}{99}
\footnotesize
\bibitem{13} Griffith, A. A. Phil. Trans. R. Soc. 1921, 221, 163.
\end{thebibliography}
which predicts an increase in CCT with a decrease in \( \theta \). This is because a decrease in the capillary pressure (due to lower \( \phi_f \)) results in lower stored elastic energy and hence requires a thicker film to crack so as to equal the increase in surface energy. The model prediction compares fairly well against the measured CCTs in that the model captures the peak close to the iep and the subsequent decrease at higher pH values. The number of contacting neighbors \( (M) \) is calculated by linearly extrapolating the model predictions (eq 2) at different pH values. The measured CCTs \( (\phi_f, \gamma) = (3.97, 0.66, 6.96), (4.98, 0.61, 6.18), (6, 0.56, 5.12), (7.25, 0.52, 4.90), (9.3, 0.18, 3.3), (10.46, 0.40, 3.82), and (11.88, 0.68, 7.02) \). A contact angle of 35° was assumed.24

Figure 3. Comparison of the measured critical cracking thickness (CCT) with the model predictions (eq 2) at different pH values. Furthermore, the values of \( \phi_f \) and \( M \) at different pH values are \( (pH, \phi_f, M) = (3.97, 0.66, 6.96), (4.98, 0.61, 6.18), (6, 0.56, 5.12), (7.25, 0.52, 4.90), (9.3, 0.18, 3.3), (10.46, 0.40, 3.82), and (11.88, 0.68, 7.02) \). A contact angle of 35° was assumed.24

In Figure 3, the experimentally measured CCTs are compared with those predicted by eq 2. The measured CCT (rer) initially decreases slightly as the pH is increased from ~4 to 6. With further increase in pH from 6 to ~10, there is a sharp increase in the CCT with the maximum observed at a pH of ~10. Finally, the CCT is found to decrease as the pH is further increased from 10 to ~12. Recall that the critical cracking thickness depends on the value of the maximum capillary pressure \( (-P_{max}) \) (eq 2), which in turn is a function of the final packing volume fraction and the wetting angle \( (\phi_f) \). The slight shift in the predicted peak can be attributed to small errors in pH measurements (about ±5%). At low pH (<6), however, the experiments exhibit a reverse trend compared to the model predictions. One plausible reason could be the high solubility of alumina at low pH21 that could lead to the precipitation of alumina at particle contacts that in turn would lead to strengthening of the network without significantly altering the final packing volume fraction. Such a phenomenon is not accounted for in our model and could be the cause of the discrepancy. Chiu et al.8 also report higher CCTs below pH 2 and have attributed this to the higher solubility of alumina at low pH, which explains the difference in the observed trend with respect to those of Carreras et al.12 Nevertheless, our model captures quite well the measured trend for the remaining pH values. However, the CCT predicted using \( \phi_f \) implied by the yield stress data predicts only a modest increase (~130 μm) close to the iep. All in all, the above results point to the importance of capillary pressure and its role in the cracking of drying films.

Figure 4 plots the dimensionless critical cracking stress against the dimensionless characteristic scale \( (M\phi_f/N^2) \) for dispersions with pH values of 3.3, 6.5, 7.8, 10.0, and 11.1. Here, the average thickness of the film \( (h) \) is used to calculate the dimensionless film thickness \( (N = h/2R) \). It should be noted that the transverse flow \( ^5 \) generated by capillary pressures at the edges leads to slight inhomogeneities in the thickness over the film. Thus, although the average thickness may be low, the actual thickness over certain regions of the film would be well above the CCT.7 The solid line in Figure 4 represents model predictions (eq 1) with no adjustable parameters.22 The experiments and model predictions are in excellent agreement, confirming that the model based on energetic arguments and proposed for stable dispersions is equally capable of predicting the cracking behavior in flocculated systems as well. However, it is important to note that the model is incapable of

(18) Murray, M. Personal communication.
(22) As in case of Singh and Tirumkudulu,3 the coefficient in eq 1 was increased by a factor of 2 while comparing this equation with the experimental results.
predicting the final packing volume fraction at which a given drying film will crack. This would require a knowledge of the force required to compress the network during consolidation, which in turn depends on the strength of the interparticle bonds and the microstructure of the network. The models describing such phenomena are still in a state of early development, and the discrepancy between our measured $\phi_f$ close to the iep and the corresponding values deduced from the reported compressive yield stress underlines this fact. However, once the final packing volume fraction of the dry film is known, the critical stress and thickness variation with respect to other system parameters (shear modulus and particle radius) are captured well by our model.

Conclusions

The cracking behavior of a model aqueous dispersion over a broad range of pH values is investigated. The measured values of critical stress and thickness in both the stable and flocculated regimes were compared with the prediction of the existing model. Whereas good agreement was found for pH > 6, some discrepancy was observed in the critical thickness at lower pH. This study highlights the importance of capillary pressure in the cracking of drying films of colloidal dispersions and demonstrates how merely varying the final packing volume fraction can drastically alter the cracking characteristics. The proposed model provides a complete theoretical framework for predicting the cracking characteristics of drying colloidal dispersions and could form the basis for the efficient design of coating formulations.

Acknowledgment. This work was financially supported by the Department of Science and Technology, India, and an IIT Bombay research grant. We thank Dr. Martin Murray of AkzoNobel for stimulating discussions and for providing the AKP-30 particles.
