The excitement of watching paints dry

Mahesh S Tirumkudulu
Department of Chemical Engineering
Coating Flows

FluID MECbAnICS

CoMLoIdS & InterFaCeS

SOLID MECbANICS

Film Formation and Cracking in Films

Craquelure
**Film Formation & Cracking**

- Paints contain pigments, binder, solvents, additives
- Traditional paints contained volatile organic compounds (VOCs)
- VOCs soften particles during deformation, **BUT**
- VOCs are health hazard, regulation to limit their use.

---

**Diagram Details:**
- **Evaporation**减少厚度
- **Particle deformation**
- **Coalescence**
- **Cracking**

**Latex:** Water-borne dispersion
Drying

\[ (\phi \geq \phi_{r cp}) \]

\[ P = -\frac{2\gamma_{wa}}{r_c} \]

uniform evaporation

transverse flow

transverse flow

Capillary rise

\[ P = 0 \]

\[ P = -\frac{2\gamma_{wa}}{R} \]

P = 0

2R

“Coffee ring” problem
Particle Deformation

Liquid menisci

Equivalent “model” film

Network of springs

Particle pairs replaced by non-linear springs

Equivalent film

\[ F = kx \]

\[ \frac{F}{\pi R^2} \sim G\varepsilon^2 \]

G: particle modulus

\varepsilon: strain

“linear”

“non-linear”
Drying and Cracking

Polymer particles (350 nm) in water

~500 microns
Why do drying films crack?

If the metal films are separate when cooled:

For the bimetallic strip:

Tensile
Compressive
Measurement of Transverse Stress

\[ \sigma_{xx} = \frac{h_s^3 G \alpha}{6 L_f H (H + h_s)} \]

- \( h_s \): substrate thickness
- \( H \): film thickness
- \( L_f \): length of film
- \( G \): Young’s modulus of substrate
Non-film forming dispersion

\[
\left( \frac{\sigma R_o}{2\gamma} \right)
\]

Critical Cracking Stress

\[
\hat{t} \equiv t E / (h_o (1 - \phi_o))
\]
Critical Stress for Cracking

• Stress-Strain relation \( \sigma \sim G \varepsilon^2 \)
  \( \text{(Stress=} \text{modulus} \times \text{strain}^2 \)\)

• Recovered Elastic energy, \( E_{\text{elastic}} \sim h^2 \sigma \varepsilon \)
  \( \text{(~stress} \times \text{strain} \times \text{vol}) \)

• Increase in Surface energy, \( E_{\text{surface}} \sim \gamma h \)

• Critical Stress for cracking, \( \sigma_c \sim G^3 \left( \frac{\gamma}{h} \right)^{\frac{2}{3}} \)

Elastic energy = Surface energy
Critical stress vs. film thickness

\[ \left( \frac{\sigma_{c,i} R_o}{2\gamma} \right) \]

Identical particles

- PPG342: Experiment
- PPG342: Short time limit
- PPG342: Long time limit
- GMA610: Experiment
- GMA610: Short time limit
- GMA610: Long time limit

\[ \sigma_c \sim G^\frac{1}{3} (\gamma/h)^\frac{2}{3} \]

\[ N \equiv \left( \frac{h_o \phi_o}{2R_o \phi_c} \right) \]

(Tirumkudulu & Russel, Langmuir, 2005)
Critical Cracking Thickness

Maximum Crack Free thickness

(Styrene Butadiene particles, \(2R_o\)=250 nm, \(T_g=65^\circ C\))

\[
\sigma \sim G \left( \frac{\gamma}{h} \right)^{\frac{1}{3}} \sim -P_{\text{max}} \Rightarrow h \sim \gamma G^2 \left( \frac{1}{-P_{\text{max}}} \right)^{\frac{3}{2}}
\]
Stress-Limited Regime

Identical particles

Gives a guideline for formulation of paints & coatings

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

Acrylic: 82-353 nm; 0.8 GPa
S-B: 250 nm; 1.0 GPa
Silica: 22, 330 nm; 31 GPa
Alumina: 230-489 nm; 156 GPa
Polystyrene: 300 nm; 1.6 GPa
Zirconia: 200 nm; 81 GPa

(Singh & Tirumkudulu, Phys Rev Lett, 2007)
Multiple Cracks

Crack spacing vs Thickness

- Alumina, 13nm (Shorlin)
- PMMA, 95nm (MT&WBR)
- Styrene-Butadiene, 250nm (IITB)
- Acrylic, 82nm (IITB)
- Acrylic, 133nm (IITB)

$2W = 3.4076 \times h$
Latex Blends

- Closer to “real” paints and coatings
- Mixture of hard and soft particles: pigments and binder
- How to predict the mechanical properties of such a film? What is the effective modulus?
- Will the same theoretical framework apply to blends?

Singh et al, Langmuir 2009(a,b)
Conclusions

• Capillary pressure is responsible for cracking.

• Scaling for the critical stress for an isolated crack agrees well with experiment for stable dispersion.

• Critical cracking thickness, measurements agree with predictions

• Blends-mixed results, more theoretical work required
Acknowledgement

Students
Karnail Singh (PhD)
Laxman Bhosale (MTech)
Girish Deoghare (DD)
V Ranganath (MTech)
Arijit Sarkar (PhD student)
T Venugopal (MTech student)

Collaborators
Martin Murray (AkzoNobel)

Funding
DST, India
AkzoNobel, UK