Lessons learned while watching paint dry: film formation, drying fronts, and cracking

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July 2007

OUTLINE

one-dimensional film formation
  regimes
  temperature dependence
observations on a cantilever
  capillary stresses
  drying fronts

cracking: theory & experiment
  critical capillary pressure
  patterns and spacing
  critical thickness

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Film Formation, Non-Uniformities, and Cracking Driven by Capillary Pressure

early time

- non-uniform evaporation
- pressure driven flow
- compression
- tension

transparent film

- water flows
- stresses

crack
Driving Forces for Homogeneous Deformation

1. **Wet sintering** (Vanderhoff, 1966)
   polymer/water surface tension
   \[ \gamma_{pw} \]

2. **Dry sintering** (Dillon, 1951)
   polymer/air surface tension
   \[ 2\gamma_{pa} \]

3. **Capillary Deformation** (Brown, 1956)
   pressure at air-water interface
   \[ -p_{cap} = -\kappa \gamma_{wa} \leq 10 - 15 \frac{\gamma_{wa}}{a} \]

In all three negative pressures put the film in tension. The substrate prevents lateral deformation, while free surface allows compression in normal direction.
MODEL FOR ONE-DIMENSIONAL FILM FORMATION

\[ F_{nm} = -\frac{16}{3} a^2 \left\{ \eta \frac{d}{dt} \left( -n_{nm} \cdot \varepsilon \cdot n_{nm} \right)^{3/2} n_{nm} \right\} \text{ viscous} \]

\[ \frac{G}{2(1-v)} \left( -n_{nm} \cdot \varepsilon \cdot n_{nm} \right)^{3/2} n_{nm} \text{ elastic} \]

\[ n \cdot \varepsilon \cdot n = \Delta R/2a \]

Hertz 1882, Matthews 1980

**Close-packed spheres**

\[ \sigma_{33} = -p_{cap} + 0.69 \frac{\phi N \gamma}{a} - \frac{\phi NG}{6\pi(1-v)} \int_{-\infty}^{t} \exp \left( \frac{G(t' - t)}{2\eta(1-v)} \right) \frac{d\varepsilon^{3/2}}{dt'} dt' = 0 \]

\[ \varepsilon = -\varepsilon_{33} = 1 - \frac{\phi_{rcp}}{\phi} \quad -p_{cap} \leq 12.5\gamma_{aw}/a \]

**Scaling**

\[ \bar{t} = \frac{\dot{E}t}{H(1-\phi_{o})} \quad \bar{\sigma}_{t} = \frac{a\phi_{cap}}{N\phi\gamma_{wa}} \]

\[ \bar{G} = \frac{HG_{\infty}^{*}}{\dot{E}_{\infty}} \quad \text{evaporation time} \]

\[ \bar{\lambda} = \frac{\eta a \dot{E}}{H\gamma_{wa}} \quad \text{viscous collapse time} \]

\[ \phi = 1 \]
Generalized Process Map

- **Viscous closure**
- **Evaporation**

- **Dry sintering**
- **Receding water front**
- **Capillary deformation**
- **Wet sintering**

- Ratios of time scales: $a\eta E\gamma_{aw}H$
- $1.0 \times 10^3$
- $1.0 \times 10^1$
- $1.0 \times 10^{-1}$

- **Evaporation relaxation**

- **Interfacial tension driving force**
  - Particle-air
  - Water-air/particle-air
  - Water-air
  - Particle-water
EFFECT OF TEMPERATURE

time to close pores
\[ t_{film} = 0.21 \frac{\eta(T) a}{\gamma_{pw}} \]

wet sintering
capillary deformation
\[ 0.36 \frac{H}{\dot{E}} \]
dry sintering
\[ 0.21 \frac{\eta(T) a}{\gamma_{pa}} \]

Cantilever Experiment for Measuring Stresses


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

- \( h_s \): substrate thickness
- \( h \): film thickness
- \( L \): length of film
- \( G \): bending modulus
(a) fluid domain

particle packed domain

contours of constant stress.

packed domain at the edge of the film.

clear film region

(b) fluid region

(c)
Film forming latices

\[ T_g < T_{amb} \]
Low $T_g$ Film Forming Latex: WCFA

$\phi_o = 0.32 - 0.35 \quad 2a = 290 \text{ nm} \quad T_{mft} = 16^\circ\text{C}$

Rel. Humidity = 12-44%
Temperature = 20-23.4 $^\circ\text{C}$
Evap'n Rate = 2.9 - 5.6 mm/min
Dry film thks. = 10 - 116 $\mu$m

decrease in stress with film thickness $\Rightarrow$ viscous response
Capillary pressure required to form film

$\varepsilon = 0.36$

elastic limit

$p_{\text{cap}}^{\text{film}} \sim \phi NG / 2(1-\nu)$

viscous limit

$p_{\text{cap}}^{\text{film}} \sim \phi N \eta \dot{E} / H$

$\frac{GH}{2(1-\nu)\eta \dot{E}}$
\[ T_{amb} < T_g \implies \text{non-film forming latices} \]

large particles => high permeability packing
Film Cracking: Large High $T_g$ Particles

$2a=342$ nm, $h_{dry}=79.5$ μm, $E=2.5$ μm/min, $RH=66\%$, $T=23.5$ °C
evaporation complete
Observations from behind the Glass Slide

Polystyrene particles, $a = 342 \text{ nm}, \phi = 0.46$
large high $T_g$ PPG342

$\Rightarrow$ cracking followed by “debonding” or failure at first layer of particles

small high $T_g$ PMMA95
When particles deform viscously, capillary stress drives film formation before onset of cracking.

\[ N = \frac{H\phi_o}{2a\phi_{rcp}} \]
$T_{amb} < T_g \Rightarrow$ non-film forming latices
small particles $\Rightarrow$ low permeability packings
Film Cracking: Small High $T_g$ Particles

$2a=95$ nm, $h_{\text{dry}}=262$ µm, $E=6.7$ µm/min, $RH=35\%$, $T=24.4$ °C
Film Cracking: Small High $T_g$ Particles

$2a=95 \text{ nm}, h_{\text{dry}}=101 \text{ µm}, E=6.7 \text{ µm/min}, RH=35\%, T=24.4 \text{ ºC}$

→ simple and reproducible results, but how to understand the mechanism?
Cracking in Thin Elastic Films

Griffiths criterion
recovery of elastic energy
\[ \sigma_{33}^o = -p_o - \frac{2}{3} \overline{G} \varepsilon_o^{3/2} = 0 \]
\[ \sigma_{11}^o = \sigma_{22}^o = \frac{1}{2} \overline{G} \varepsilon_o^{3/2} \]

cost of surface energy
\[ \sigma_{11} + \sigma_{33} = 0 \]
relaxation in plane

• one-dimensional base state
  compression normal to film
  \[ \overline{G} = \frac{\phi NG}{2\pi(1 - \nu)} \]
tension in plane of film

• perturbed stress fields after cracking without dilation
  stress-free air-water interface
  \[ \langle \sigma'_{33} \rangle = -\langle p' \rangle - \frac{5}{8} \overline{G} \varepsilon_o^{1/2} \langle \varepsilon'_{11} \rangle = 0 \]
  \[ \langle p' \rangle = -\frac{5}{8} \overline{G} \varepsilon_o^{1/2} \langle \varepsilon'_{11} \rangle \]
  \[ \langle \sigma'_{11} \rangle = \frac{3}{4} \overline{G} \varepsilon_o^{1/2} \langle \varepsilon'_{11} \rangle \]
  \[ \langle \sigma'_{13} \rangle = \frac{1}{2} \overline{G} \varepsilon_o^{1/2} \langle \varepsilon'_{13} \rangle \]
homogeneous linearly elastic film

- vertically averaged stress balance

\[
\frac{\partial \langle \sigma'_{11} \rangle}{\partial x_1} = \left. \frac{\sigma'_{13}}{H} \right|_{z=0}
\]

"lubrication" approximation

\[ u' \equiv 3 \langle u_1' \rangle \frac{x_3}{H} \left( 1 - \frac{x_3}{2H} \right) \]

\[ \varepsilon'_{13} \bigg|_{z=0} \equiv 3 \langle u_1' \rangle / 2H \quad \text{and} \quad \langle \varepsilon'_{13} \rangle \equiv 3 \langle u_1' \rangle / 4H \]

- equation for displacement

\[
\frac{\partial^2 \langle u_1' \rangle}{\partial x_1^2} = \frac{\langle u_1' \rangle}{H^2} \quad \text{with} \quad \frac{p_{\text{cap}}}{\varepsilon_0 G} + \frac{\partial \langle u_1' \rangle}{\partial x_1}(0) = 0 \quad \langle u_1' \rangle(\infty) = 0
\]

stress-free crack
uniform film

surface
• solve boundary value problems
• evaluate recovery of elastic energy
• equate to surface energy

minimum capillary pressure for opening crack

\[-\frac{H_{P_{\text{cap}}}^{\text{crack}}}{\gamma} \equiv 1.3 \left( \frac{\phi NGH}{2(1-\nu)\gamma} \right)^{2/5} + 2.9 \frac{\gamma}{\phi N\eta\dot{E}} \frac{\phi NGH}{2(1-\nu)\gamma} \]
Direct Measurement of Stresses

high pressure filter chamber:

gas in \quad \text{camera} \quad \text{pressure meter}

Teflon o-ring

polycarbonate chamber

film

porous support

membrane

water out
Capillary Pressure Required for Cracking

- pressure at first crack independent of particle radius
  \[ \text{two dimensionless variables } \frac{ph}{\gamma} \frac{Gh}{(1-v)\gamma} \]
  one must be function of the other

- energy criterion
  \[ \frac{hp_{\text{cap}}^{\text{crack}}}{\gamma} \approx 2.0 \left( \frac{Gh}{(1-v)\gamma} \right)^{2/5} \]

- energy criterion
  \[ \rightarrow \text{lower bound} \]

- packing flaws
  \[ \rightarrow \text{initiate cracks} \]

- grain boundaries and notches
  \[ \rightarrow \text{nucleation sites} \]

variables
\[ p \; \text{kg/m-s} \]
\[ h \; \text{m} \]
\[ \gamma \; \text{kg/s} \]
\[ G/(1-v) \; \text{kg/m-s} \]
smooth top surface
fracture surface from below
junction of two fractures

ordered films
91 nm PS
Normalized spacing as function of excess stress

\[
\frac{p_{\text{cap}}^{\text{crack}}}{p_{\text{cap}}} = \left\{ \tanh \left( \frac{W}{2H} \right) - \frac{W}{2H} \right\}^{11} \cosh^2 \left( \frac{W}{2H} \right)^{3/5}
\]

- Debonding terminates cracking by relaxing stress.
- Theory for parallel cracks misses phenomenon.

→ Subsequent cracking controlled by distribution of flaws
Data implies flaws with $L \ll h$ for randomly close packed layers, but $L \geq h$ for ordered dispersion.
hypothesis: When capillary pressure exceeds $12.5 \frac{\gamma}{a}$ without causing cracking, the water front simply recedes into film.

$$- \frac{p_{\text{cap}}^{\text{max}} H}{\gamma} = 1.30 \left( \frac{\phi NGH}{2(1 - v) \gamma} \right)^{2/5} \Rightarrow \frac{H_{\text{crit}}}{a} = 0.023 \left( \frac{\phi NGa}{2(1 - v) \gamma} \right)^{2/3}$$
SUMMARY

• **Mode of film formation** depends on rate of evaporation relative to rate of viscous deformation driven by capillary pressure.

• Particles that deform too slowly allow the capillary pressure to cause **cracking before the water front** recedes into the film.

• The **capillary pressure required for cracking** decreases with increasing film thickness and elastic compliance but is independent of particle size. The density of cracks increases with excess pressure.

• The onset of **cracking** and additional cracking at higher pressures **appears to be flaw/nucleation controlled**.

• **Cracking is not favorable below a minimum thickness** even for layers of hard particles.