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

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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

Collaborators

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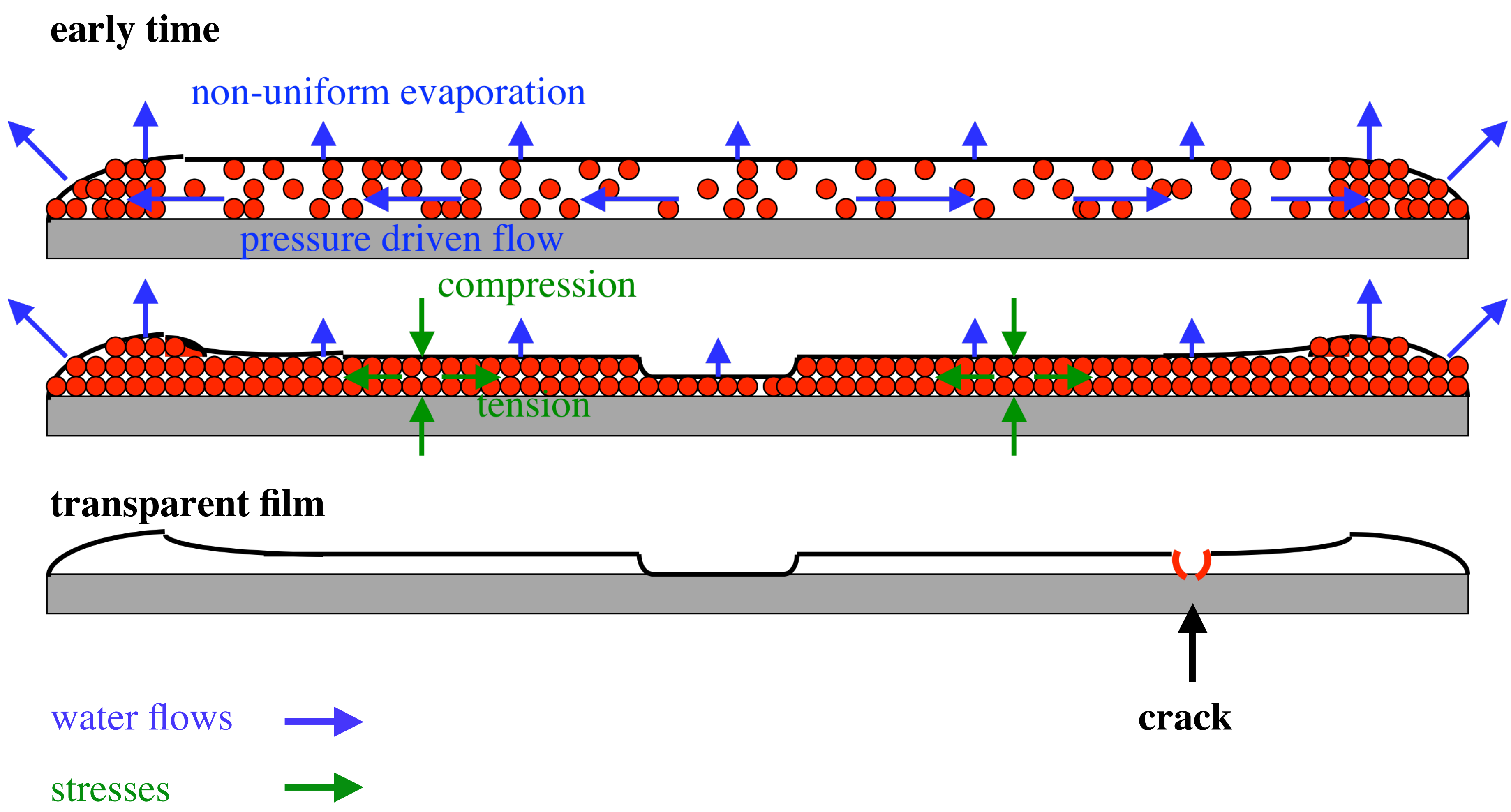
Weining Man *05

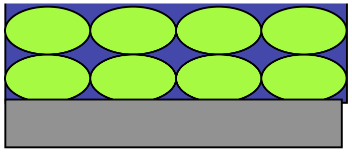
Film Formation, Non-Uniformities, and Cracking Driven by Capillary Pressure



Driving Forces for Homogeneous Deformation

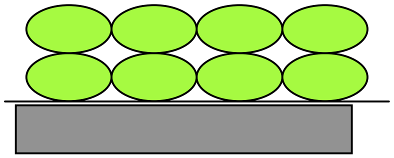
1. **Wet sintering** (Vanderhoff, 1966)

   polymer/water surface tension $\frac{\gamma_{pw}}{a}$



2. **Dry sintering** (Dillon, 1951)

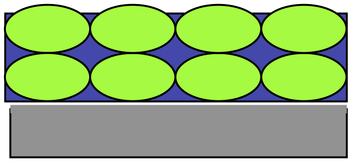
   polymer/air surface tension $\frac{2\gamma_{pa}}{a}$



3. **Capillary Deformation** (Brown, 1956)

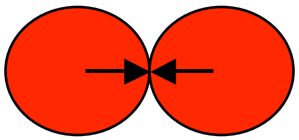
   pressure at air-water interface

$$-p_{cap} = -\kappa\gamma_{wa} \leq 10 - 15\frac{\gamma_{wa}}{a}$$



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



$$\boldsymbol{n}\cdot\boldsymbol{\varepsilon}\cdot\boldsymbol{n} = \Delta R/2a$$

Hertz 1882, Matthews 1980

contact force

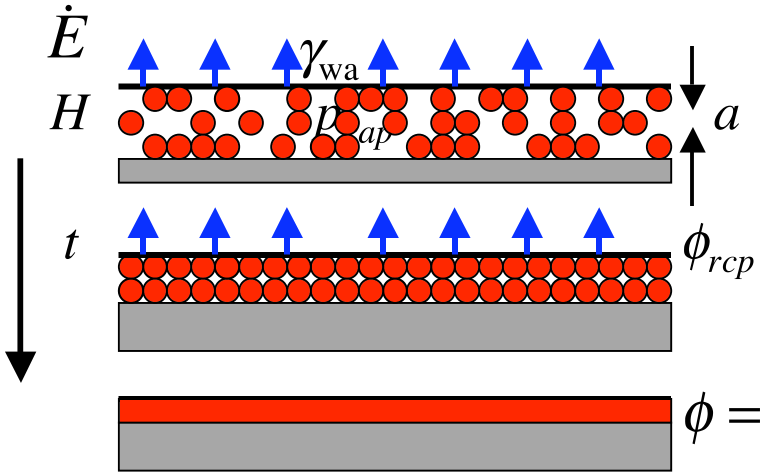
$$\boldsymbol{F}_{nm} = -\frac{16}{3}a^2\begin{cases}\eta\dfrac{d}{dt}\left(-\boldsymbol{n}_{nm}\bullet\boldsymbol{\varepsilon}\bullet\boldsymbol{n}_{nm}\right)^{3/2}\boldsymbol{n}_{nm} & \text{viscous}\\ \dfrac{G}{2(1-\nu)}\left(-\boldsymbol{n}_{nm}\bullet\boldsymbol{\varepsilon}\bullet\boldsymbol{n}_{nm}\right)^{3/2}\boldsymbol{n}_{nm} & \text{elastic}\end{cases}$$

---

close-packed spheres

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

$$\varepsilon = -\varepsilon_{33} = 1-\phi_{rcp}/\phi \qquad -p_{cap} \le 12.5\gamma_{aw}/a$$



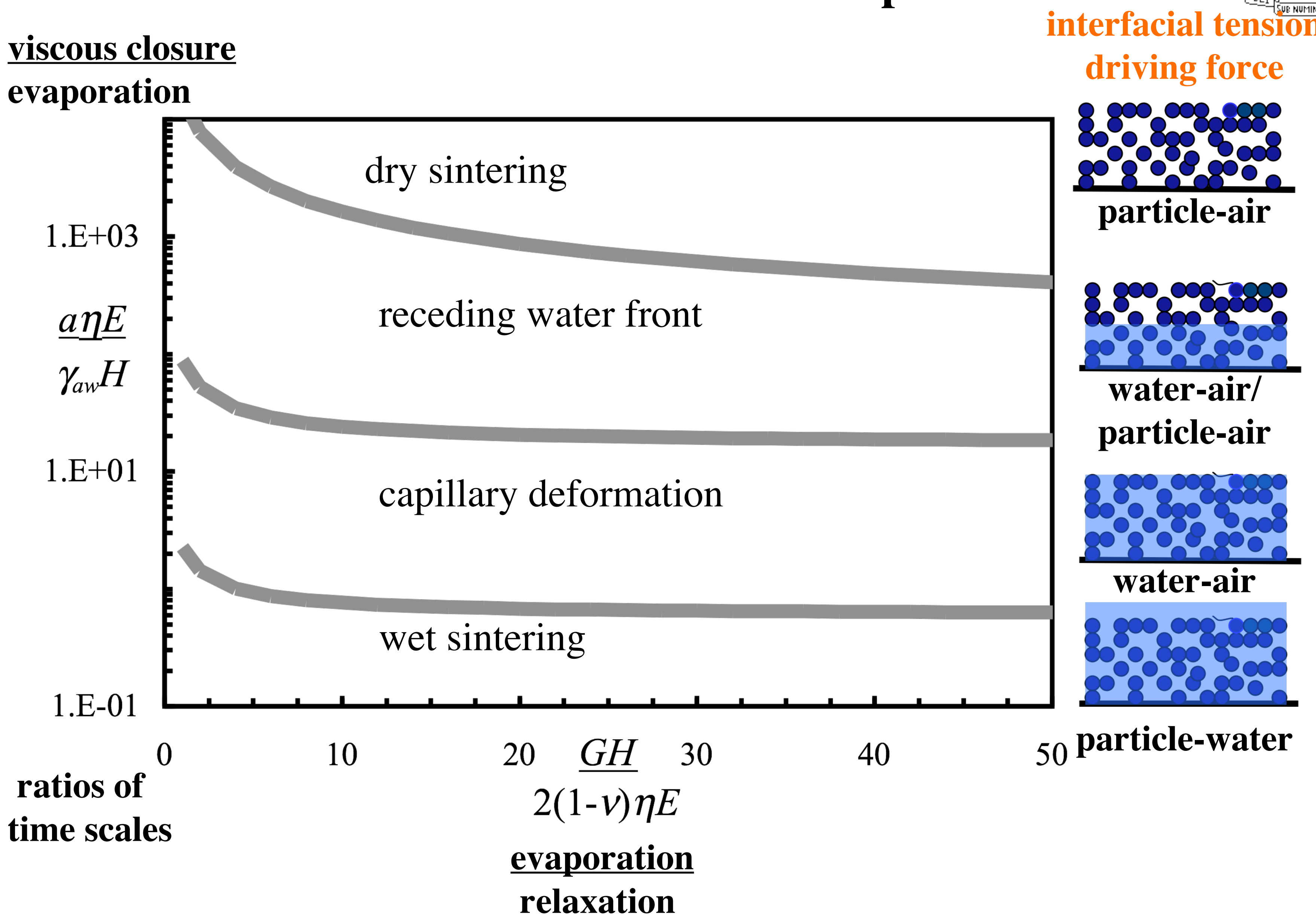
scaling

$$\bar{t} = \frac{\dot{E}t}{H(1-\phi_o)} \qquad \bar{\sigma}_t = \frac{ap_{cap}}{N\phi\gamma_{wa}}$$

$$\bar{G} = \frac{HG'_{\infty}}{\dot{E}\eta} \qquad \frac{\text{evaporation time}}{\text{relaxation time}}$$

$$\bar{\lambda} = \frac{\eta a\dot{E}}{H\gamma_{wa}} \qquad \frac{\text{viscous collapse time}}{\text{evaporation time}}$$

Generalized Process Map



EFFECT OF TEMPERATURE

P.R. Sperry, et al., *Langmuir* **10** 2619 (1994)

time to close pores

t_{film}

wet sintering

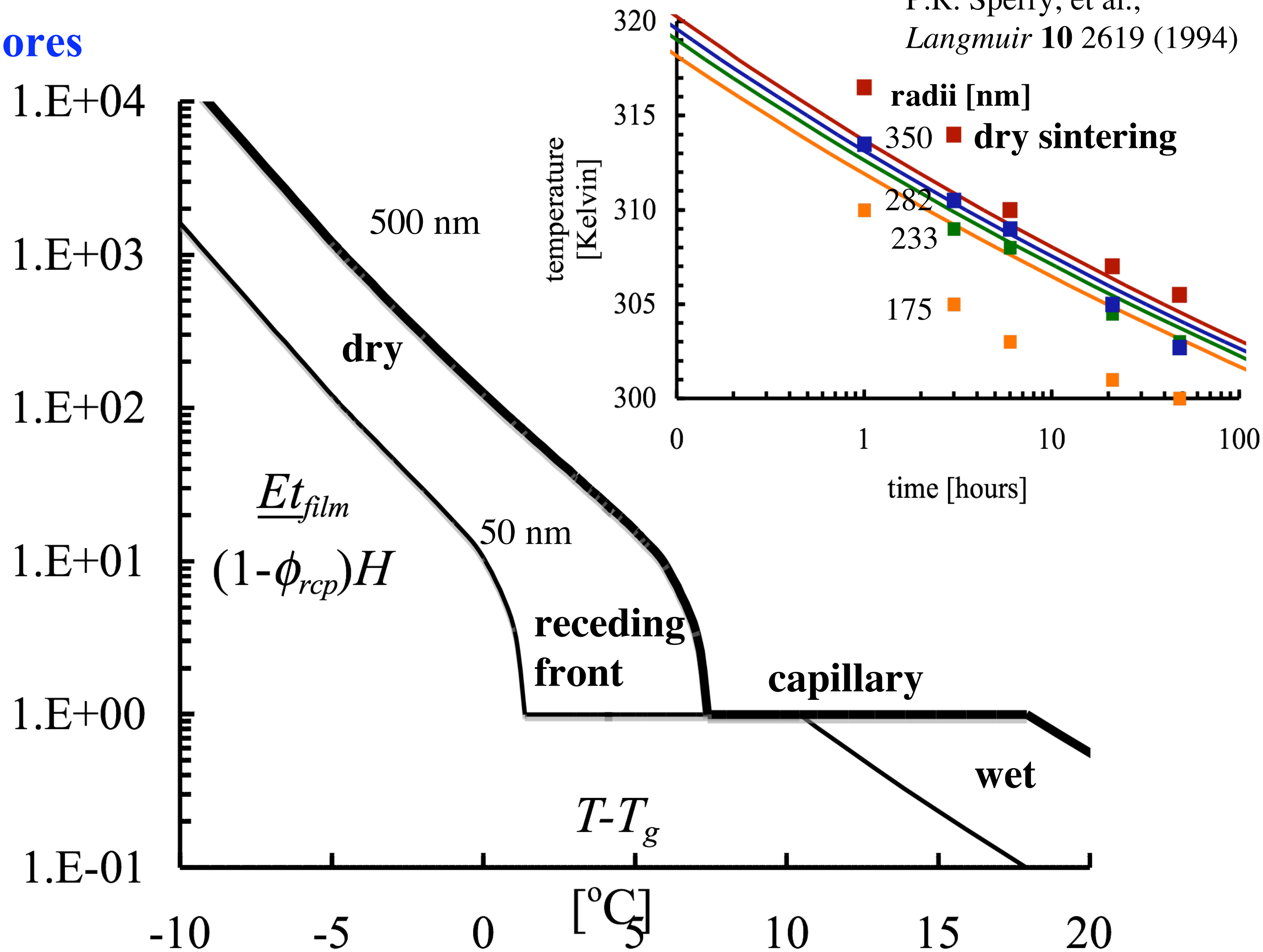
$$0.21\frac{\eta(T)a}{\gamma_{pw}}$$

capillary deformation

$$0.36\frac{H}{\dot{E}}$$

dry sintering

$$0.21\frac{\eta(T)a}{\gamma_{pa}}$$

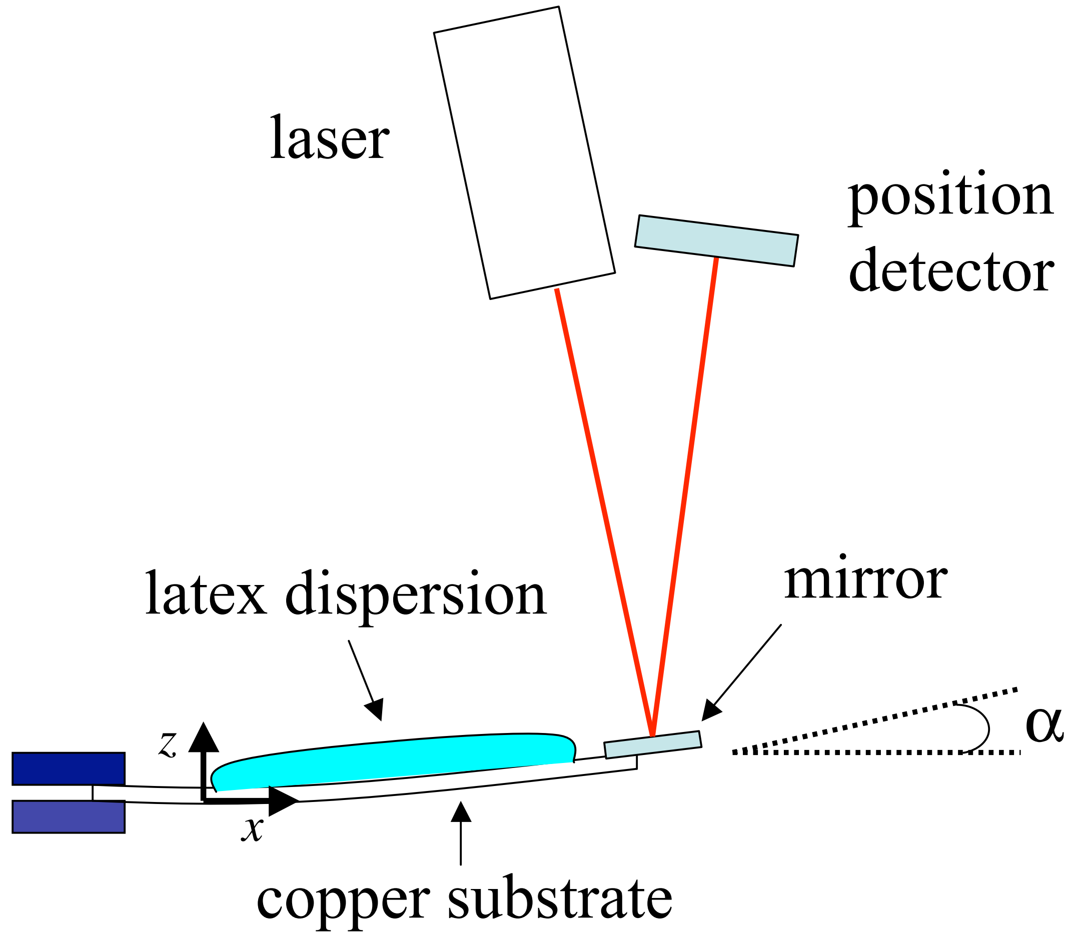


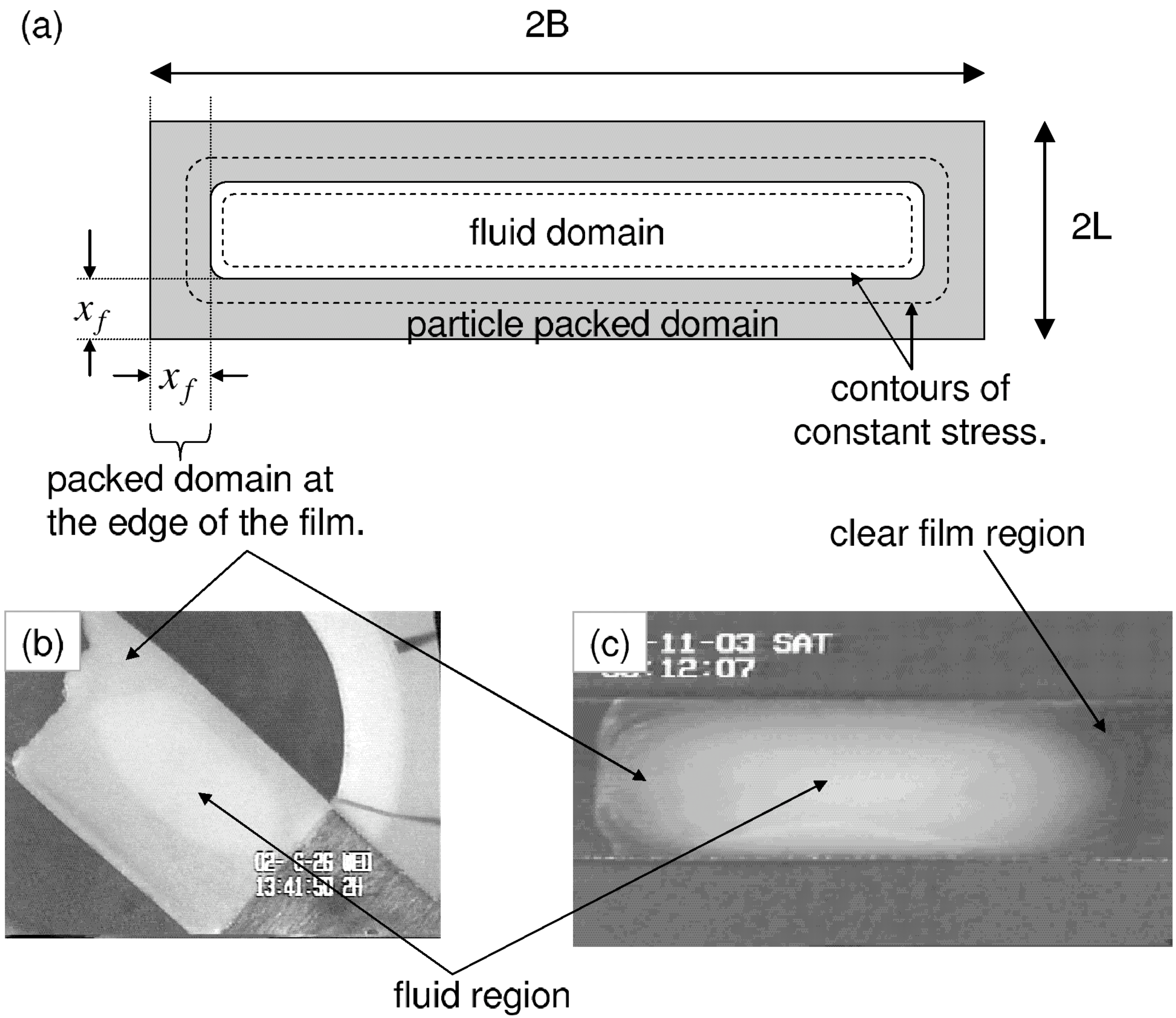
Cantilever Experiment for Measuring Stresses

Chiu *et al. J. Am. Ceramic Soc.* (1993); Peterson, *et al. Langmuir* (1999); Martinez, *et al. Langmuir* (2000)

$$\sigma_{xx} = \frac{h_s^3 G\alpha}{6\,L\,h\left(h + h_s\right)}$$

h_s : substrate thickness
h : film thickness
L : length of film
G : bending modulus



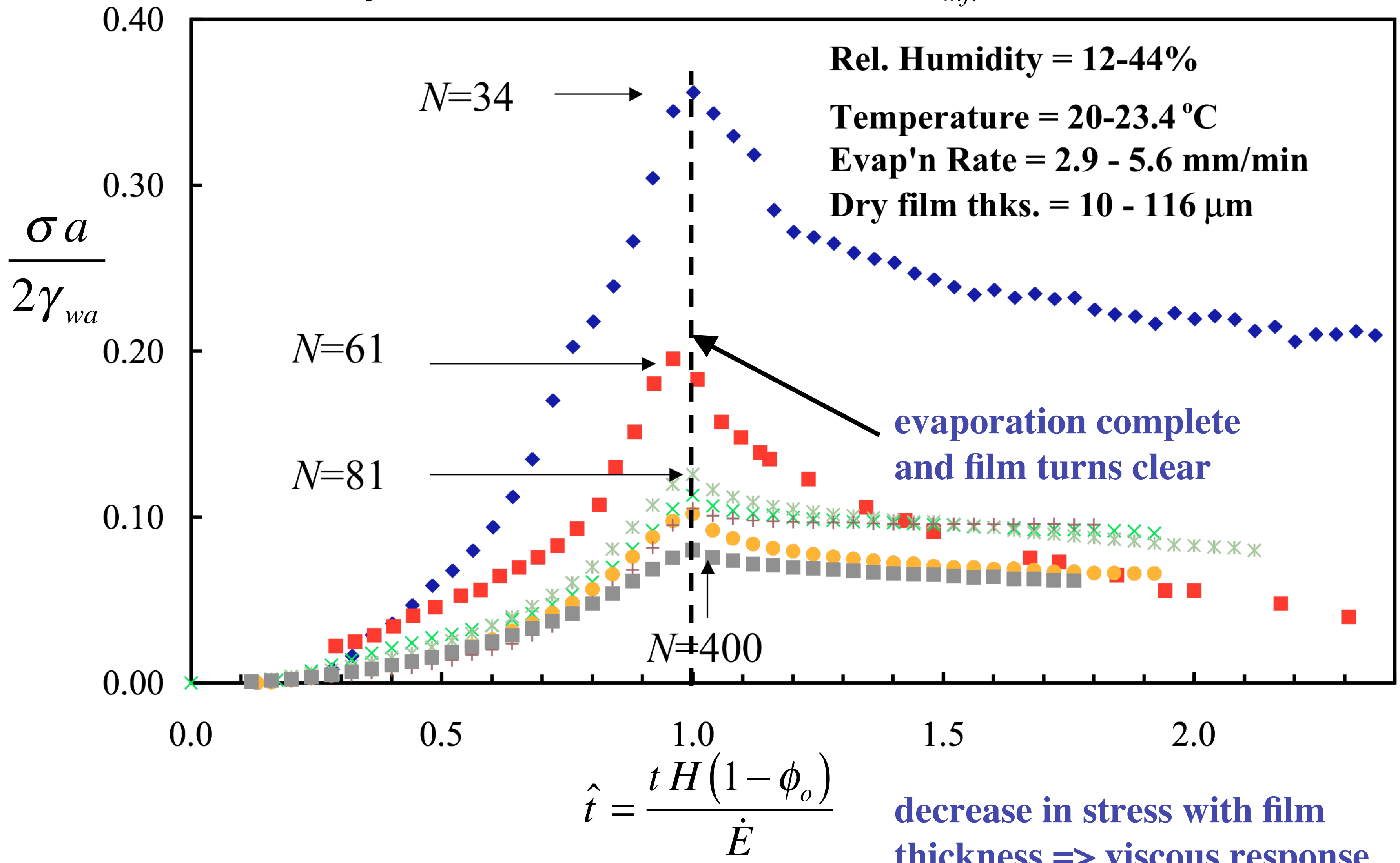

(a)
2B
2L
fluid domain
particle packed domain
x_f
x_f
contours of
constant stress.
packed domain at
the edge of the film.
clear film region
(b)
(c)
fluid region

Film forming latices

$$T_g < T_{amb}$$

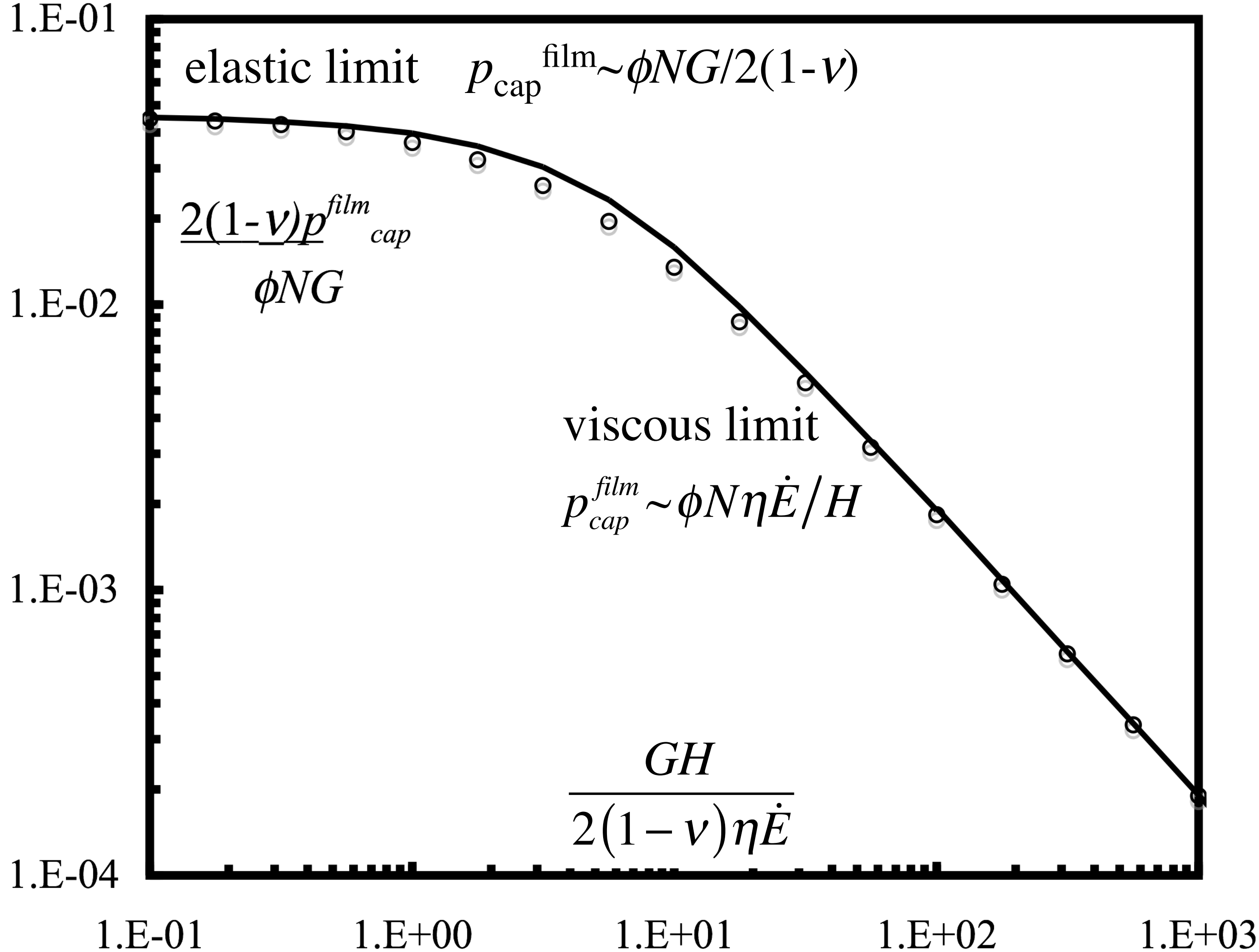
Low T_g Film Forming Latex: WCFA

ϕ_o=0.32–0.35 $2a$ = 290 nm T_{mft} =16°C



decrease in stress with film thickness => viscous response

Capillary pressure required to form film
$\varepsilon = 0.36$

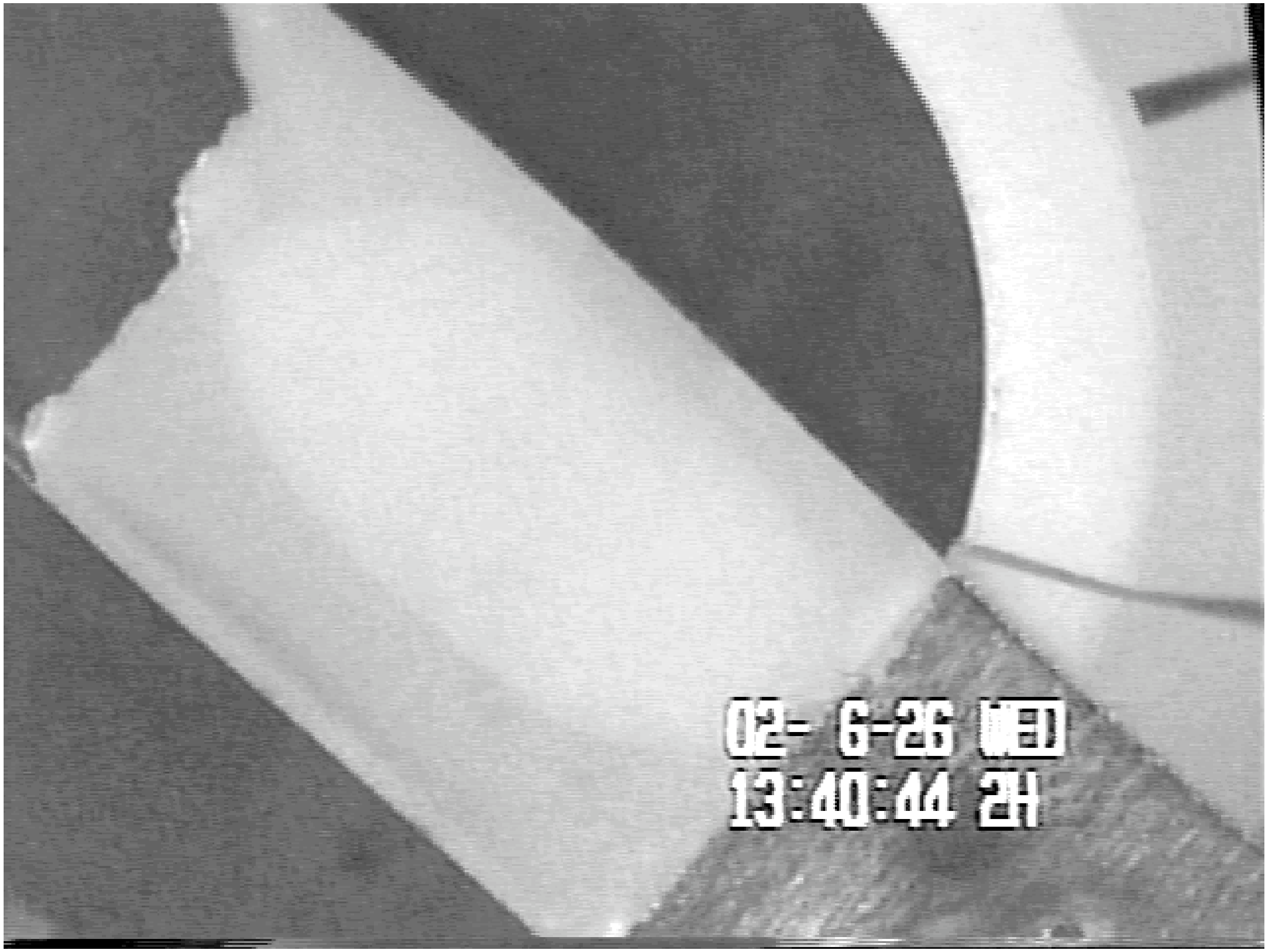


$T_{amb} < T_g$ => **non-film forming latices**

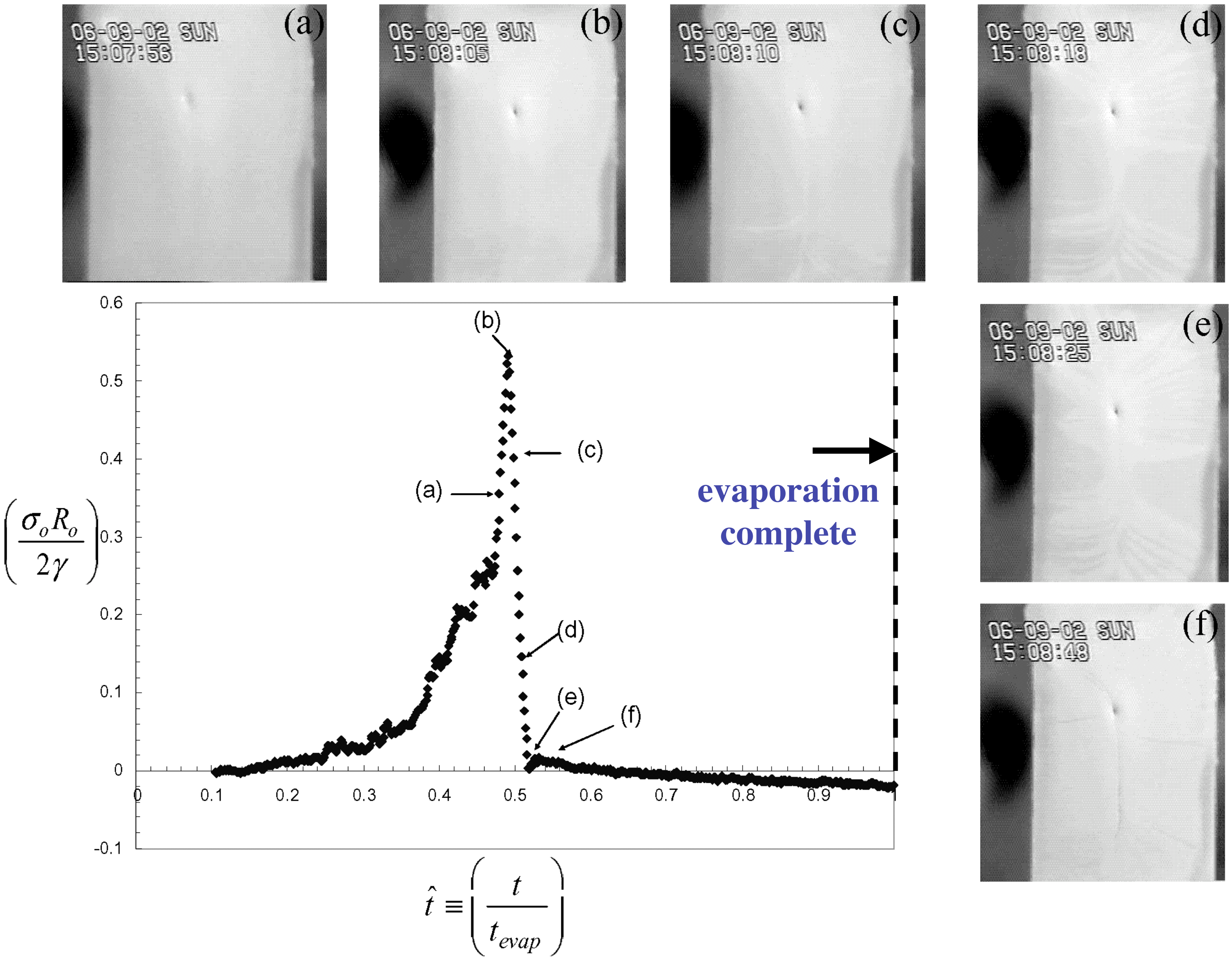
large particles => high permeability packing

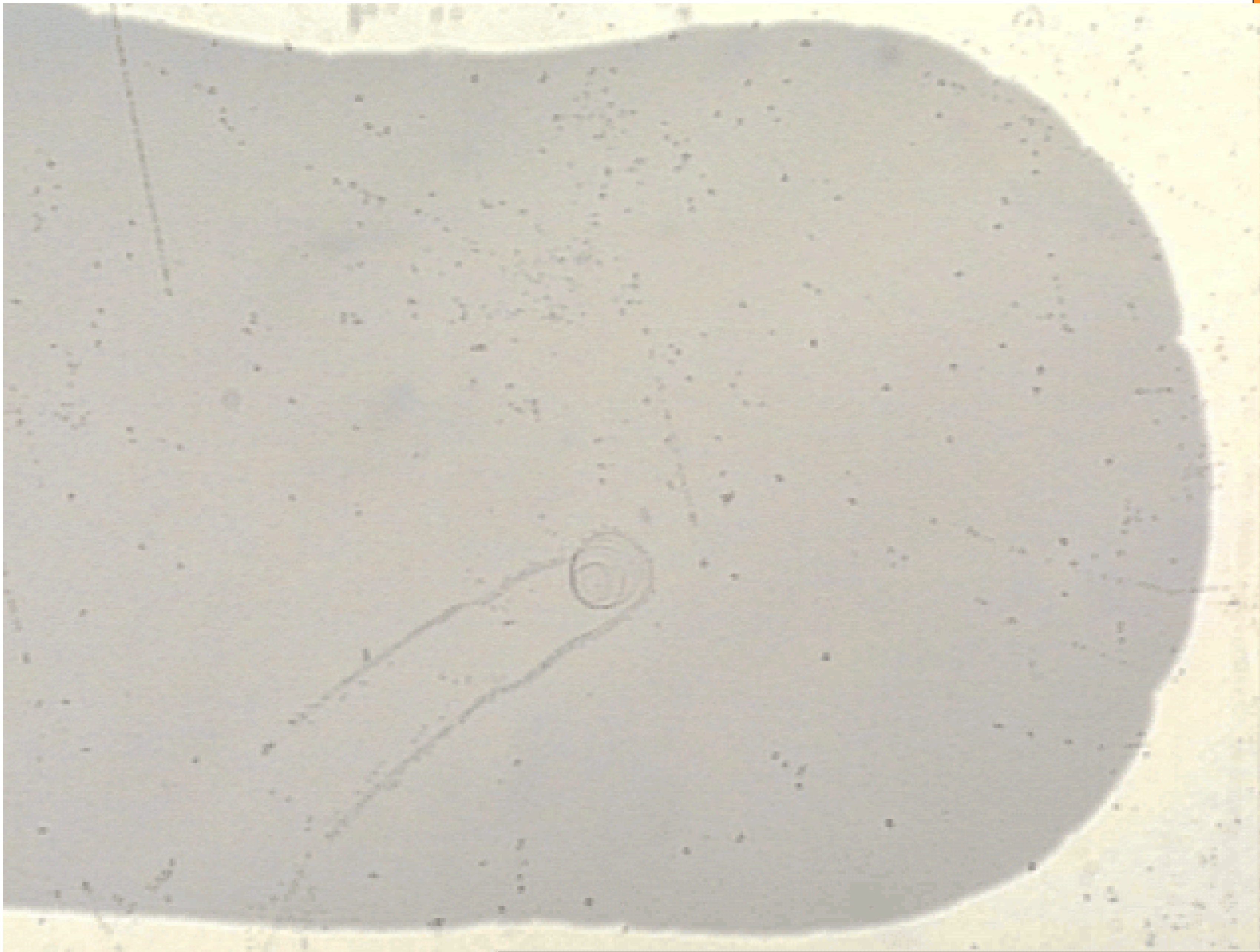
Film Cracking: Large High T_g Particles

$2a$=342 nm, h_{dry}=79.5 μm, E=2.5 μm/min, RH=66%, T=23.5 ^oC

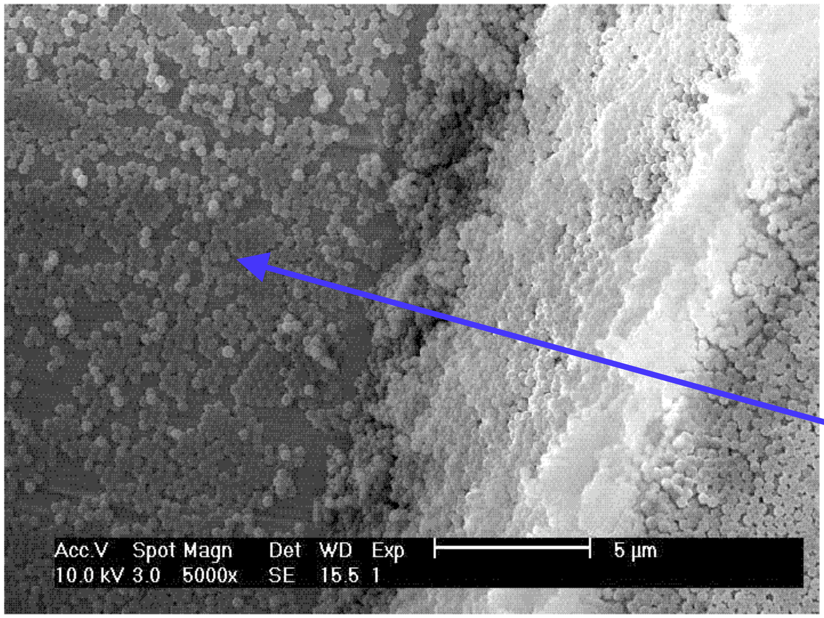


(PS342-062602b)

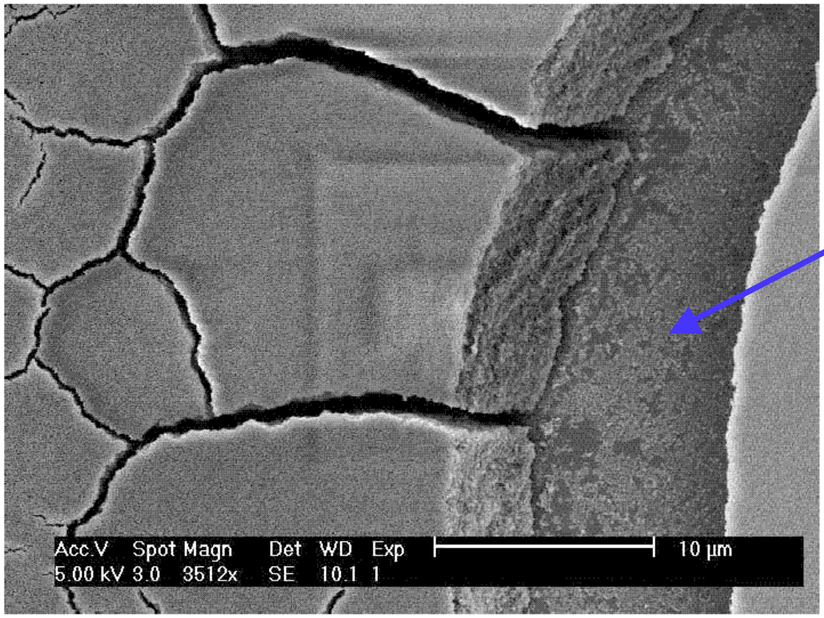

(a)
06-09-02 SUN
15:07:56
(b)
06-09-02 SUN
15:08:05
(c)
06-09-02 SUN
15:08:10
(d)
06-09-02 SUN
15:08:18
(e)
06-09-02 SUN
15:08:25
(f)
06-09-02 SUN
15:08:48
$\left(\frac{\sigma_o R_o}{2\gamma}\right)$
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
$\hat{t} \equiv \left(\frac{t}{t_{evap}}\right)$
evaporation complete



(a)



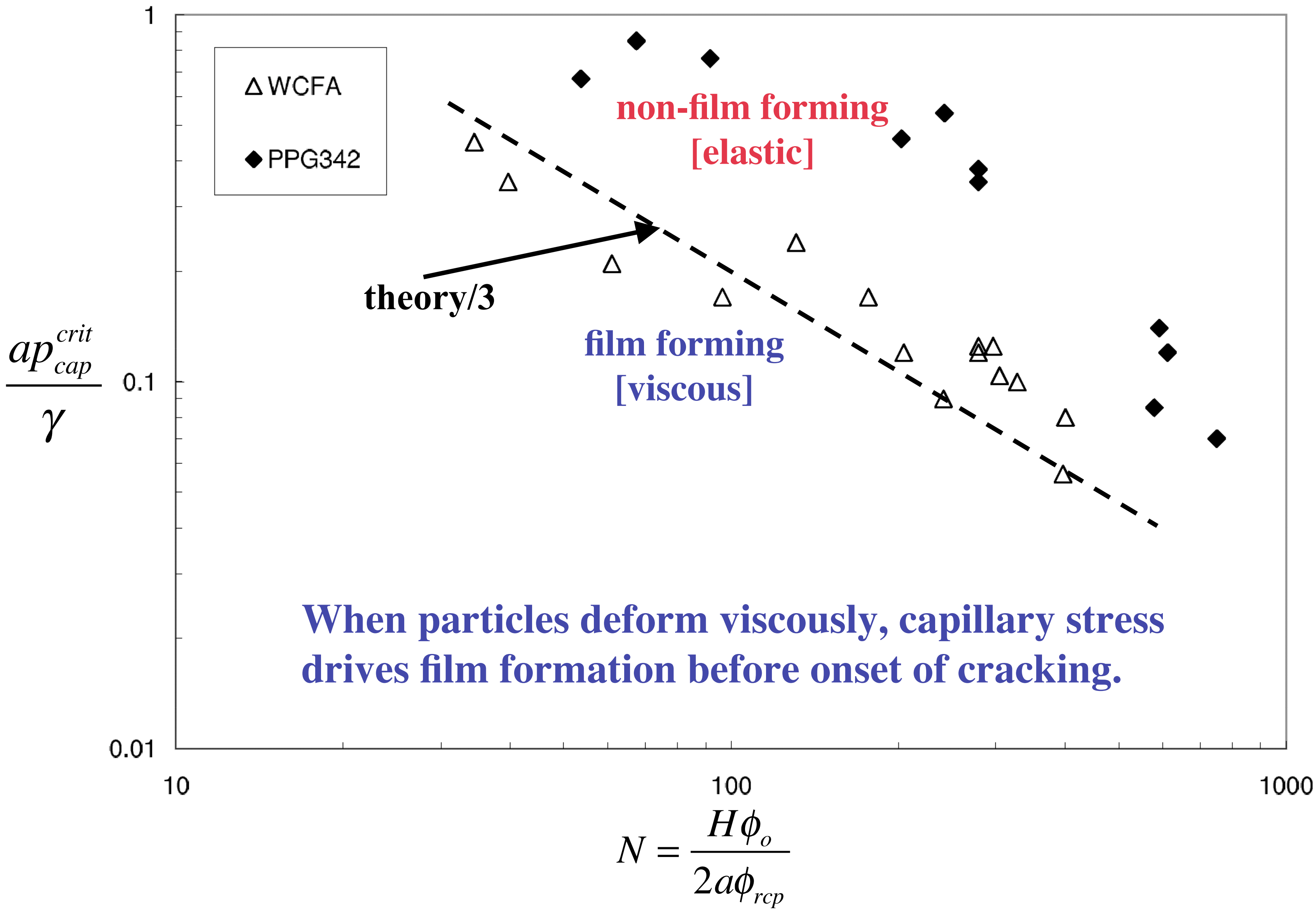
(b)



large high T_g PPG342

⇒ **cracking followed by "debonding" or failure at first layer of particles**

small high T_g PMMA95



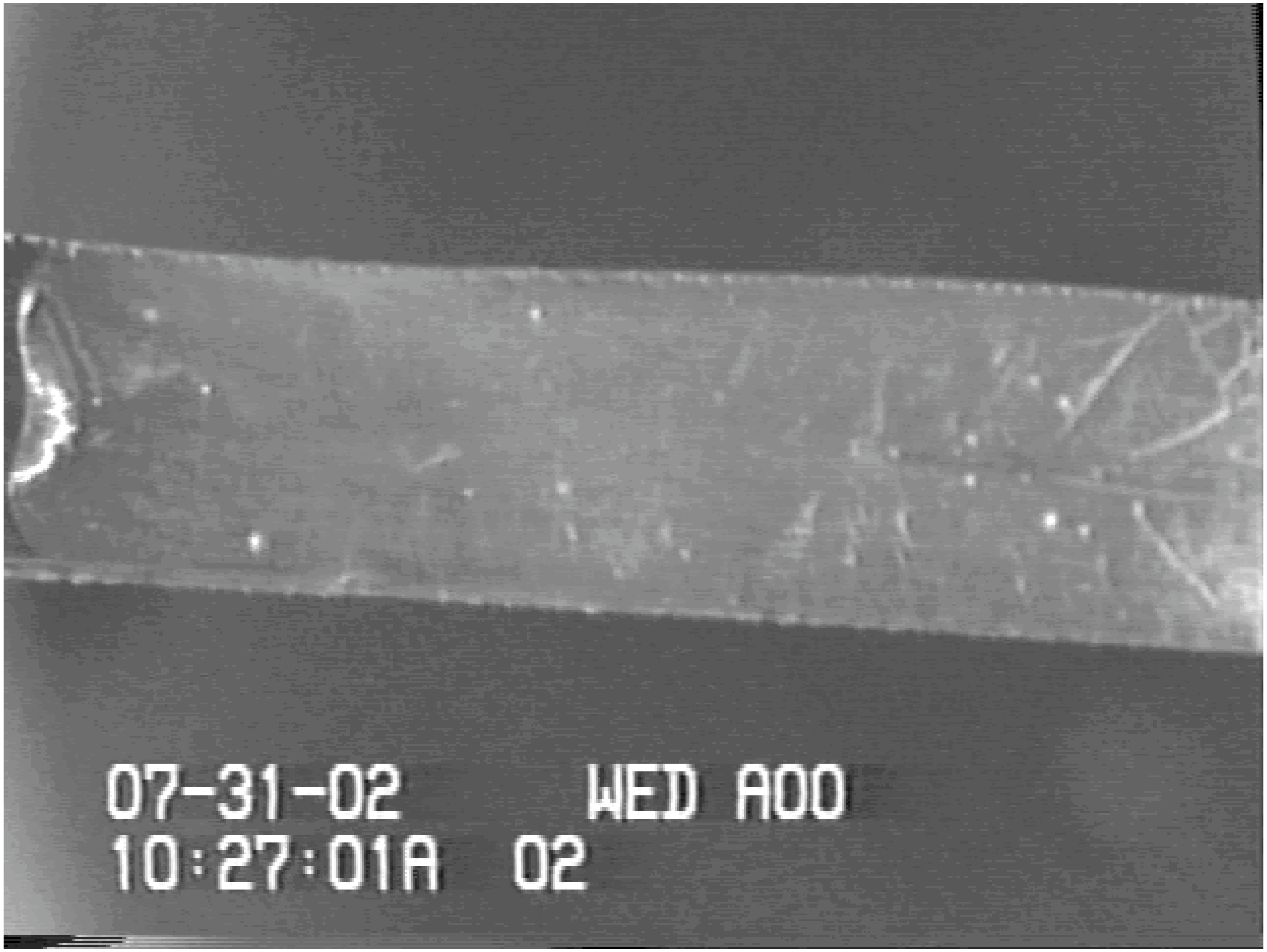
WCFA
PPG342
non-film forming
[elastic]
theory/3
film forming
[viscous]
When particles deform viscously, capillary stress
drives film formation before onset of cracking.
1
0.1
0.01
10
100
1000
$\frac{a p_{cap}^{crit}}{\gamma}$
$N = \frac{H\phi_o}{2a\phi_{rcp}}$

$T_{amb} < T_g$ **=> non-film forming latices**

small particles => low permeability packings

Film Cracking: Small High T_g Particles

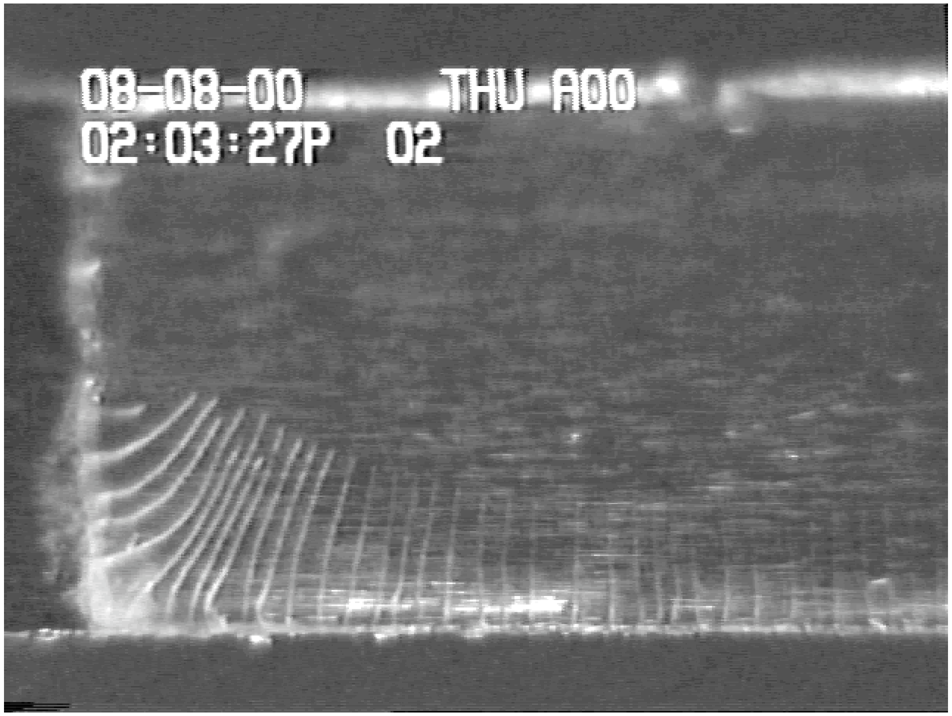
$2a$=95 nm, h_{dry}=262 µm, E=6.7 µm/min, RH=35%, T=24.4 °C

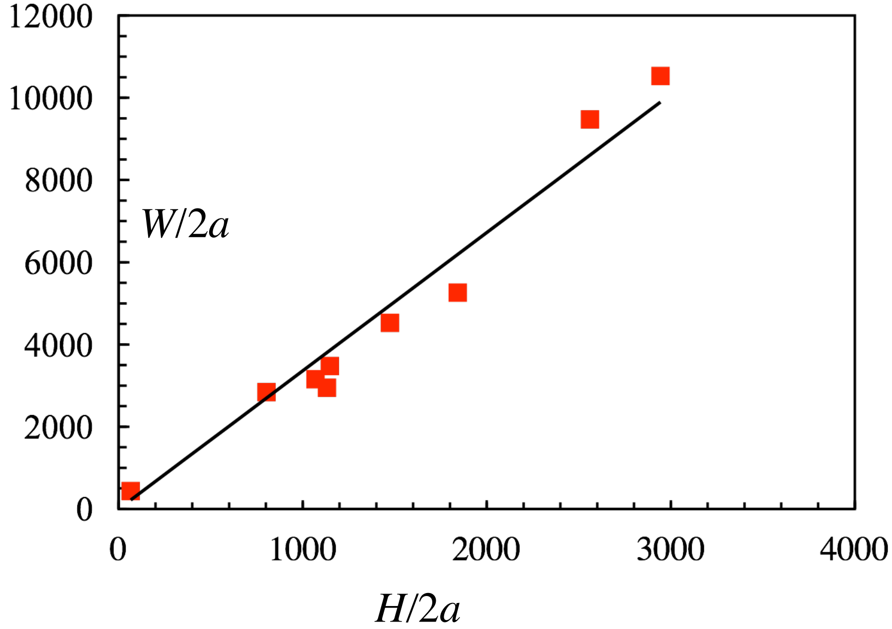


(PMMA95-080802b)

Film Cracking: Small High T_g Particles

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





→ **simple and reproducible results, but how to understand the mechanism?**

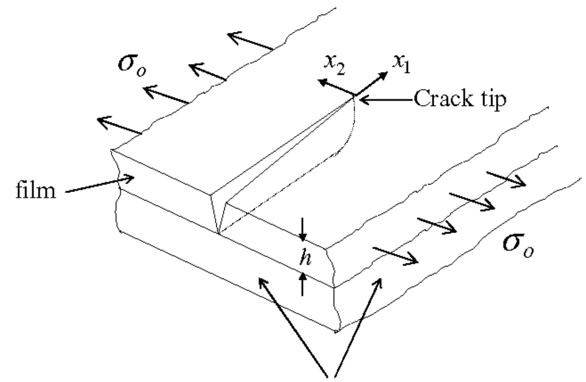
Cracking in Thin Elastic Films

Griffiths criterion

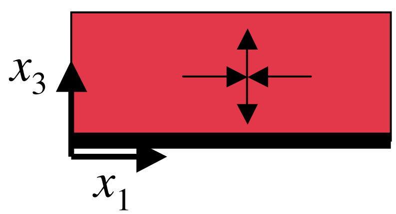
recovery of elastic energy

||

cost of surface energy



- **one-dimensional base state**



compression normal to film

$$\sigma_{33}^{o} = -p_o - \tfrac{2}{3}\bar{G}\varepsilon_o^{3/2} = 0$$

$$\bar{G} = \frac{\phi N G}{2\pi(1-\nu)}$$

tension in plane of film

$$\sigma_{11}^{o} = \sigma_{22}^{o} = \tfrac{1}{2}\bar{G}\varepsilon_o^{3/2}$$

- **perturbed stress fields after cracking without dilation** $\varepsilon_{11} + \varepsilon_{33} = 0$

stress-free air-water interface

$$\langle \sigma_{33}' \rangle = -\langle p' \rangle - \tfrac{5}{8}\bar{G}\varepsilon_o^{1/2}\langle \varepsilon_{11}' \rangle = 0$$

$$\Rightarrow \quad \langle p' \rangle = -\tfrac{5}{8}\bar{G}\varepsilon_o^{1/2}\langle \varepsilon_{11}' \rangle$$

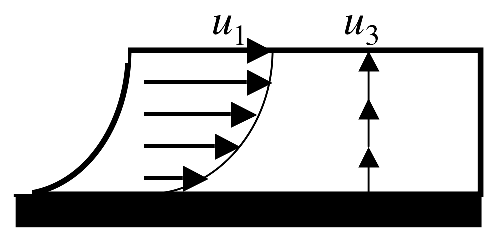
relaxation in plane

$$\langle \sigma_{11}' \rangle = \tfrac{3}{4}\bar{G}\varepsilon_o^{1/2}\langle \varepsilon_{11}' \rangle$$

$$\langle \sigma_{13}' \rangle = \tfrac{1}{2}\bar{G}\varepsilon_o^{1/2}\langle \varepsilon_{13}' \rangle$$

homogeneous linearly elastic film

A.G. Evans, M.D. Drory, and M.S. Hu, *J. Materials Res* **3** 1043 (1988)
J.L. Beuth, *Int. J. Solids Structures* **29** 1657 (1992)
X.C. Xia and J.W. Hutchinson, *J. Mech. Phys. Solids* **48** 1107 (2000)



- **vertically averaged stress balance**

$$\frac{\partial \langle \sigma'_{11} \rangle}{\partial x_1} = \frac{\sigma'_{13}\big|_{z=0}}{H}$$

"lubrication" approximation $u'_1 \cong 3\langle u'_1 \rangle \dfrac{x_3}{H}\left(1 - \dfrac{x_3}{2H}\right)$

$$\varepsilon'_{13}\big|_{z=0} \doteq 3\langle u'_1 \rangle / 2H \quad \text{and} \quad \langle \varepsilon'_{13} \rangle \doteq 3\langle u'_1 \rangle / 4H$$

- **equation for displacement**

$$\frac{\partial^2 \langle u'_1 \rangle}{\partial x_1^2} = \frac{\langle u'_1 \rangle}{H^2} \quad \text{with} \quad \frac{p_{cap}}{\varepsilon_o \bar{\bar{G}}} + \frac{\partial \langle u'_1 \rangle}{\partial x_1}(0) = 0 \qquad \langle u'_1 \rangle (\infty) = 0$$

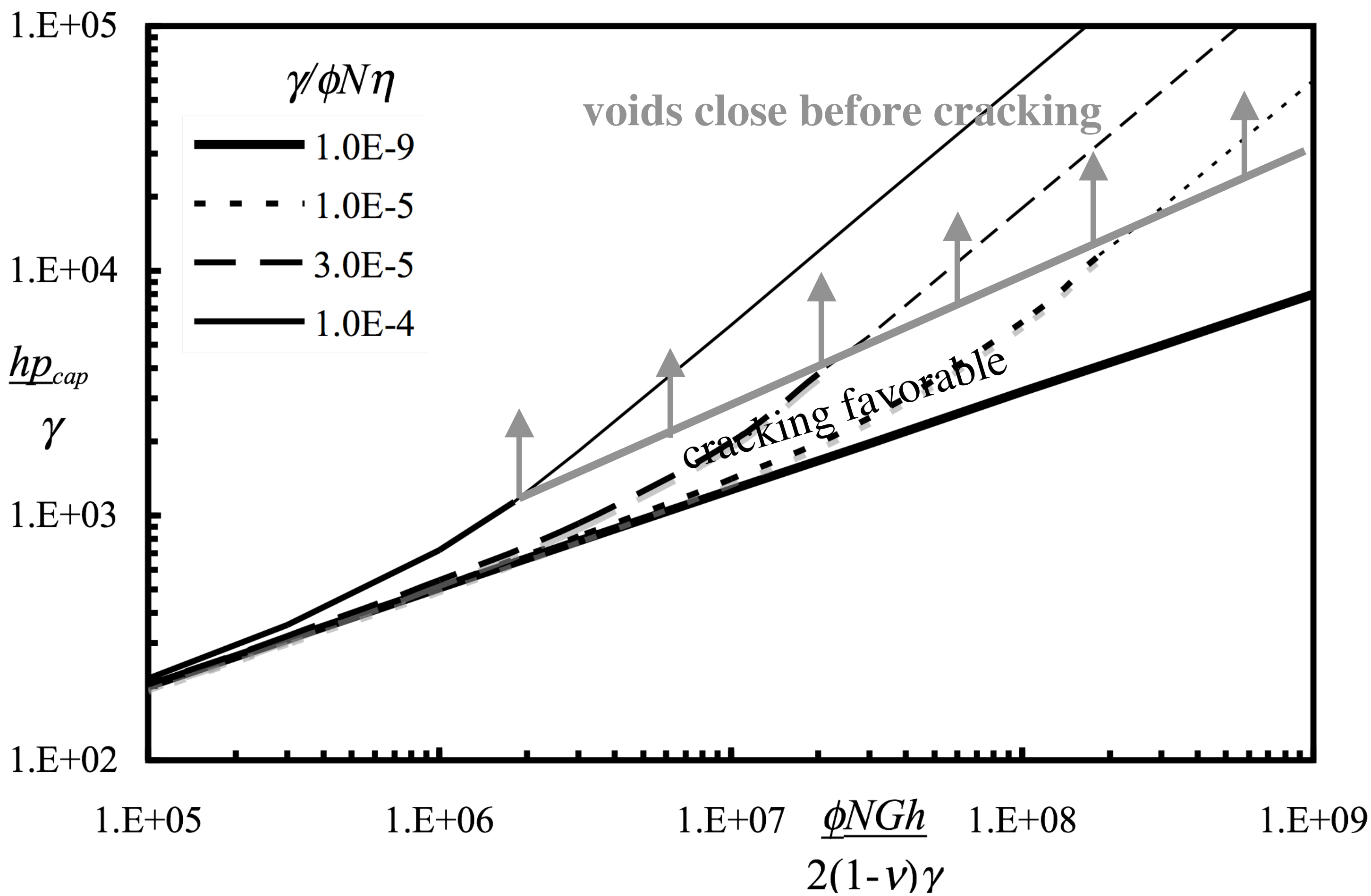
stress-free crack surface

uniform film

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

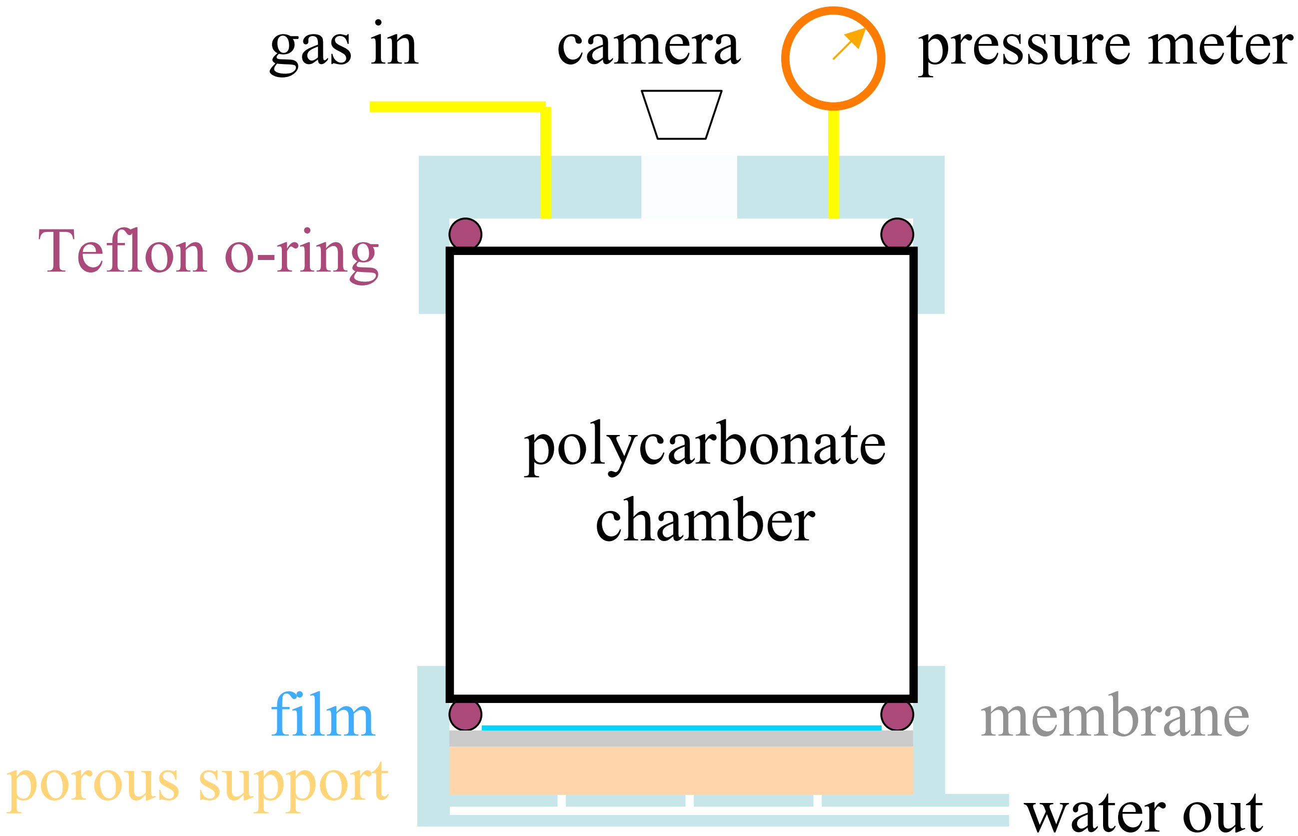
minimum capillary pressure for opening crack

$$-\frac{Hp_{cap}^{crack}}{\gamma} \cong 1.3\left(\frac{\phi NGH}{2(1-\nu)\gamma}\right)^{2/5} + 2.9\frac{\gamma}{\phi N\eta\dot{E}}\frac{\phi NGH}{2(1-\nu)\gamma}$$



Direct Measurement of Stresses

high pressure filter chamber:



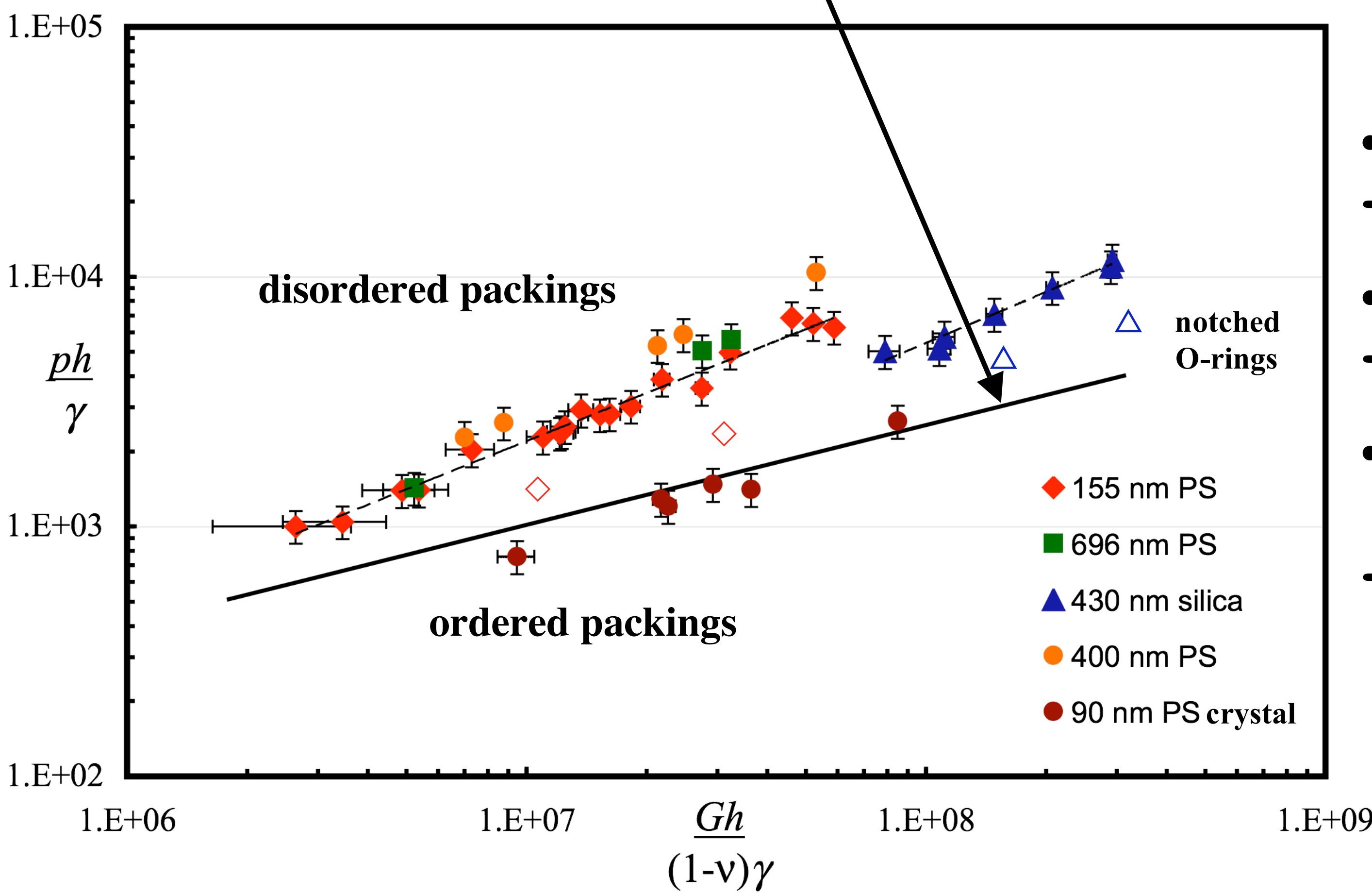
Capillary Pressure Required for Cracking

- pressure at first crack independent of particle radius
  ➜ two dimensionless variables ph/γ $Gh/(1\text{-}\nu)\gamma$
  one must be function of the other
- energy criterion

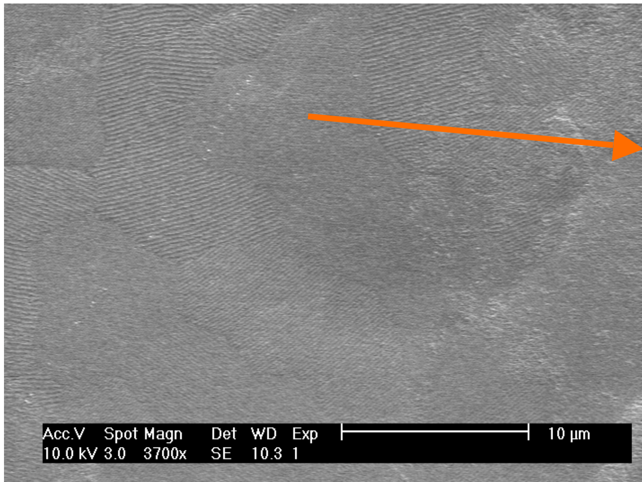
$$-\frac{hp_{cap}^{crack}}{\gamma} \cong 2.0\left(\frac{Gh}{(1-\nu)\gamma}\right)^{2/5}$$

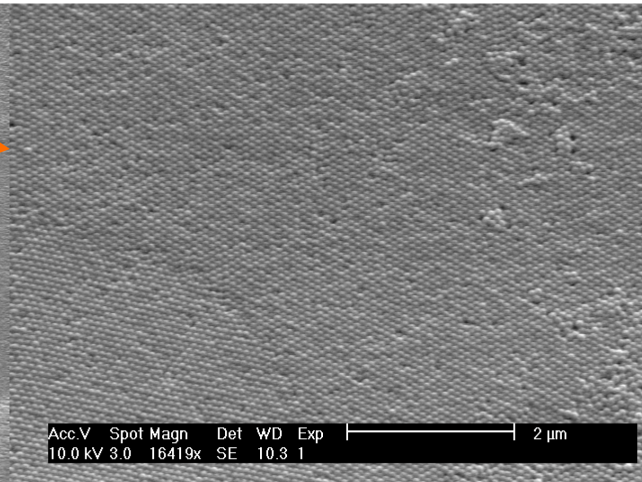
variables

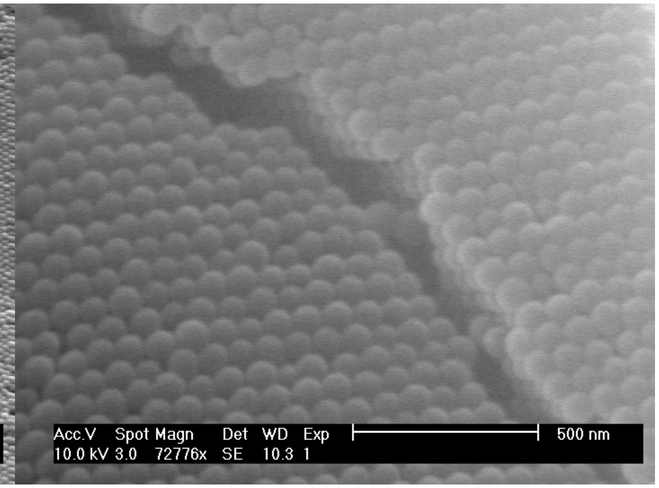
p	kg/m-s
h	m
γ	kg/s
$G/(1-\nu)$	kg/m-s

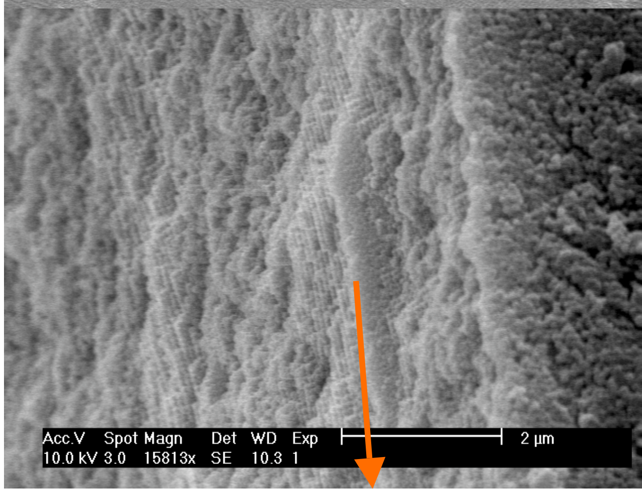


- energy criterion
  ➜ **lower bound**
- packing flaws
  ➜**initiate cracks**
- grain boundaries
  and notches
  ➜ **nucleation sites**





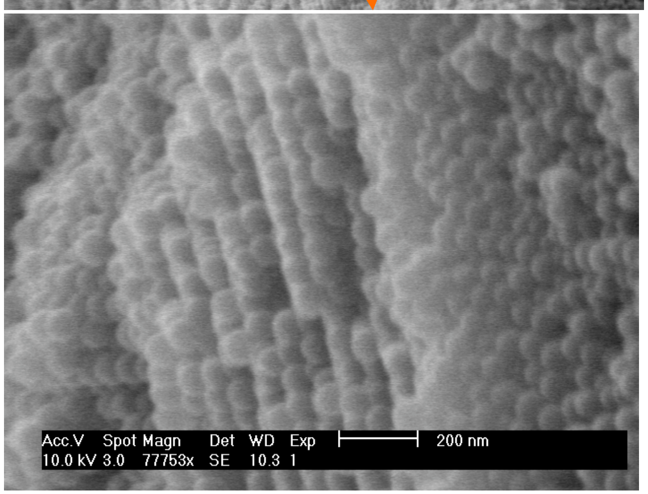


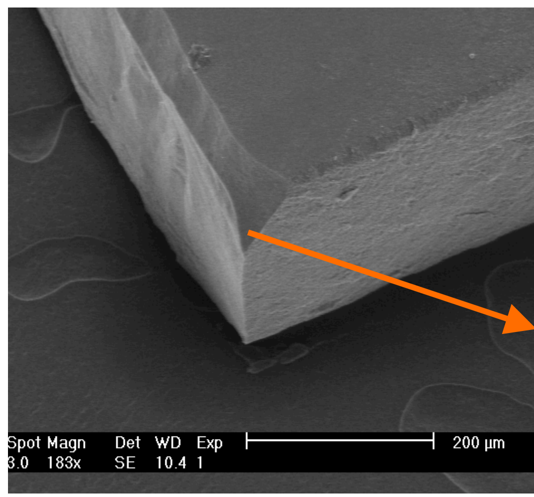


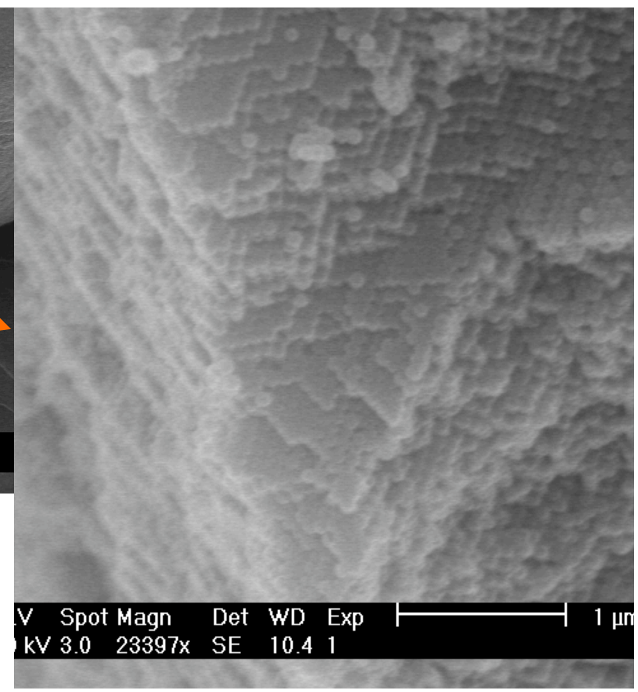
↑ smooth top surface

← fracture surface from below

↓ junction of two fractures



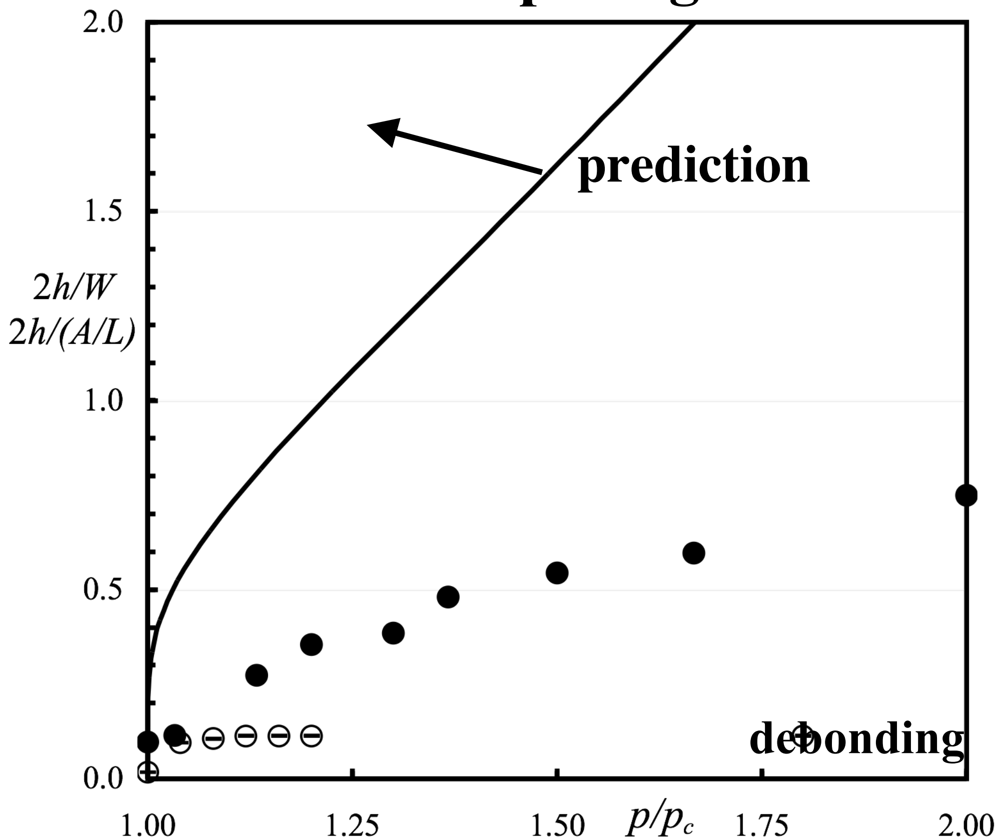


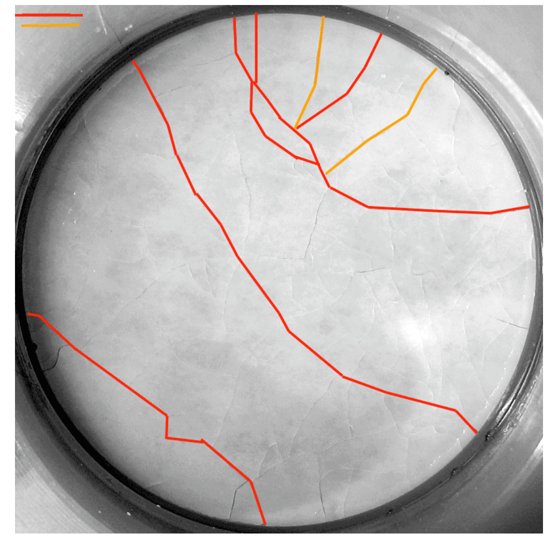


ordered films

91 nm PS

Normalized spacing as function of excess stress





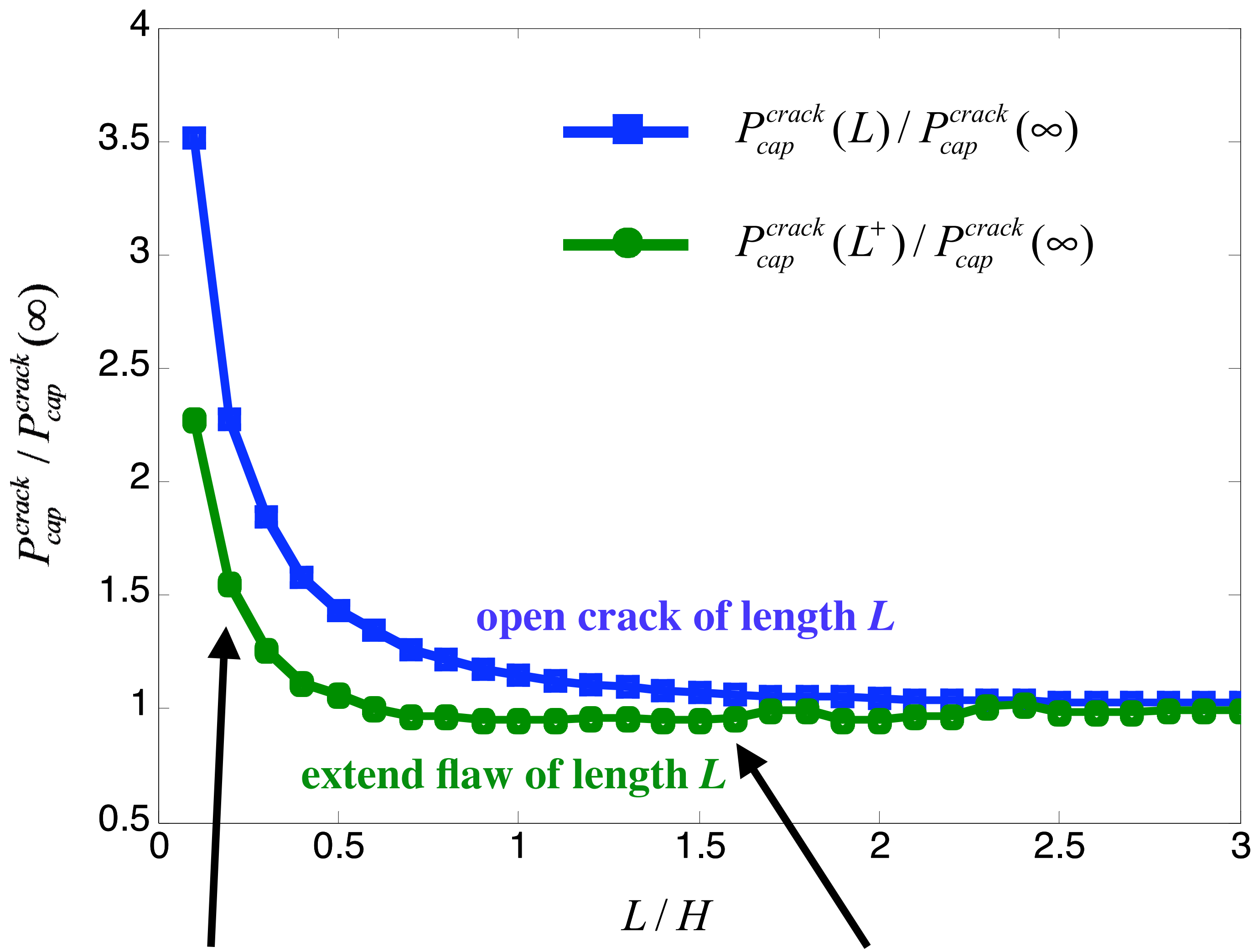
spacing *W* between cracks as function of excess stress

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

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

→ Subsequent cracking controlled by distribution of flaws

Capillary Pressure to Open or Extend Finite Crack

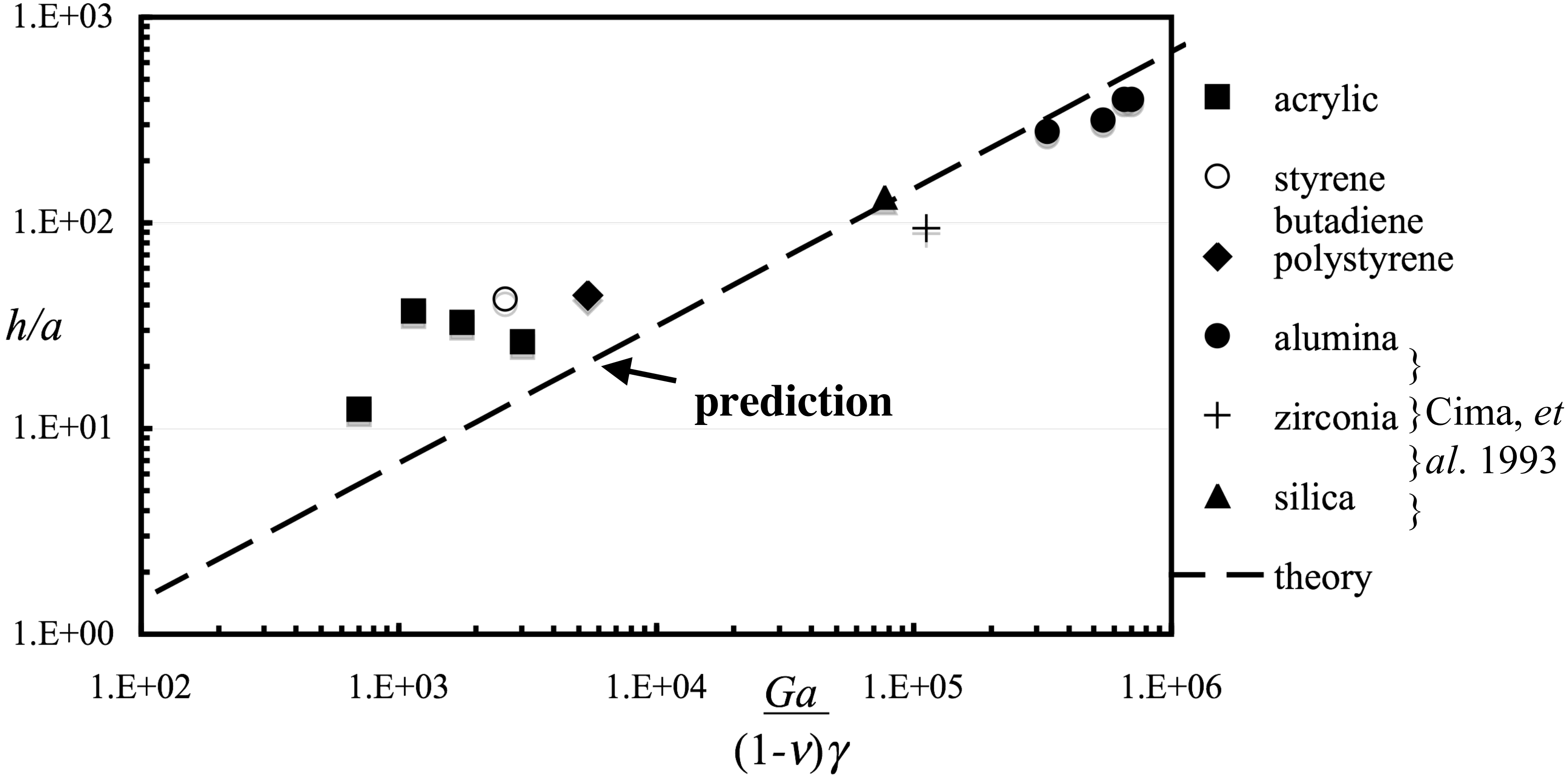


Data implies flaws with *L*<< *h* for randomly close packed layers,

but *L* ≥ *h* for ordered dispersion.

Critical Thickness via Spin Coating

K.B. Singh & M.S. Tirumkudulu (in preparation)



hypothesis: When capillary pressure exceeds $12.5\gamma/a$ without causing cracking, the water front simply recedes into film.

$$-\frac{p_{cap}^{max} H}{\gamma} = 1.30\left(\frac{\phi N G H}{2(1-\nu)\gamma}\right)^{2/5} \Rightarrow \frac{H_{crit}}{a} = 0.023\left(\frac{\phi N G a}{2(1-\nu)\gamma}\right)^{2/3}$$

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.