LESSONS FROM WATCHING PAINT DRY:
film formation, moving fronts, and cracking

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ICSCS 2006
Beijing

OUTLINE

one-dimensional film formation
- regimes
- temperature dependence

measurements with cantilever
- capillary stresses
- drying fronts

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

Collaborators

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A.F. Routh *97 Cambridge Univ.
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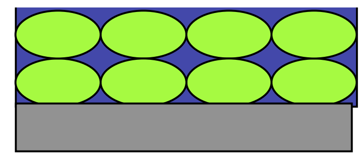
Weining Man *05

Driving Forces for Homogeneous Deformation

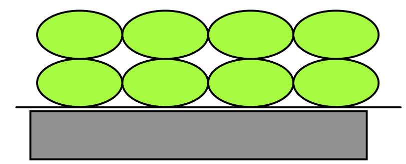
1. **Wet sintering** (Vanderhoff, 1966)

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



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

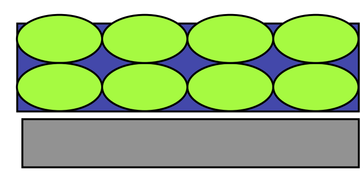
polymer/air surface tension $$\frac{2\gamma_{pa}}{a}$$



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

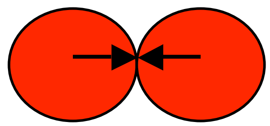
pressure at air-water interface

$$-p_{cap} = -\kappa\gamma_{wa} \leq 10-12\frac{\gamma_{wa}}{a}$$



In all three **negative pressure** puts the film in **tension**. The substrate prevents lateral deformation, while free surface allows **compression** in normal direction.

MODEL FOR ONE-DIMENSIONAL FILM FORMATION



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

$$\boldsymbol{F}_{nm} = -\frac{16}{3}a^2\left\{\frac{G}{2(1-\nu)}+\eta\frac{d}{dt}\right\}\left(-\boldsymbol{n}_{nm}\bullet\boldsymbol{\varepsilon}\bullet\boldsymbol{n}_{nm}\right)^{3/2}\boldsymbol{n}_{nm}$$

contact force — non-linear viscoelastic response → Hertzian contact (Matthews 1980)

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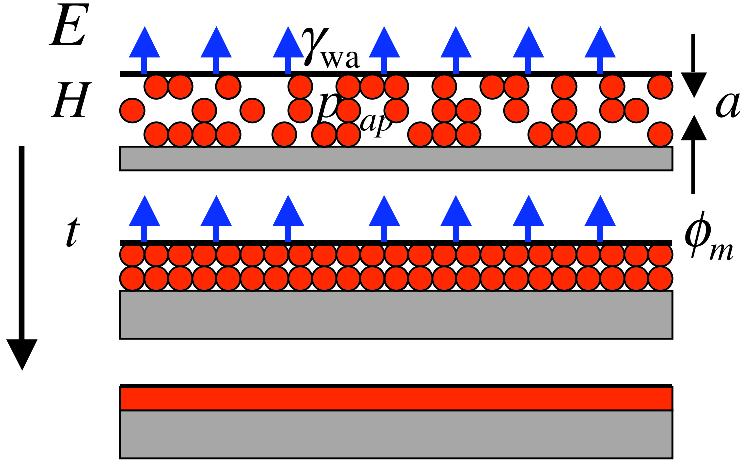
initially isotropic thin film of close-packed spheres

$$\sigma_{33} = -p_{cap} - \frac{2}{3\pi}\phi N\left\{\frac{G}{2(1-\nu)}+\eta\frac{d}{dt}\right\}\varepsilon^{3/2} = 0$$

$$\varepsilon = -\varepsilon_{33} = 1-\phi_m/\phi$$



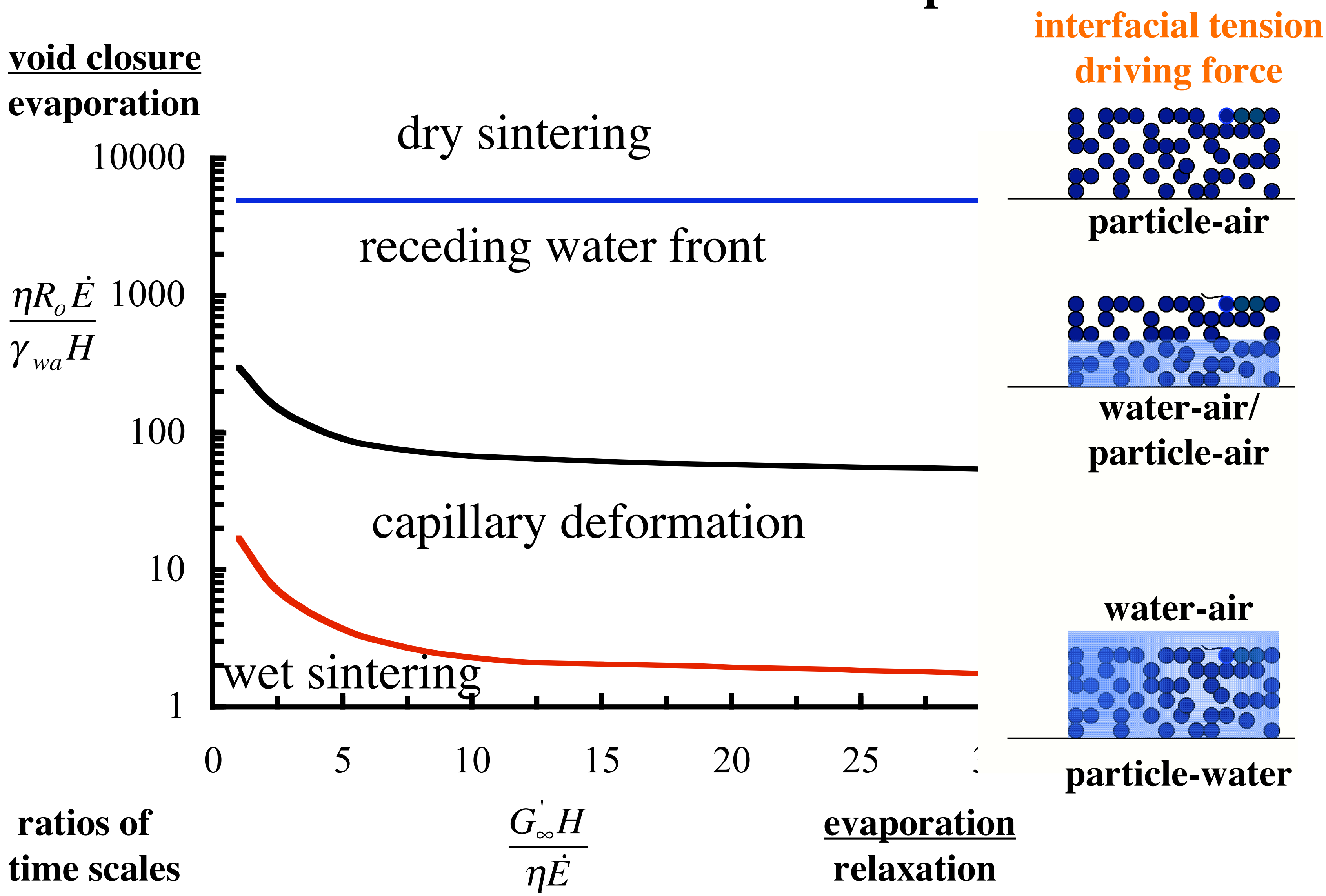
scaling

$$\bar{t} = \dot{E}t/H \qquad \bar{\sigma}_t = \frac{128ap_{cap}}{15N\phi_m^2\gamma_{wa}}$$

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

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

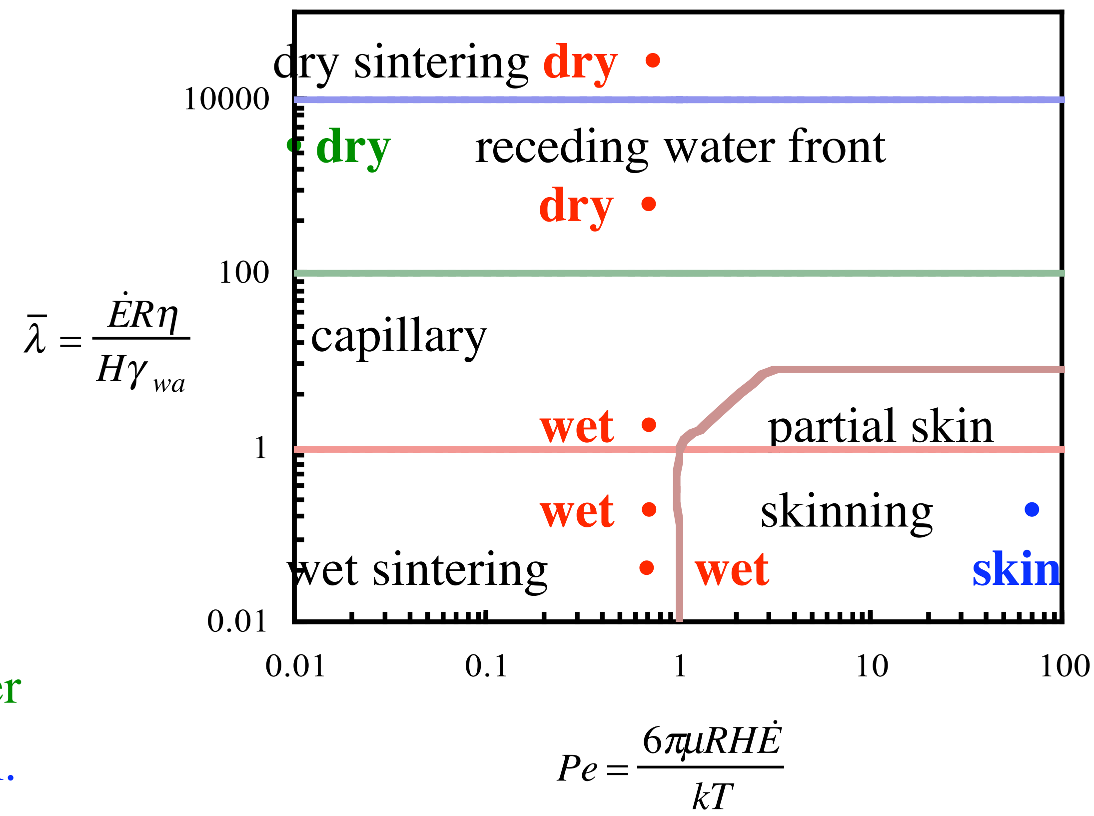
Generalized Process Map



REGIMES OF DEFORMATION

key dimensionless groups

$$\bar{\lambda} = \frac{\text{time for viscous collapse}}{\text{time for evaporation}} \qquad Pe = \frac{\text{time for evaporation}}{\text{time for diffusion}}$$



Keddie
Lin & Meier
Dobler et al.

EFFECT OF TEMPERATURE

time to close pores

wet sintering

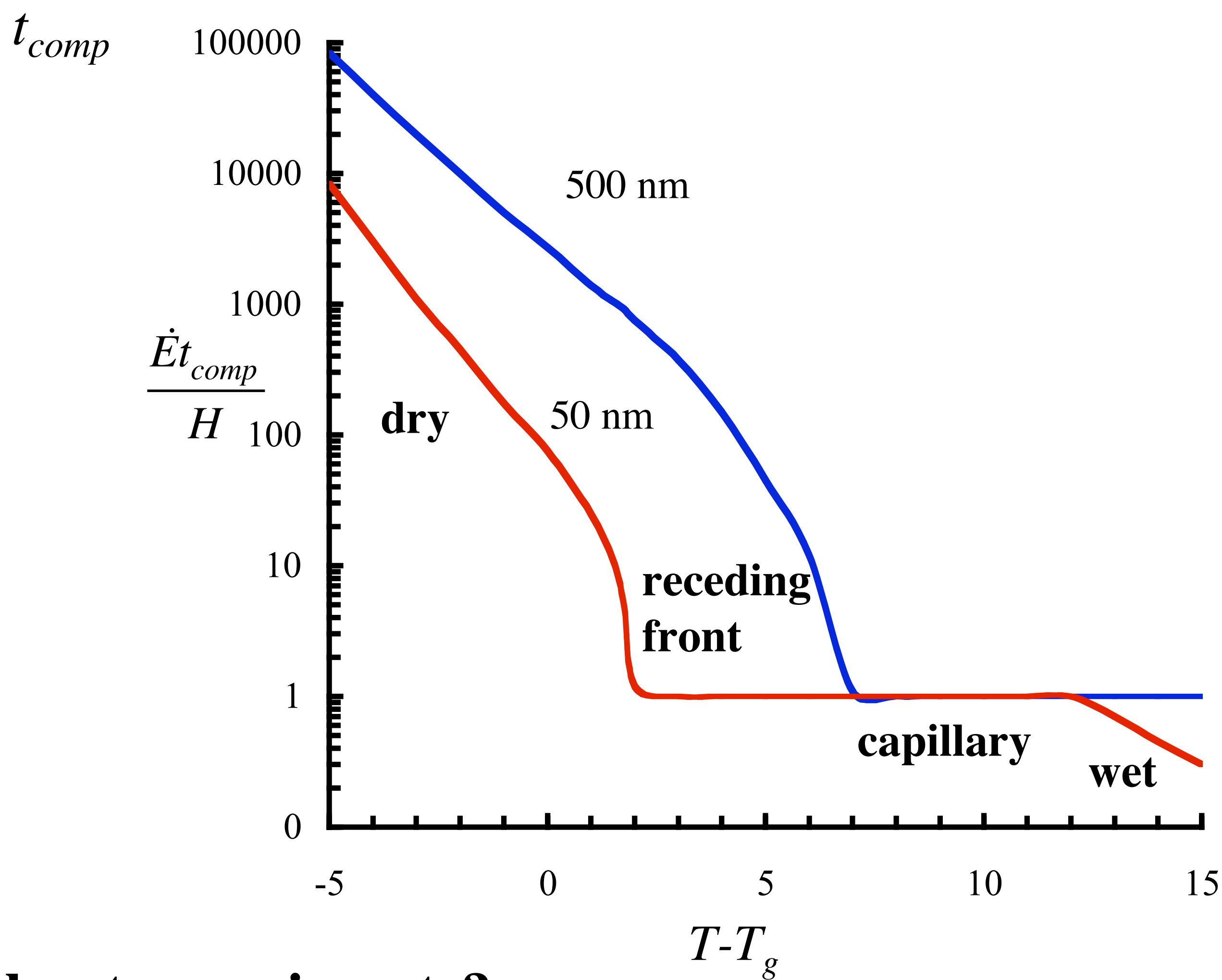
$$0.26\frac{\eta(T)R_o}{\gamma_{pw}}$$

capillary deformation

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

dry sintering

$$0.26\frac{\eta(T)R_o}{\gamma_{pa}}$$



What about experiments?

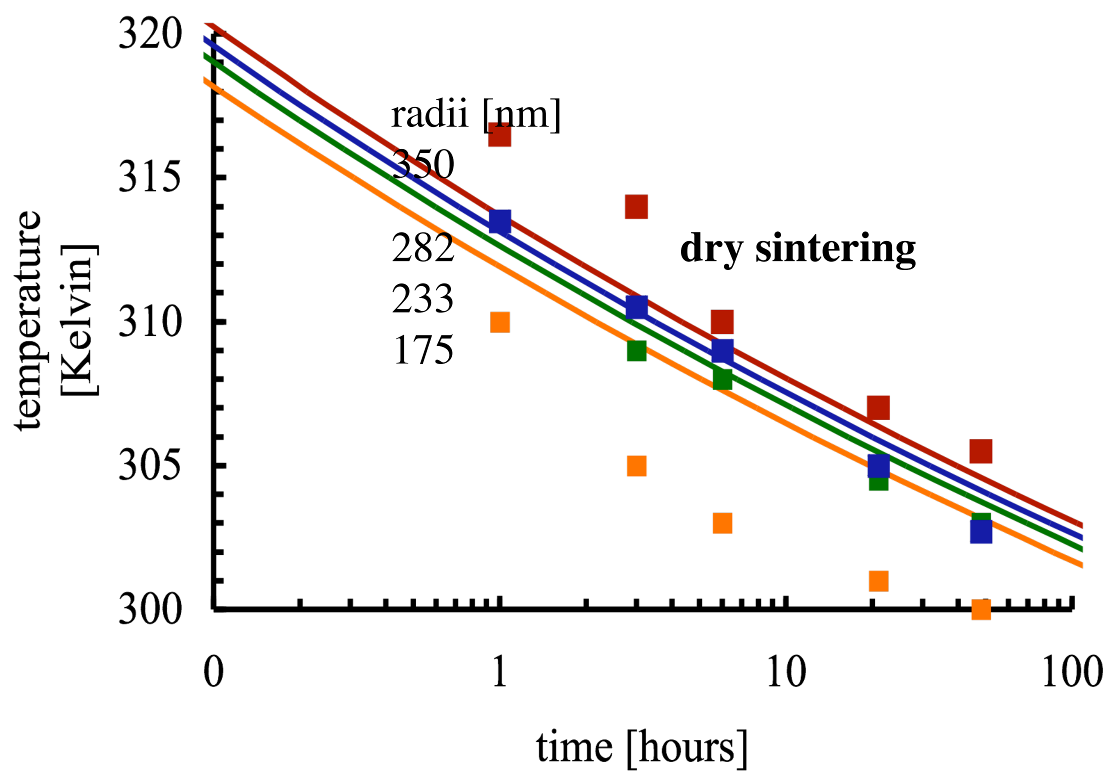
P.R. Sperry, B.S. Snyder, M.L. O'Dowd, P.M. Lesko,
"Role of water in particle deformation and compaction in latex film formation" *Langmuir* **10** 2619 (1994)

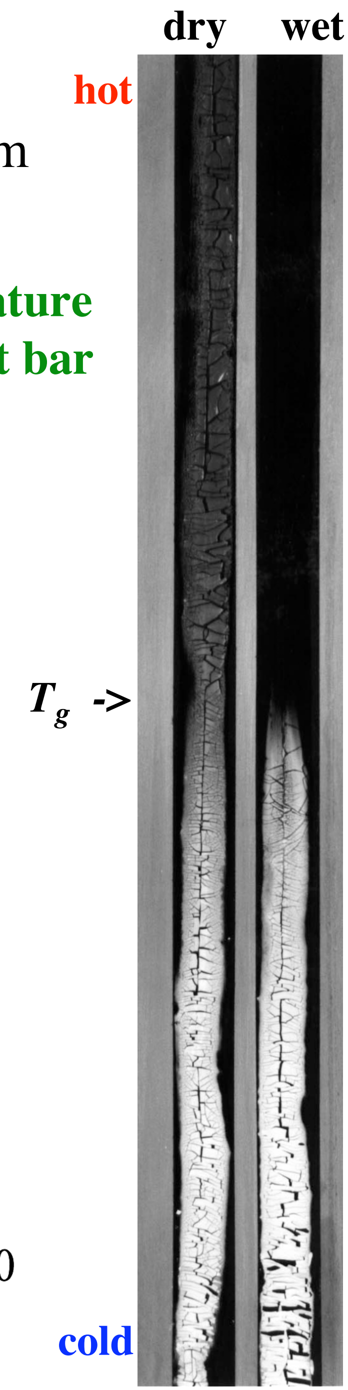
minimum film formation temperature depends on

glass transition temperature

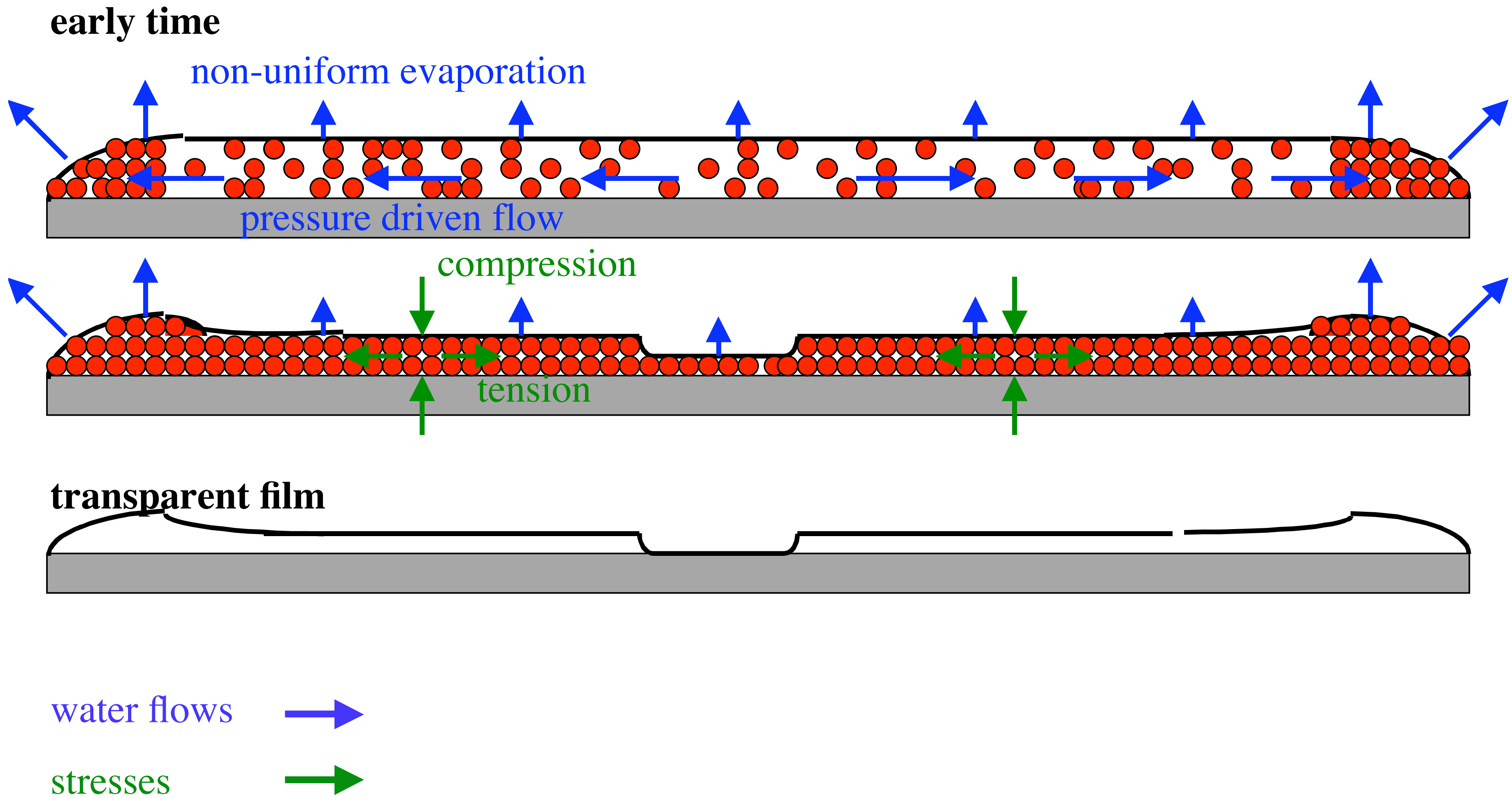
diameter of particles

time





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

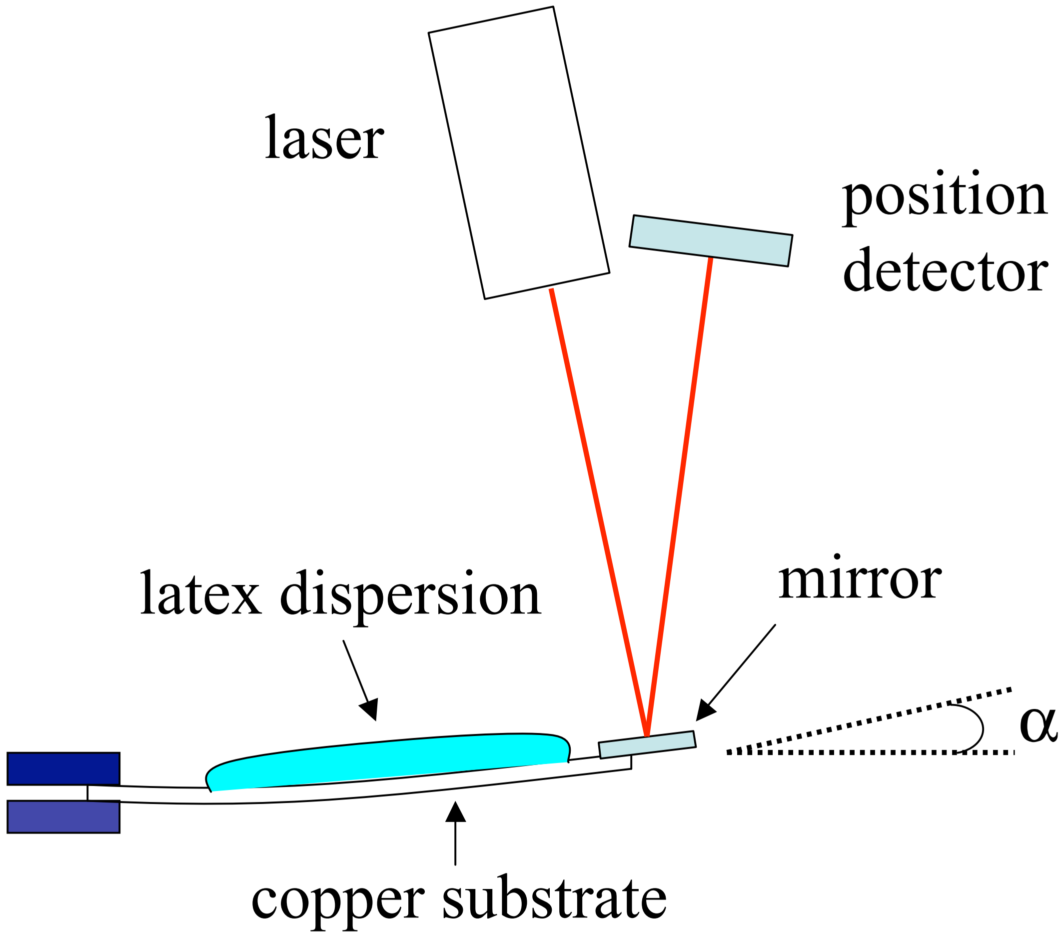


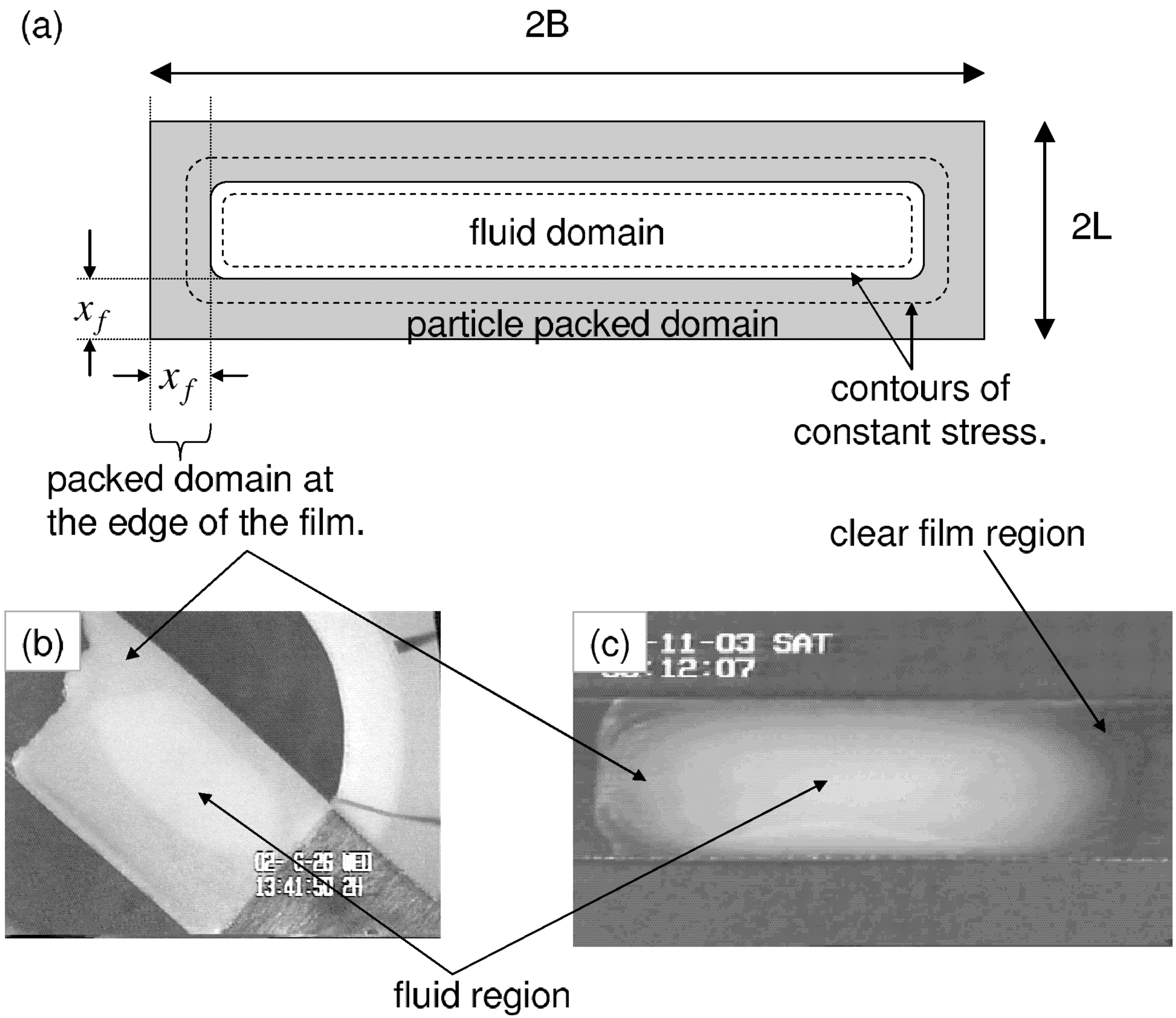
Cantilever Experiment for Measuring Stresses

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



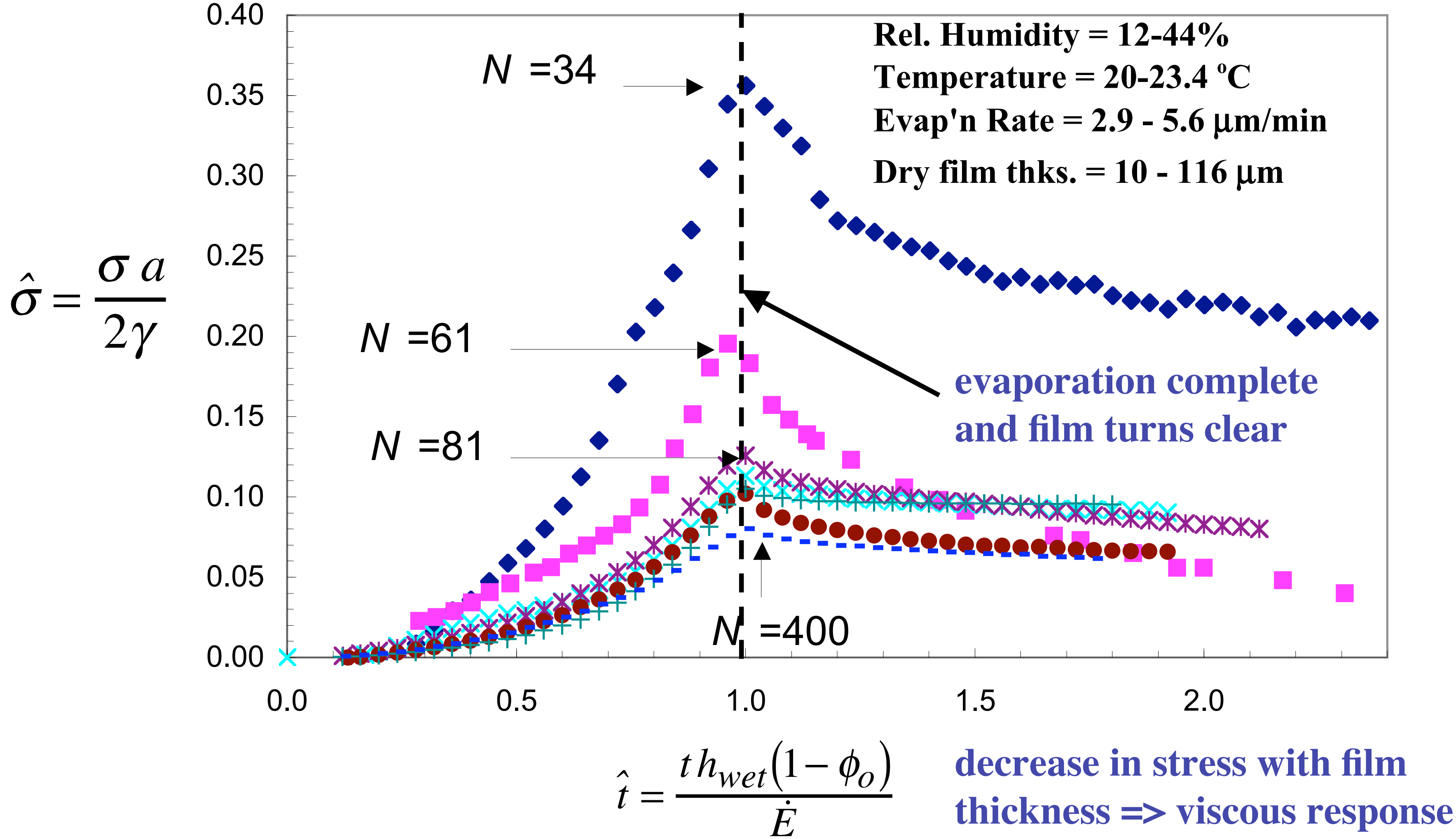

(a)
2B
2L
fluid domain
x_f
x_f
particle packed domain
contours of constant stress.
packed domain at the edge of the film.
clear film region
(b)
02- 6-26 WED
13:41:50 2H
(c)
-11-03 SAT
:12:07
fluid region

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

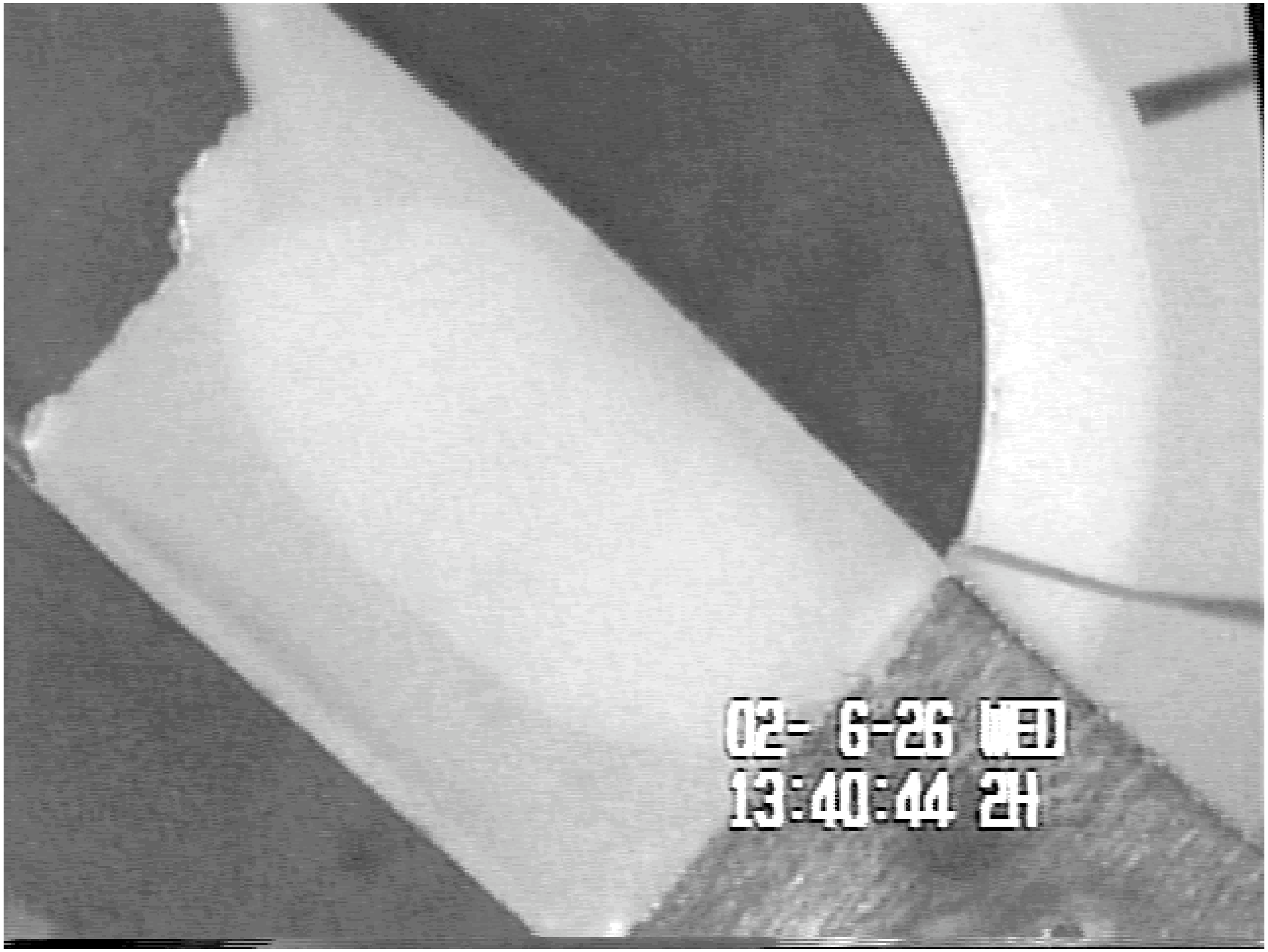


$T_{amb} < T_g$ => **non-film forming latices**

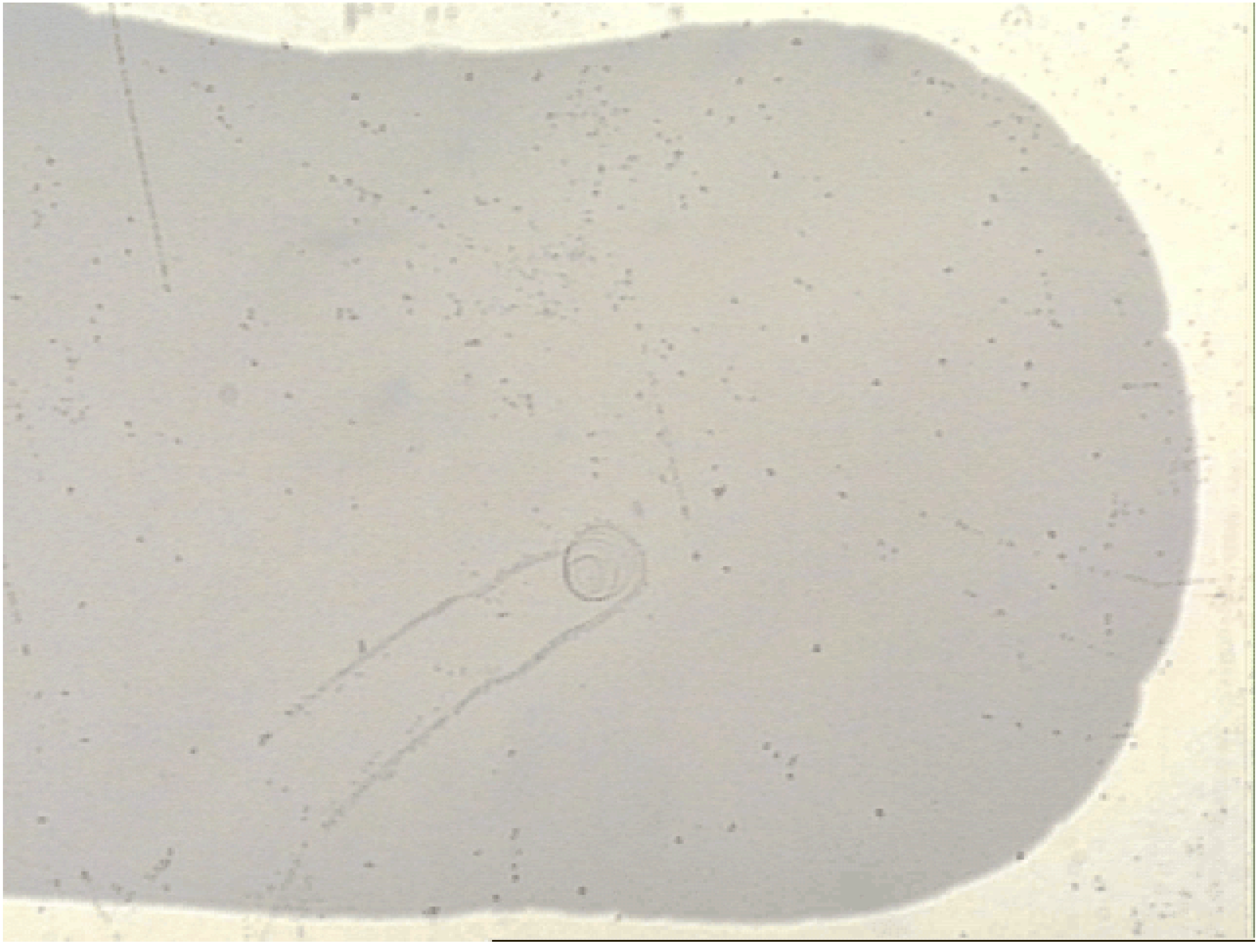
large particles => high permeability packing

Film Cracking: Large High T_g Particles

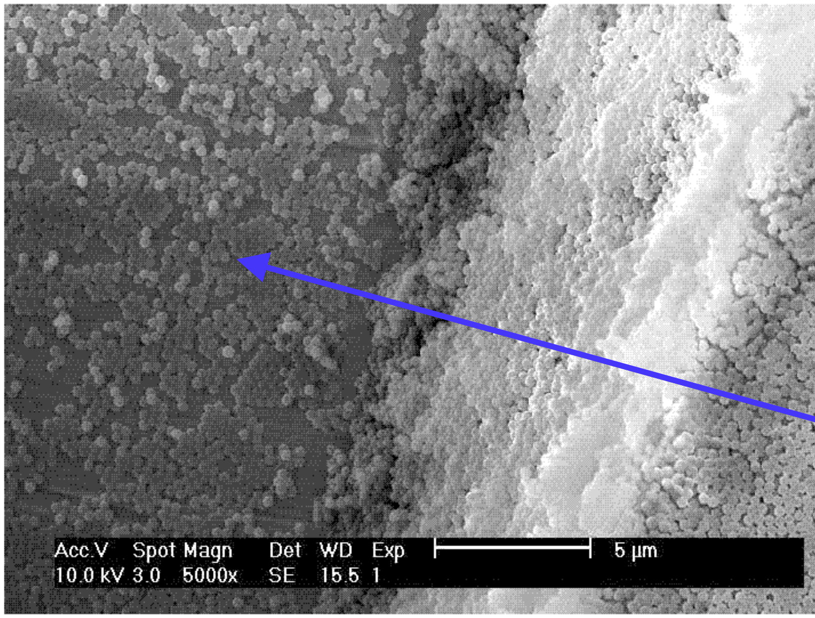
$2a$=342 nm, h_{dry}=79.5 µm, E=2.5 µm/min, RH=66%, T=23.5 °C



(PS342-062602b)

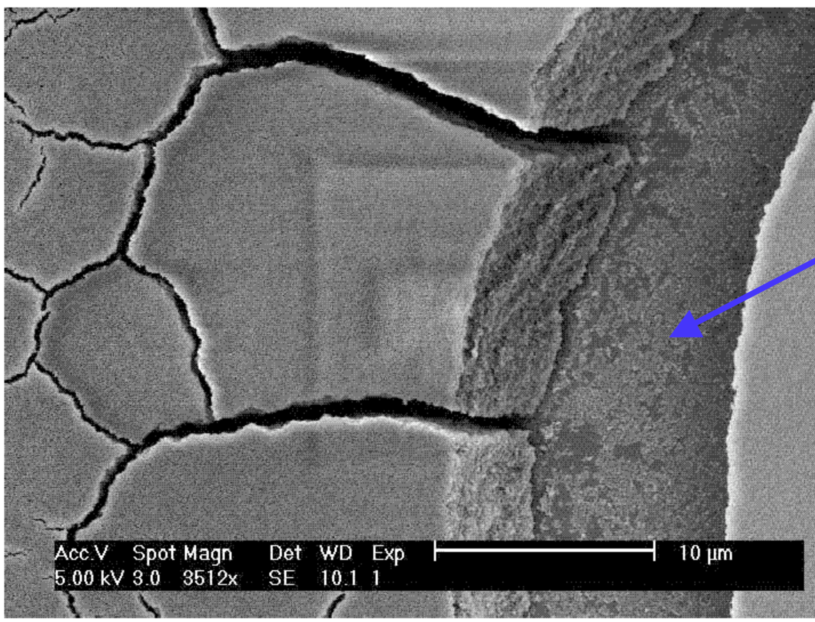


(a)



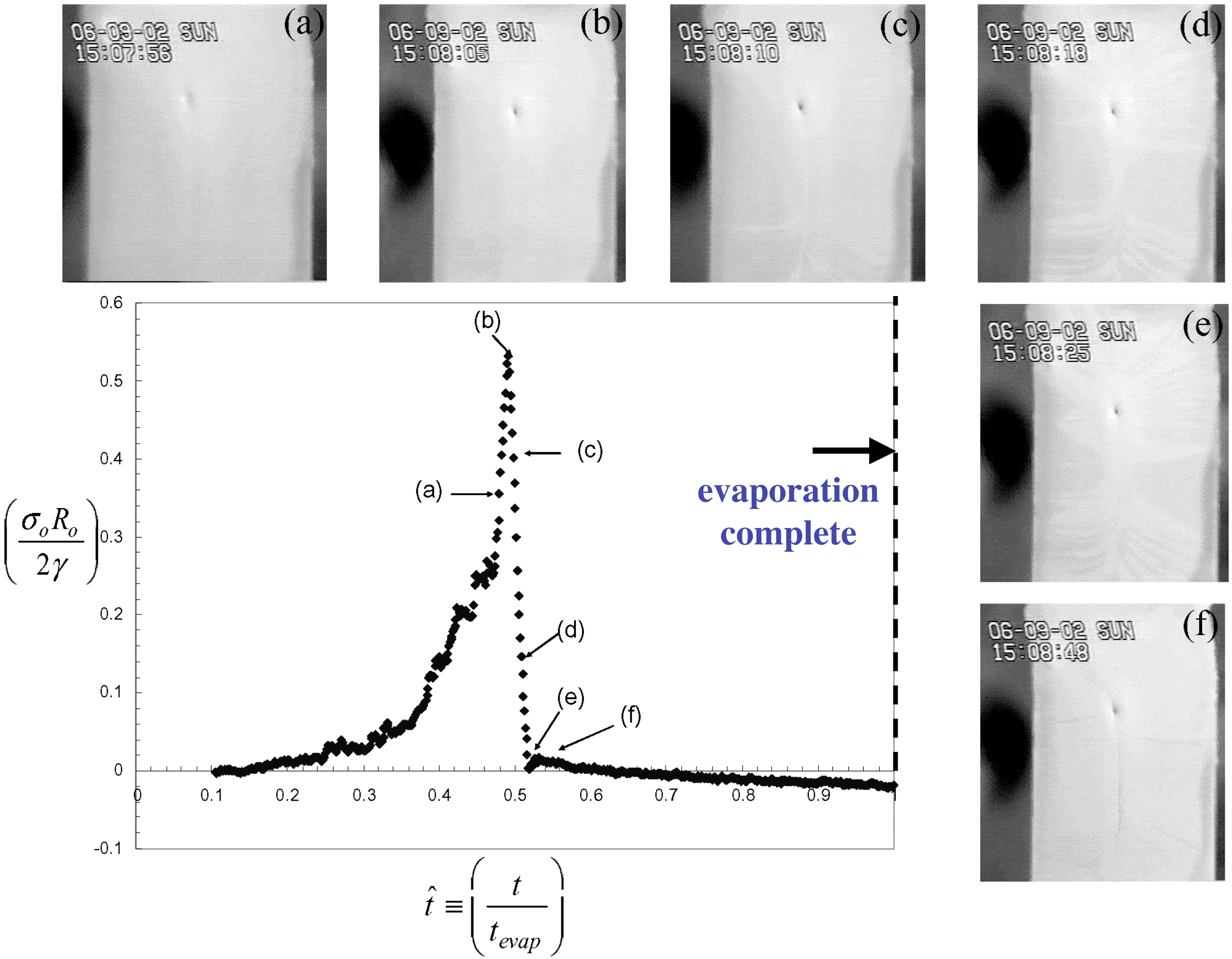
large high T_g PPG342

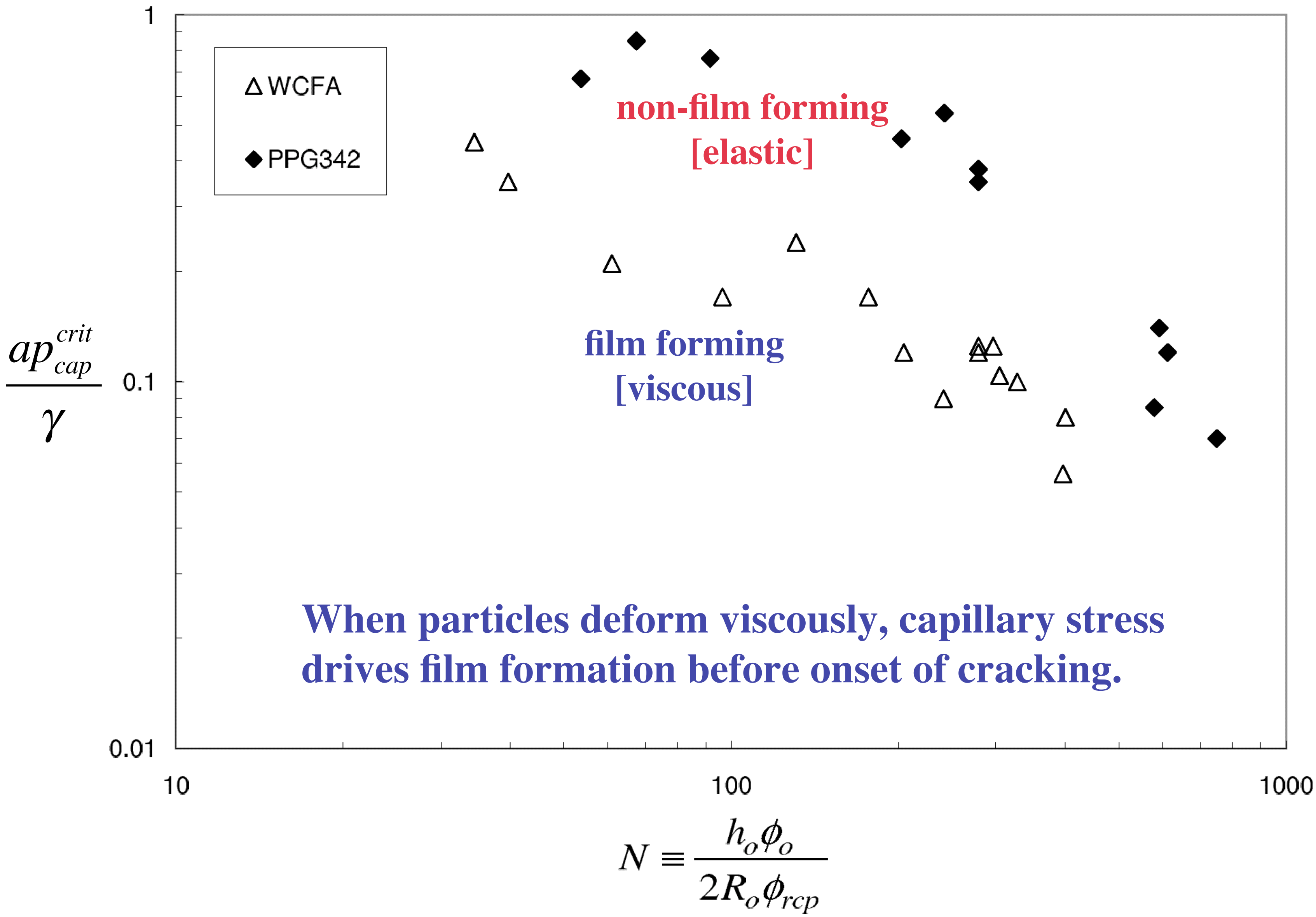
(b)



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

small high T_g PMMA95


(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
evaporation complete
$\left(\frac{\sigma_o R_o}{2\gamma}\right)$
$\hat{t} \equiv \left(\frac{t}{t_{evap}}\right)$
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



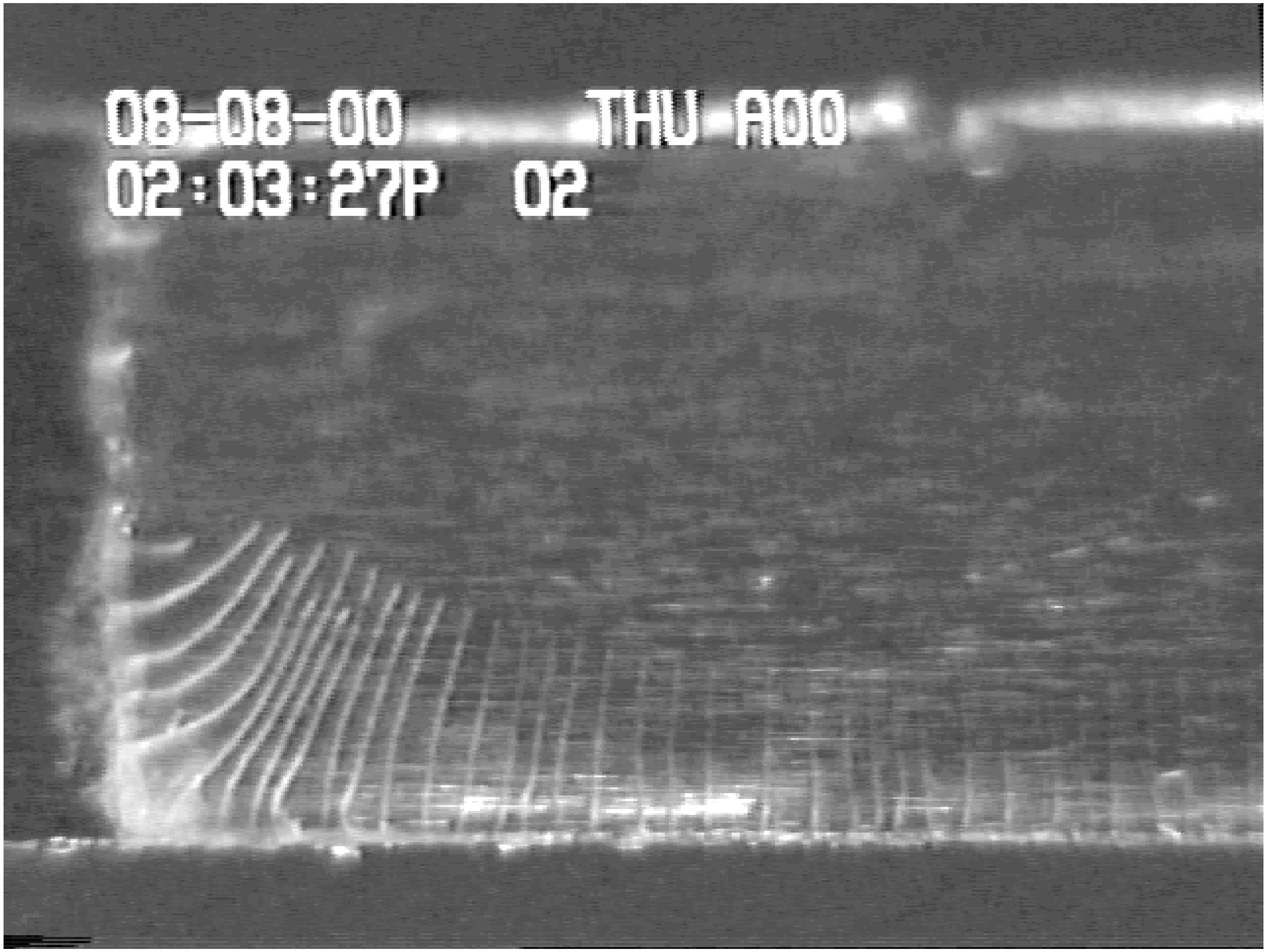
When particles deform viscously, capillary stress drives film formation before onset of cracking.

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

small particles => low permeability packings

Film Cracking: Small High T_g Particles

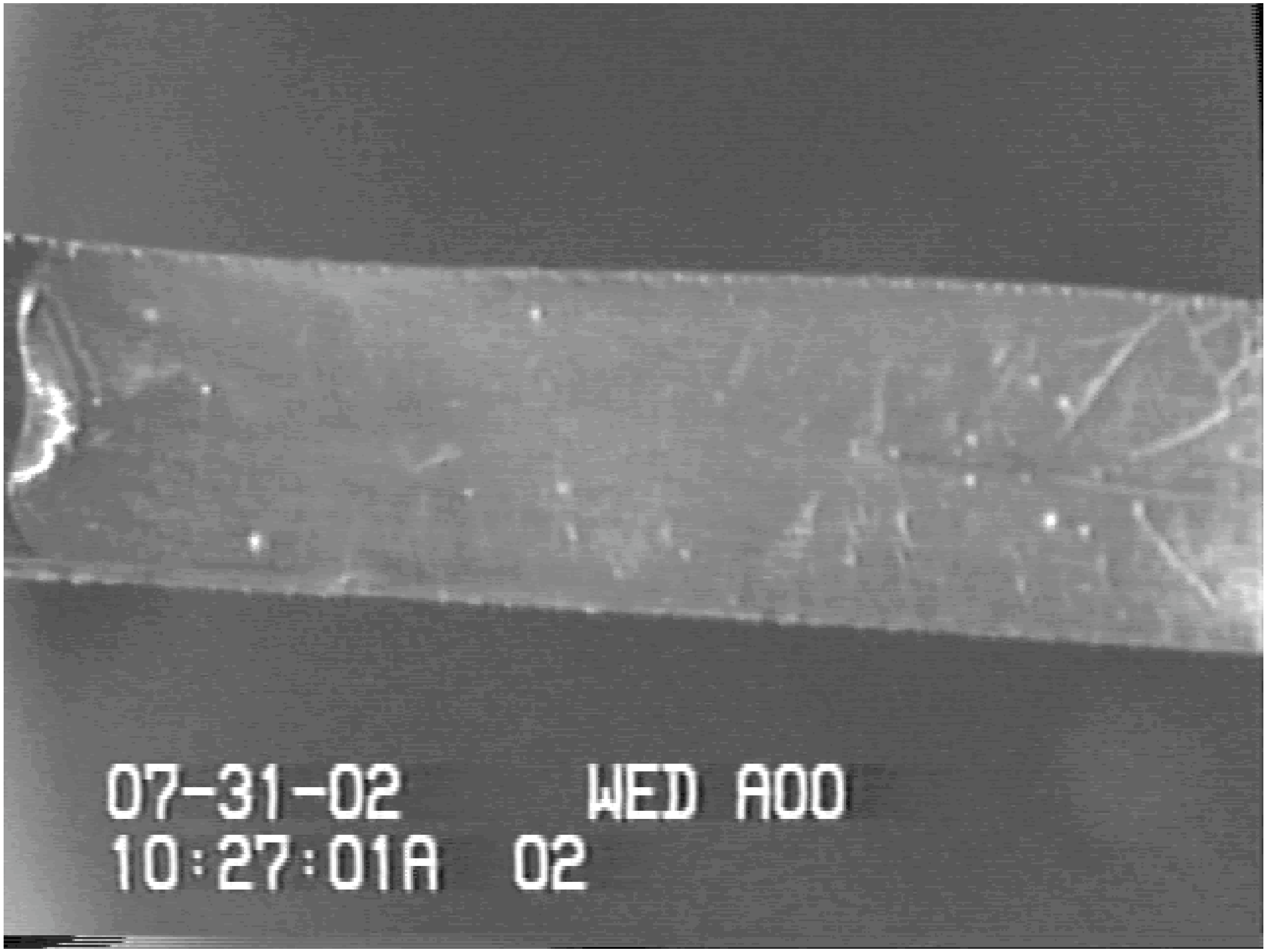
$2a$=95 nm, h_{dry}=101 µm, E=6.7 µm/min, RH=35%, T=24.4 °C



(PMMA95-080802a)

Film Cracking: Small High T_g Particles

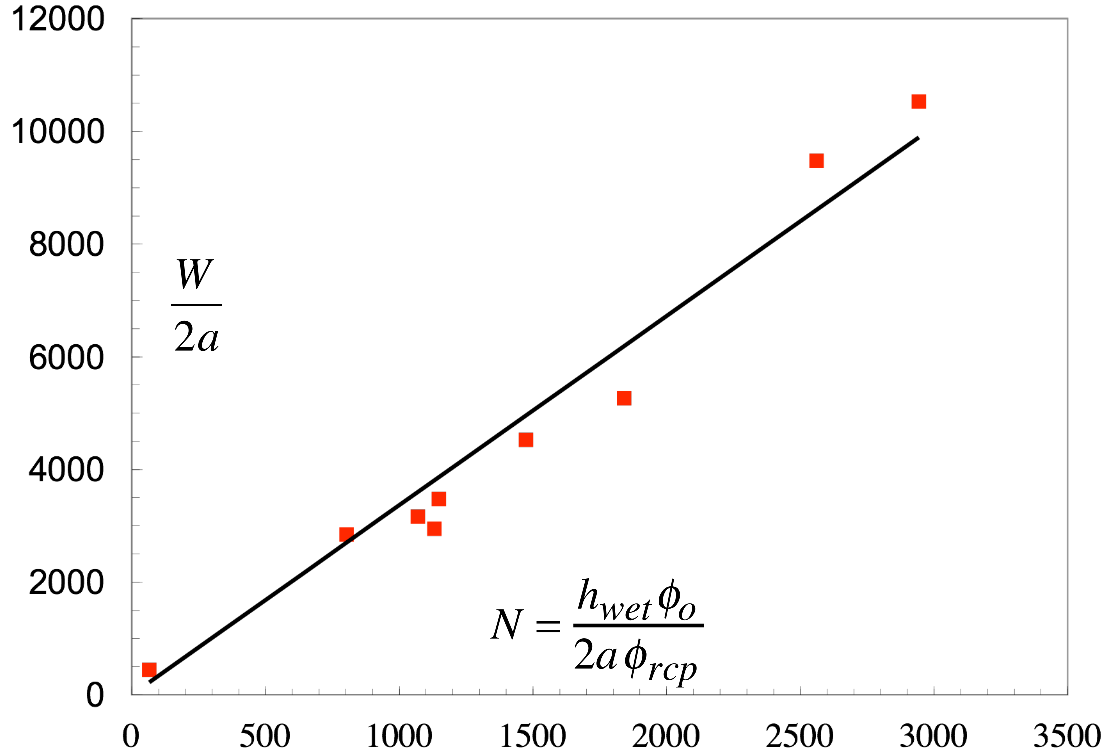
$2a$=95 nm, h_{dry}=262 μm, E=6.7 μm/min, RH=35%, T=24.4 °C



(PMMA95-080802b)

Crack Spacing

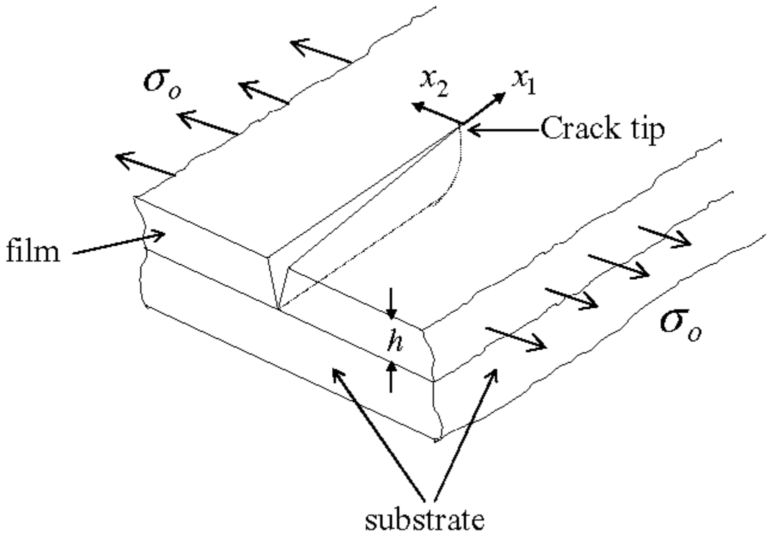
PMMA95: 2*a*=95 nm



→ simple and reproducible results, but how to

- **measure in more controlled manner**
- **understand the mechanism**

Cracking in Thin Films



homogeneous linearly elastic films

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)

Griffiths criterion

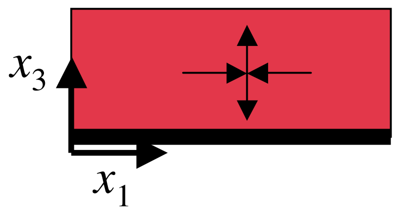
recovery of elastic energy $\Delta E = h\iint \left\{ \sigma_{33} d\varepsilon'_{33} + \sigma_{22} d\varepsilon'_{22} + 2\sigma_{23} d\varepsilon'_{23} \right\} dx_2$

|| ||

cost of surface energy $2h\gamma$

==> critical stress as function of film thickness for isolated crack spacing as function of film thickness and excess stress

- **one-dimensional base state**



compression normal to film

$$\sigma_{33}^{o} = -p_o - \frac{2}{3\pi}\phi N \frac{G}{2(1-\nu)}\varepsilon_o^{\;3/2} = 0$$

tension in plane of film

$$\sigma_{11}^{o} = \sigma_{22}^{o} = \frac{\phi N}{2\pi}\frac{G}{2(1-\nu)}\varepsilon_o^{\;3/2}$$

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

stress-free air-water interface

$$\sigma_{33}^{'} = -p' - \frac{3}{4\pi}\phi N \frac{G}{2(1-\nu)}\varepsilon_o^{\;1/2}\varepsilon_{11}^{'} = 0$$

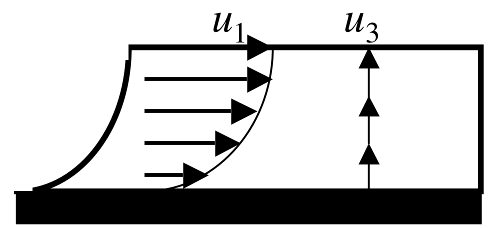
$$\Rightarrow \quad p' = \frac{3}{4\pi}\phi N \frac{G}{2(1-\nu)}\varepsilon_o^{\;1/2}\varepsilon_{11}^{'}$$

relaxation in plane

$$\sigma_{11}^{'} = \frac{5}{16\pi}\phi N \frac{G}{2(1-\nu)}\varepsilon_o^{\;1/2}\varepsilon_{11}^{'}$$

$$\sigma_{13}^{'} = \frac{1}{2\pi}\phi N \frac{G}{2(1-\nu)}\varepsilon_o^{\;1/2}\varepsilon_{13}^{'}$$

• **vertically averaged stress balance**



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

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

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

• **equation for displacement**

$$\frac{\partial^2 \left\langle u'_1 \right\rangle}{\partial x_1^2} = \frac{6}{7}\frac{\left\langle u'_1 \right\rangle}{h^2} \quad \text{with} \quad \varepsilon_o + \frac{7}{4}\frac{\partial \left\langle u'_1 \right\rangle}{\partial x_1}(0) = 0 \qquad \left\langle u'_1 \right\rangle(\infty) = 0$$

stress-free crack surface — uniform film

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

critical stress for isolated crack

$$\frac{p_{cap}^{crit}a}{\gamma}=1.17\left(\frac{a}{h}\right)^{3/5}\left(\frac{GN\phi_o a}{(1-\nu)\gamma}\right)^{2/5} \Rightarrow \frac{p_{cap}^{crit}h}{\gamma}=2.0\left(\frac{Gh}{(1-\nu)\gamma}\right)^{2/5}$$

spacing W between parallel cracks as function of excess stress

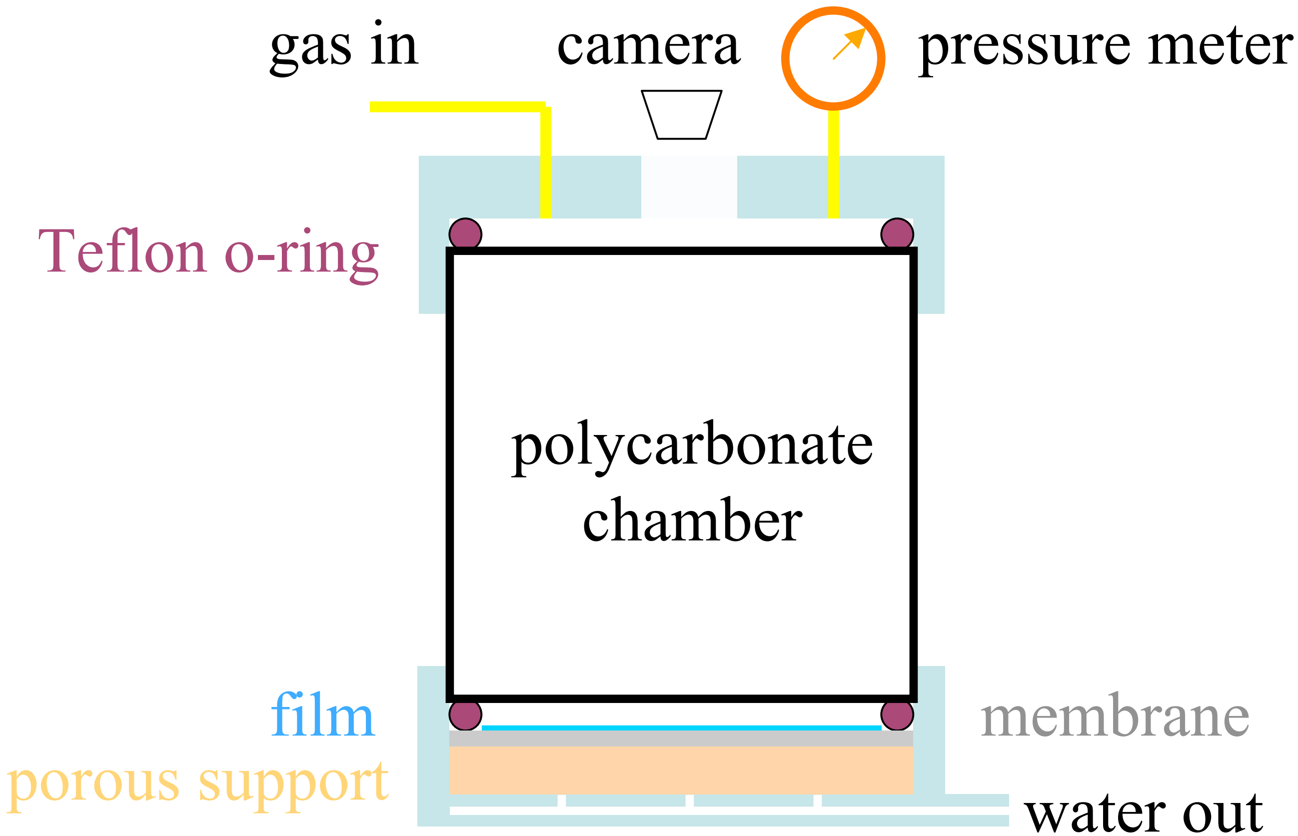
$$\frac{p_{cap}^{crit}}{p_{cap}}=\left\{\frac{3}{8}tanh\left(\sqrt{\frac{6}{7}}\frac{W}{2h}\right)-\left[5\,sinh\left(\sqrt{\frac{6}{7}}\frac{W}{h}\right)-\sqrt{\frac{6}{7}}\frac{W}{h}\right]\Big/6\,cosh^2\left(\sqrt{\frac{6}{7}}\frac{W}{2h}\right)\right\}^{3/5}$$

minimum thickness for cracking $p_{cap}^{crit}=10\gamma/a$

$$\frac{h_{crit}}{a}=0.068\left(\frac{Ga}{(1-\nu)\gamma}\right)^{2/3}$$

Direct Measurement of Stresses

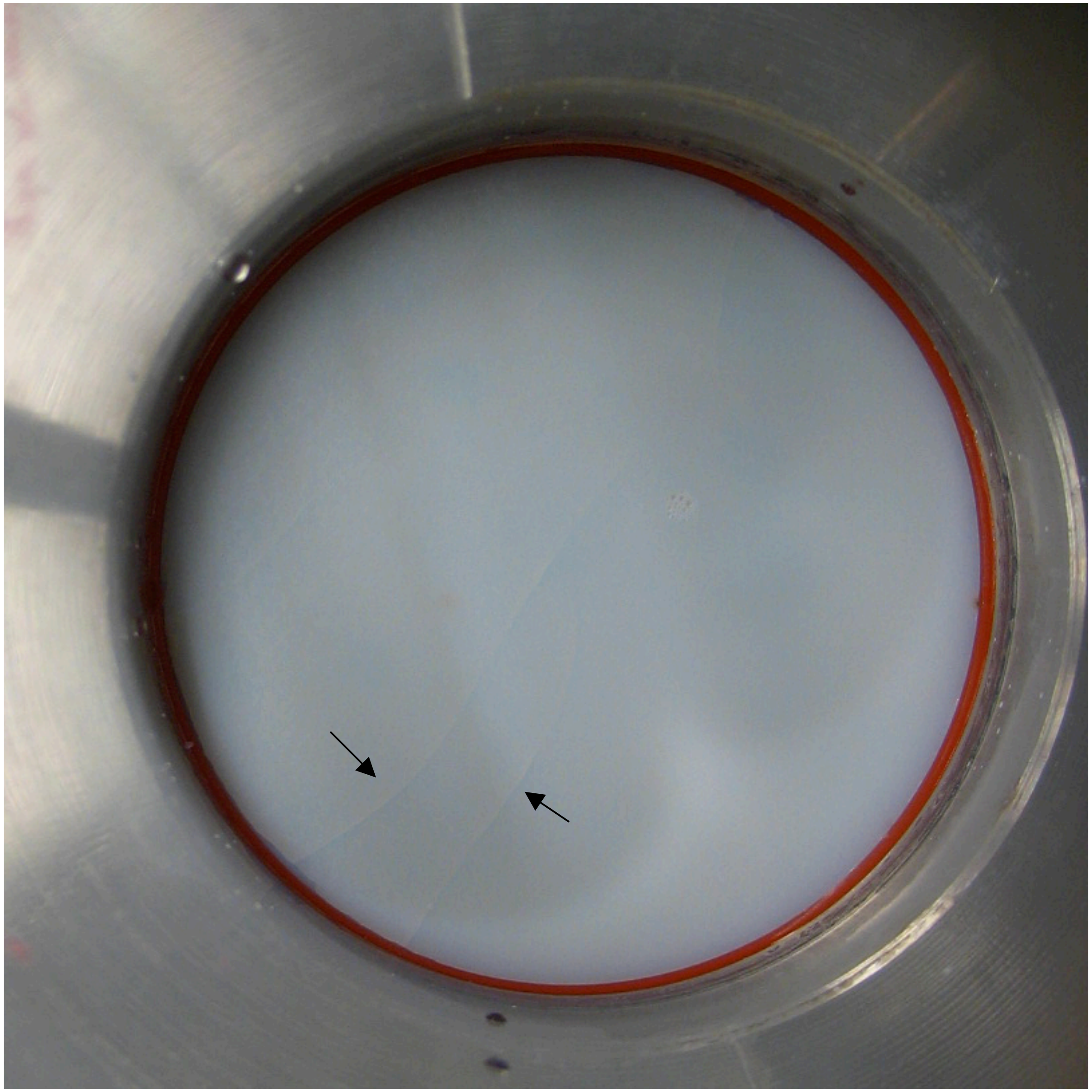
high pressure filter chamber:



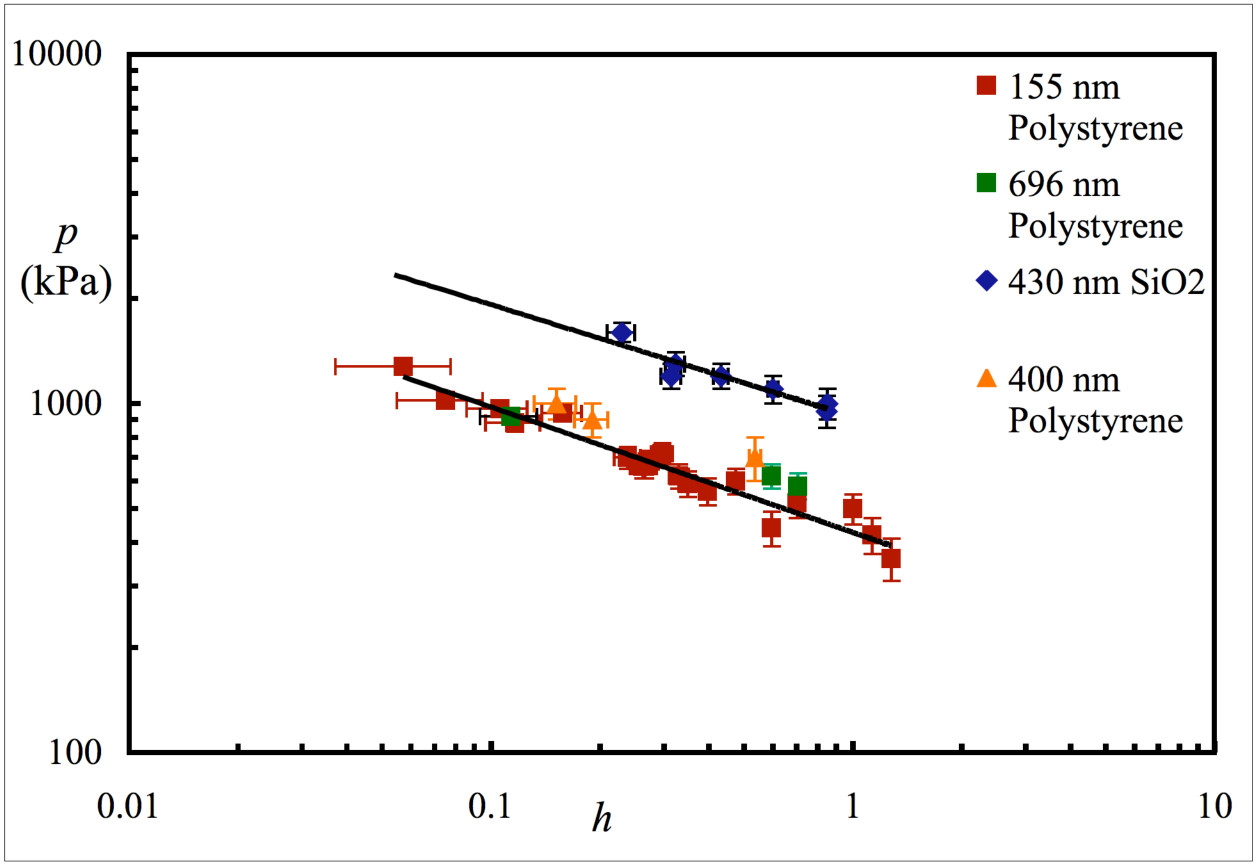
Experimental Procedure

- Dispersions consist of polymer latices below T_g or silica.
- Push water out slowly at low pressure (50 kPa) to create close packing.
- Water vapor saturates air inside the chamber, stopping evaporation.
- Gradually increase pressure until the film cracks to determine directly the critical capillary pressure.
- Continue increasing pressure in steps and photograph cracks to determine dependence of crack spacing on pressure.
- Remove film and weigh while still wet and then after drying to determine volume fraction and thickness of film.

Film as onset of cracking



Parametric Dependence of Cracking Stress



→ cracking pressure independent of particle radius

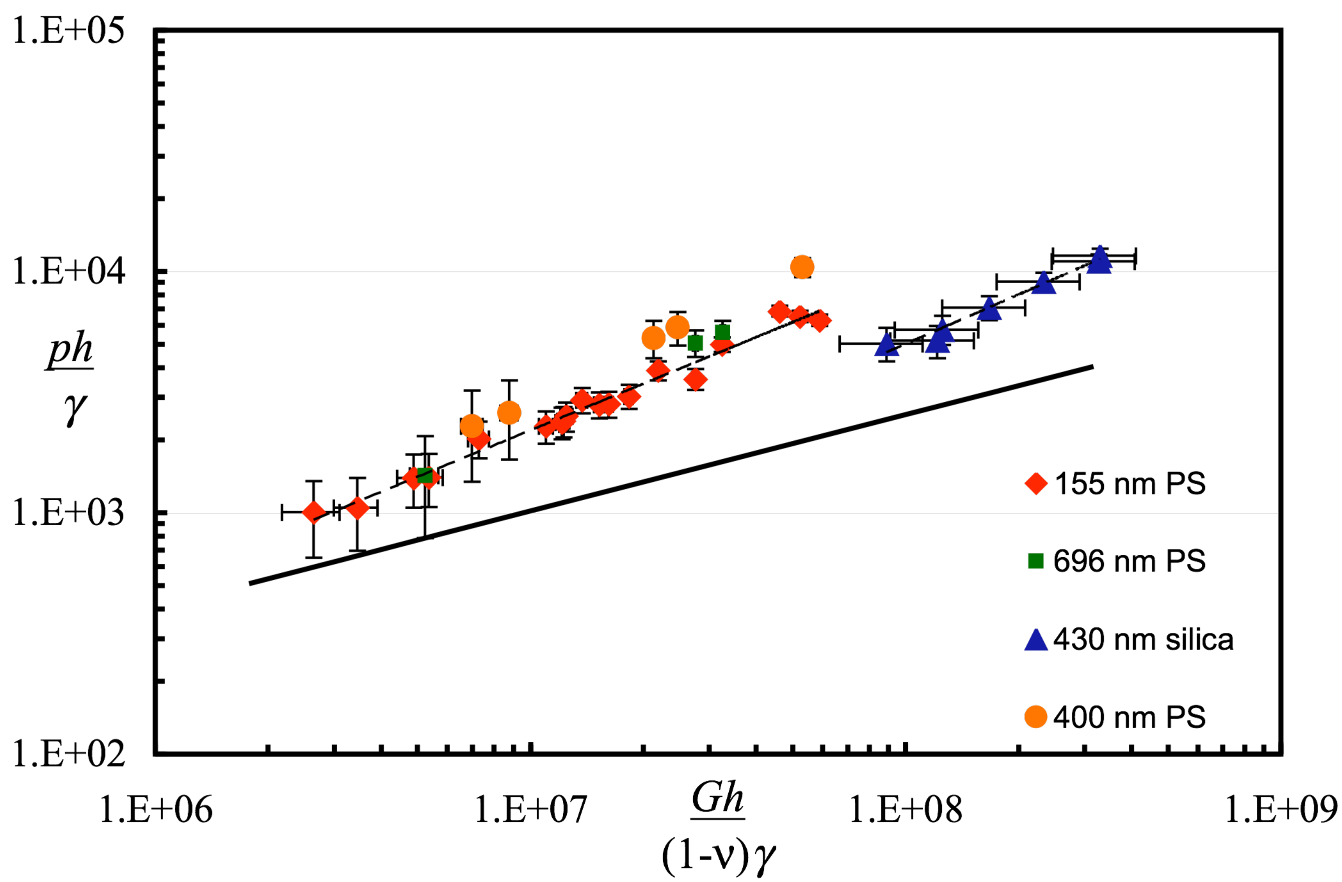
variables

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

dimensional analysis → two dimensionless variables one a function of the other

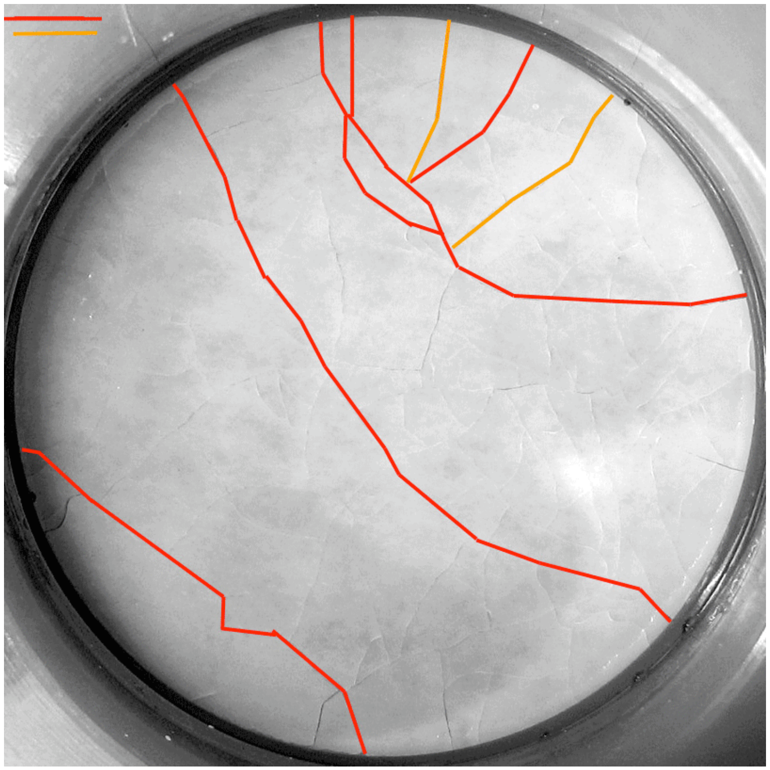
$$\frac{ph}{\gamma} = f\left(\frac{Gh}{(1-\nu)\gamma}\right)$$

Dimensional Analysis



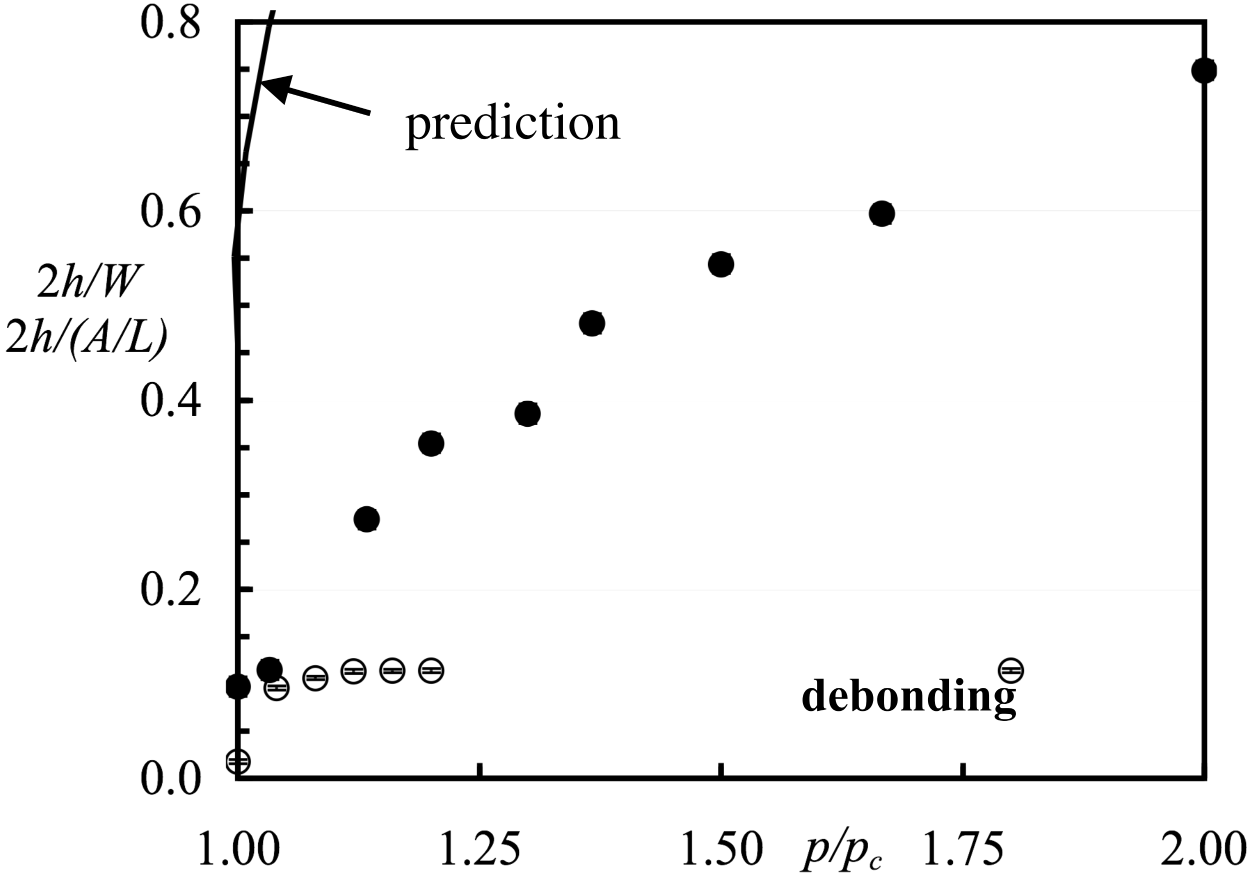
Balancing elastic energy recovered by cracking against the additional surface energy (———) provides **lower bound** on capillary pressure that produces cracking.

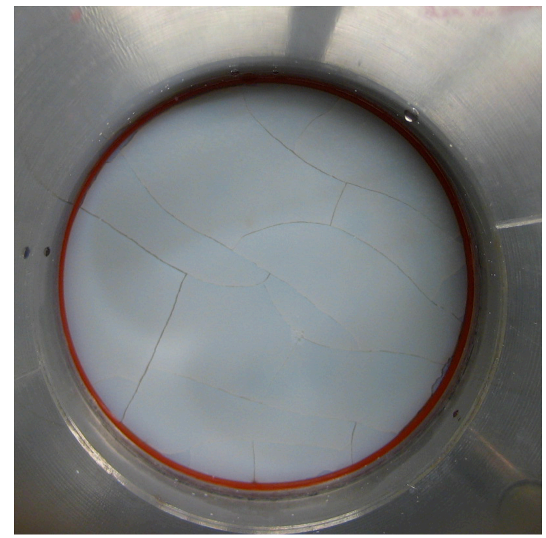
Cracking spacing at pressures above p_{crit}



A = area of film	parallel cracks	$W=A/L$
L = total length of cracks	orthogonal cracks	$W=2A/L$
	triangular cracks	$W=3A/L$

Normalized spacing as function of excess stress



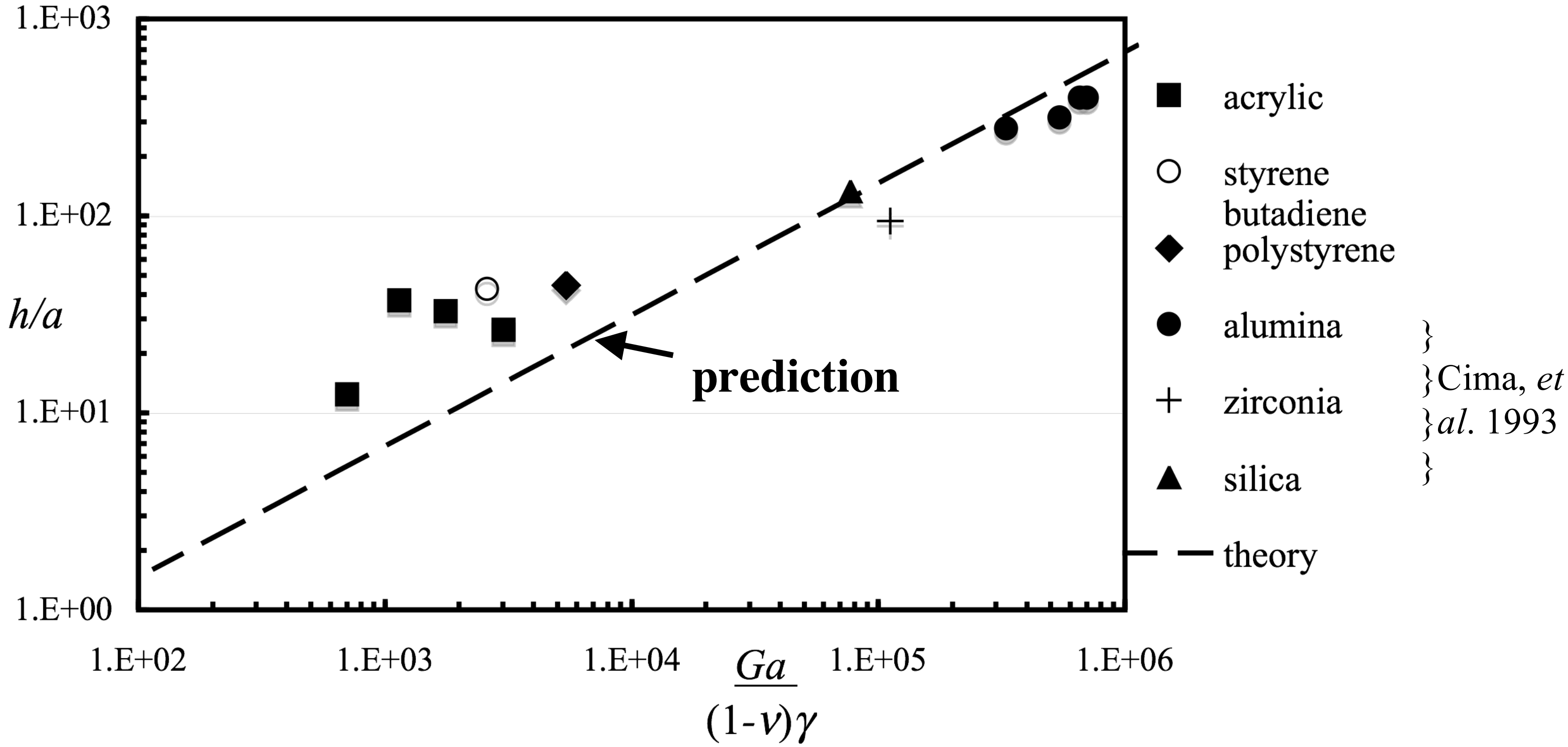


- Debonding terminates cracking by relaxing stress.
- Theory for parallel cracks misses phenomenon.

→ Subsequent cracking controlled by distribution of flaws?

Critical Thickness via Spin Coating

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



hypothesis: When capillary pressure exceeds $10\gamma/a$ without causing cracking, the water front simply recedes into film.

$$\frac{10\gamma}{a} \times \frac{h}{\gamma} = 2\left(\frac{Gh}{(1-\nu)\gamma}\right)^{2/5} \quad \rightarrow \quad \frac{h_{crit}}{a} = 0.068\left(\frac{Ga}{(1-\nu)\gamma}\right)^{2/3}$$

SUMMARY

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

• Edges cause gradients in capillary pressure that draw fluid from the center to sustain mass transfer limited evaporation.

• 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 with excess pressure but appears to be nucleation controlled.

• There exists a thickness below which films of even hard particles do not crack.