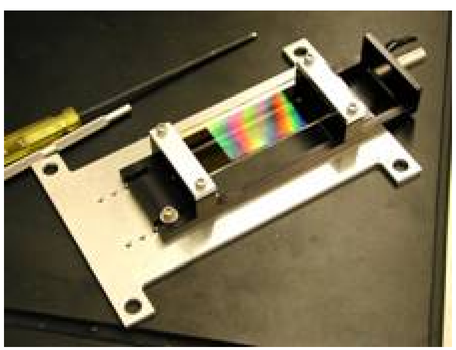
Polymers Division

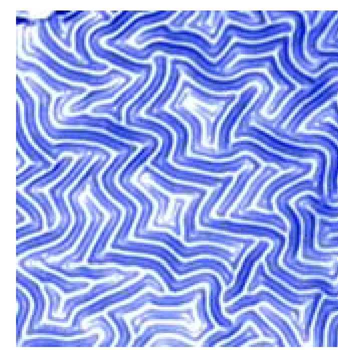
NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Surface wrinkling as a metrology tool

Christopher M. Stafford
Polymers Division
National Institute of Standards and Technology



MEASUREMENT • ANALYSIS • INFORMATICS • DESIGN • FABRICATION



ASME Applied Mechanics and Materials Conference
June 3-7, 2007
University of Texas at Austin

Motivation

Mechanical properties are critical in many applications

- predictive modeling of complex systems
- performance and reliability

Measuring mechanical properties of sub-micron (nano) films remains difficult

Nanomechanics

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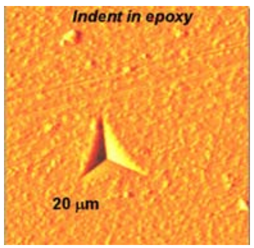
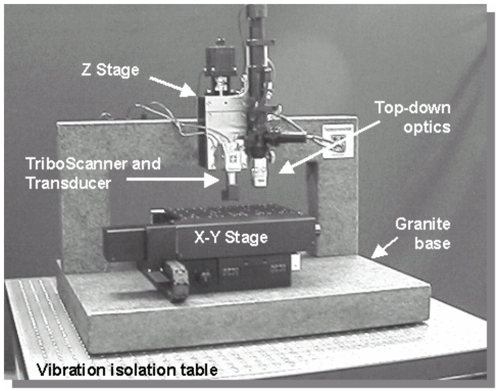
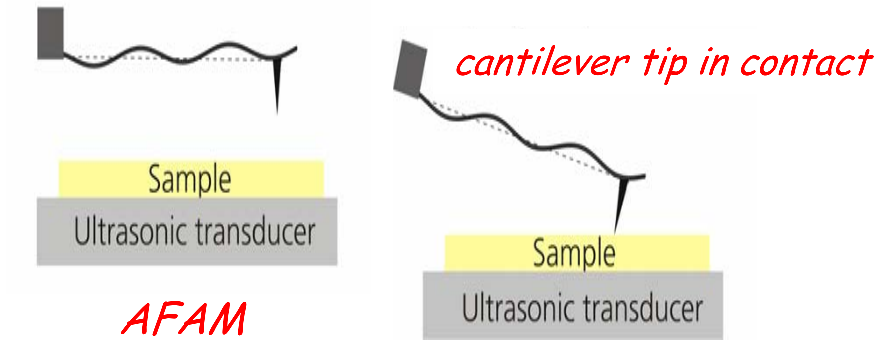
Indentation



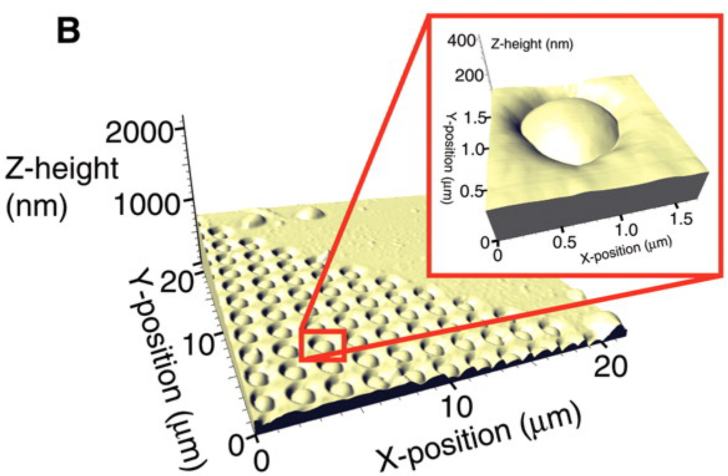


clamped-free AFM cantilever



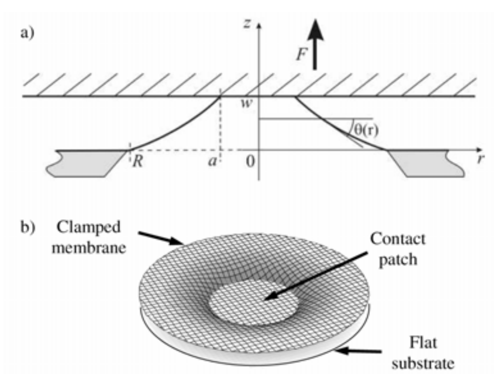
Rabe et al. *J Vac Sci Technol B* **15** 1506 (1997)
Hurley et al. *J Appl Phys* **94** 2347 (2003)

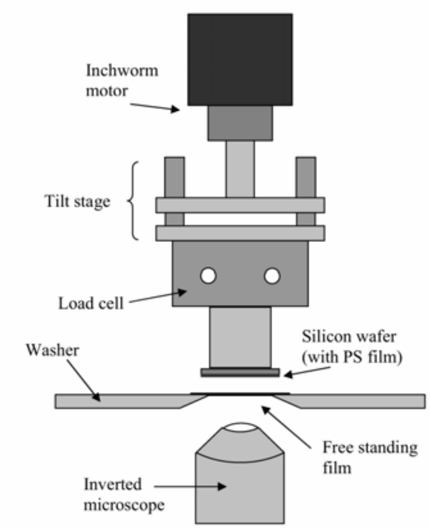
Nanobubbles



O'Connell and McKenna, *Science* **307**, 1760-1763 (2005).

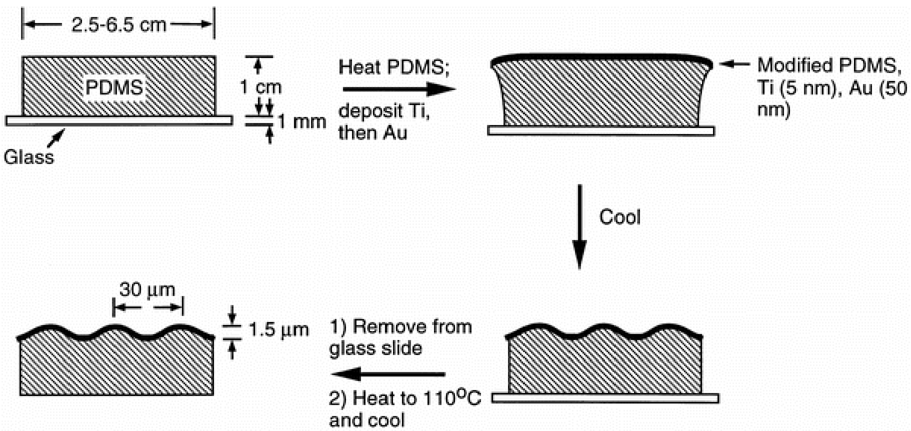
Membrane punch



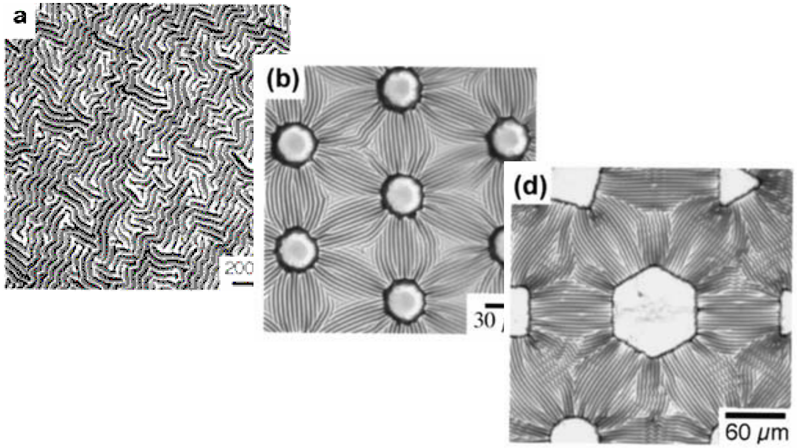


Raegan et al. *Eur. Phys. J. E* **19**, 453-459 (2006).

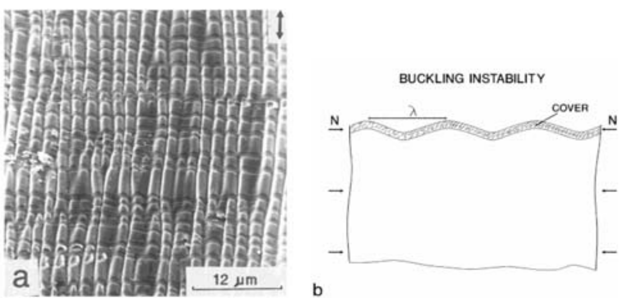
Surface wrinkling



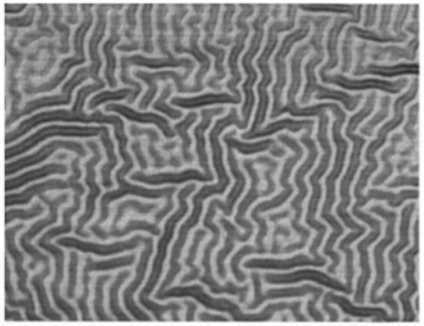
Bowden *et al. Nature* **393**, 146 (1998).



Bowden *et al. Appl. Phys. Lett.* **75**, 2557 (1999).

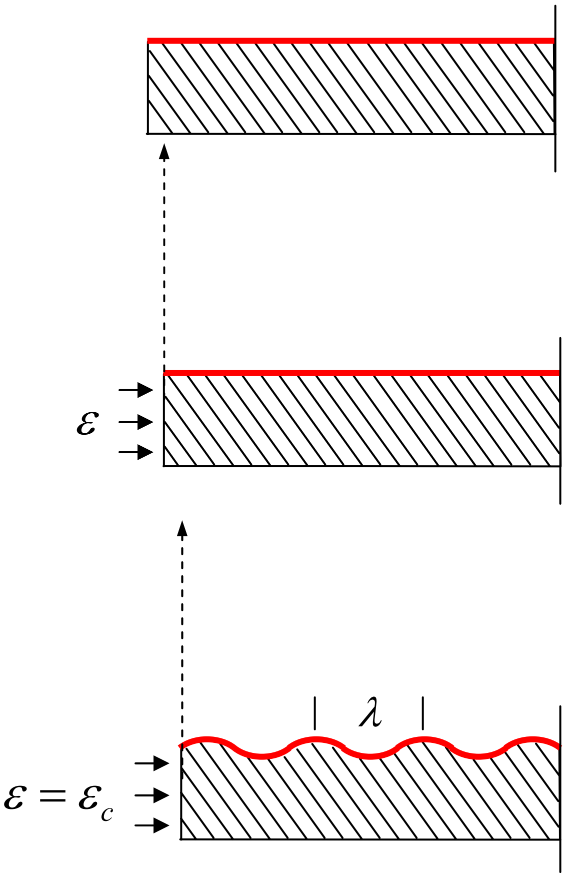


Volynskii *et al. J. Appl. Polym. Sci.* **72**, 1267 (1999).



Lacour, *et al. Appl. Phys. Lett.* **82**, 2404 (2003).

Surface wrinkling



Bending of an elastic layer on an elastic foundation:

$$\frac{E_f I}{(1-\nu_f^2)}\frac{d^4 z}{dx^2} + F\frac{d^2 z}{dx^2} + kz = 0$$

Assume sinusoidal deflection of the coating:

$$z = A\sin\frac{2\pi x}{\lambda}$$

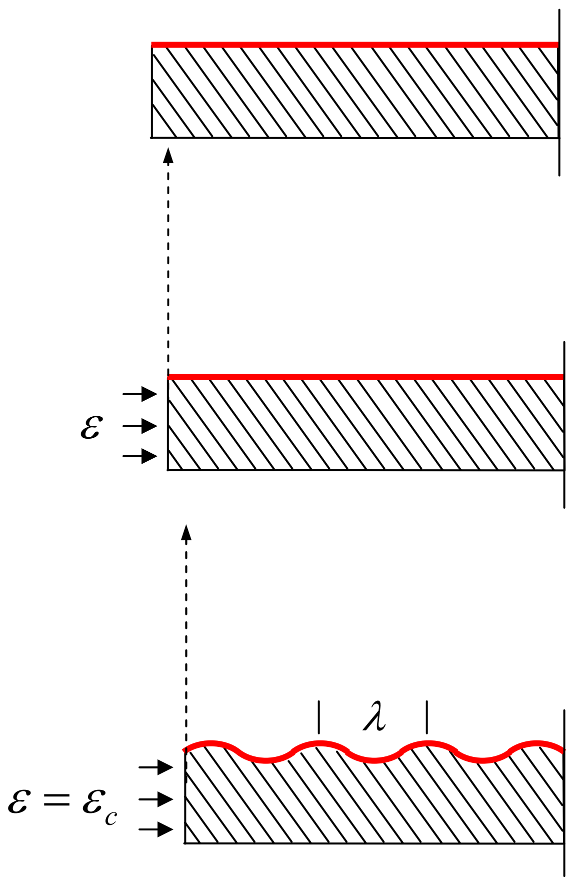
Minimize the compressive force in the coating:

$$\frac{dF}{d\lambda} = 0$$

$$\lambda = 2\pi h \sqrt[3]{\frac{(1-\nu_s^2)E_f}{3(1-\nu_f^2)E_s}}$$

M.A. Biot, *J. Applied Mechanics* **4**, A1 (1937).
A.L. Volynskii *et al. J. Material Science* **25**, 547 (2000).
R. Huang, *J. Mechanics and Physics of Solids* **53**, 63 (2005).

Surface wrinkling



Governing Equations

$$\varepsilon_c = -\frac{1}{4}\left(\frac{3\overline{E}_s}{\overline{E}_f}\right)^{2/3} \qquad \sigma_c = \left(\frac{9\overline{E}_f\overline{E}_s^2}{64}\right)^{1/3}$$

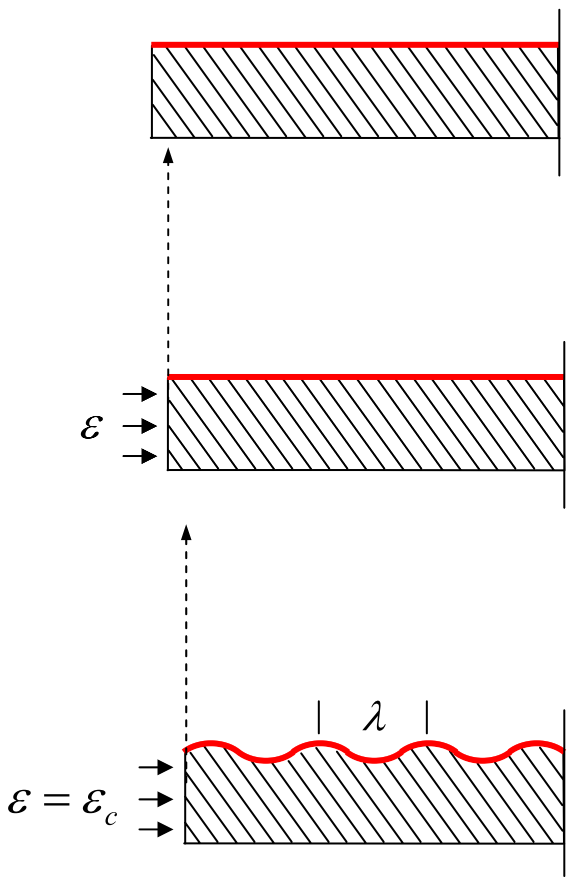
$$\lambda_e = 2\pi h_f\left(\frac{\overline{E}_f}{3\overline{E}_s}\right)^{1/3} \qquad A_e = h_f\left(\frac{\varepsilon}{\varepsilon_c} - 1\right)^{1/2}$$

where $\overline{E} = E/(1-\nu^2)$

Assumptions:

- thick substrate ($h_s \gg h_f$)
- soft substrate ($E_s \ll E_f$)
- interface must be well-bonded.
- materials behave elastically

Surface wrinkling



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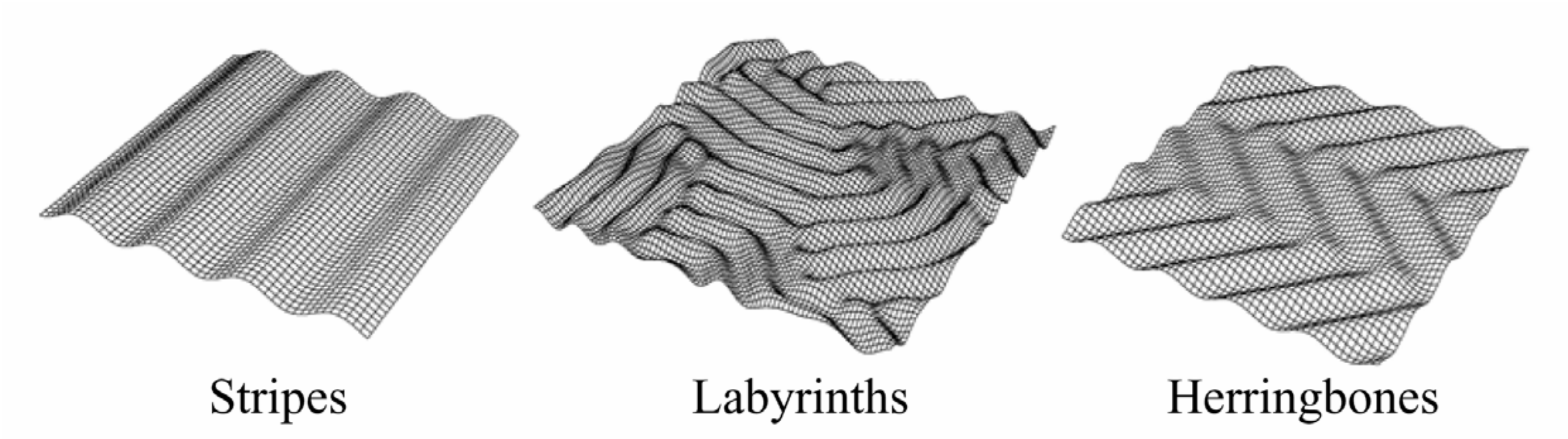
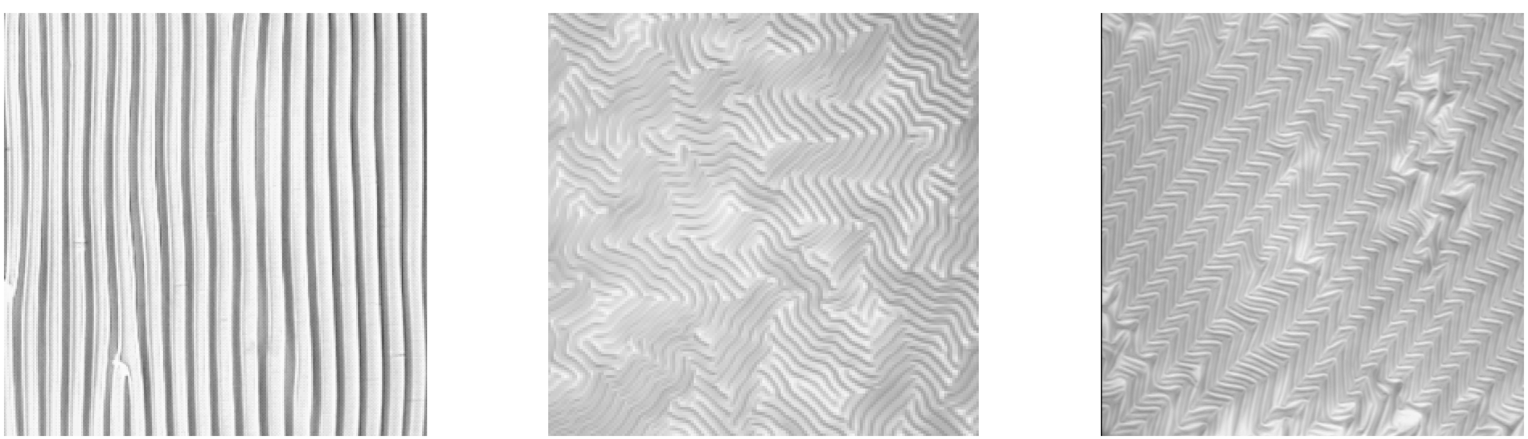
where $\bar{E} = E/(1-\nu^2)$

$$\bar{E}_f = 3\bar{E}_s \left(\frac{\lambda_e}{2\pi h_f}\right)^3$$

Surface wrinkling



Huang, Hong, and Suo, *J. Mech. Phys. Solids* **53**, 2101 (2005).



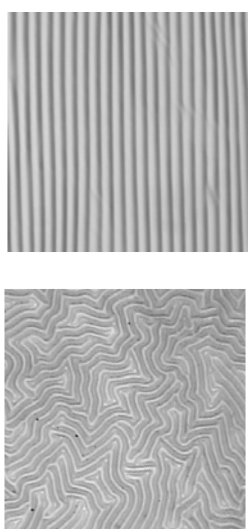
Chung and Stafford, unpublished data.

Metrology platform

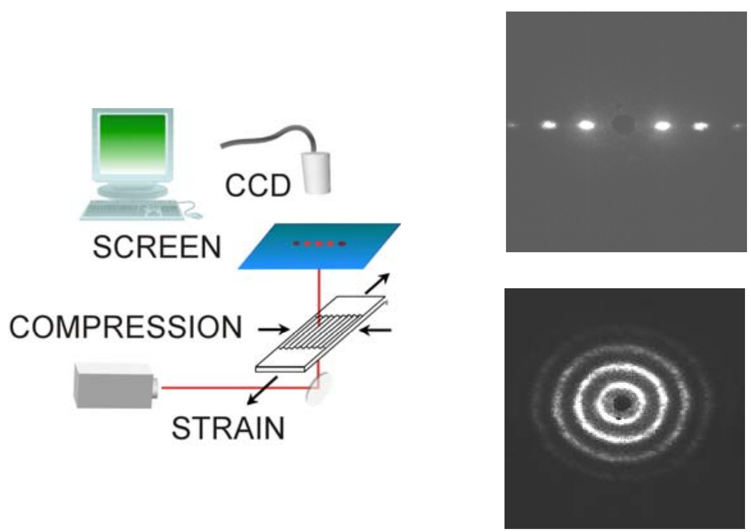
$$\overline{E}_f = 3\overline{E}_s\left(\frac{\lambda_e}{2\pi h_f}\right)^3$$

How to ascertain wavelength?

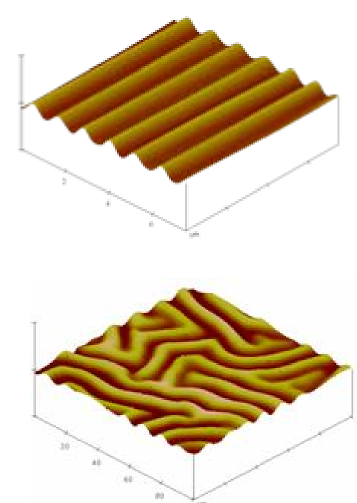
Optical microscopy



Small angle light scattering

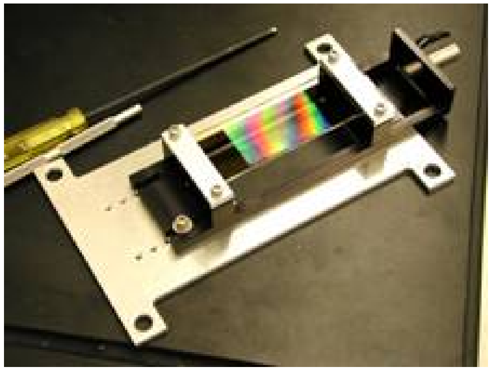


AFM



Stafford *et al. Encyclopedia of Materials: Science and Technology Online Updates* (2006).

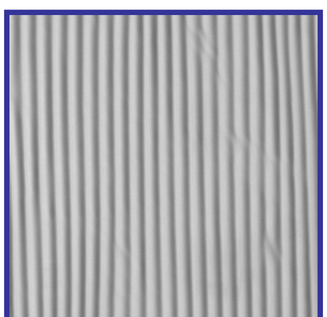
Validation



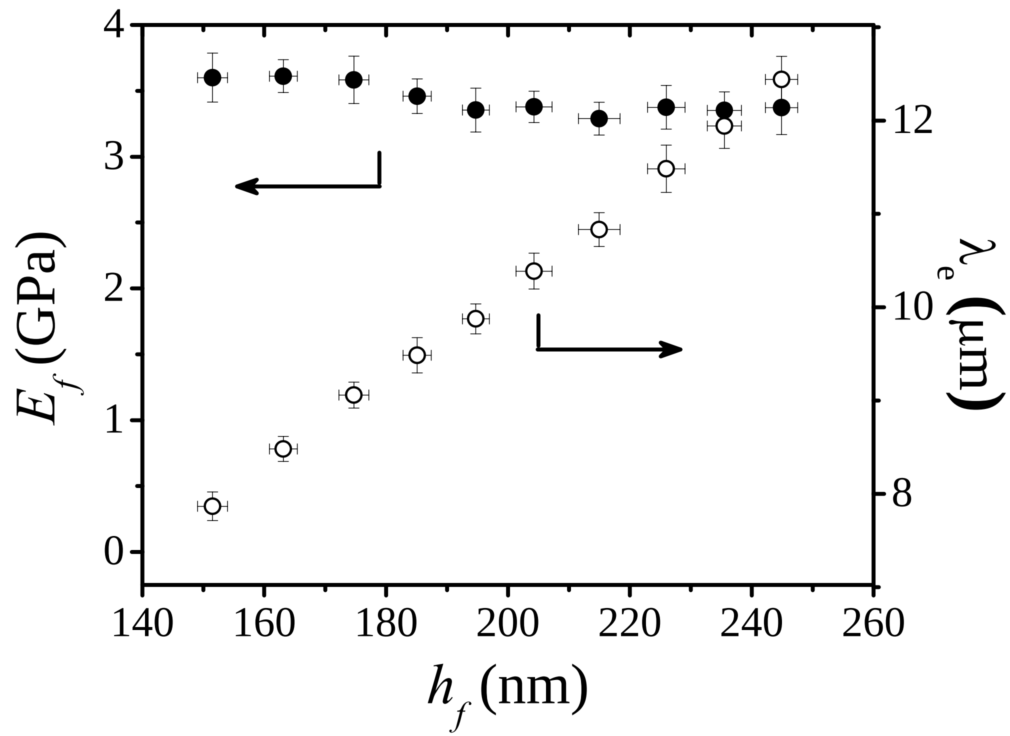
(mechanical compression)

$$\overline{E}_f = 3\overline{E}_s\left(\frac{\lambda_e}{2\pi h_f}\right)^3$$

h_f, E_s

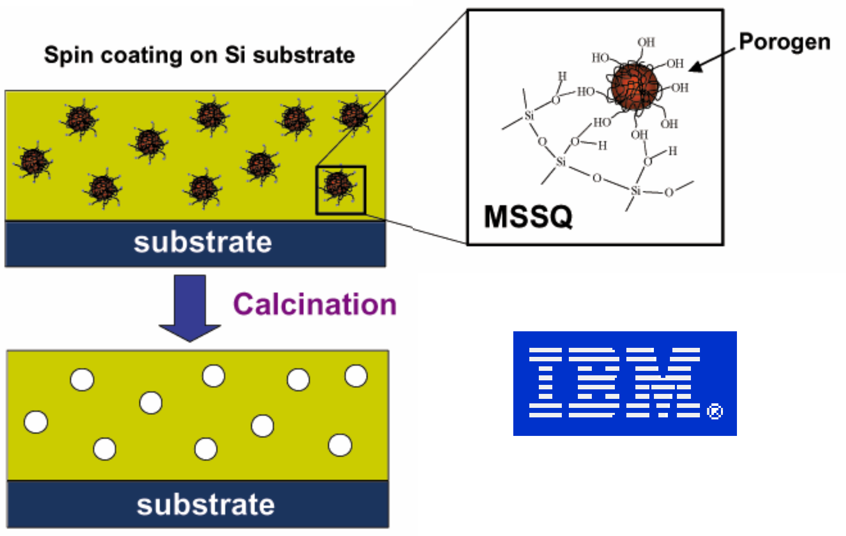


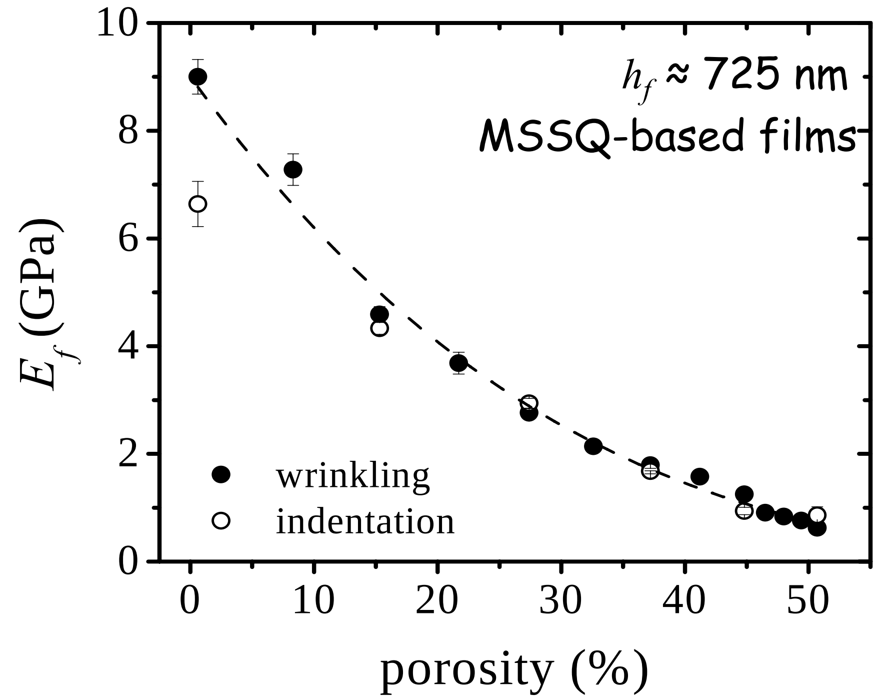
λ_e



Stafford et al. *Nat. Mater.* **3**, 545 (2004).
Stafford et al. *Rev. Sci. Instrum.* **76**, 062207 (2005).

Inorganic materials



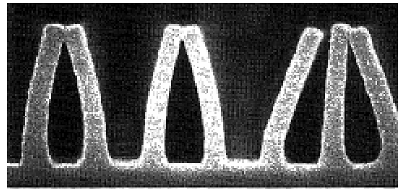


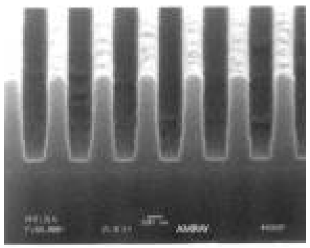
- Films cast on polished salt plates to facilitate film transfer.
- Wrinkling metrology could measure films down to 100 nm; indentation could not.
- Semiconductor industry needs $E_f > 4$ GPa to withstand CMP.

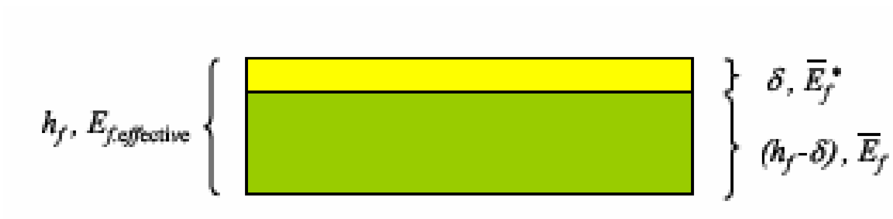
Stafford et al. *Nat. Mater.* **3**, 545 (2004).

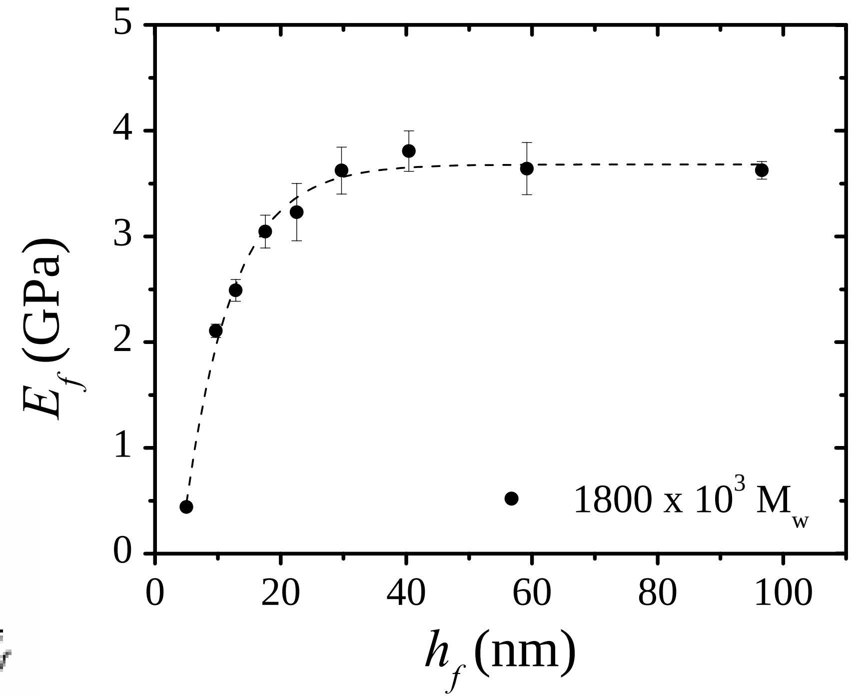
Ultrathin films

insufficient mechanical strength







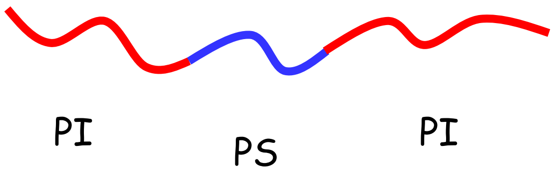


- Observe dramatic decrease in E_f below 30 nm
- Data can be explained by a surface layer (h*=2 nm) with reduced modulus (almost rubbery).

$$\lambda_e = 2\pi h_f \left(\frac{\bar{E}'_f}{3\bar{E}_s} \right)^{1/3}$$

Stafford et al. *Macromolecules* **39**, 5095-5099 (2006).
R. Huang et al. *J. Aerospace Eng.* **20**, 38-44 (2007).

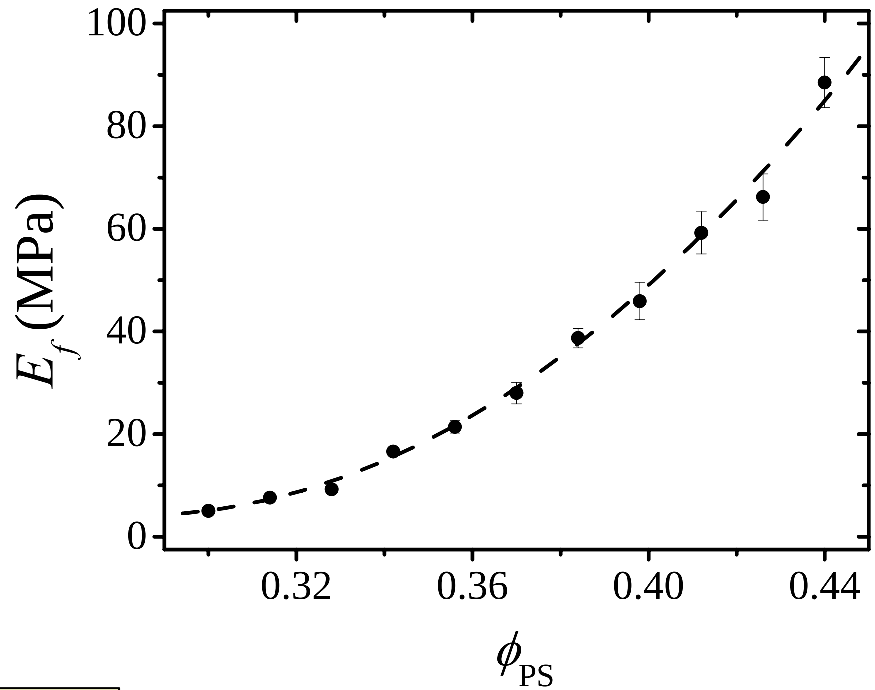
Soft materials



Sample 1 $\phi_{PS} = 0.30$

Sample 2 $\phi_{PS} = 0.44$

Solution blended prior to spin-coating.



$$\lambda_e = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

$$0.78\mu m < \lambda_e < 2.0\mu m$$
$$(h_f = 100nm)$$

$$7.8\mu m < \lambda_e < 20.0\mu m$$
$$(h_f = 1\mu m)$$

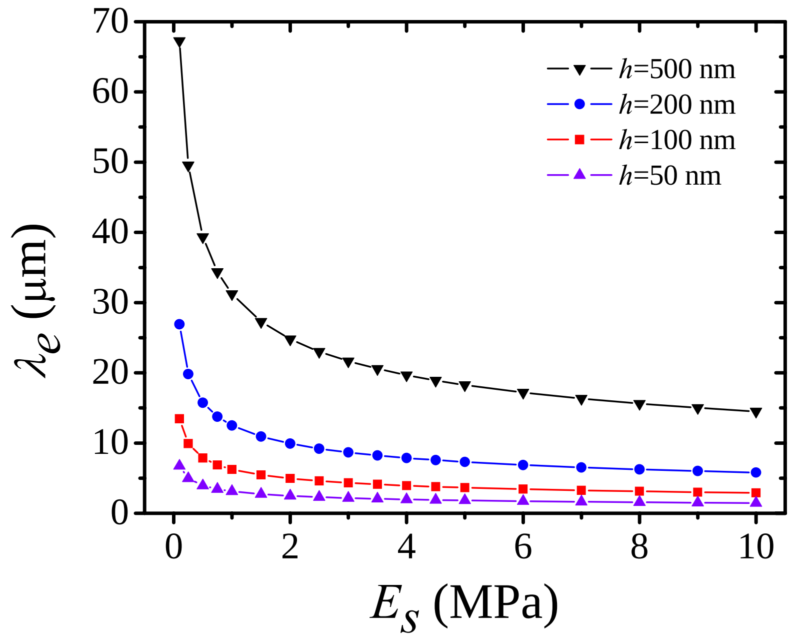
$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\overline{E}_s}{\overline{E}_f} \right)^{2/3}$$

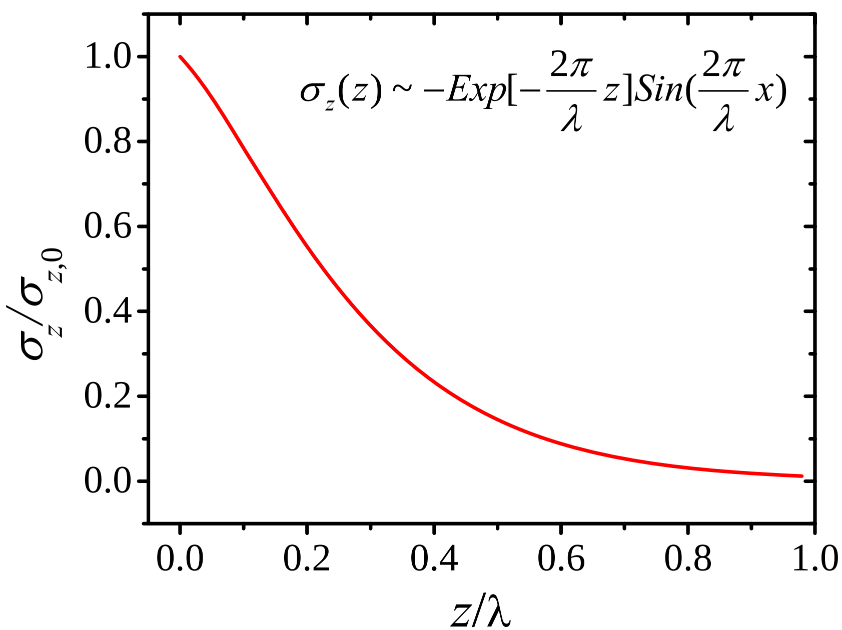
$$0.024 < \varepsilon_c < 0.179$$

Reverse metrology

Employ a 'sensor' film of known modulus and thickness to report back the substrate modulus:

$$\bar{E}_f = 3\bar{E}_s\left(\frac{\lambda_e}{2\pi h_f}\right)^3 \longrightarrow \bar{E}_s = \frac{\bar{E}_f}{3}\left(\frac{\lambda_e}{2\pi h_f}\right)^{-3}$$

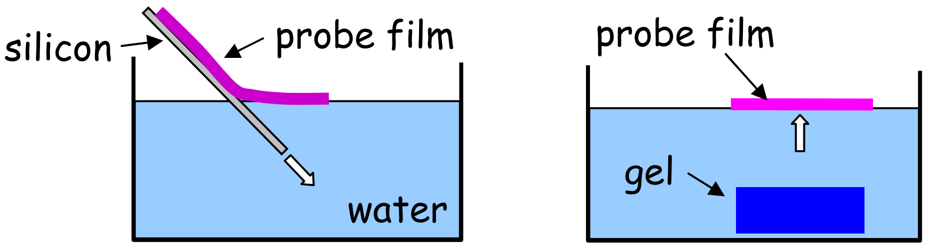


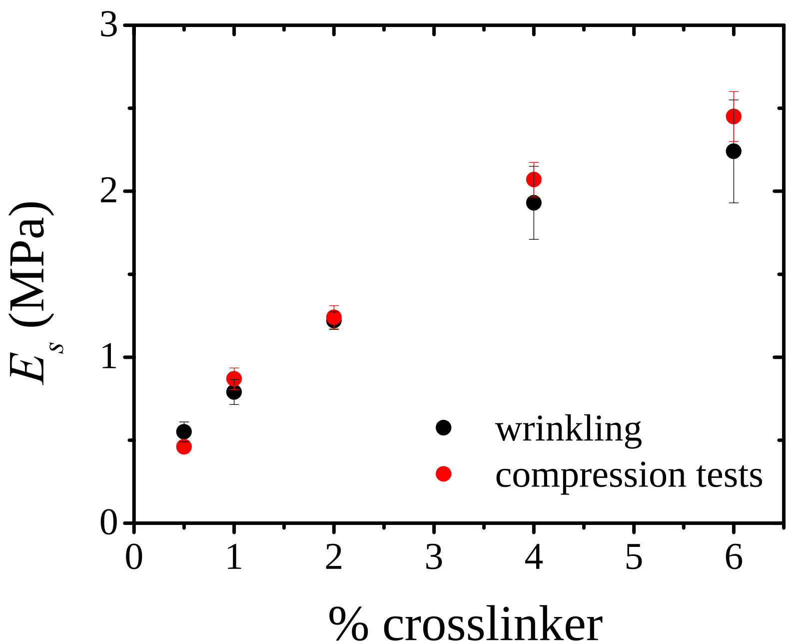


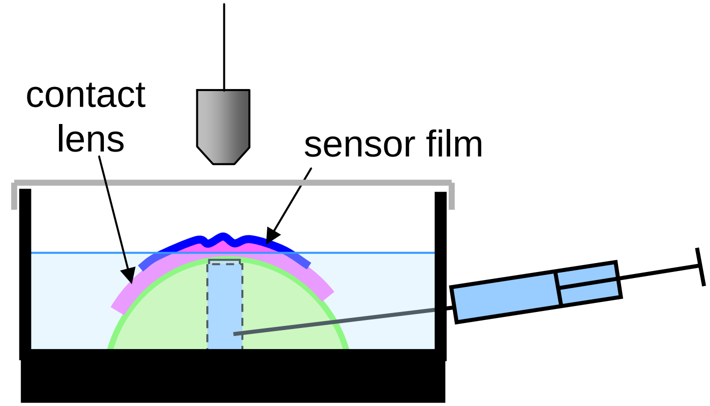
- Approach is most sensitive for Es < 2 MPa
- Thickness of sensor film is critical for measurement sensitivity

- Stress decays into the substrate on the order of a wavelength (λ_e)

Reverse metrology





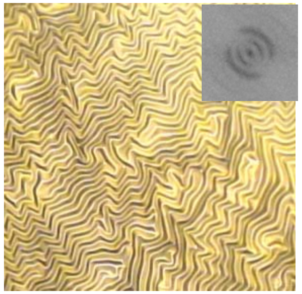


PMMA/contact lens

<u>NCMC Focus Project</u>

Surevue Etafilcon A

$$E_s = 0.41 \pm 0.02 MPa$$



Vistakon Division
of Johnson & Johnson Vision Care, Inc.

Wilder et al. *Macromolecules* **39**, 4138-4143 (2006).

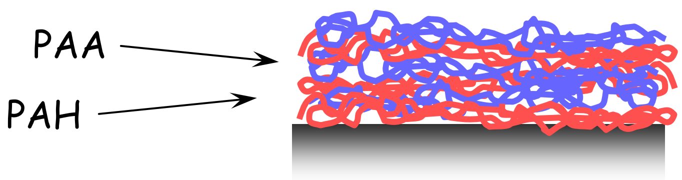
New directions

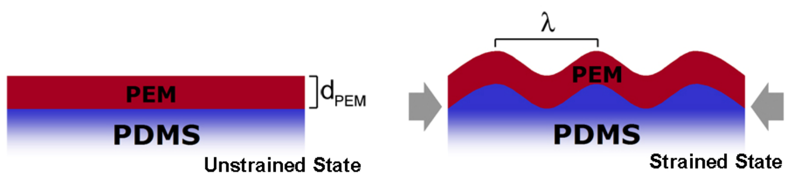
- Application to new materials
  - LbL assemblies
  - polymer brushes

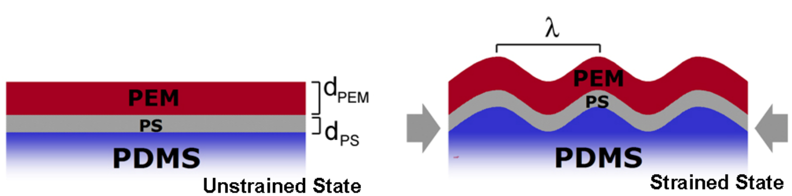
- Extend metrology to new measurements
  - critical strain
  - viscoelastic wrinkling

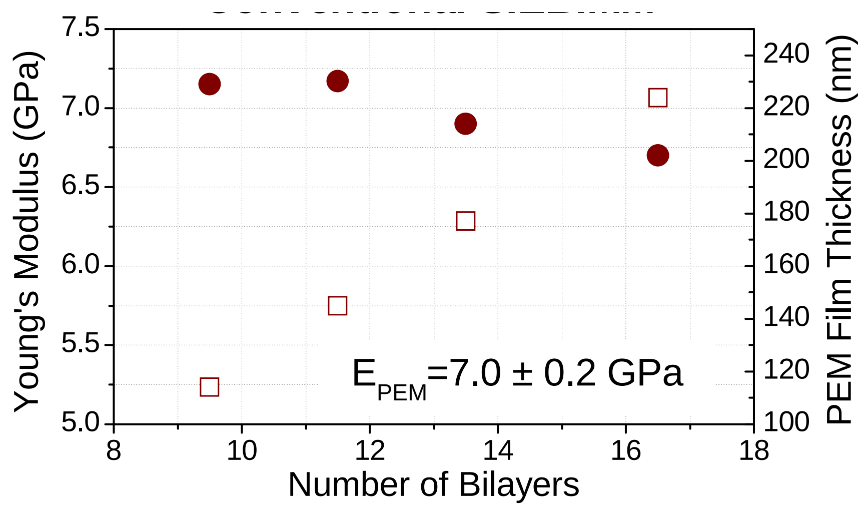
Wrinkling of PEMs

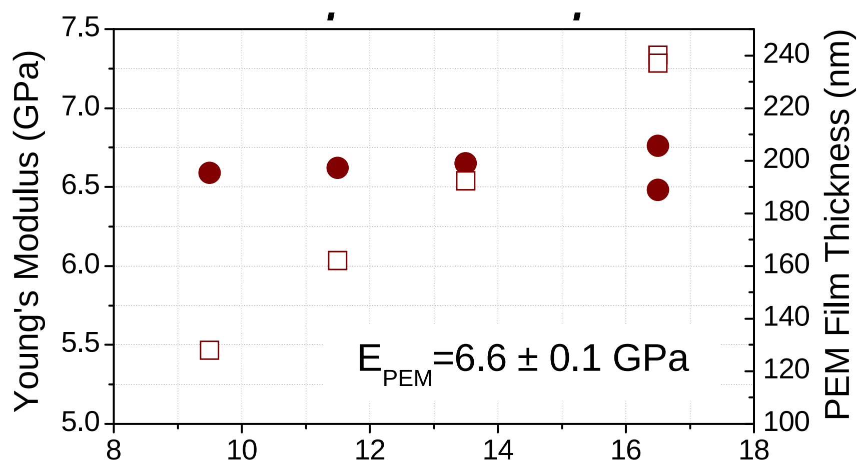
LbL assembly of polyelectrolytes directly on PDMS







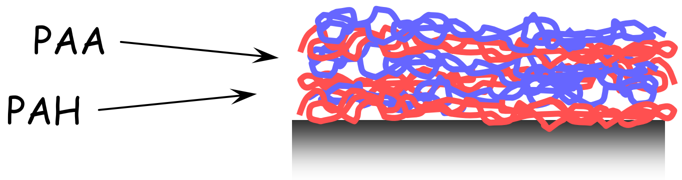


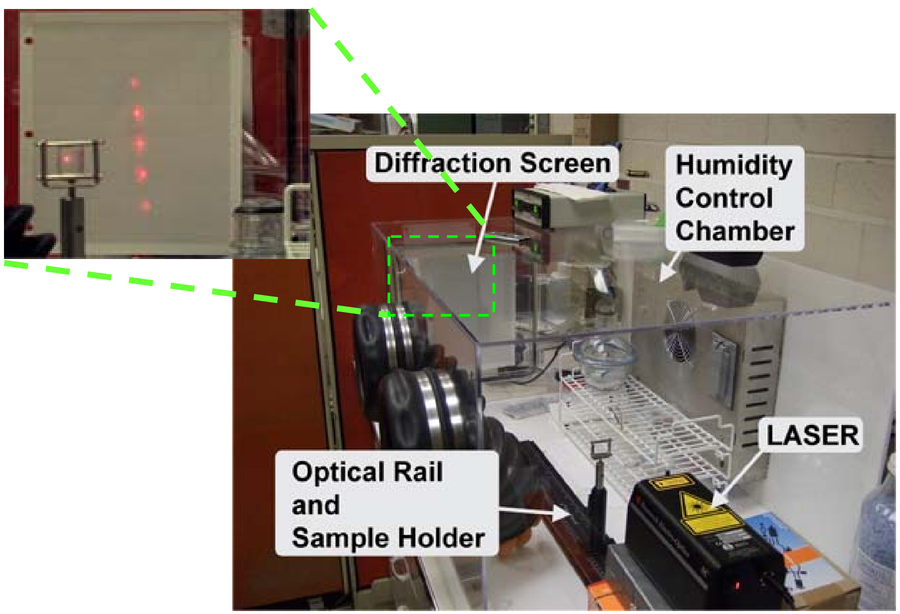


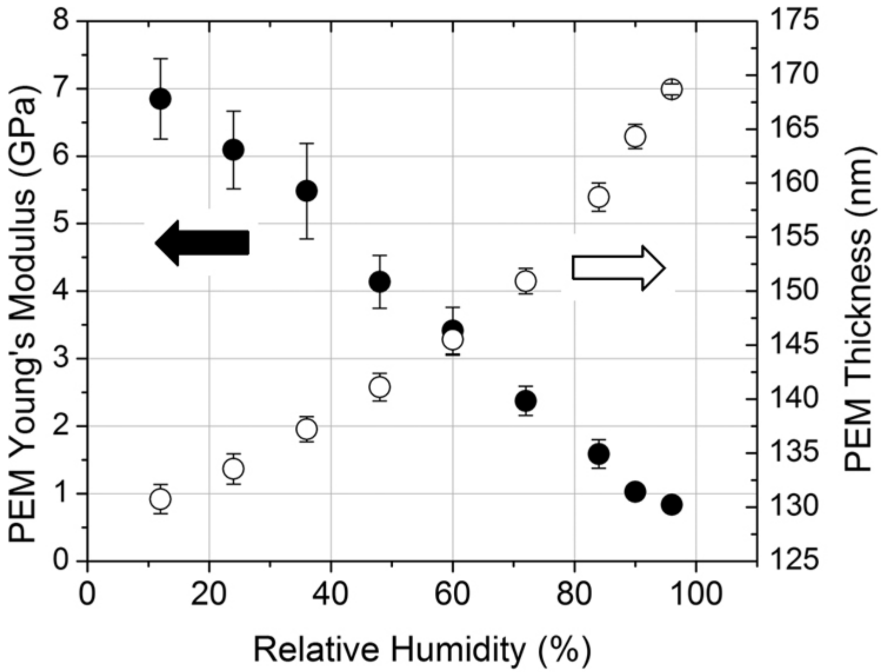
Nolte et al. *Macromolecules* **38**, 5367 (2005).
Nolte et al. *Macromolecules* **39**, 4841 (2006).

Wrinkling of PEMs

LbL assembly of polyelectrolytes directly on PDMS

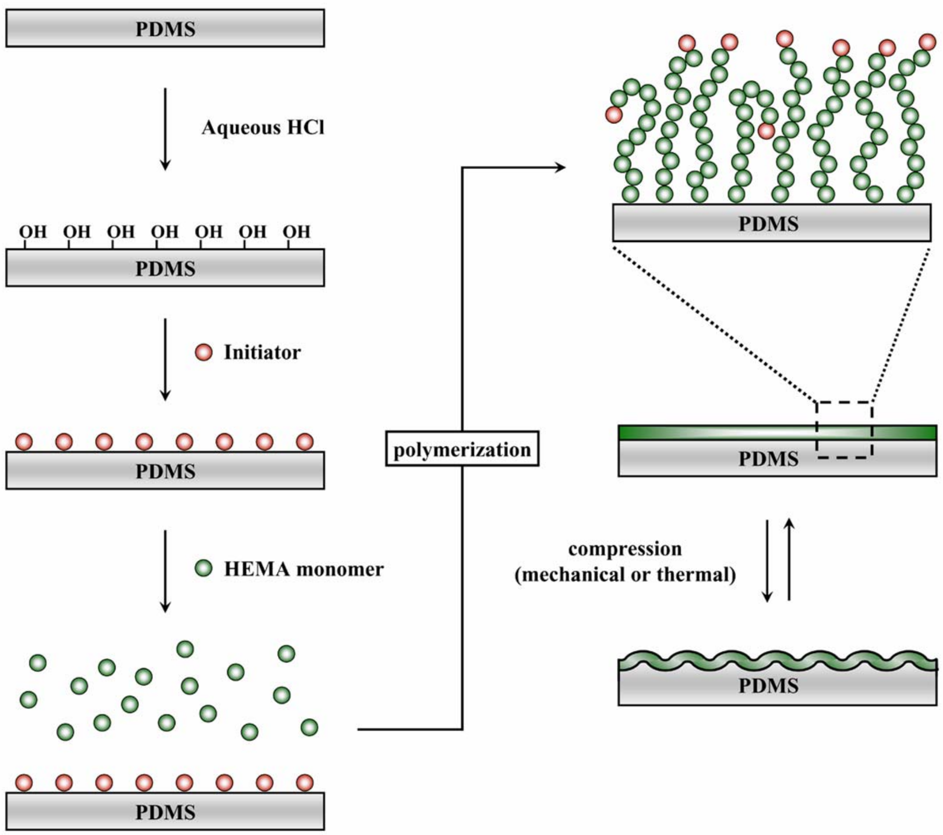


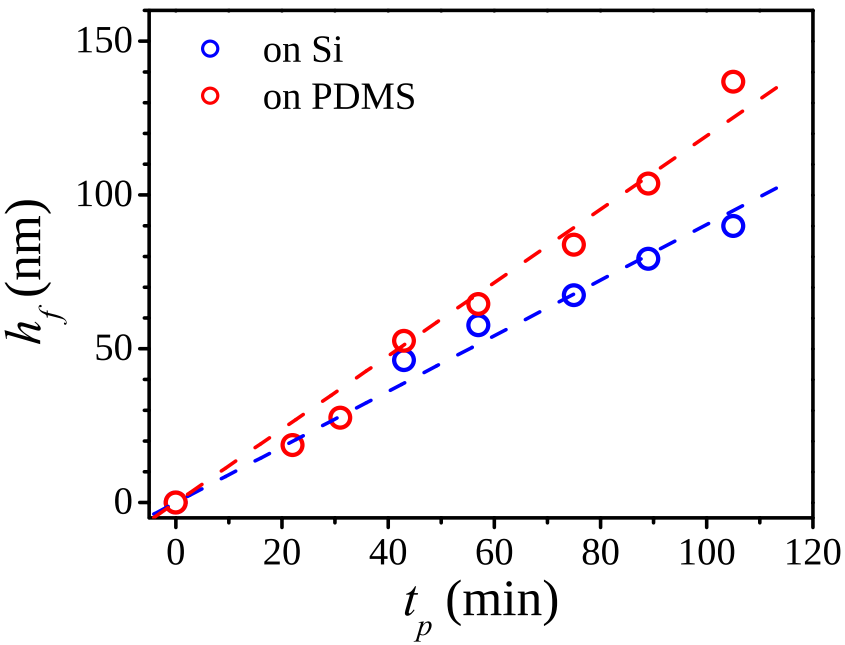




Nolte et al. *in preparation* (2007).

Wrinkling of brushes

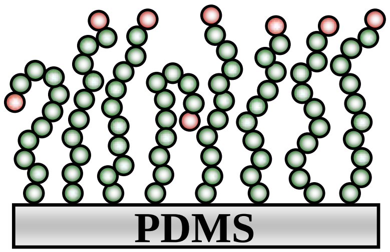




- thickness grows linearly with reaction time (t_p)
- comparable thickness on PDMS as silicon.

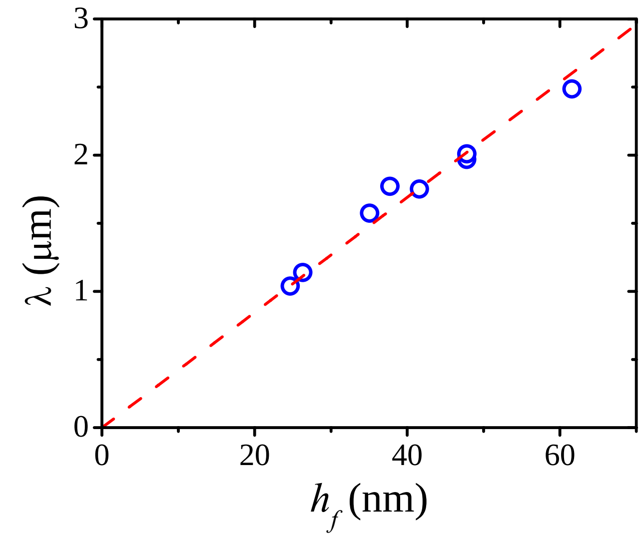
Wrinkling of brushes

Thermal wrinkling

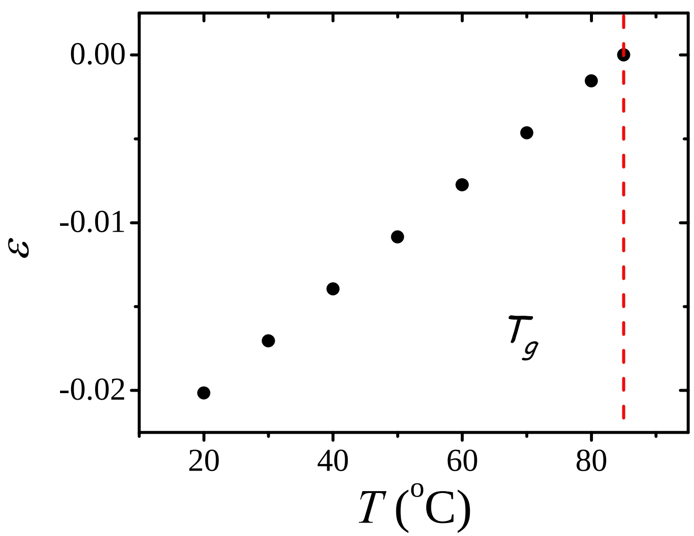


$$\lambda_e = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

Wrinkling wavelength on PDMS:

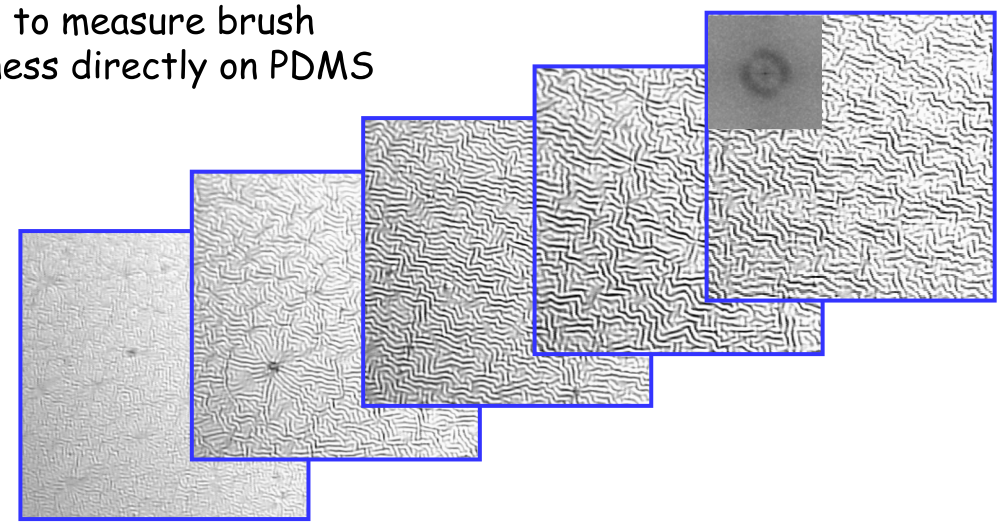


- Heat film/substrate above T_g for pHEMA (~85 °C)
- Upon cooling, compressive stress/strain is generated



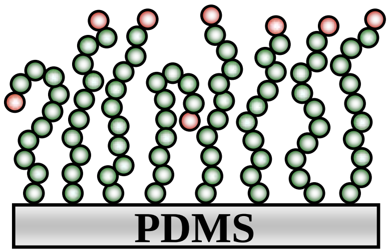
$\varepsilon_c = -0.008$ for pHEMA on PDMS

- need to measure brush thickness directly on PDMS



H. Huang et al. *in preparation* (2007).

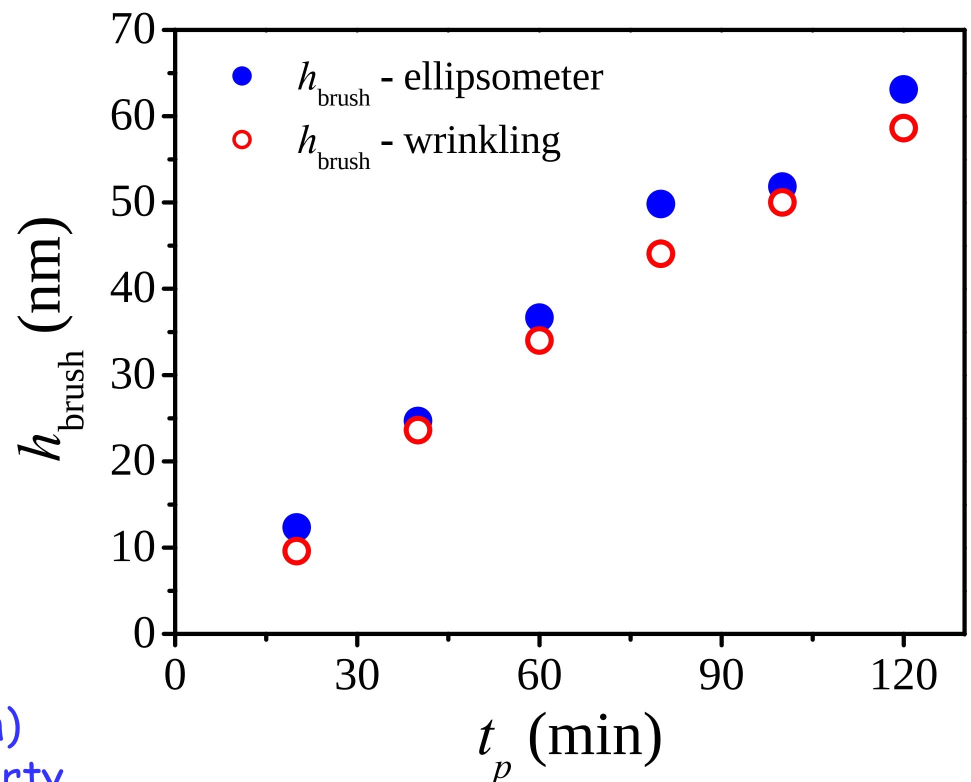
Wrinkling of brushes



$$h_f = \frac{\lambda_e}{2\pi}\left(\frac{\overline{E}_f}{3\overline{E}_s}\right)^{-1/3}$$

Measure brush thickness via wrinkling!

- assume bulk modulus
- wavelength → thickness



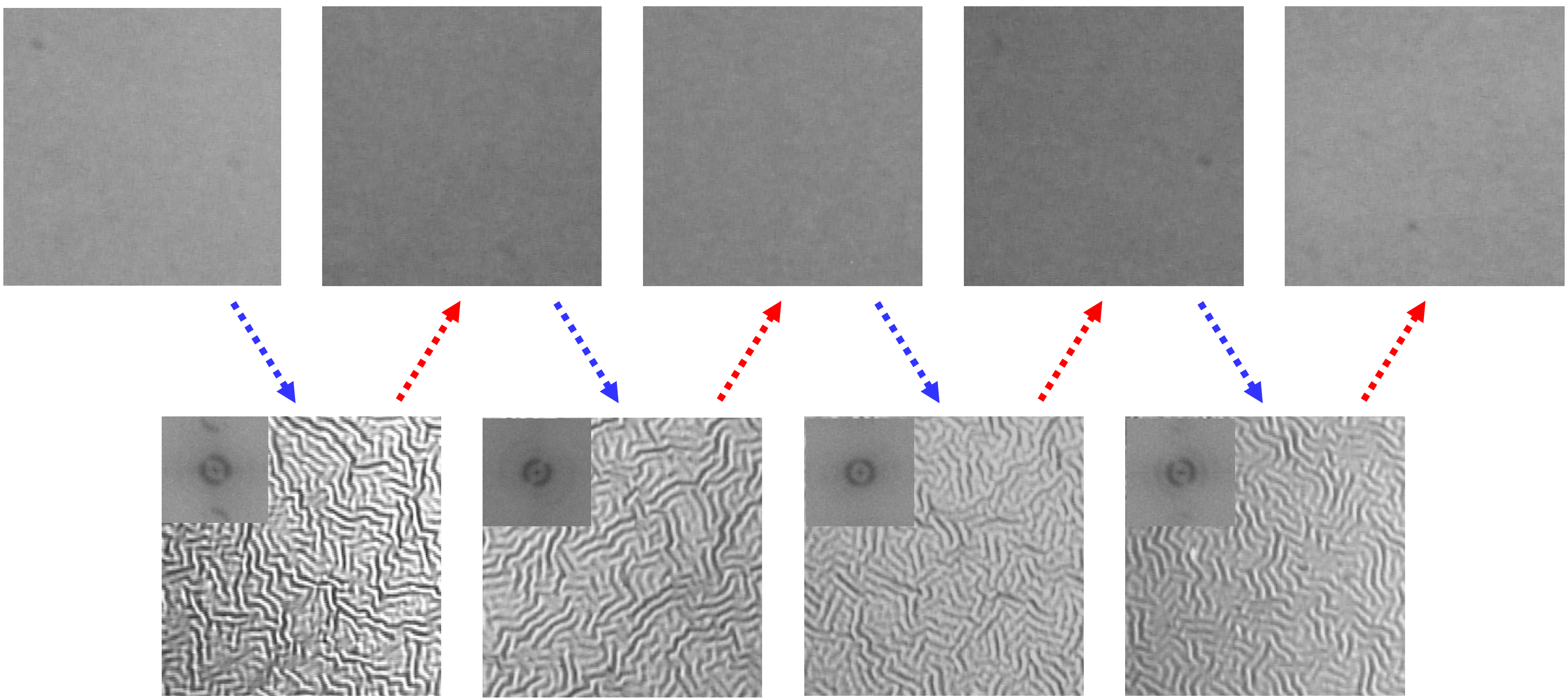
A macroscopic measurement (wavelength) can provide accurate measure of a property at the nanometer scale (thickness)

H. Huang et al. *in preparation* (2007).

Reversibility in wrinkled brushes

Heating/cooling cycle

Rinse with solvent (DMF/methanol)



λ = 1.78 ± 0.19 mm λ = 1.92 ± 0.10 mm λ = 1.89 ± 0.14 mm λ = 1.88 ± 0.06 mm

Critical strain

$$\lambda_e = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

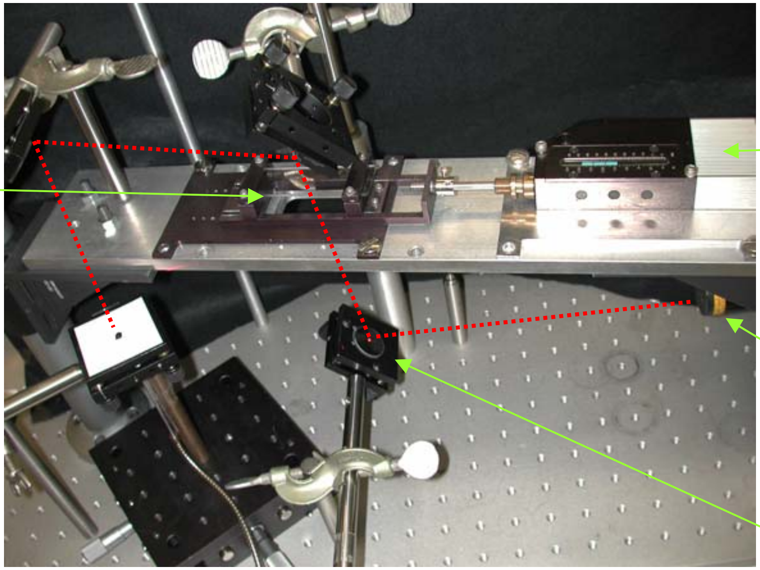
- thickness dependence (linear)
- modulus ratio to the 1/3

$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\overline{E}_s}{\overline{E}_f} \right)^{2/3}$$

- no thickness dependence
- modulus ratio to the 2/3

o One way to detect critical strain (ε_c) is through OM or LS….

sample



custom-built strain stage

laser

mirror

Measure the scattered intensity as a function of compressive strain.

Critical strain - LS

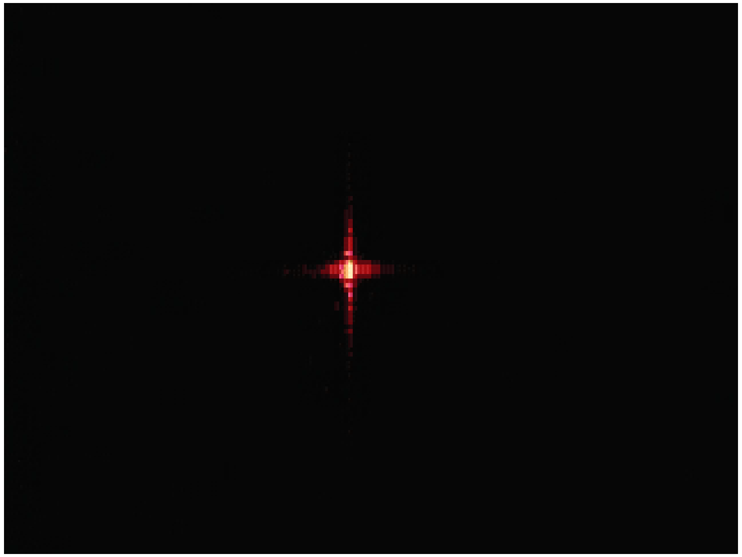
$$\lambda_e = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

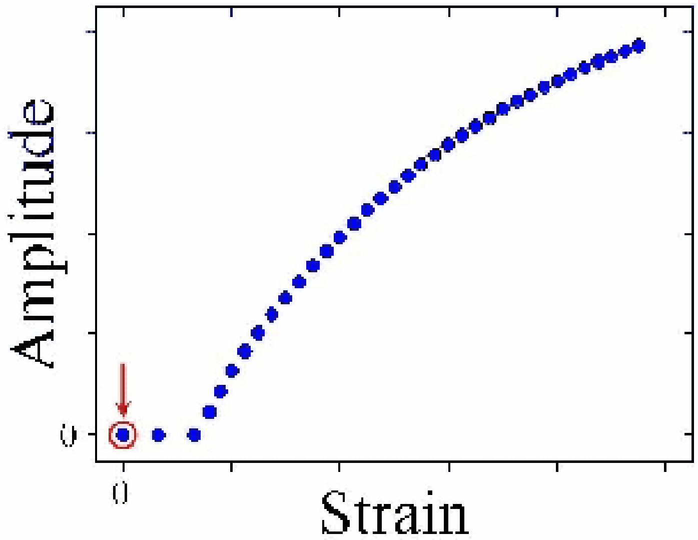
- thickness dependence (linear)
- modulus ratio to the 1/3

$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\overline{E}_s}{\overline{E}_f} \right)^{2/3}$$

- no thickness dependence
- modulus ratio to the 2/3

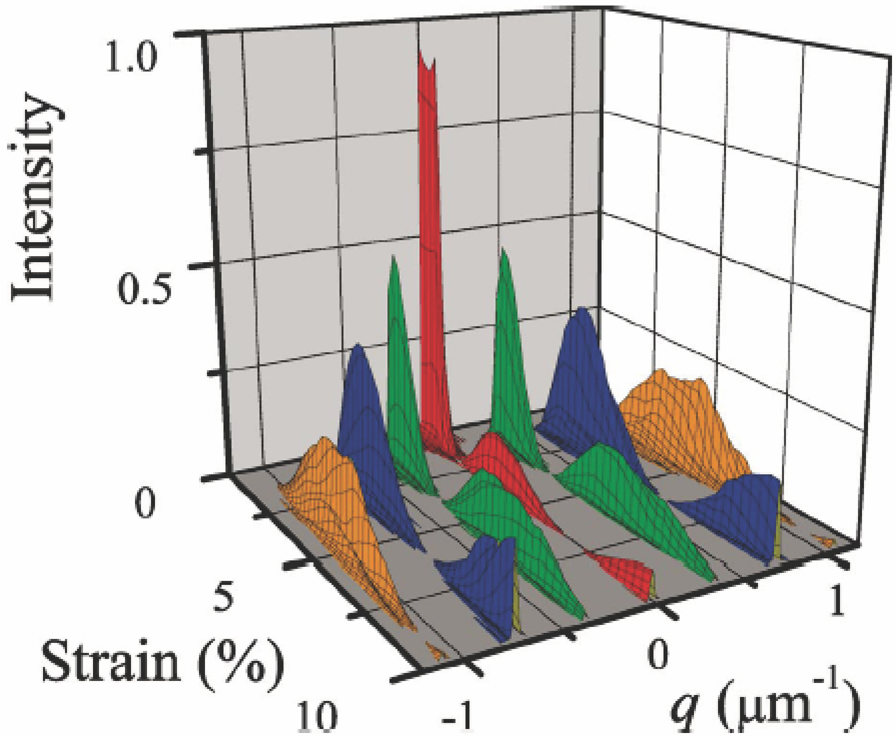
o One way to detect critical strain (ε_c) is through OM or LS….





Stafford, *et al. Encyclopedia of Materials: Science and Technology Online Updates* (2006).

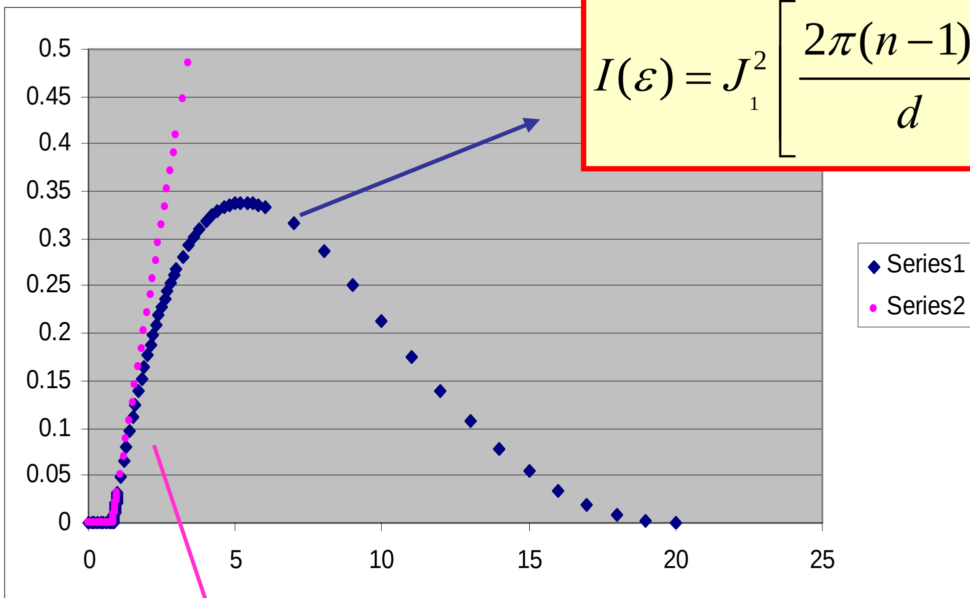
Critical strain



$$I[q] \approx \sum_{p=-\infty}^{\infty} J_p^2\left(\frac{m}{2}\right)\operatorname{sinc}^2\left[\frac{W}{\pi}\left(q-\frac{2p\pi}{d}\right)\right],$$

Harrison et al. *Appl. Phys. Lett.* **85**, 4016 (2004).

Critical strain



$$I(\varepsilon)=J_1^2\left[\frac{2\pi(n-1)h_f}{d}\left(\frac{\varepsilon}{\varepsilon_c}-1\right)^{1/2}\right]$$

$$\left\{\begin{aligned}\lambda &= 2\pi h_f\left(\frac{\overline{E}_f}{3\overline{E}_s}\right)^{1/3}\\ \varepsilon_c &= -\frac{1}{4}\left(\frac{3\overline{E}_s}{\overline{E}_f}\right)^{2/3}\\ A &= h_f\left(\frac{\varepsilon}{\varepsilon_c}-1\right)^{1/2}\end{aligned}\right.$$

$$I(\varepsilon)=\left(\frac{\pi(n-1)h_f}{d}\right)^2\left(\frac{\varepsilon}{\varepsilon_c}-1\right)$$

For small argument, $0 < x << \sqrt{2}, \quad J_1(x)\rightarrow x/2$

The intensity of the first order diffracted beam follows the linear dependence on the applied strain when $\varepsilon < 1.25\varepsilon_c$.

Critical strain

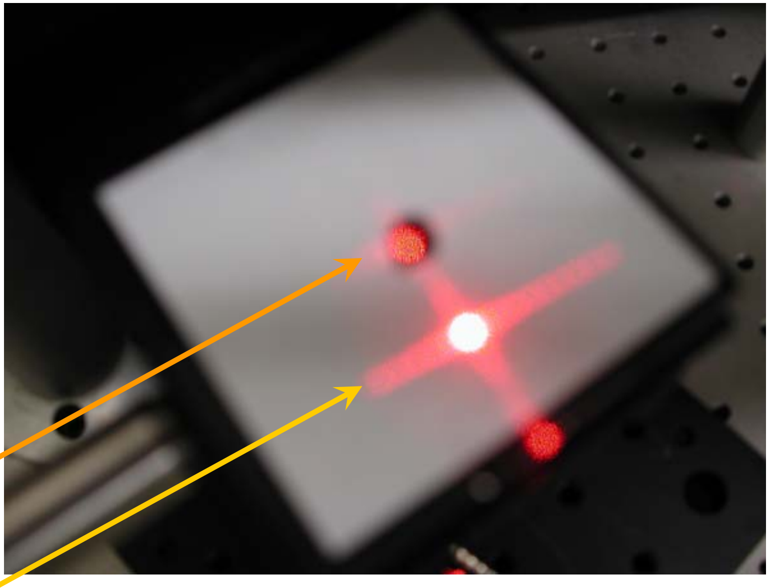
$$\lambda_e = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

- thickness dependence (linear)
- modulus ratio to the 1/3

$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\overline{E}_s}{\overline{E}_f} \right)^{2/3}$$

- no thickness dependence
- modulus ratio to the 2/3

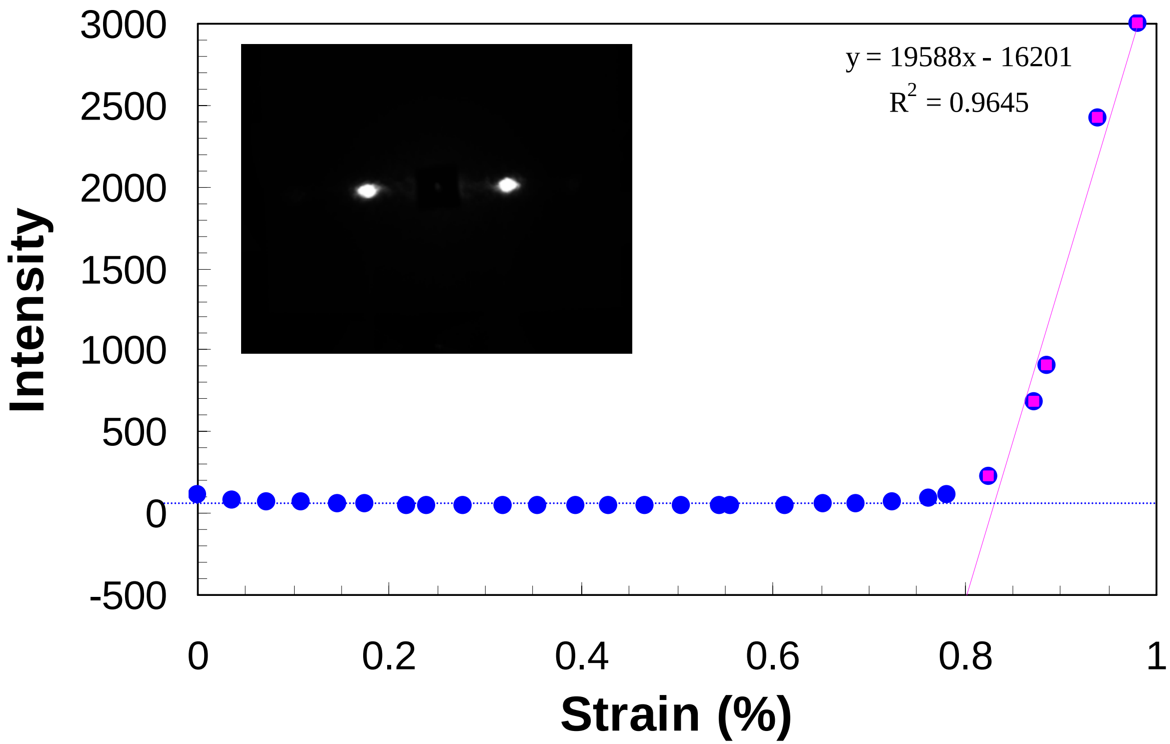
o One way to detect critical strain (ε_c) is through OM or LS....



1st order diffraction spot

wavenumber (~wavelength)

Critical strain – PS/PDMS



$h \sim 197$ nm

$\lambda \sim 9.4\ \mu$m (measured)

$$\lambda = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

$E_f \sim 3.1$ GPa (calculated)

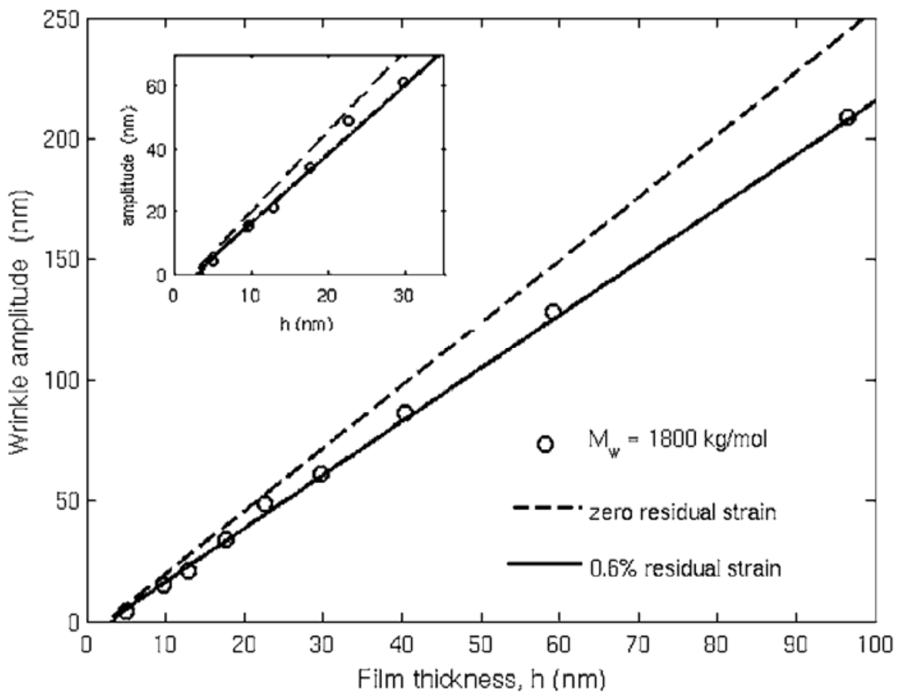
$$\varepsilon_c = -\frac{1}{4}\left(\frac{3\overline{E}_s}{\overline{E}_f} \right)^{2/3}$$

Residual strain (or stress) ?

$\varepsilon_c \sim 0.44\%$ (calculated)

$\varepsilon_c \sim 0.83\%$ (measured)

Critical strain



$$A = h_f \sqrt{\frac{\varepsilon + \eta}{\varepsilon_c + \eta} - 1}$$

η is a residual surface strain

$h \sim 197$ nm

$\lambda \sim 9.4\ \mu$m (measured)

$$\lambda = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3}$$

$E_f \sim 3.1$ GPa (calculated)

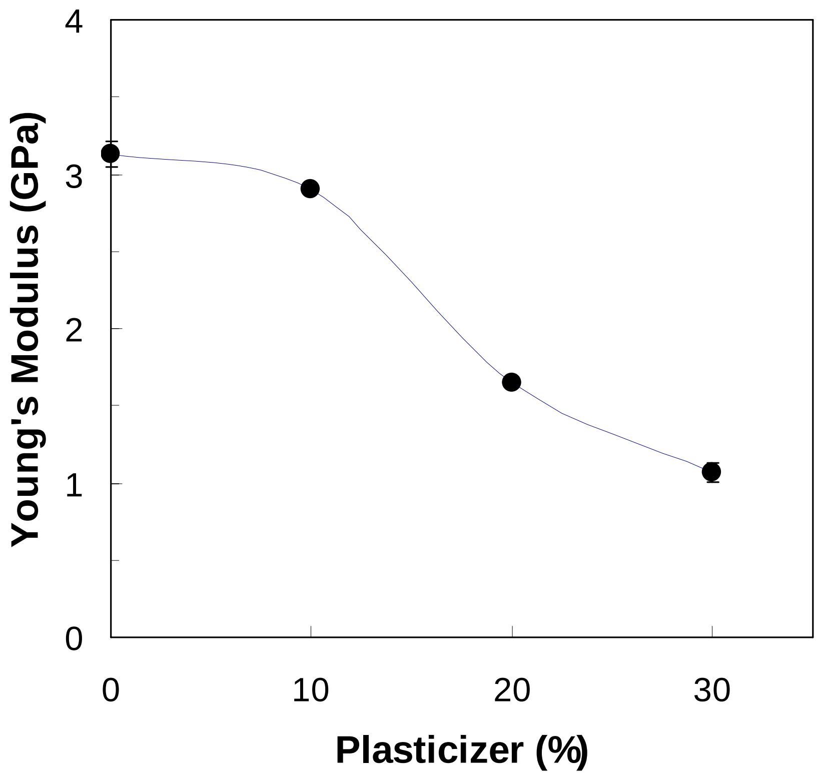
$$\varepsilon_c = -\frac{1}{4} \left(\frac{3\overline{E}_s}{\overline{E}_f} \right)^{2/3}$$

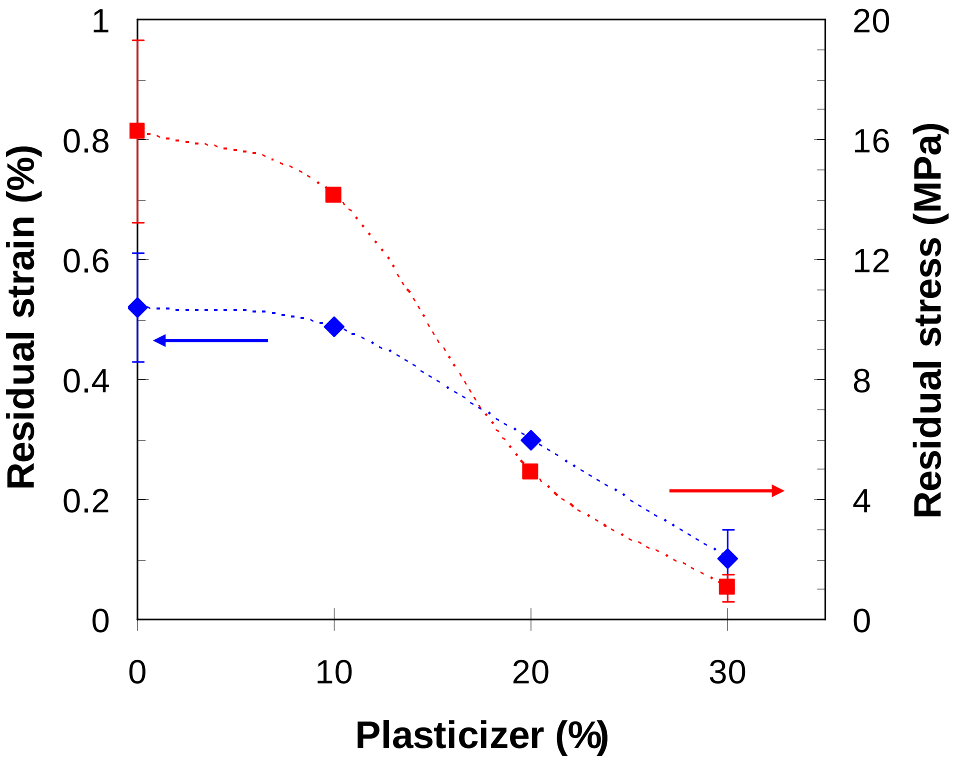
$\varepsilon_c \sim 0.44\%$ (calculated)

$\varepsilon_c \sim 0.83\%$ (measured)

R. Huang et al. *J. Aero. Eng.* **20**, 38 (2007).

Critical strain - pPS/PDMS





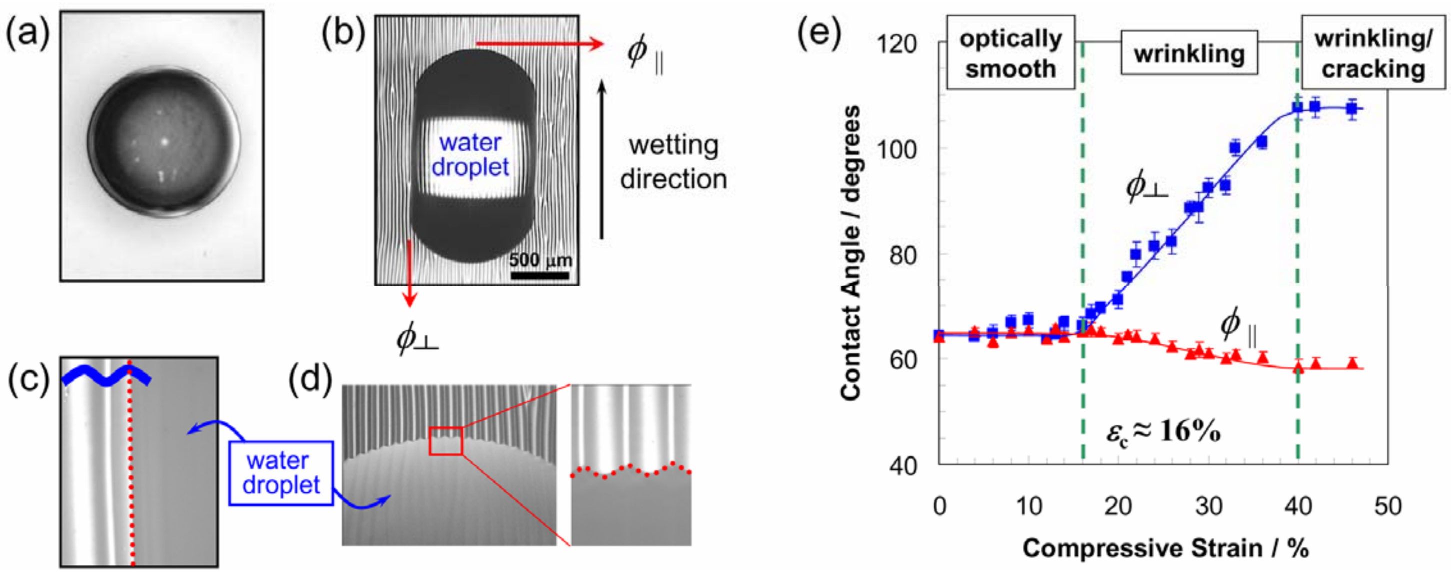
* Moduli were determined using the wrinkling wavelength

** Residual strains were determined by taking the difference between the measured and calculated critical strains.

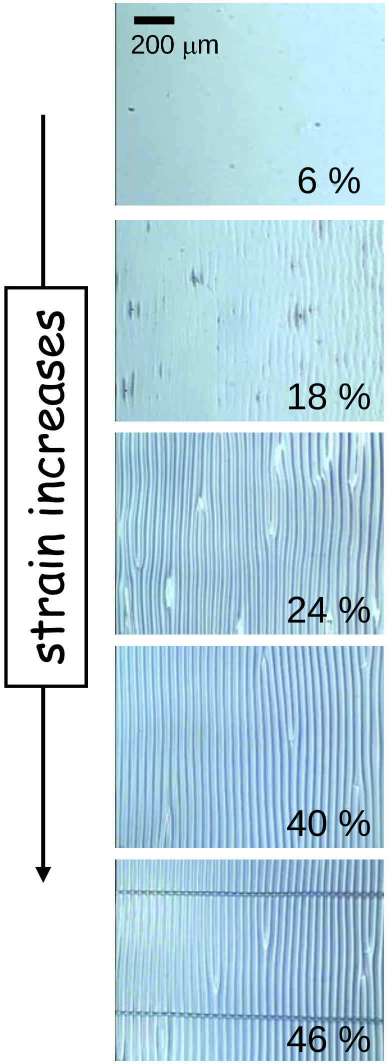
Future Plans → ***Critical strain/stress vs Film annealing time***

Critical strain - wettability

- Another way is through wettabilitiy



$$\frac{A}{\lambda} \propto \varepsilon^{1/2}$$



UVO / PDMS

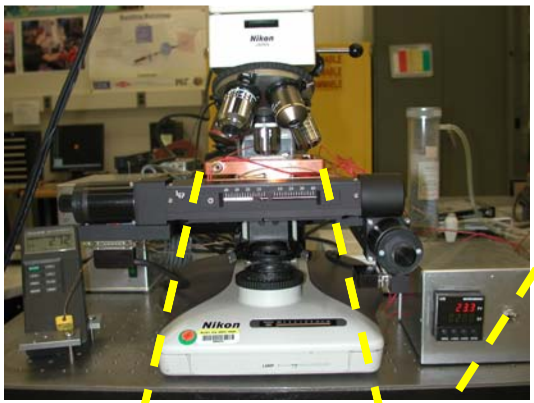
Chung et al. *Soft Matter* accepted (2007).

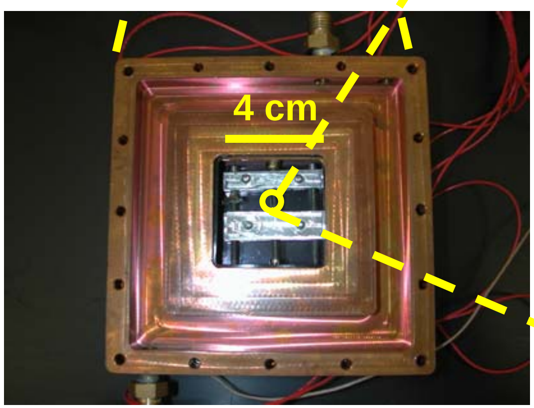
Thermal wrinkling

Access to temperature dependent properties

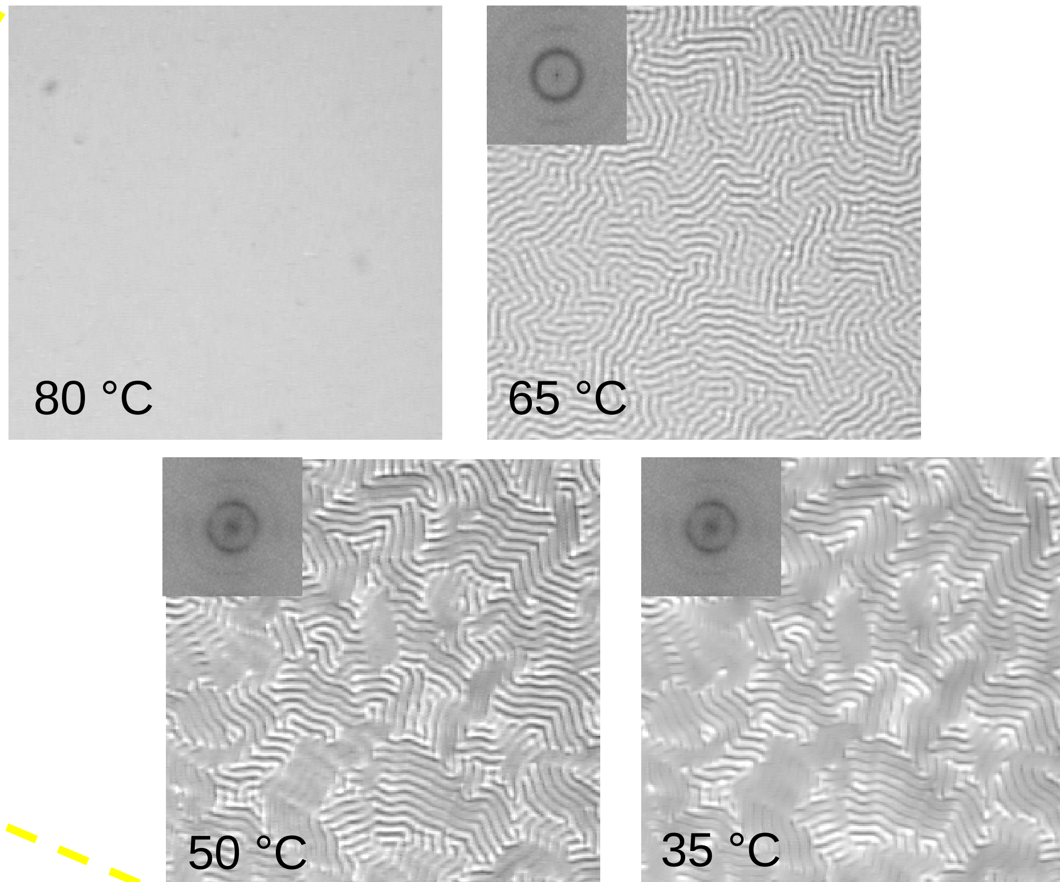
PS Film / PDMS

$$\bar{E}_f(T) = 3\bar{E}_s\left(\frac{\lambda(T)}{2\pi h_f}\right)^3$$





Miniaturized strain stage in a temperature controlled chamber

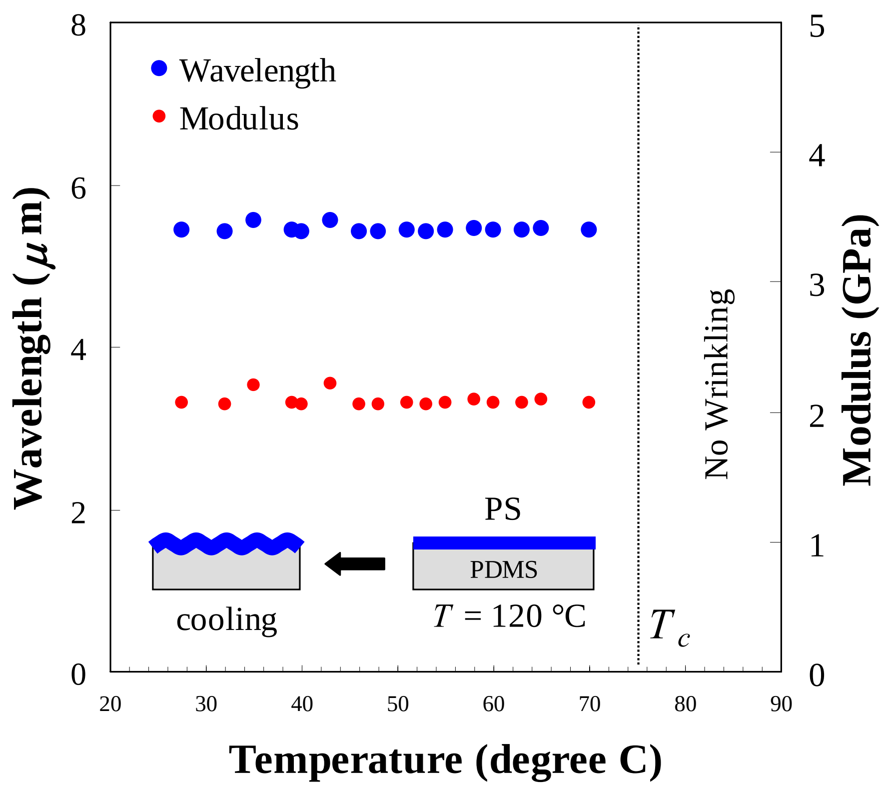


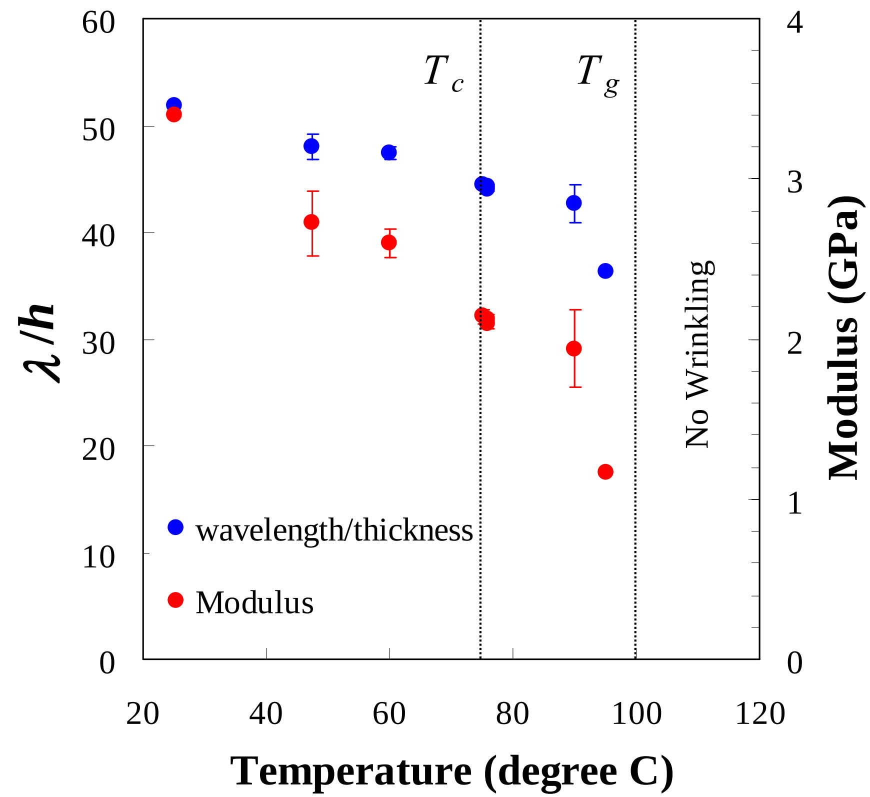
Chung and Stafford, unpublished data

Thermal wrinkling

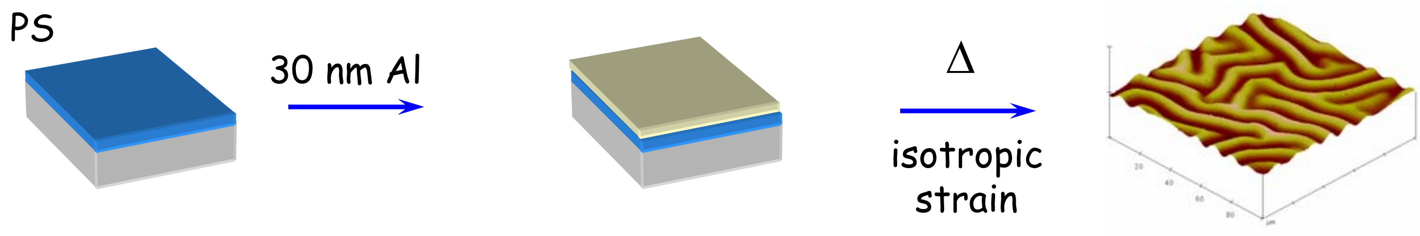
Access to temperature dependent properties

PS Film / PDMS

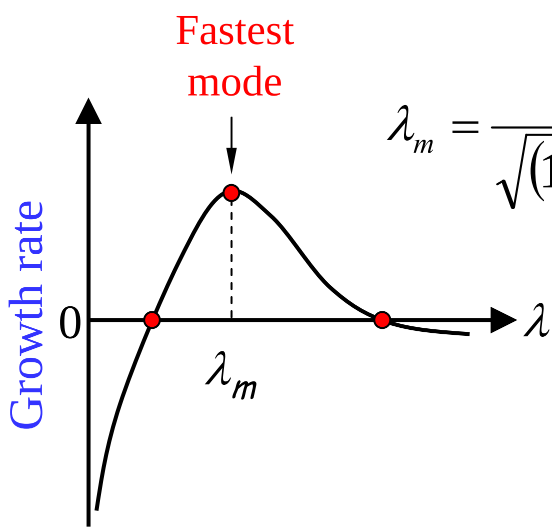




Viscoelastic wrinkling



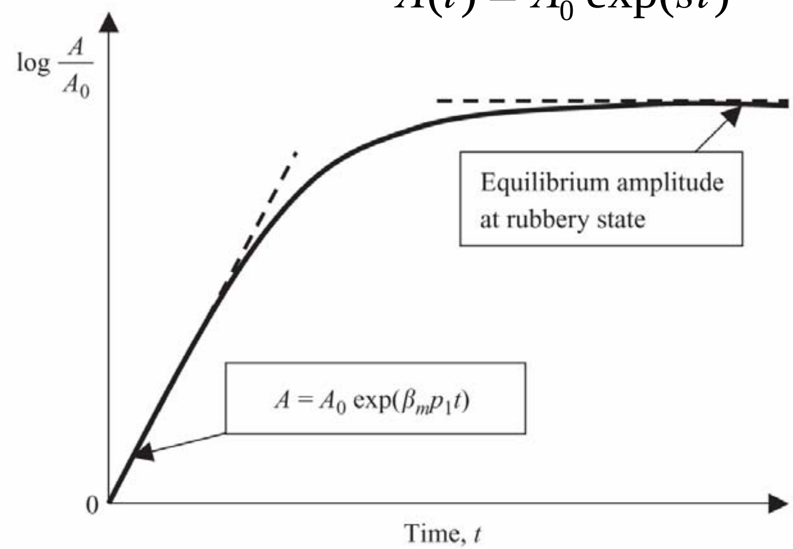
The wavelength of the instability is initially selected by the magnitude of the compressive strain and the thickness of the Al layer.



$$\lambda_m = \frac{\pi h_f}{\sqrt{(1+\nu)|\varepsilon|}}$$

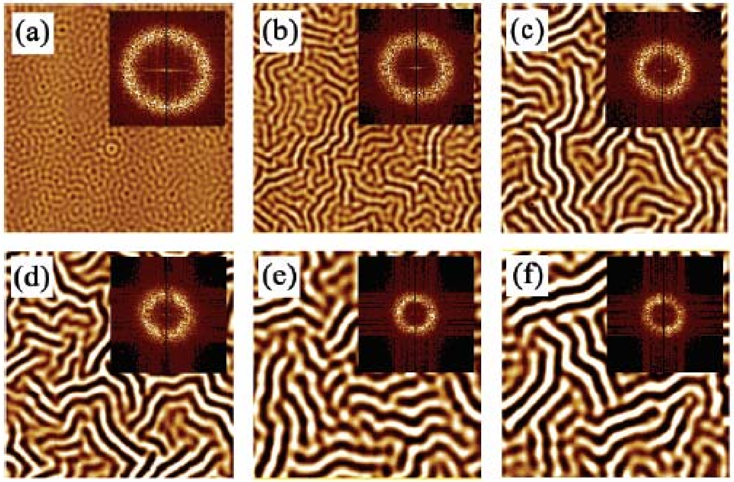
The amplitude of the instability grows exponentially with time until it saturates at the rubber state.

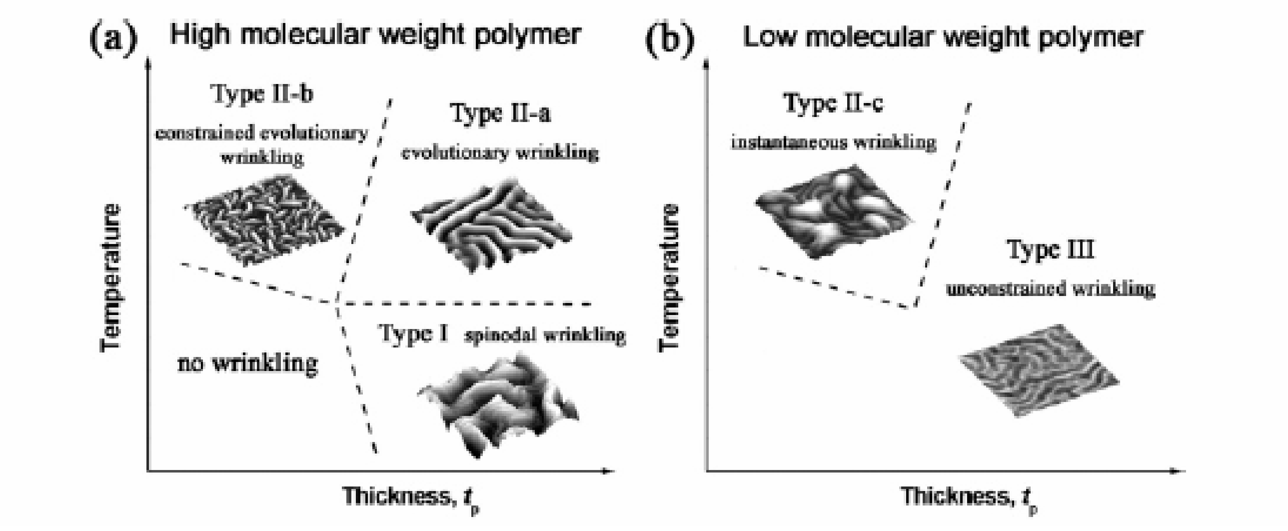
$$A(t) = A_0 \exp(st)$$



R. Huang, J. Mech. Phys. Solids **53**, 63-69 (2005).

Thermal (viscoelastic) wrinkling

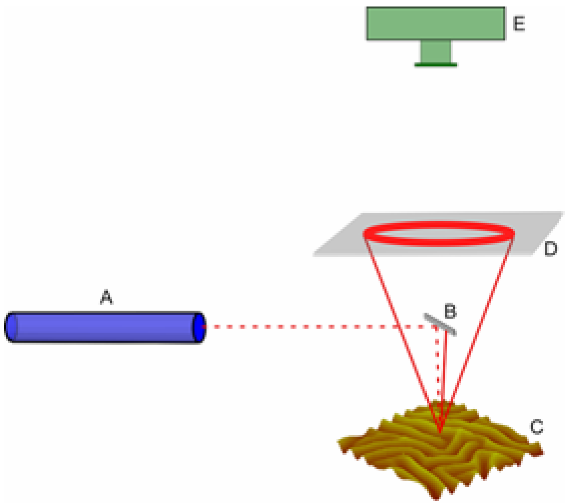




Yoo P.J. and Lee, H. H.Macromolecules **2005**, *38*, 2820-2831

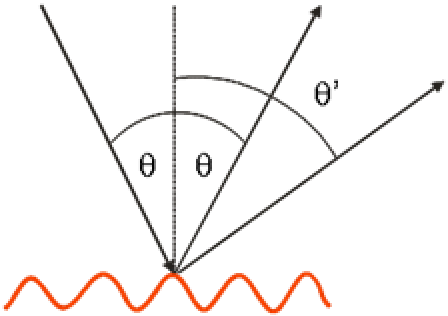
Thermal (viscoelastic) wrinkling

Scattering Set-up

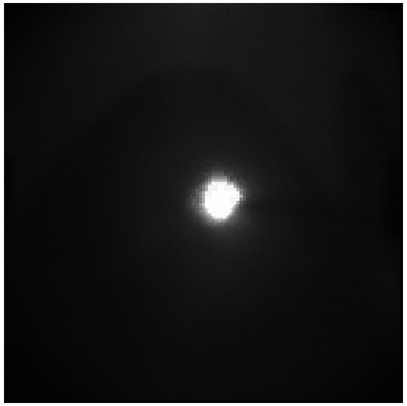


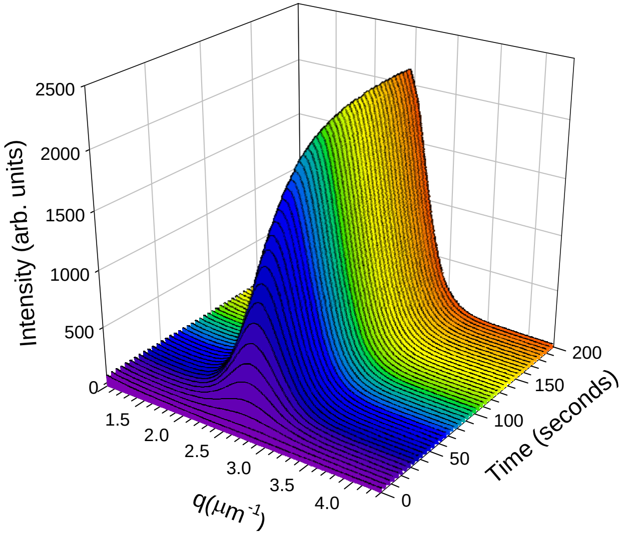
Scattering From Surface Grating

$$n\lambda = d\left(\sin[\theta] \pm \sin[\theta']\right)$$

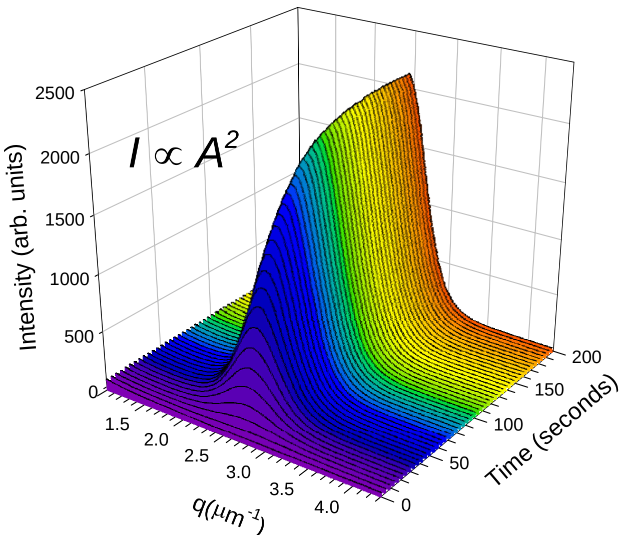


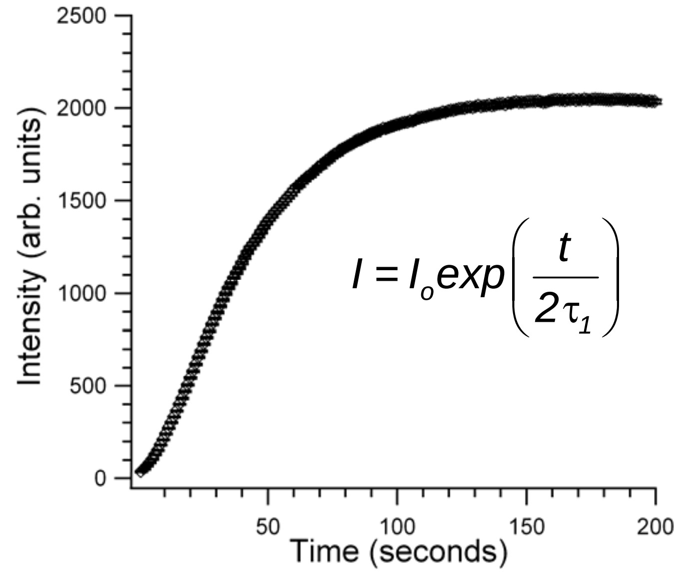
Real-time Scattering

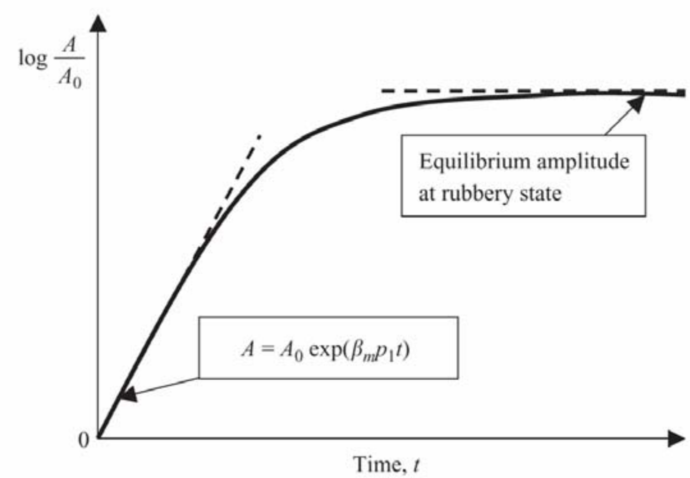




Real-Time Surface Scattering



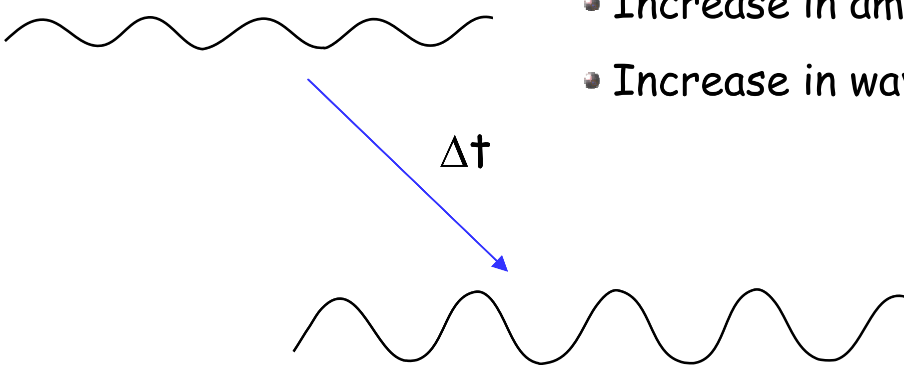




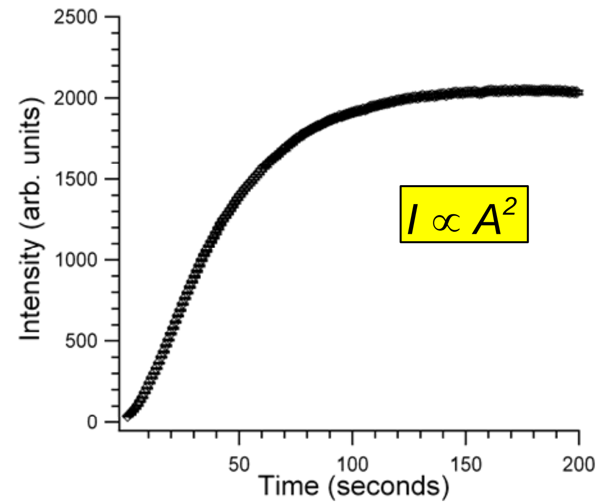
- Scattering data is easily reduced
- Exponential growth of intensity with time
- Excellent agreement with theory

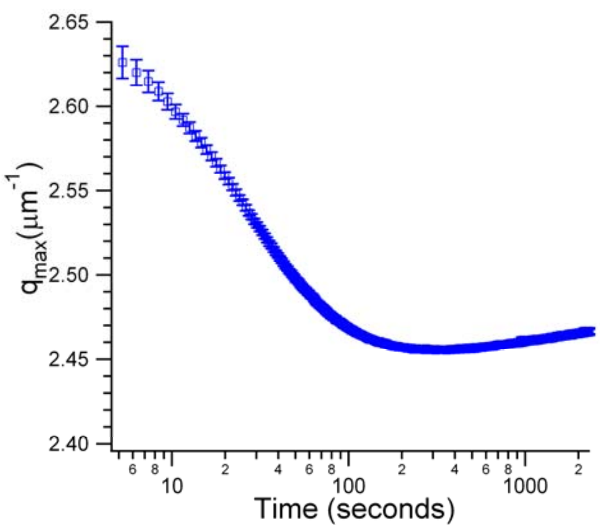
R. Huang, J. Mech. Phys. Solids **53**, 63-69 (2005).

Scattering Data

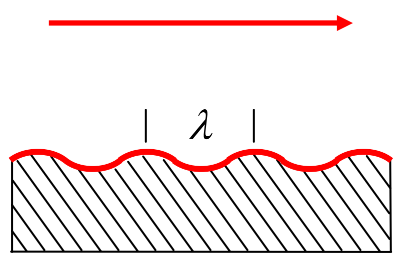


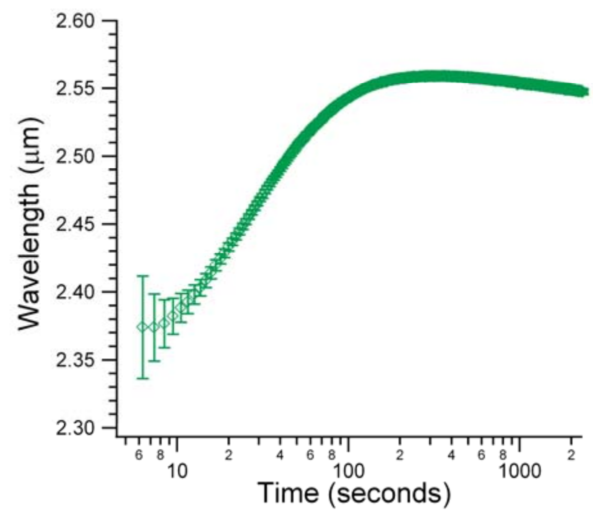
- Increase in amplitude
- Increase in wavelength





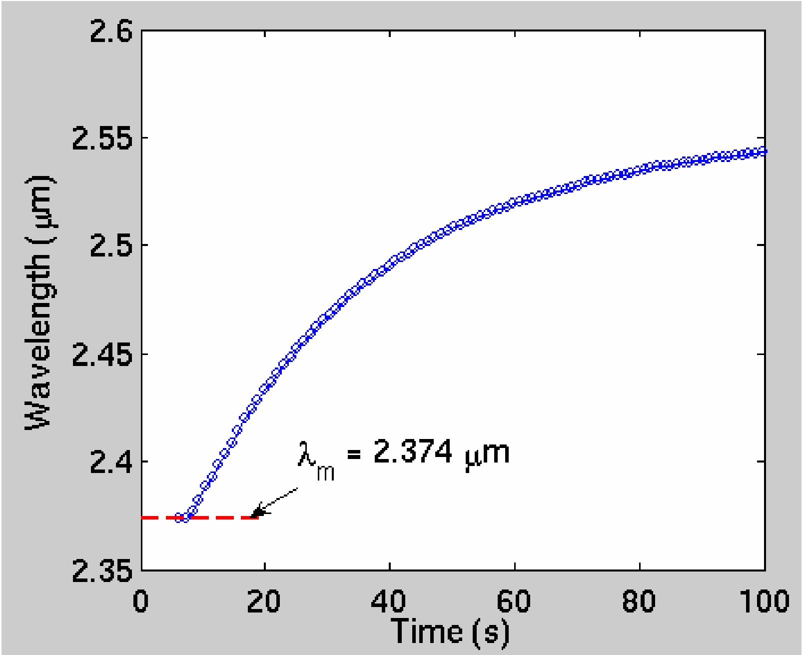
$$\lambda = \frac{2\pi}{q_{max}}$$

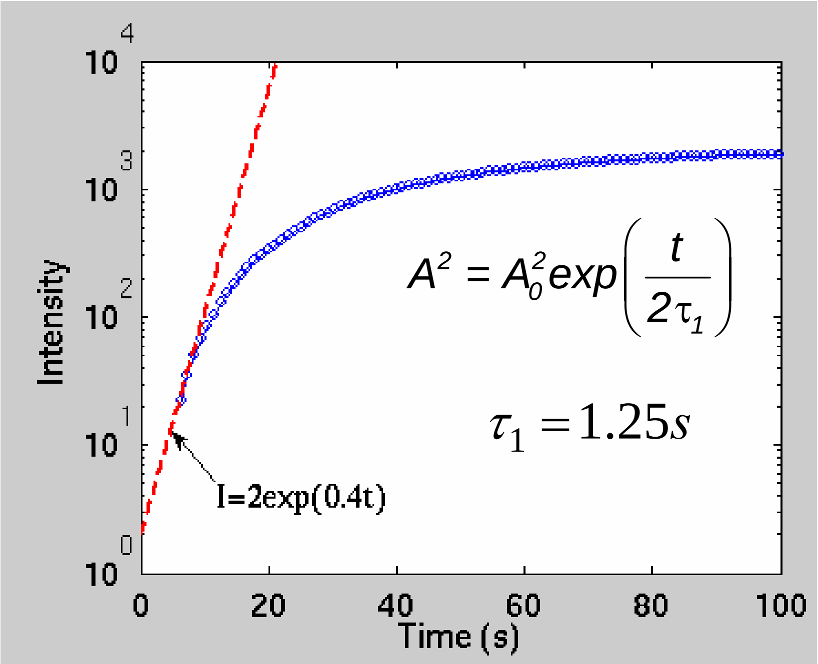




Early Wrinkling and Viscosity

Initial stage (constant wavelength, exponential growth in amplitude):





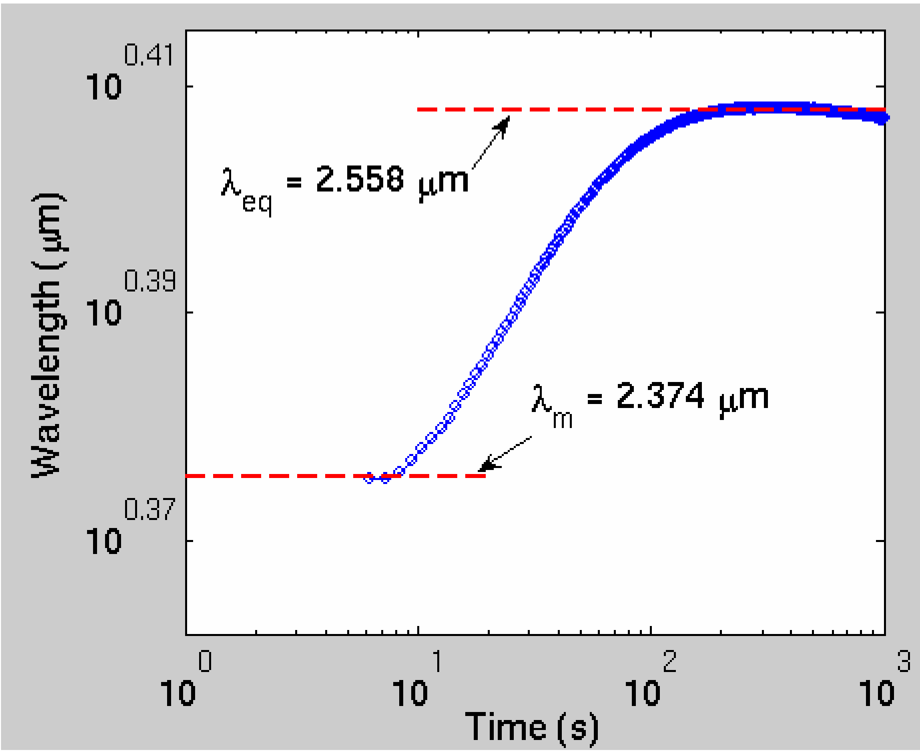
$$\lambda_m = \sqrt{-\frac{4\pi^2 \mu_f h_f^2}{3(1-\nu_f)\sigma_0}}$$

$$\tau_1 = \frac{(1-\nu)h_f \mu_f \eta}{3(1-2\nu)(1-\nu_f)H\sigma_0^2}$$

$$\sigma_0 = 58.4MPa$$

$$\eta = 6.28\times10^5\, Pa\cdot s$$

Wrinkling



- AFM results yield ~ 6.4 nm

Equilibrium wavelength:

$$\lambda_{eq} = 2\pi h_f \left[\frac{(1-2\nu)\mu_f H}{12(1-\nu)(1-\nu_f)\mu_R h_f} \right]^{1/4}$$

$$\mu_R = 0.0931 MPa$$

Critical stress:

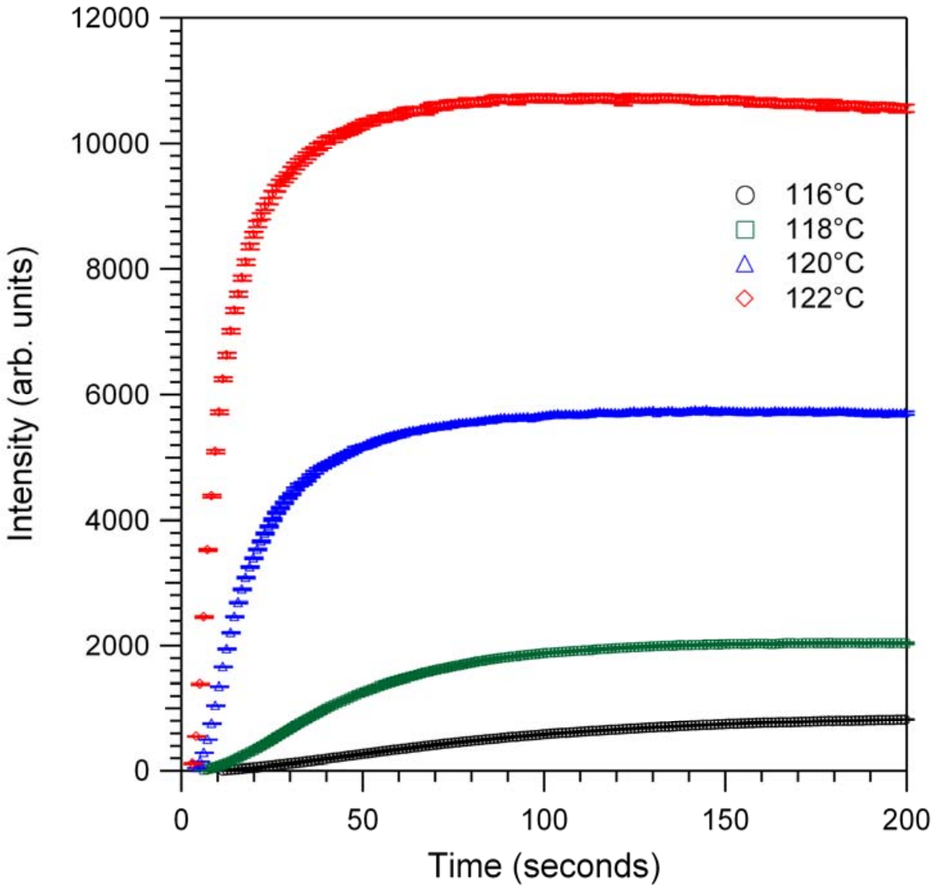
$$\sigma_c = -\sqrt{\frac{4(1-\nu)}{3(1-2\nu)(1-\nu_f)} \frac{h_f}{H} \mu_f \mu_R}$$

$$= 50.3 MPa$$

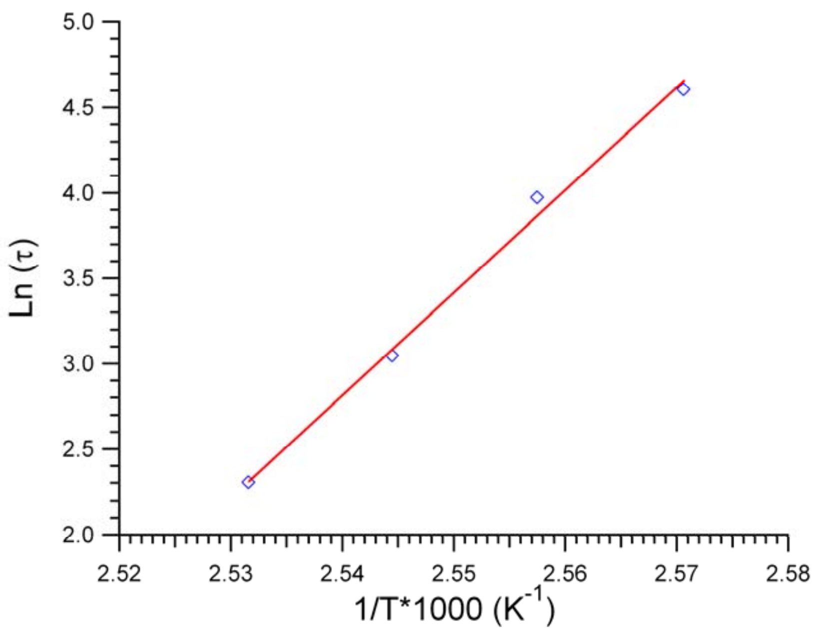
Equilibrium amplitude:

$$A_{eq} = h_f \sqrt{\frac{2}{3}\left(\frac{\sigma_0}{\sigma_c} - 1\right)} \quad = 8.19\,nm$$

Temperature Dependence

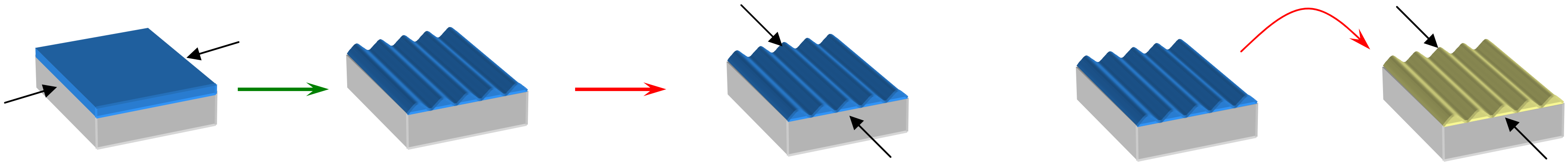


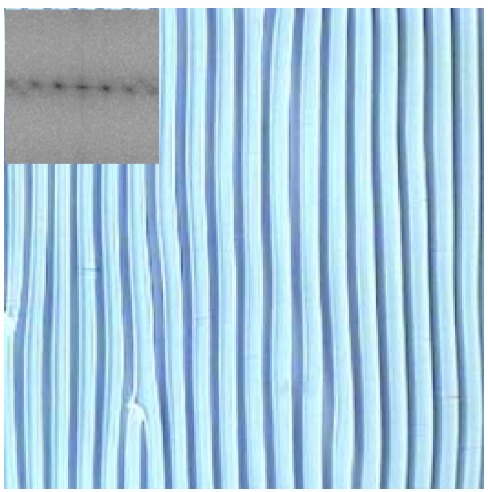
- Rate increases with T
- Equilibrium intensity increases with T



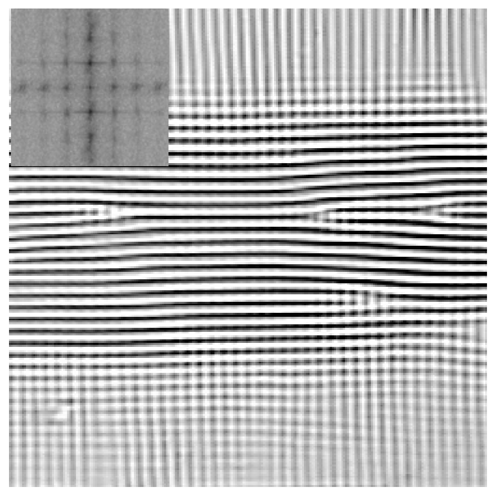
Patterning

Mechanical strain + *Thermal strain* or *Replicate + Mechanical*

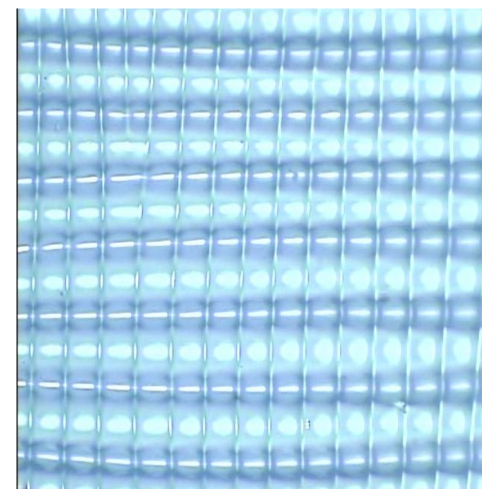




stripes



checkerboard



λ_1 selected by h_f, E_f
λ_2 selected by h_f, $E_f(T_c)$

λ_1 selected by h_{f1}, E_{f1}
λ_2 selected by h_{f2}, E_{f2}

Polymers Division

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Project Team:

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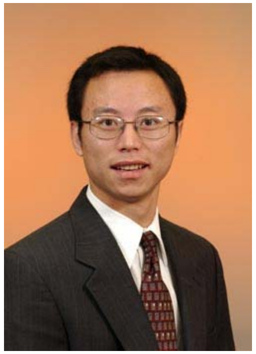
Heqing Huang

Adam J. Nolte

Kirt A. Page

Collaborators:



Rui Huang
UT Austin

This work was carried out at the
NIST Combinatorial Methods Center
www.nist.gov/combi