

# Some experiments on Slip, Adhesion and Friction

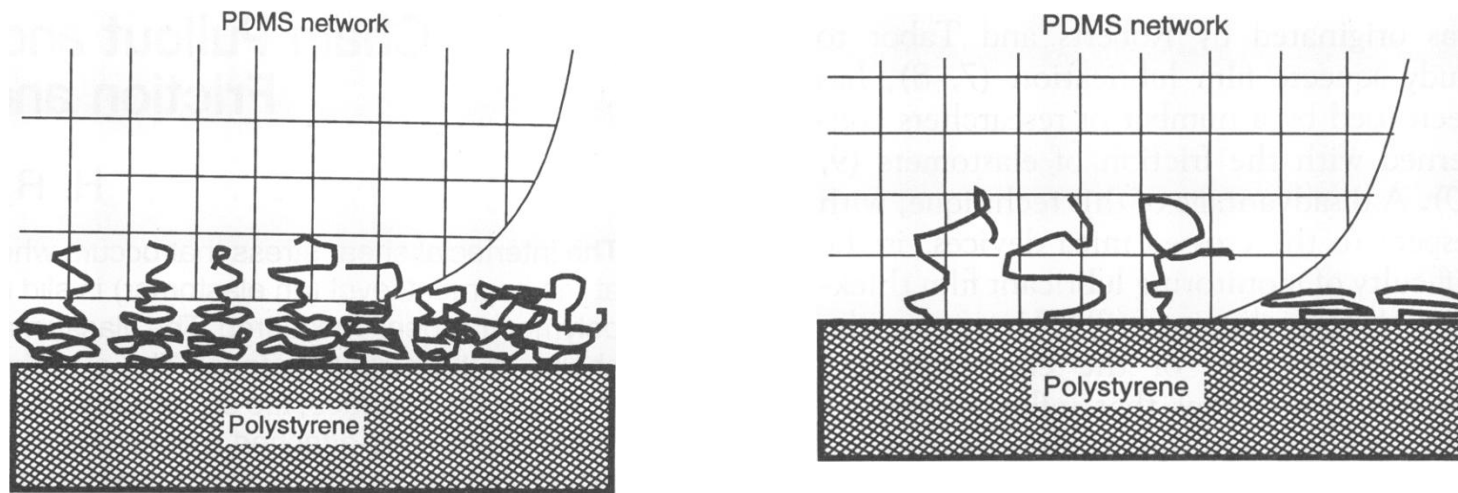
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Australia



# Outline of Talk

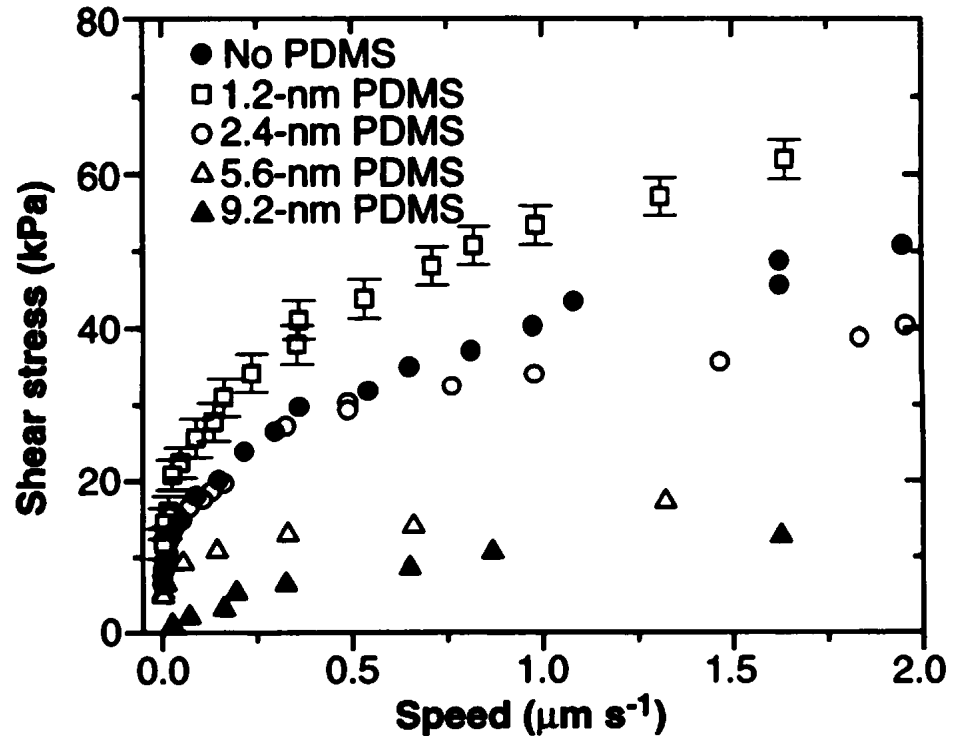
- Tethered chain pull-out and friction in an elastomer
- Effect of interfacial slip on adhesion
- Friction induced orientation in a polyimide
- Interfacial friction processes in polystyrene and PMMA

# Effect of the pullout of tethered chains of slip resistance



End tethered PDMS chains on polystyrene and a crosslinked PDMS lens slider

The PDMS lens was made by the technique developed by Manoj Chaudhury



At low coverage of end-tethered chains on the polystyrene the friction increases due to tethered chain penetration and chain pullout. Pullout approximately agreed with the model of Ajdari et. al..

At high coverage the friction decreases as the situation is now mobile-on-mobile with little chain penetration.

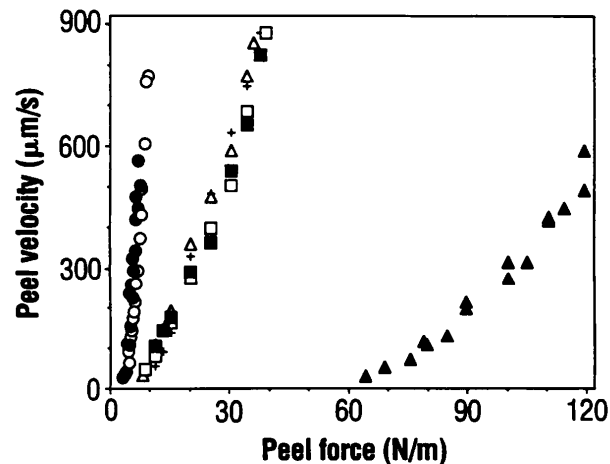
There is much more recent work from Liliane Leger's group and others.



# Effect of Interfacial Slippage on Adhesion

Work done with Manoj Chaudhury and Bi-min Zhang Newby.  
Just talk about first paper – initial adhesion measurements and model.  
Manoj will talk about later work this afternoon.

Newby, Chaudhury and Brown, *Science* **269**, 1407 (1995)

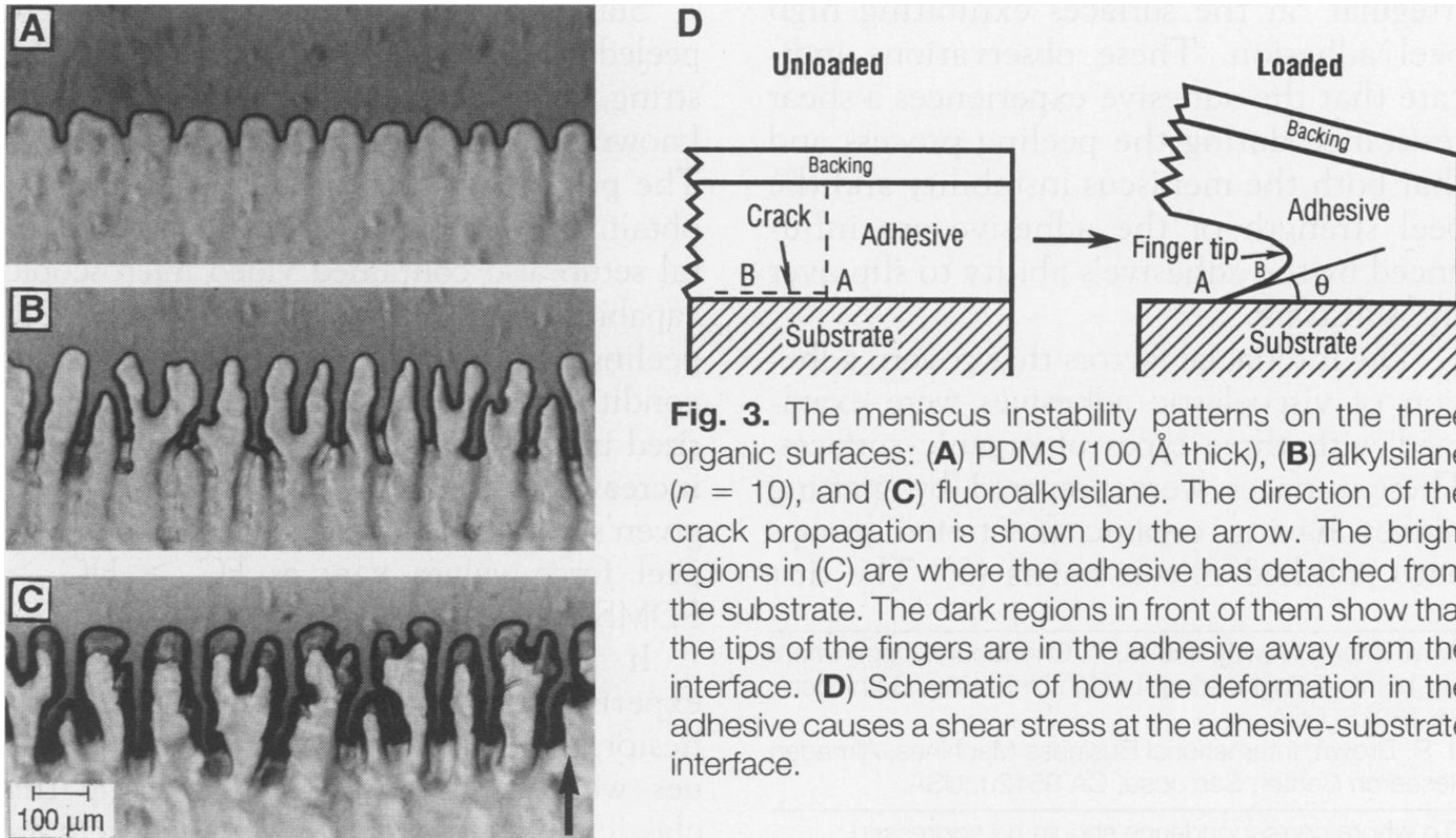


**Fig. 1.** The peel adhesion results of a viscoelastic adhesive on three types of surfaces at a peel angle of 40°. Within a certain class of organic film, the adhesion does not depend significantly on film thickness. PDMS: 50 Å thick (○), 100 Å thick (●); hydrocarbons: C<sub>10</sub> (△), C<sub>11</sub> (+), C<sub>14</sub> (□), and C<sub>16</sub> (■); fluorocarbon (▲).

Fluorocarbon (FC), Hydrocarbon (HC) and Siloxane surfaces.

The peel force was FC>HC>PDMS  
But surface energy implied the opposite would happen.

Peel force varied inversely with the mobility of the surface. So peel force varied with resistance to slip.



Optical observation showed that the crack tunneled as shown schematically in D above.

It was assumed that the peel energy was dissipated in viscoelastic deformation in the adhesive. This was crudely modeled by using a simple elastic model to find the contact angle  $\theta$  and a viscous model for the dissipation in the wedge.

$$\tan \theta = \frac{2G}{\sigma_s \left[ 1 - \left( \frac{G}{\sigma_s} \right)^2 \right]}$$

Elastic shape.  $\sigma_s$  is slip resistance

$$\dot{Q} = \frac{3\eta u^2}{\tan \theta} \ln \left| \frac{x_{\max}}{x_{\min}} \right|$$

Viscous dissipation in a wedge

$$G_o = \frac{\dot{Q}}{u} = \frac{3\eta u \alpha \sigma_s}{2G}$$

Fracture energy varies as slip resistance-  
gives reasonable numbers

# Recent developments

A number of recent experimental papers from Robert McMeeking's group in UCSB on the role of frictional sliding in peeling.

Finite deformation calculation of the crack tip shape with and without slip with soft elastomer adhesive.

T. H. Lengyel, Rong Long and P. Schiavone, *Proc Roy. Soc A* **470**, 20140497 (2014)

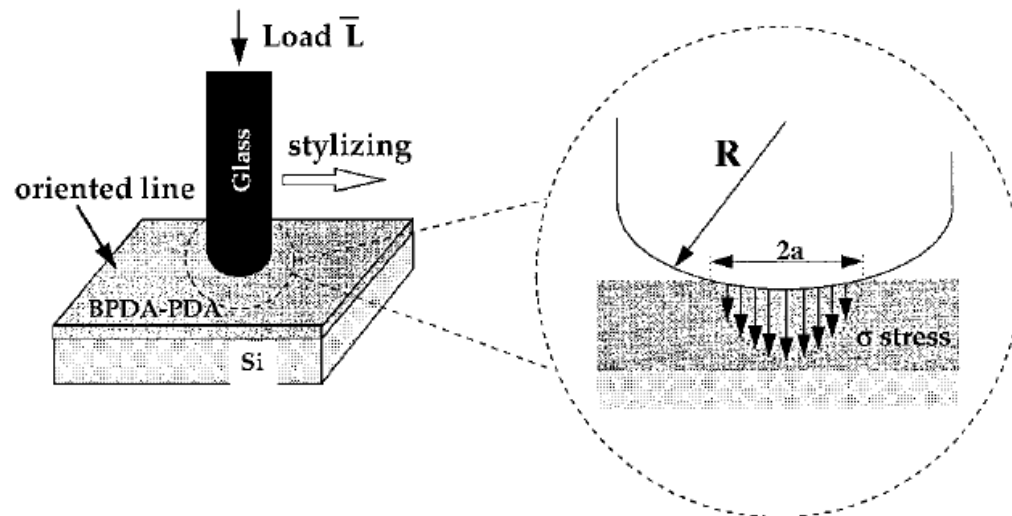
They showed that no slip increased the wedge angle from the  $90^\circ$  in the perfect slip case.

They said

“it is speculated that the wedge angle should depend on the slippage as shown in the rough model of Newby et. al.”

# Friction induced polymer orientation

Liquid crystal display screens sometimes require that the liquid crystal molecules are oriented in a defined direction at the surfaces of the cell. This is (or was) done by coating the glass with a polyimide (PI) and buffing it with a nylon cloth.



**Figure 1.** Schematic of the stylizing process. The light-shaded parallelepiped represents the Si wafer on top of which the polyimide layer has been spin coated (dark-shaded parallelepiped). A glass lens is rubbed across the polyimide film creating a track of oriented chains of width  $2a$ . The glass lens tip has a curvature radius  $R$  and is pressed on the polyimide with a force  $\bar{L}$ . The local stress  $\sigma$  across the track is ellipsoidal.<sup>23</sup>

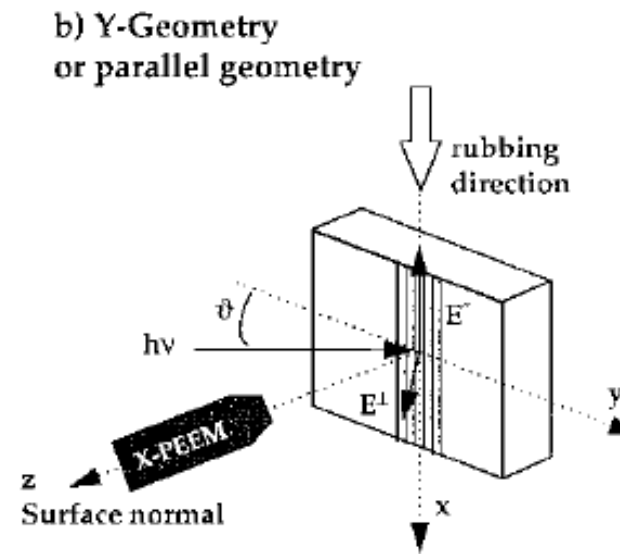
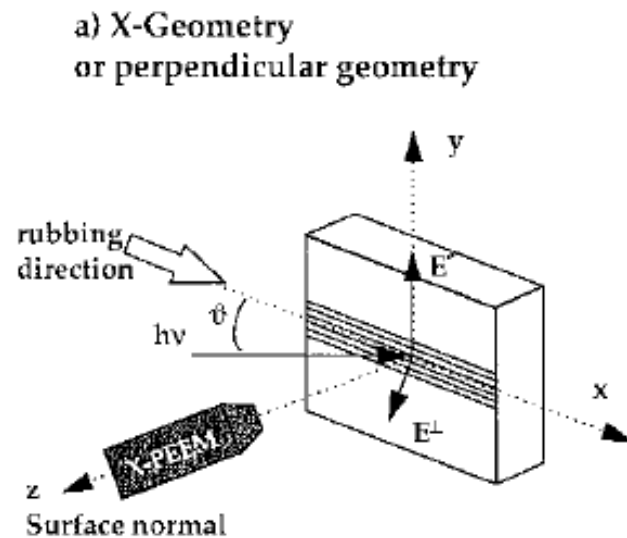
The buffing orients the PI in spite of its high yield stress ( $\sim 200$  MPa).

NEXAFS has shown that the orientation is much higher in the top 1 nm than the top 10 nm.

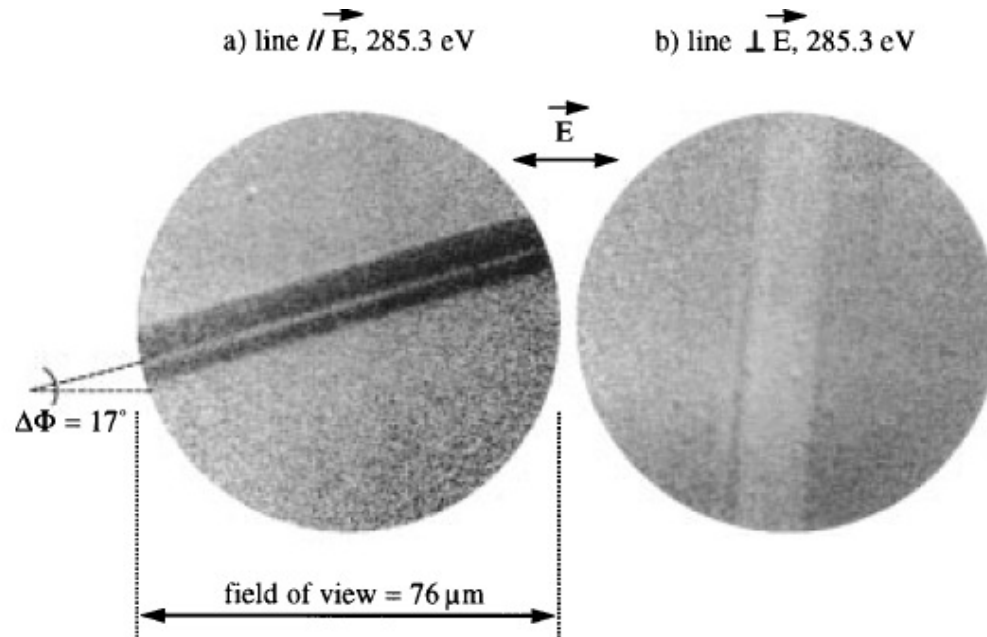
What shear stress is required for orientation of the PI?

# Principle of the experiment

- We know the stress under the spherical indenter as a function of position so the width of the orientated line can give the normal force required for orientation.
- The oriented line can be seen by X-ray photoemission microscopy (X-PEEM) using monochromatic polarized soft X-rays.



# Images of the oriented line



The 'scratch' was not visible by optical or scanning probe microscopy.

The difference in contrast shows that it is a strip of orientated polymer

# Results

From the normal load the contact patch had a width of 16  $\mu\text{m}$  but the lines were 12  $\mu\text{m}$  wide. Hence, from Hertzian contact, the normal stress at the edge of the line was 45 MPa. This must be the minimum normal stress to cause orientation.

The measured coefficient of friction was 0.75 so perhaps the minimum shear stress for orientation was 34 MPa.

This is to be compared with an estimated yield stress of 200-300MPa.

A. Cossy-Favre et. al. *Macromolecules* **31**, 4957-62 (1998)



# Polymer entanglement density and its influence on interfacial friction

Philip Whitten

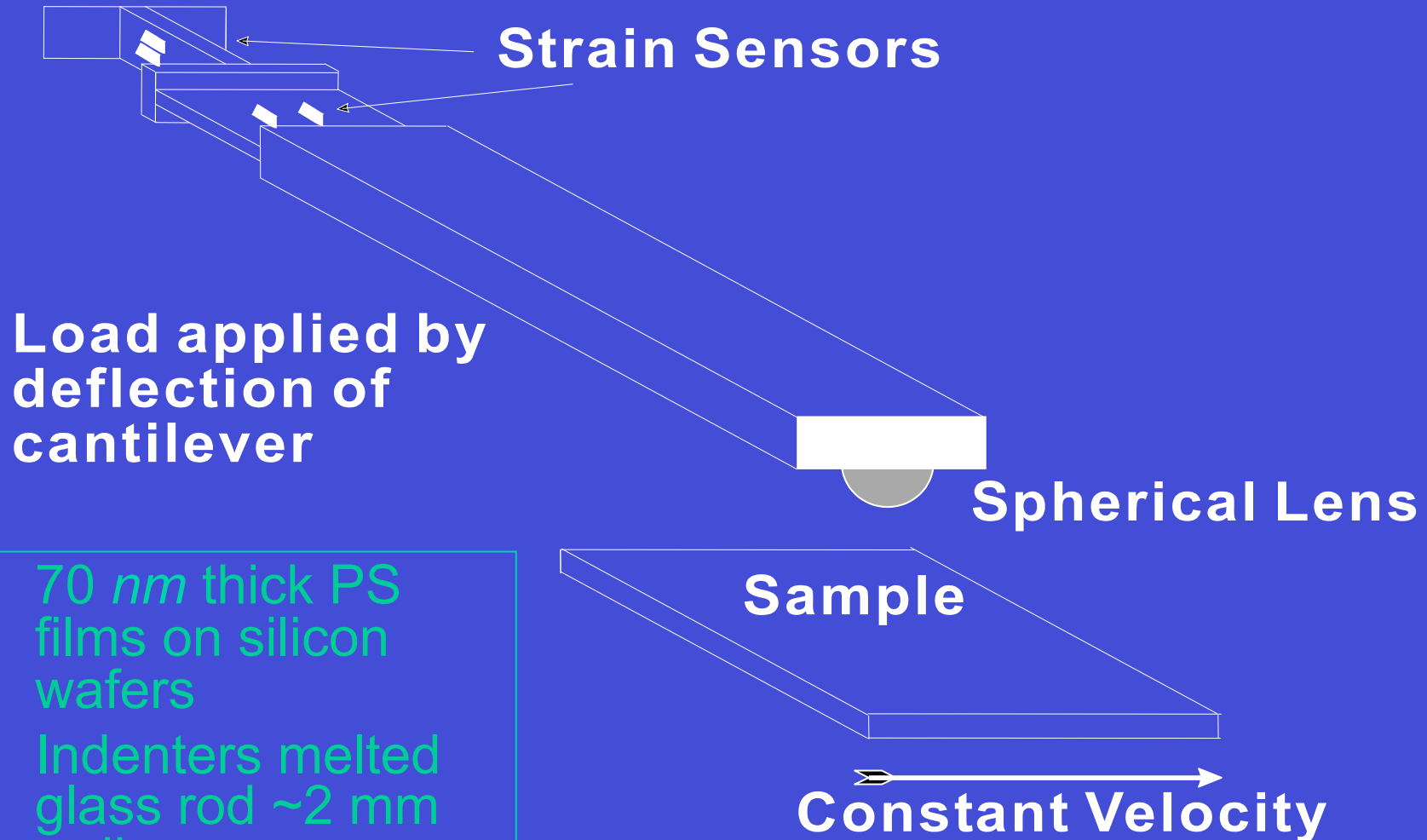
Hugh R. Brown

P. G. Whitten and H. R. Brown, *Phys. Rev. E*, **76**, 026101 (2007)

# Background

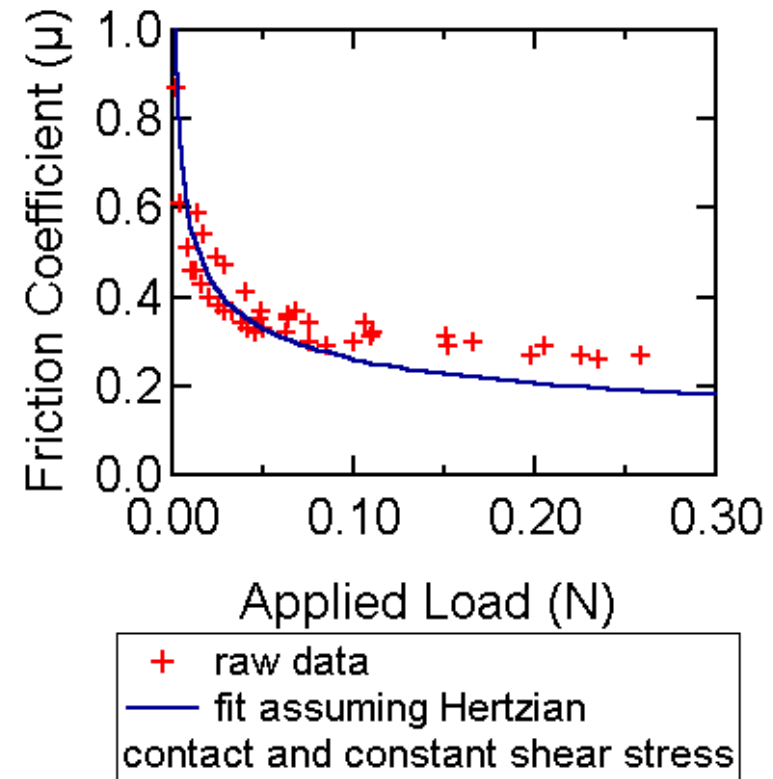
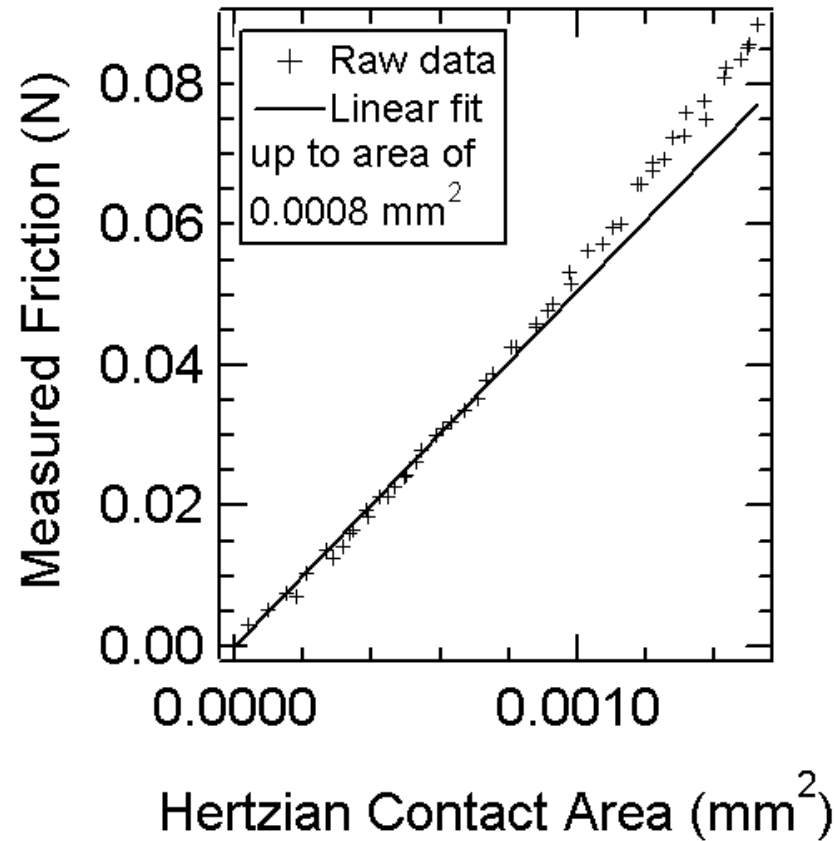
- Glassy polymer surfaces are oriented by brushing with a velour cloth in liquid crystal display production
- Sliding on a polymer surface with a smooth indenter has two modes: 1) an interfacial friction mode with high friction, often described as elastic as no damage is visible optically and 2) a normal friction mode with visible damage
- This work concerned with mode 1). Sliding cannot be elastic – what is the friction process?

# Macroscopic Friction Experiments



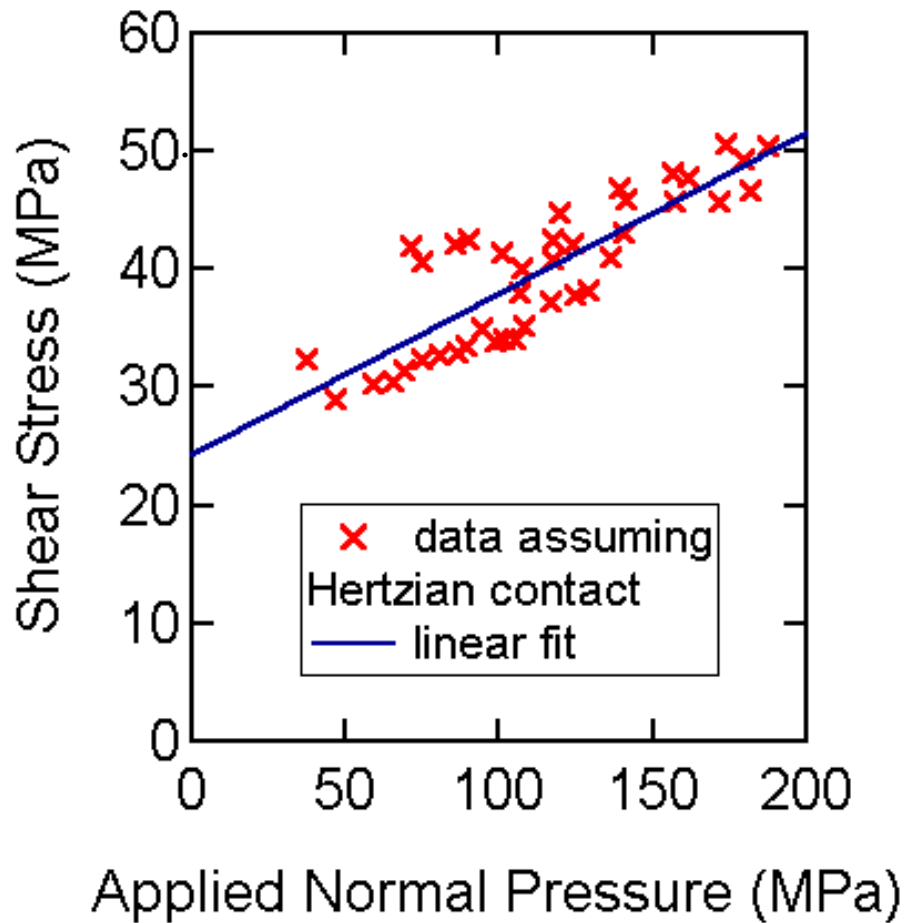
- 70 nm thick PS films on silicon wafers
- Indenters melted glass rod ~2 mm radius
- 2  $\mu\text{m/s}$  sliding velocity

# Variation of Friction with Contact Area and Coefficient of Friction



At high loads the friction increased above the linear relation.

# Pressure Dependent Shear Stress



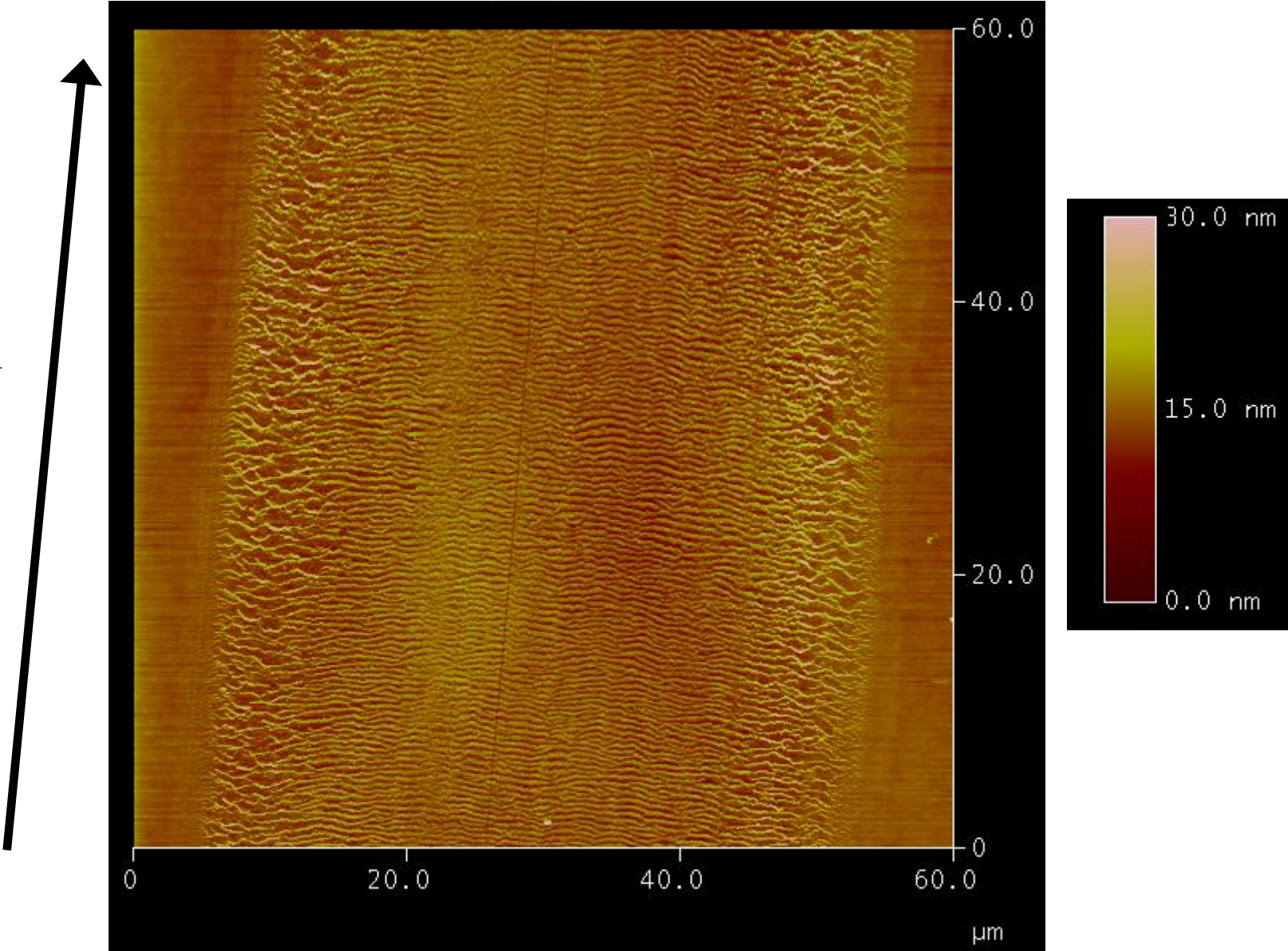
$$F = \tau A = A(S_c + \alpha \sigma)$$

$\uparrow$   
 Normal pressure

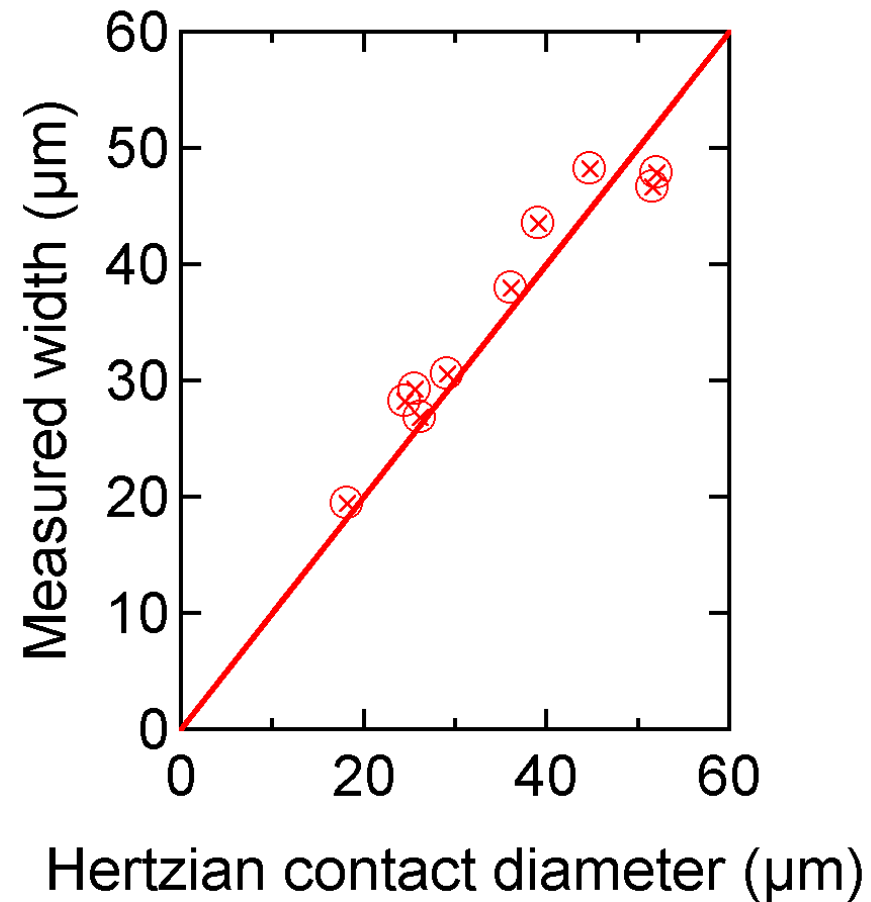
| Polymer | $S_c$<br>(MPa) | $\alpha$<br>(MPa · MPa <sup>-1</sup> ) |
|---------|----------------|--|
| PMMA    | 38.6 ± 1.4     | 0.10 ± 0.01                            |
| PS      | 24.5 ± 1.4     | 0.13 ± 0.01                            |
| PPO     | 19.6 ± 1.0     | 0.05 ± 0.01                            |
| PC      | 16.6 ± 5.2     | 0.06 ± 0.08                            |

# Ripples on PS surface

Sliding  
direction  
of  
indenter

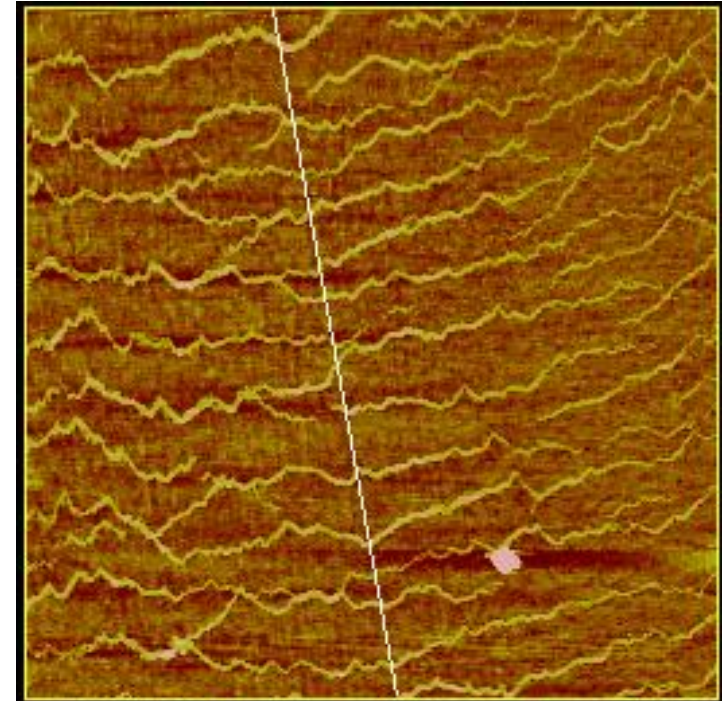


# Width of rippled region matches Hertzian contact area

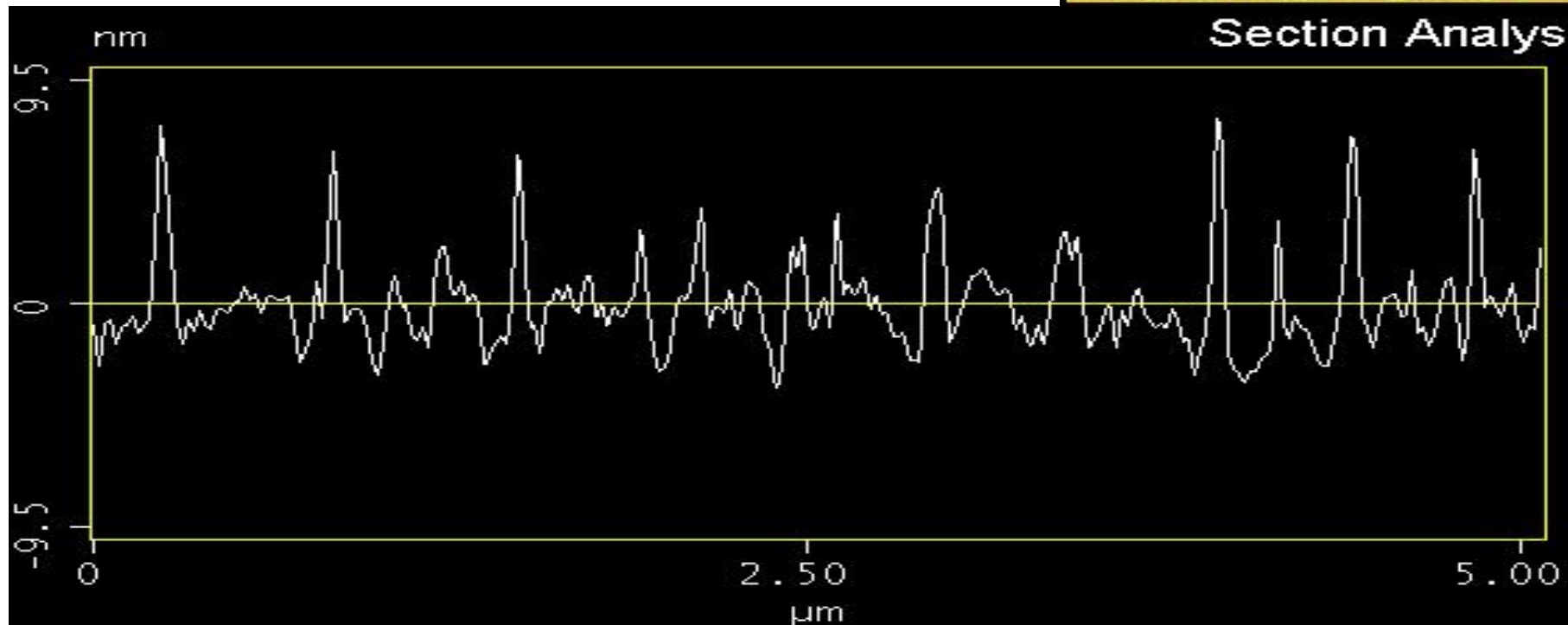


The red line is a  
1:1 relationship

# Profile of ripples on Polystyrene

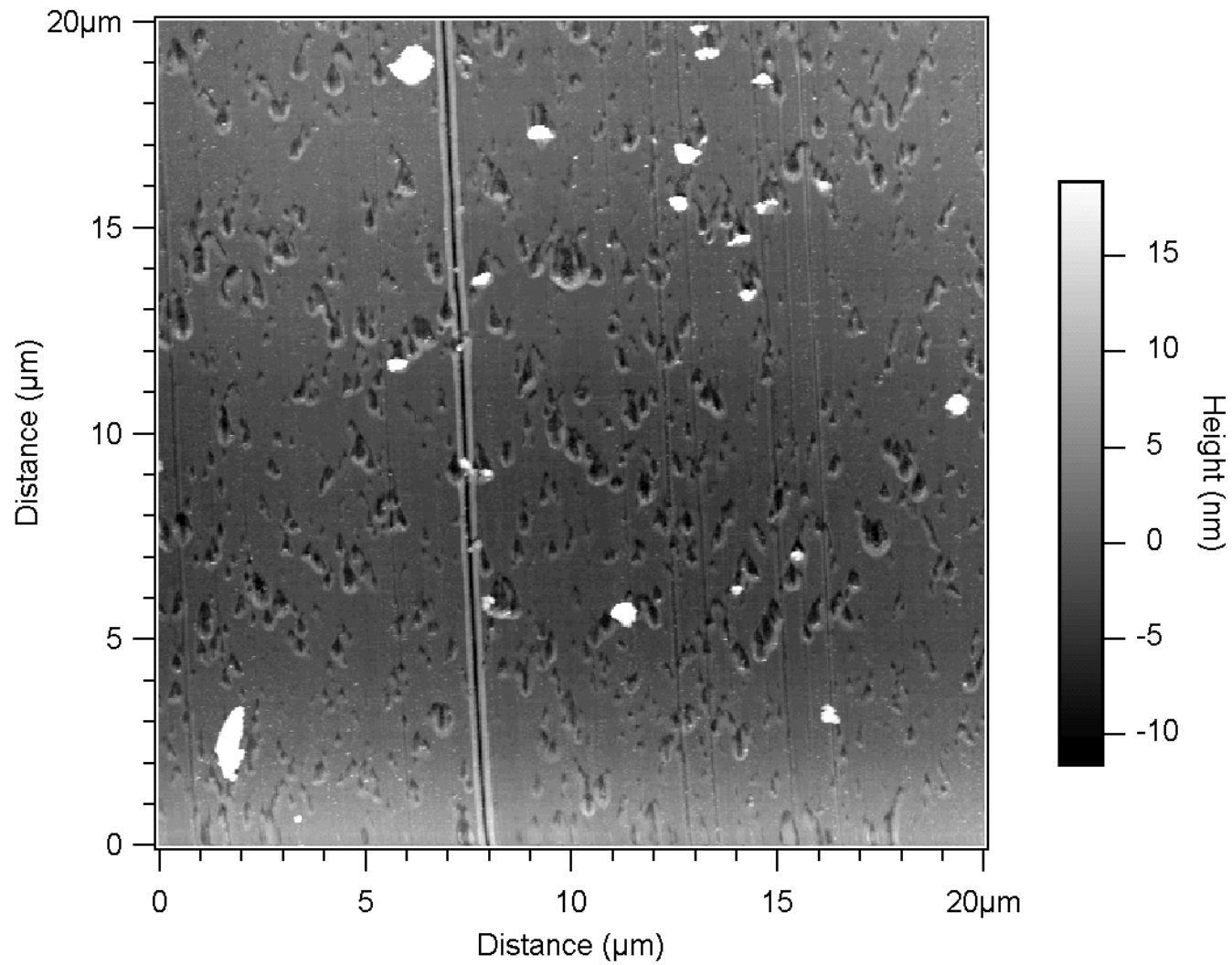


Section Analysis

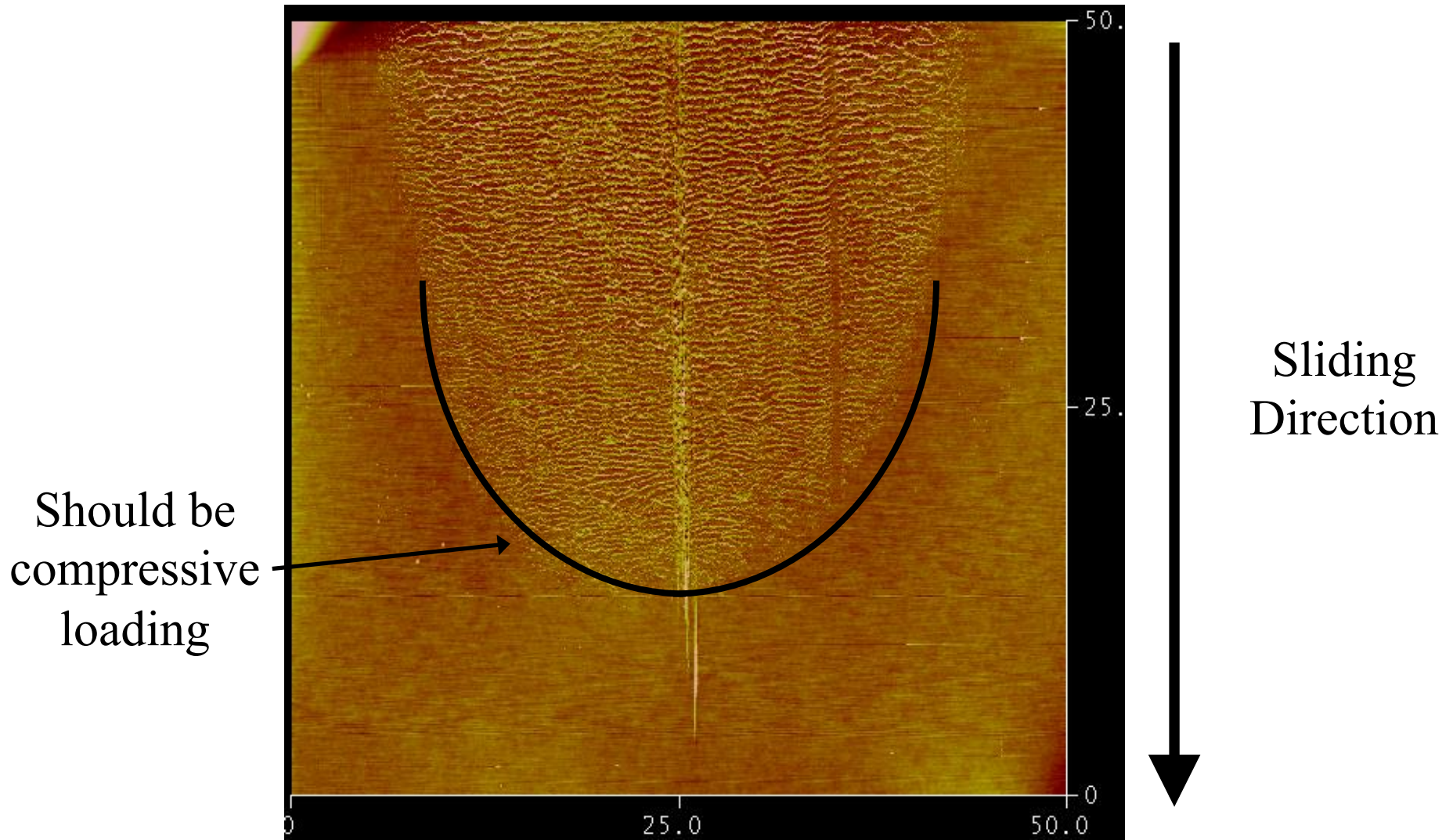




# Holes in PMMA Surface



# Ripples form at leading edge of contact



## Ripples and Brittle Failure

- Damage (ripples and holes) only occurred in PS and PMMA, not in PPO and PC.
- PS and PMMA show brittle failure, PC and PPO are more ductile
- Suspect ripples related to brittle failure

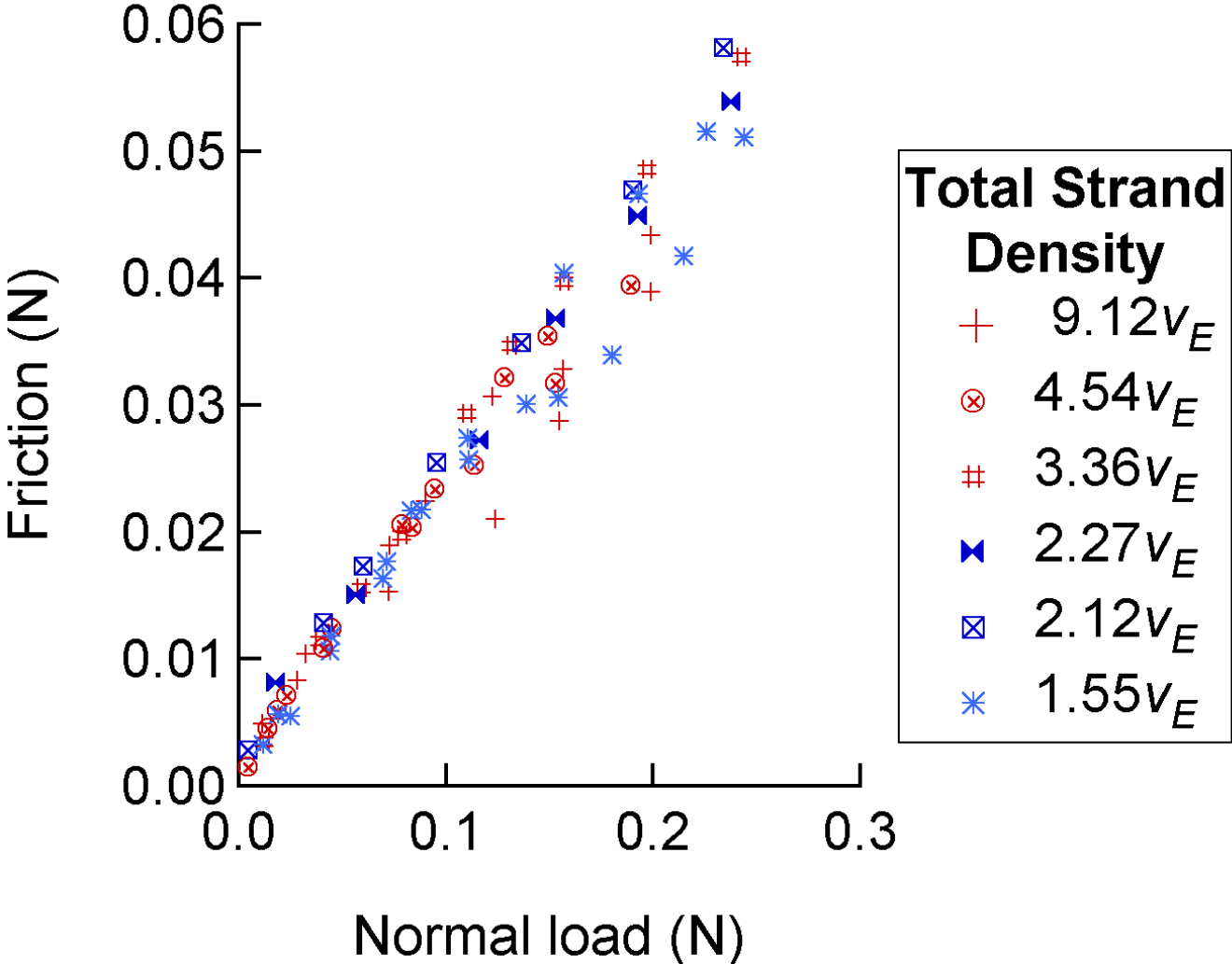
# Brittle failure of glassy polymers

- Many glassy polymers fail in a macroscopically brittle manner under tensile loading
- Cracks nucleate from crazes
- Ironically, crazes form through large-strain plastic deformation at a small scale (strain localization)
- The extension ratio of a deformation or craze zone decreases with increasing entanglement density – suppress crazing by increasing entanglement density
- Can change effective entanglement density by crosslinking PS using the e-beam of an SEM

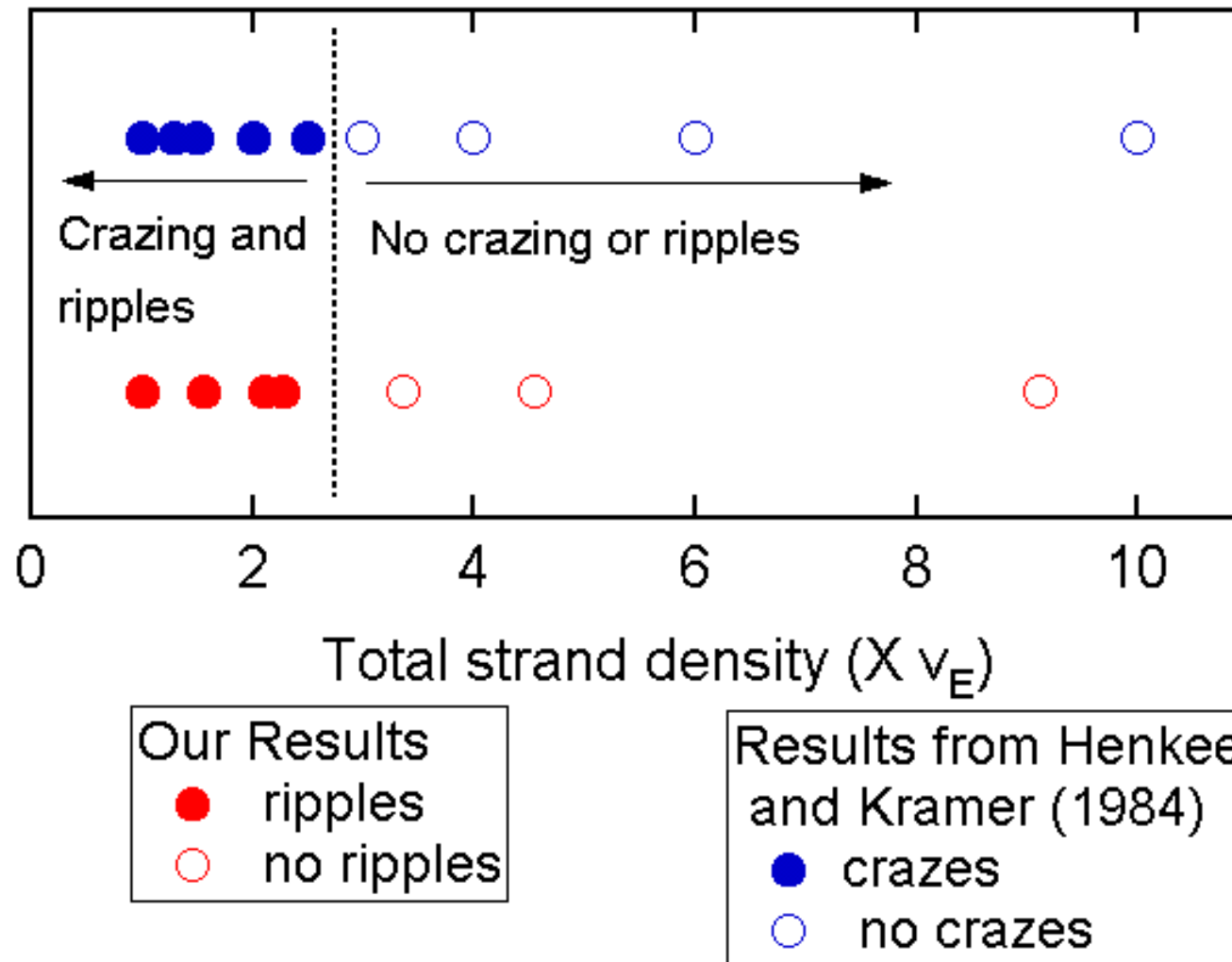
C. Henkee, E. Kramer, Journal of Polymer Science: Polymer Physics edition, Vol. 22, 721-737 (1984)

L. Berger, E. Kramer, Journal of Materials Science, Vol. 23, 3536-3543 (1988)

# Frictional Force is Independent of the Crosslink Density



# The ripples are due to strain localization



## Mechanisms of ripple formation and friction

- Ripples are related to strain localisation and crazing, probably caused by accumulation of wear debris that come from brittle failure
- If there was no slip or uniform slip, tension would only exist towards the rear of the contact patch. But ripples form at the front of the contact patch showing there must be tensile stresses all over the contact
- There are probably stick regions and slip regions all over the contact with tension (and failure) occurring behind each stick region

## Conclusions

- The frictional shear stress of glass on polystyrene is independent of the crosslink density
- Glassy polymers that fail by a brittle manner under tensile loading produce debris under sliding friction
- The entanglement density of a polymer has a dramatic affect on the processes occurring at the sliding interface
- Substantial plastic deformation at the polymer surface must take place

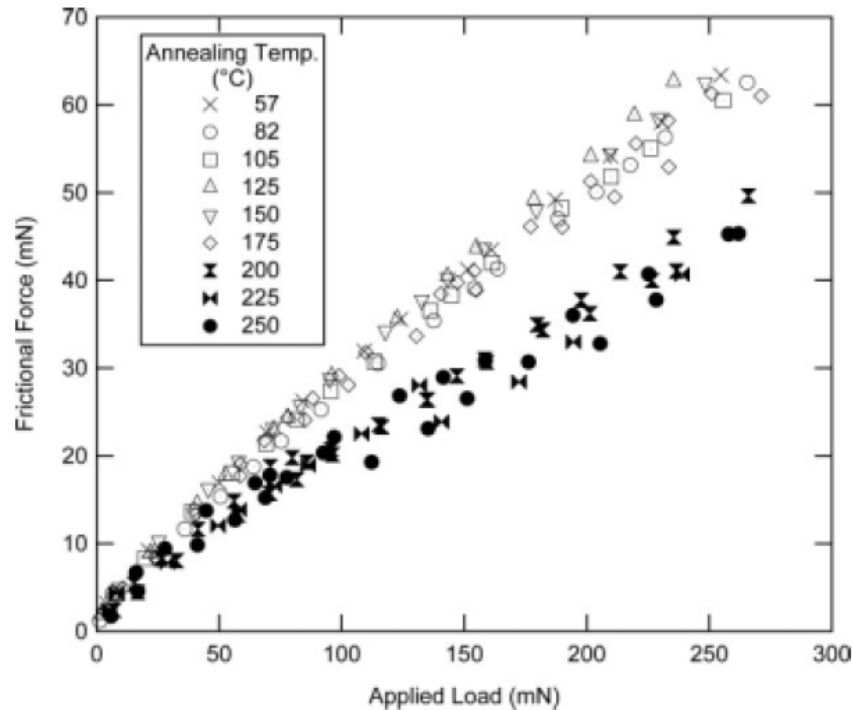


# Interfacial Friction and Structure of PPO

Philip G. Whitten and H. R. Brown

P. G. Whitten and H. R. Brown, J. Polym. Sci. B. **47**, 1637-43 (2009)

# Effect of Annealing Temperature on the Frictional Properties of PPO



**Figure 1.** The effect of annealing temperature on the macroscopic friction properties of PPO.

The PPO was spin coated onto silicon wafers from a solution in toluene and dried (annealed) in a vacuum oven.

**Table 1.** Fitting Parameters for a Linear Fit of the Shear Stress versus the Mean Contact Pressure

| Annealing Temperature (°C) | $S_c$ (MPa)    | $\alpha$ (MPa/MPa) |
|----------------------------|----------------|--------------------|
| $\leq 175$                 | $23.7 \pm 1.0$ | $0.11 \pm 0.01$    |
| $\geq 200$                 | $17.1 \pm 1.2$ | $0.08 \pm 0.01$    |

$S_c$  is the shear stress at zero applied pressure;  $\alpha$  is the rate at which the shear stress increases with contact pressure. The presented error is 1 standard deviation.

What happens when the annealing temperature is  $\geq 200$ C?

# Surface topography

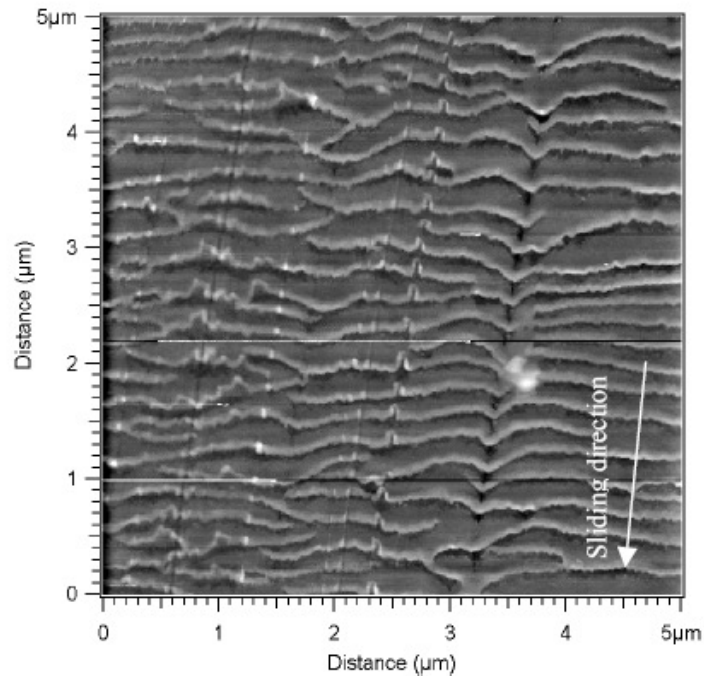


Figure 4-58. The surface topography of an annealed (125°C) PPC following a single sliding pass by a glass indenter.

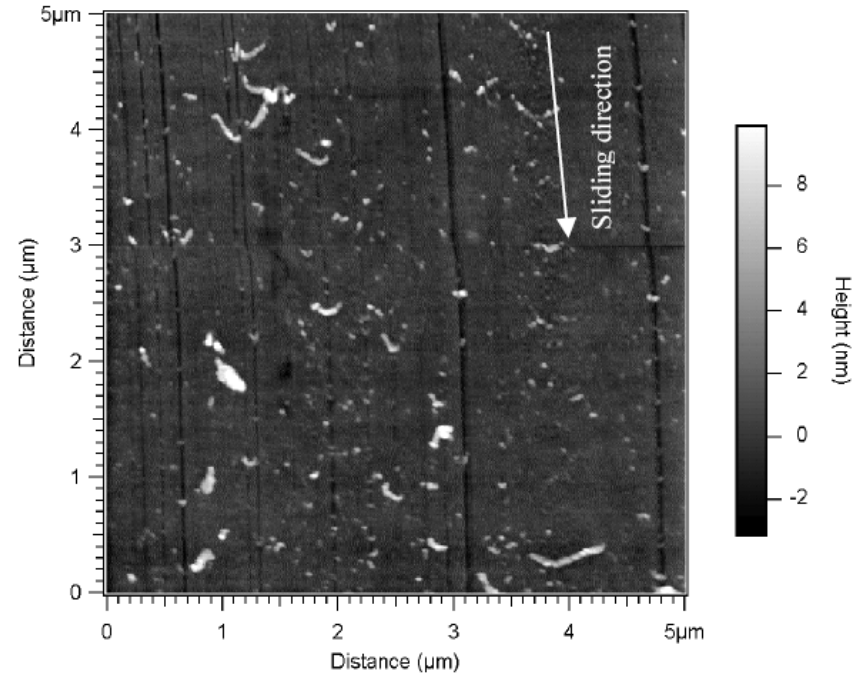
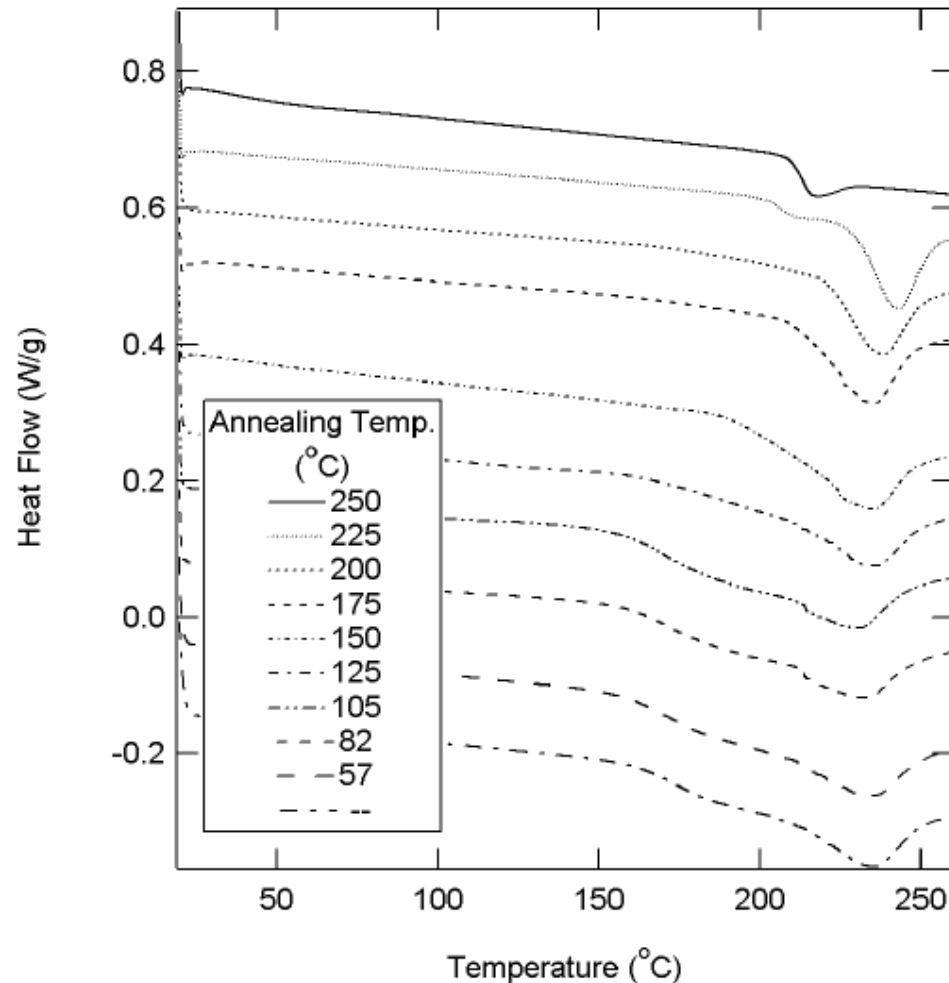


Figure 4-60. The surface topography of an annealed (200°C) PPO sample following a single sliding pass by a glass indenter.

Ripples formed for annealing temperatures less than 200C.

# DSC Results



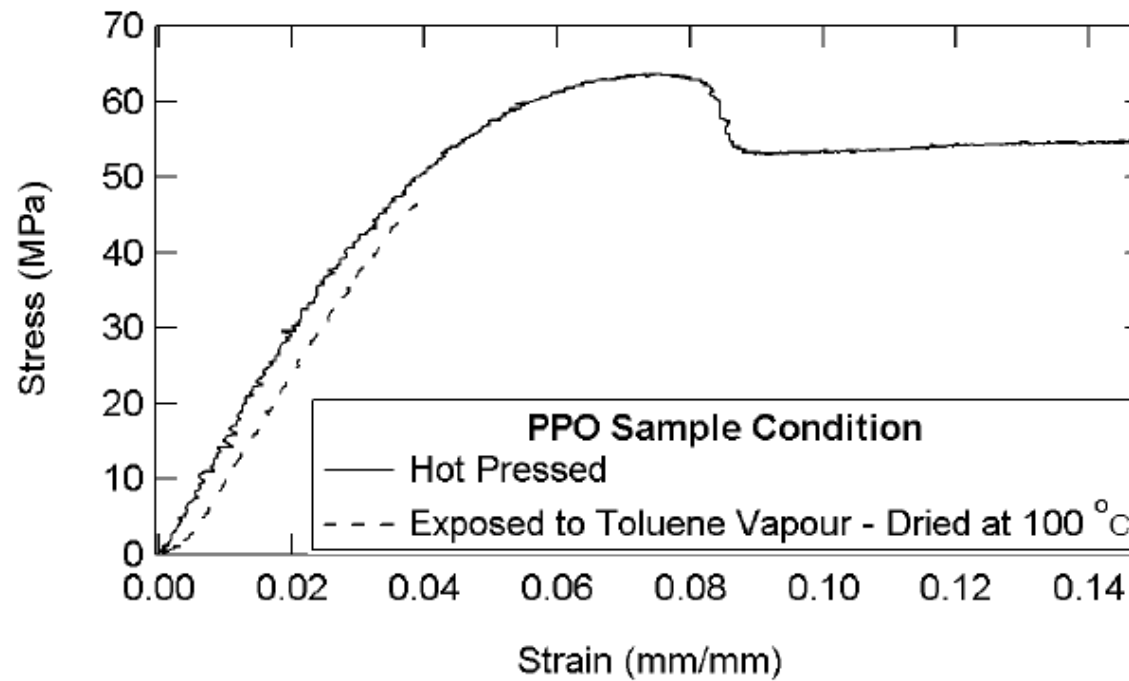
The PPO crystallizes when cast from toluene. No T<sub>g</sub> is visible for annealing at less than 200C – rigid amorphous phase is present.

Only the 250C annealed sample is fully amorphous.

The difference between the two groups cannot be caused by crystallization. Presumably it is caused by the elevated yield stress and brittle nature of the rigid amorphous phase.

# Tensile Properties

PPO bar exposed to toluene for 5h then dried for 2 days at 100C.  
Mass increase 1.8%. Material highly brittle.

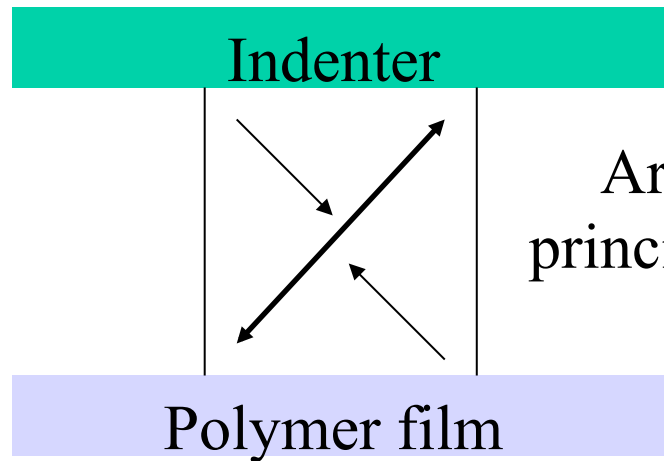


## Conclusion

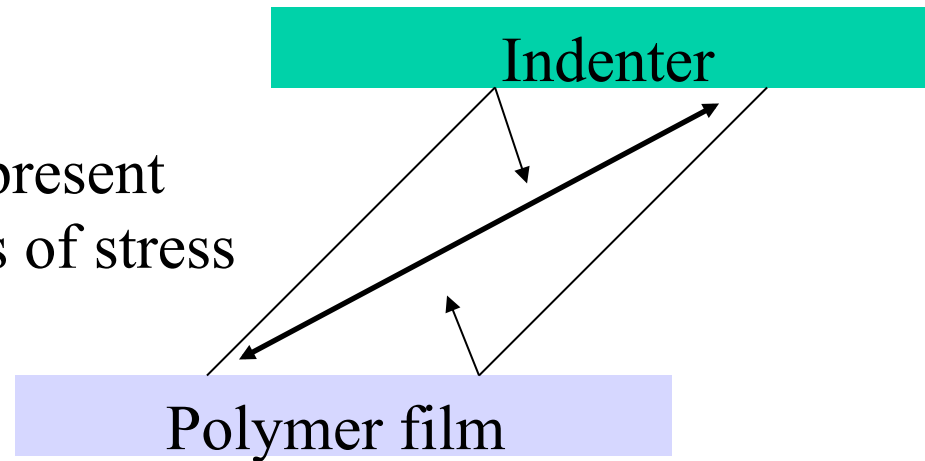
- PPO shows a brittle-ductile transition in friction properties when cast from toluene.
- The brittle form appears to be caused by the existence of a rigid amorphous phases rather than crystallization or residual toluene.
- There is a strong correlation between frictional and tensile properties – implies loading during interfacial friction is tensile.

# Mechanism of ripple formation

Indenter is sliding over  
the PS film

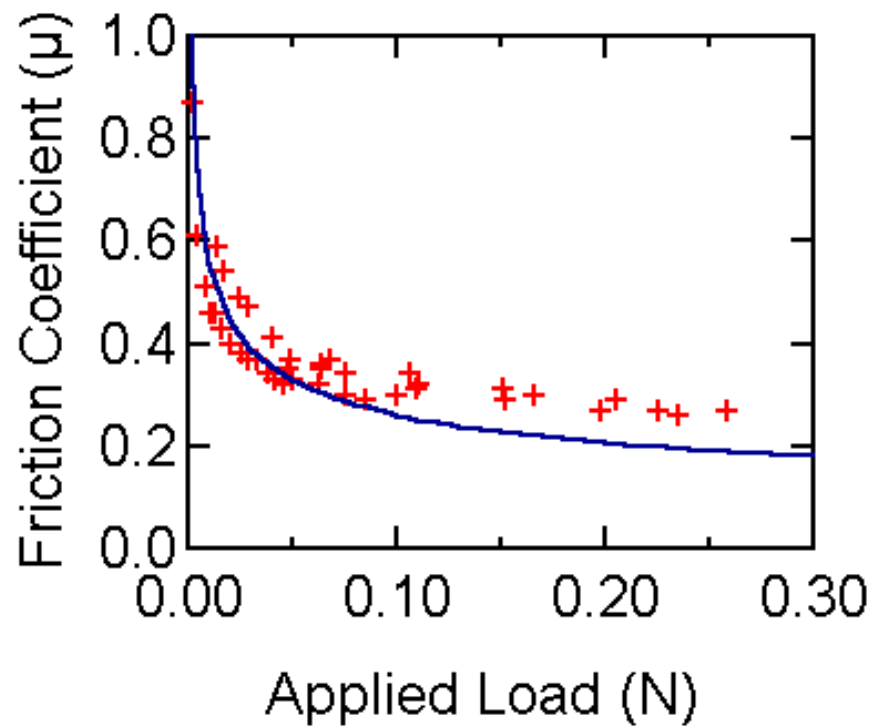


Indenter is sticking to  
the PS film



Arrows represent  
principal axes of stress

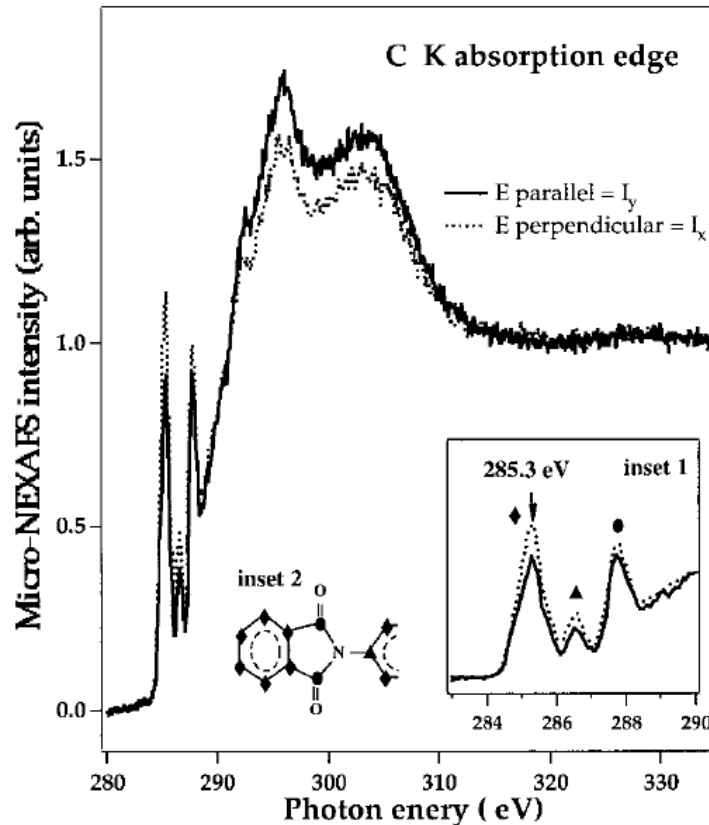
- High amounts of deformation at a local scale
- Loading changes from shear to tensile
- Cohesive failure occurs in tensile regime



+ raw data  
— fit assuming Hertzian  
contact and constant shear stress



# Micro-NEXAFS Results



The image signal comes from the carbon atoms shown as diamonds

**Figure 6.** Micro-NEXAFS spectra from an area within the stylized lines for the lines parallel (full curve) and perpendicular (dotted curve) to the electric field vector  $\vec{E}$ . The data have been normalized as discussed in the text. Inset 1 shows the  $\pi^*$  resonance at an enlarged scale. The three intensity maxima at 285.3, 286.5 and 287.7 eV correspond to phenyl C atoms (diamonds), phenyl C atoms with bonds to N (triangles), and carbonyl carbon atoms (circles), respectively. Inset 2 is a schematic representation of the BPDA-PDA molecule.