

Combinatorial  
Methods Group

# Combinatorial Investigations of Polymer Adhesion

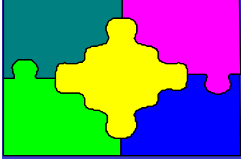
Alfred J. Crosby

Alamgir Karim

Eric J. Amis

Polymers Division

National Institute of Standards and Technology



Combinatorial  
Methods Group

# Combinatorial Investigations of Polymer Adhesion

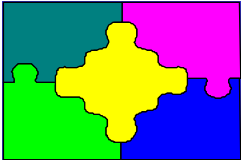
## Motivation

- Adhesion influences numerous industries
- Myriad of variables control adhesion
- Existing techniques have disadvantages

- Surface Energy
- Molecular Weight
- Time
- Temperature
- Humidity
- Roughness
- Geometry

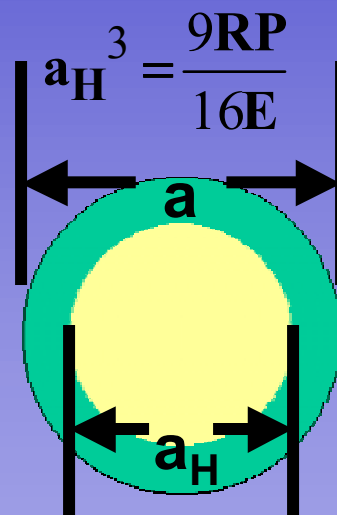
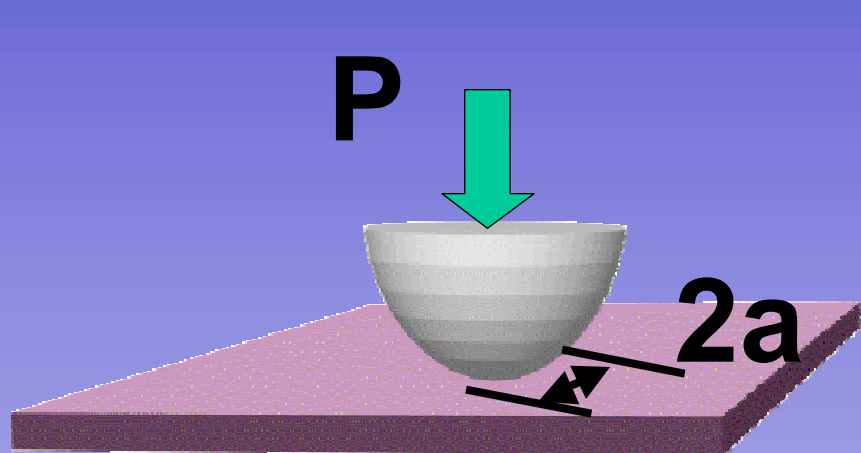
## Objective

- Develop methodology for quantitative high-throughput measurements of adhesive strength of polymer interfaces

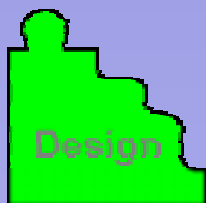


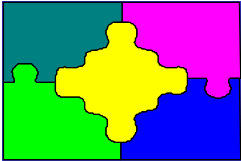
# How do we study polymer adhesion?

## JOHNSON, KENDALL, & ROBERTS (JKR)



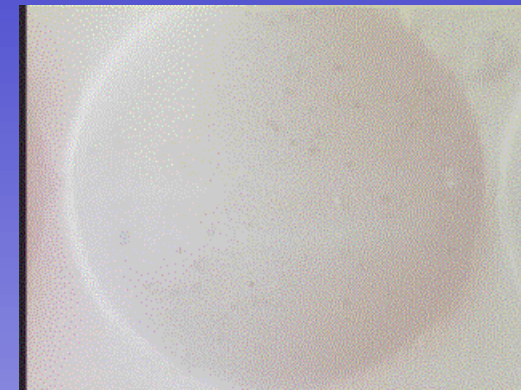
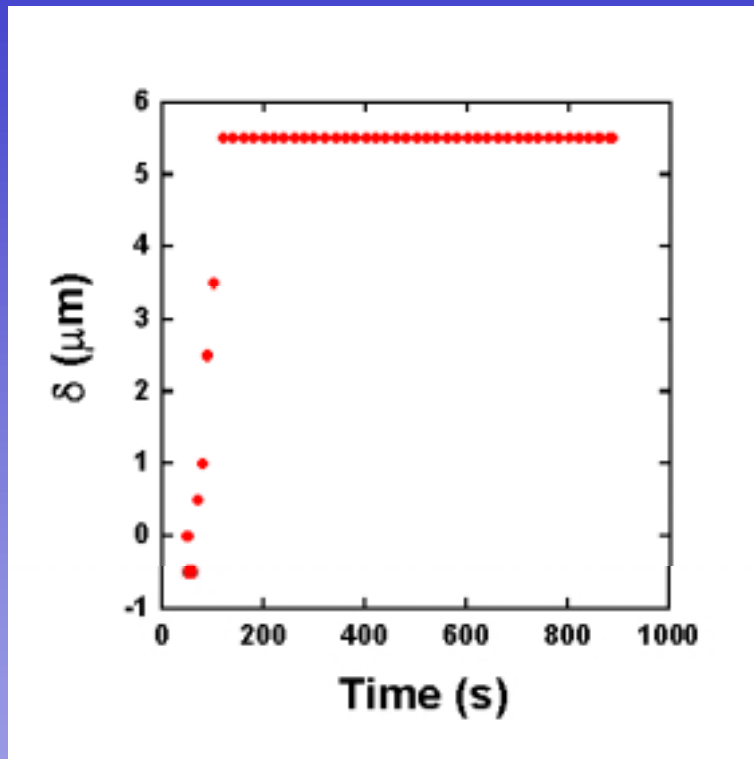
$$a^3 = \frac{9R}{16E} \left[ P + 3\pi GR + \sqrt{6GRP + (3\pi GR)^2} \right]$$





Combinatorial  
Methods Group

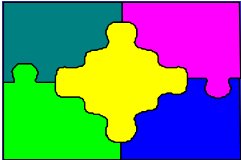
# Why choose JKR?



PDMS contacting glass

Classical Use:

- Fundamental studies of adhesion of soft polymers
- Limited to elastic materials and geometries where  $a \ll h, R$



Combinatorial  
Methods Group

# Why choose JKR?

Recent Developments have allowed JKR to be applied to a wide range of issues

## Finite-Size Corrections (for $a > h$ )

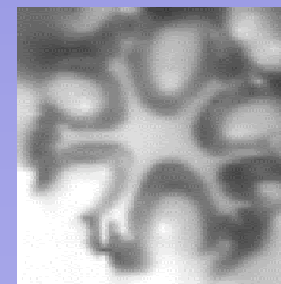
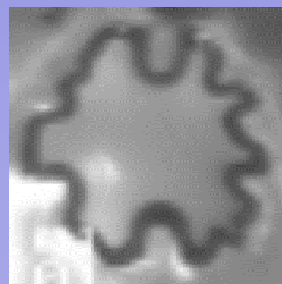
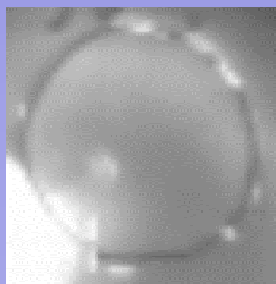
Shull, K.R., et al, *Macromol. Chem. Phys.*, 1998, **199**, 489-511.

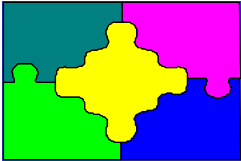
Crosby, A.J. et al, *Journal of Applied Physics*, 2001, **88**, 2956-2966.

## Viscoelasticity Corrections

Lin, Y.Y., et al, *Journal of Applied Physics*, 1999, **32**, 2250-2260.

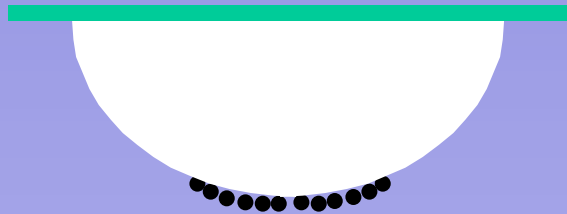
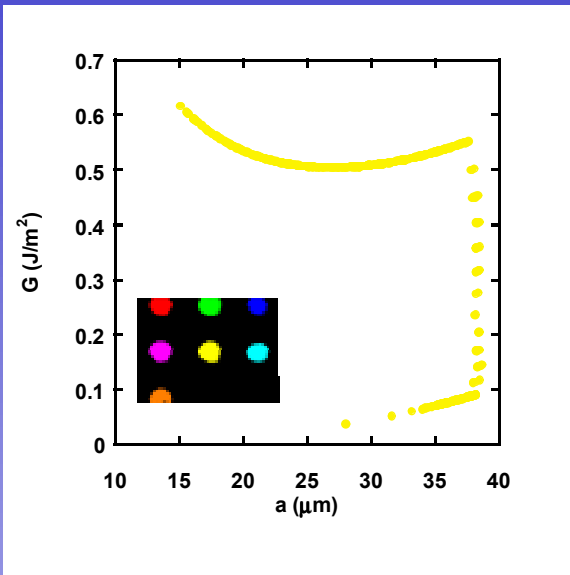
Johnson, K.L., ACS publication, 2000.

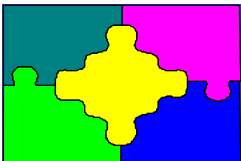




Combinatorial  
Methods Group

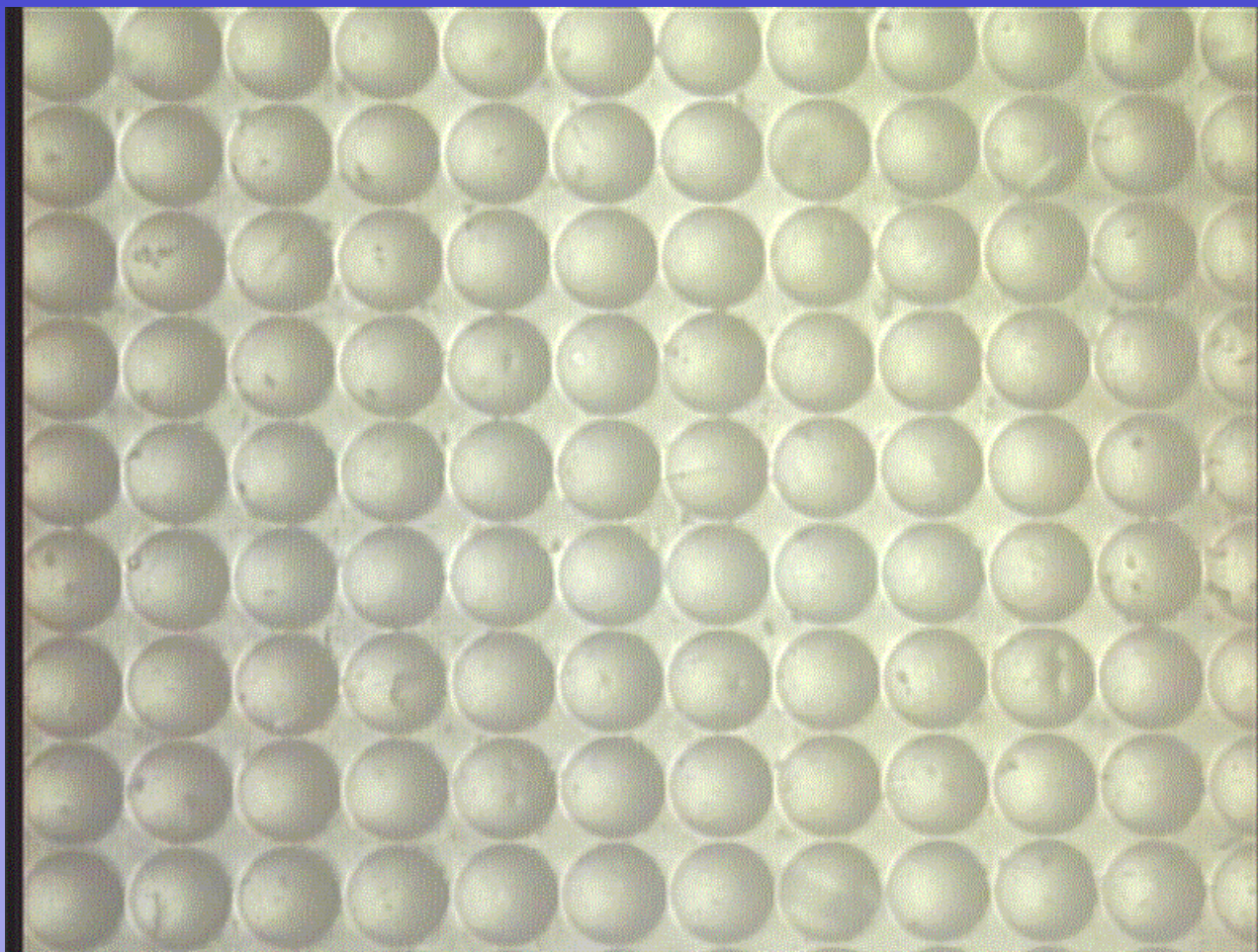
# What about an array of lenses?

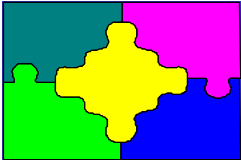




Combinatorial  
Methods Group

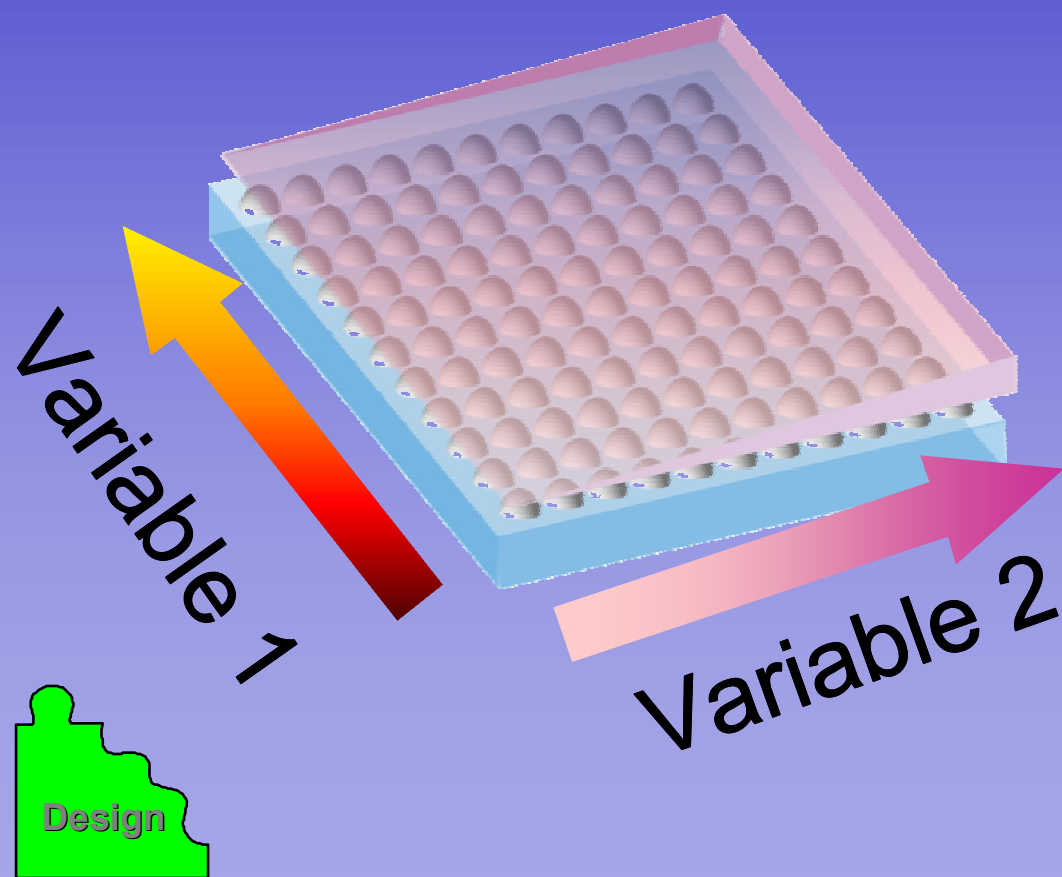
# Why not more?





Combinatorial  
Methods Group

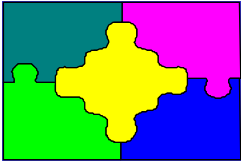
# How do we design a *combinatorial* JKR test?



- Measure  $a$ ,  $\delta$
- Determine  $\mathcal{G}$

- Possible Variables:
  - Temperature
  - Thickness
  - Strain
  - Surface Energy



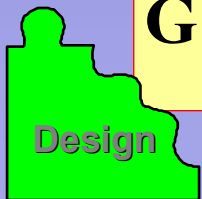
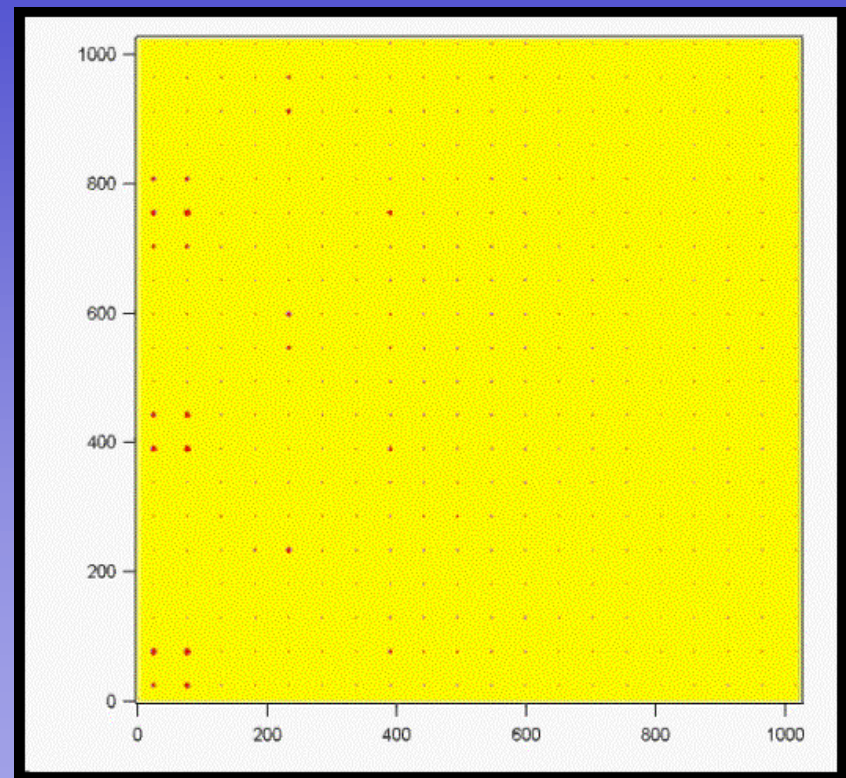


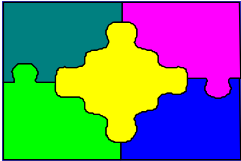
# How do we calculate $\mathcal{G}$ ?

$$a^3 = \frac{9R}{16E} \left[ P + 3\pi GR + \sqrt{6GRP + (3\pi GR)^2} \right]$$

$$C = \frac{3}{8Ea} = \frac{d\delta}{dP} = \frac{\delta' - \delta}{P' - P}$$

$$G = \frac{2E(\delta' - \delta)^2}{3\pi a} \cdot f_{\delta}(a, h)$$

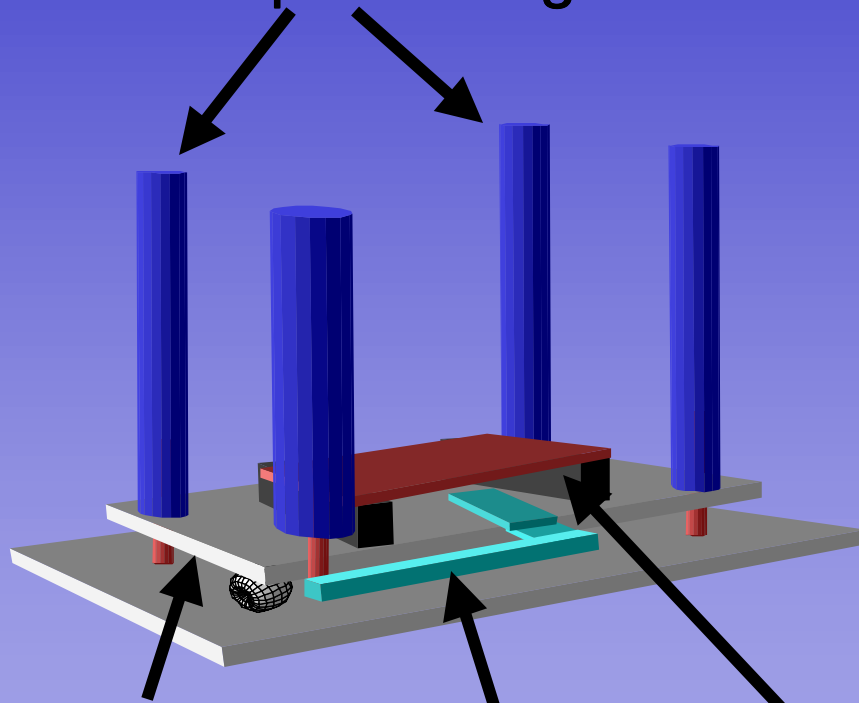




Combinatorial  
Methods Group

# How do we control contact?

Nanopositioning Actuators



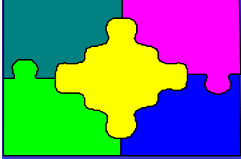
Tip/Tilt Stage

Thermal Gradient Stage

Multilens Probe Holder



Programmable X-Y Stage

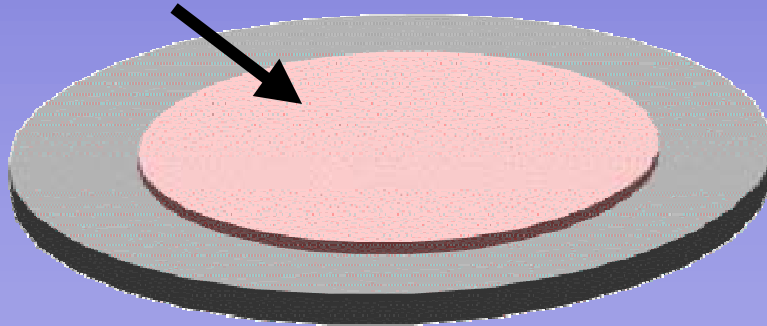


# What problem to consider first?

- The Adhesion of Glassy Polymers to Elastomers  
- Specifically, PS to PDMS

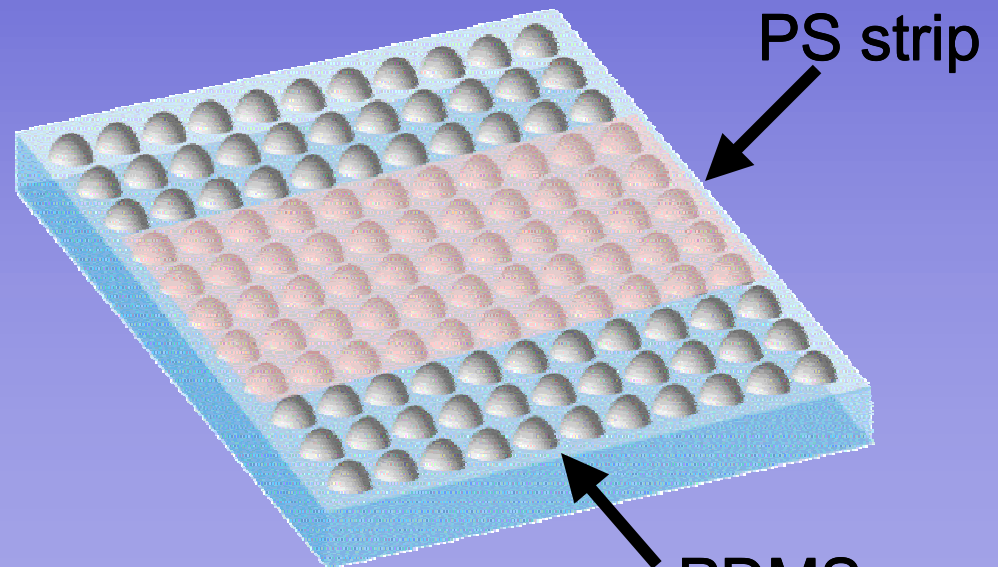
## Our Libraries:

PS film  
 $h = 30 \text{ nm}$

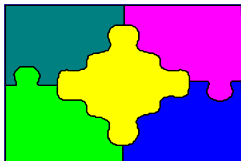


Library  
Generation

Si substrate

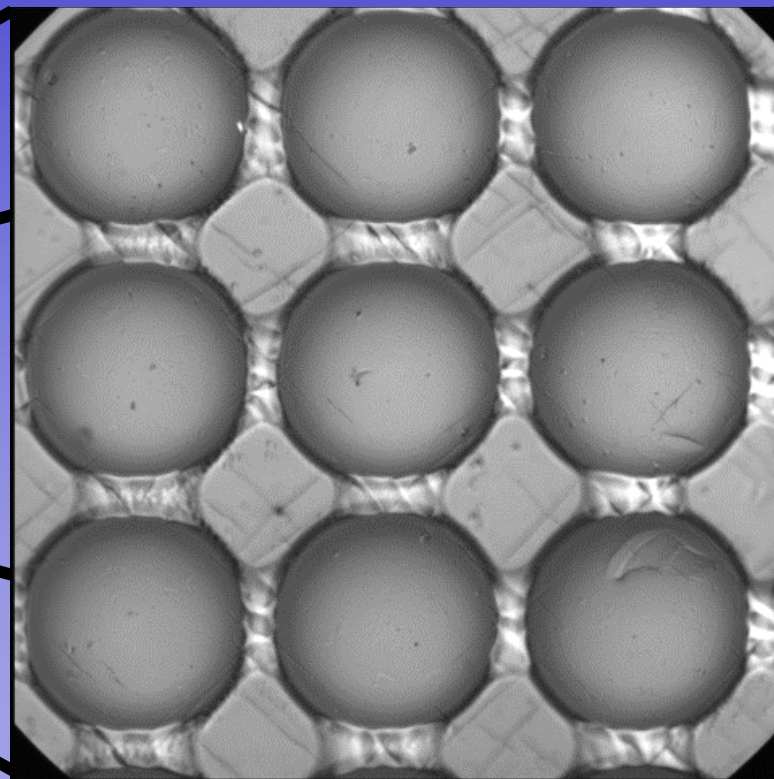
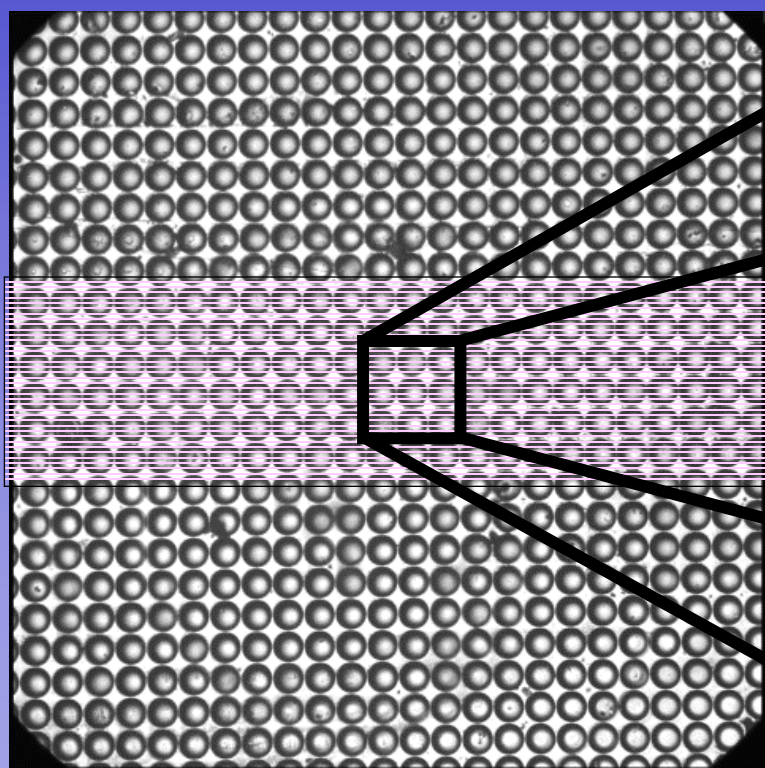


PDMS



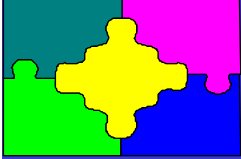
Combinatorial  
Methods Group

# What do our libraries look like?



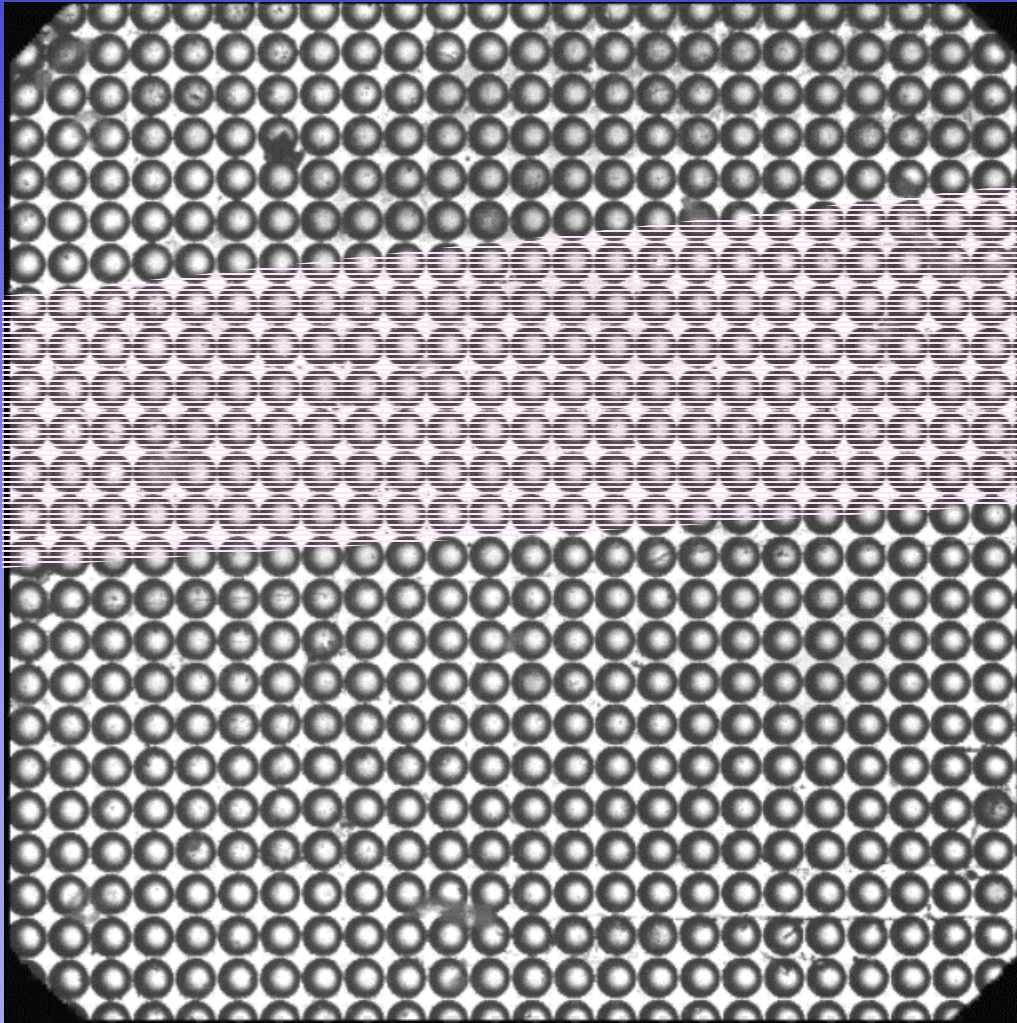
100  $\mu\text{m}$

Library  
Generation



Combinatorial  
Methods Group

# What do we observe?



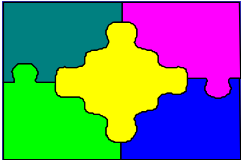
## Conditions:

$$d\delta/dt = 1 \mu\text{m/s}$$

$$h_{\text{PS strip}} = 30 \text{ nm}$$

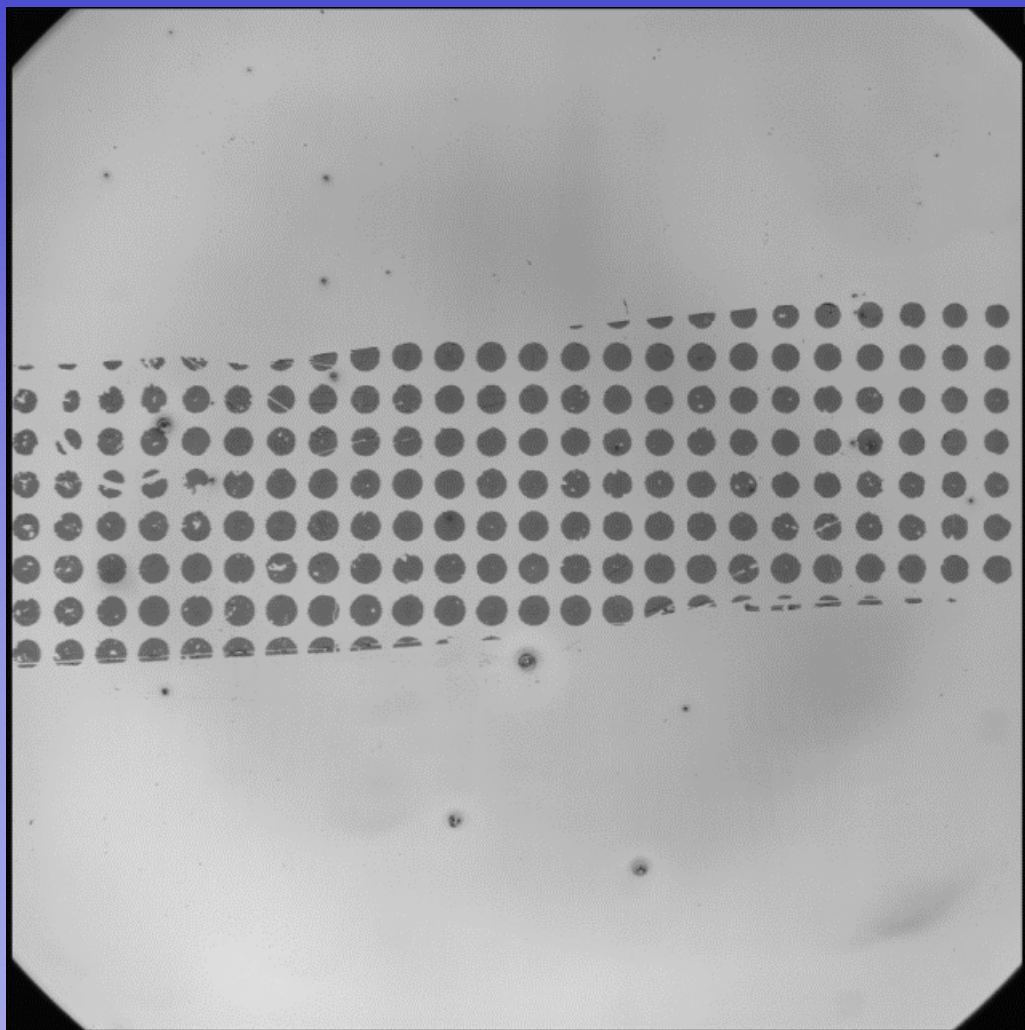
$$\text{Temperature} = 25^\circ\text{C}$$

Library  
Evaluation



Combinatorial  
Methods Group

# What happens at elevated temperature?



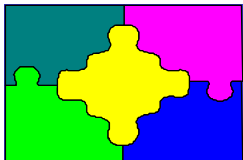
## Conditions:

$$d\delta/dt = 1 \mu\text{m/s}$$

$$h_{\text{PS strip}} = 30 \text{ nm}$$

Temperature  $\sim 80^\circ\text{C}$

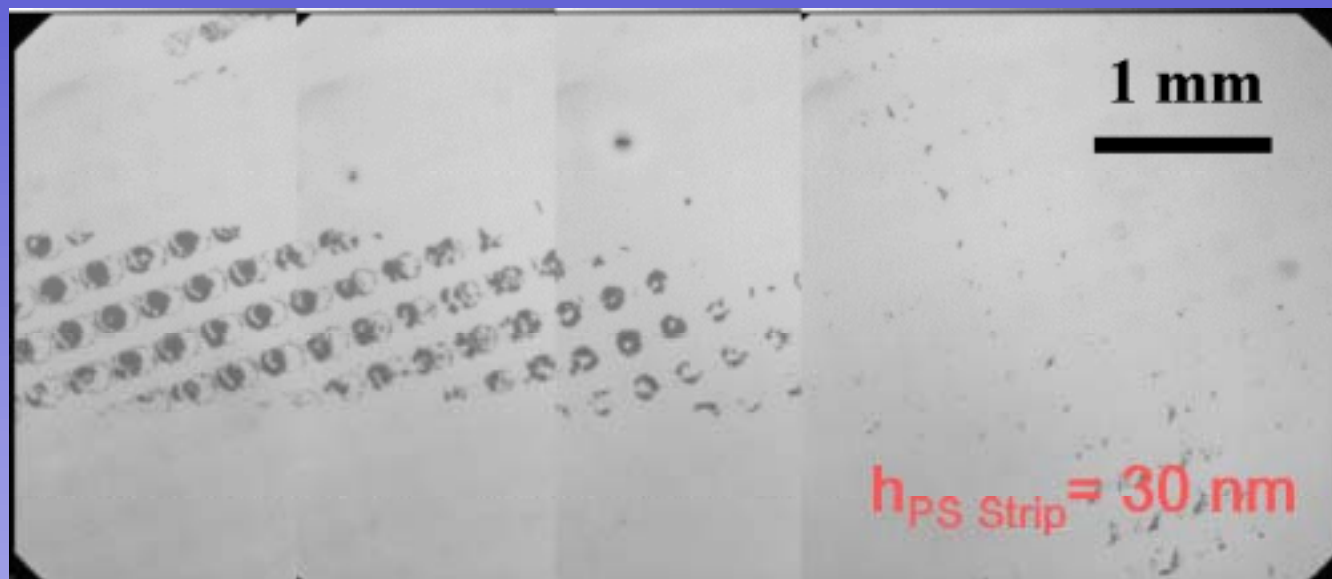
Library  
Evaluation



Combinatorial  
Methods Group

# What is the critical temperature for PS welding?

## Let's use combi!

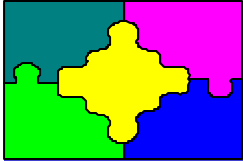


80°C

75°C

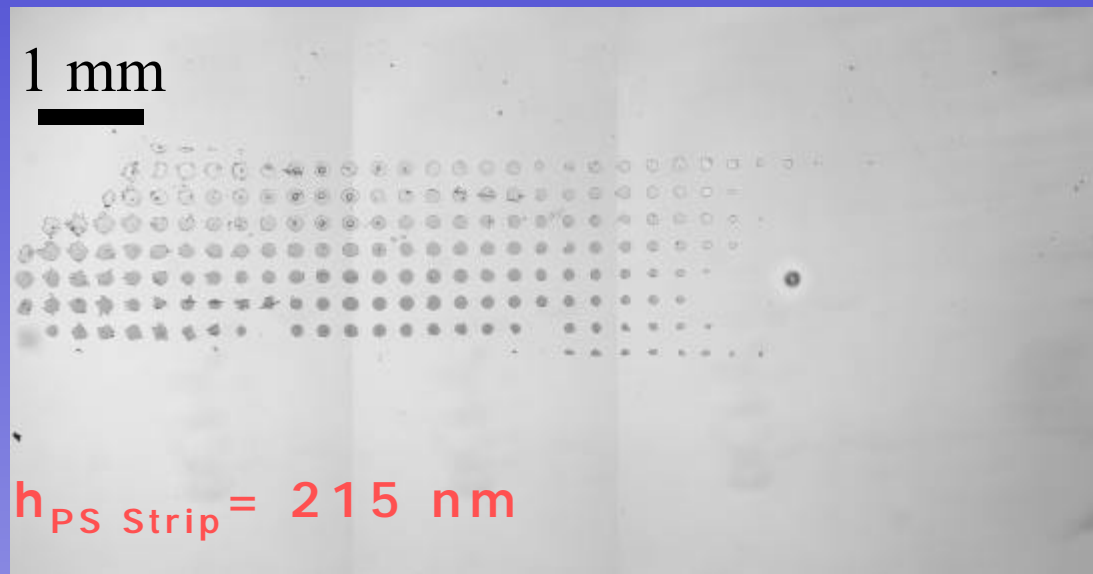
70°C

Library  
Evaluation



Combinatorial  
Methods  
Group

# Does the critical temperature depend on thickness?



100°C

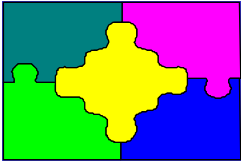
95°C

90°C

85°C

Library  
Evaluation

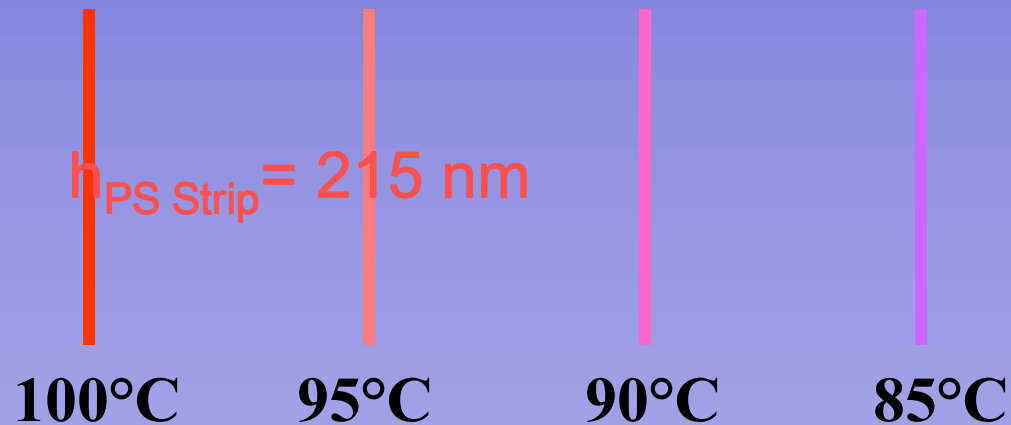


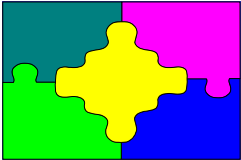


Combinatorial  
Methods Group

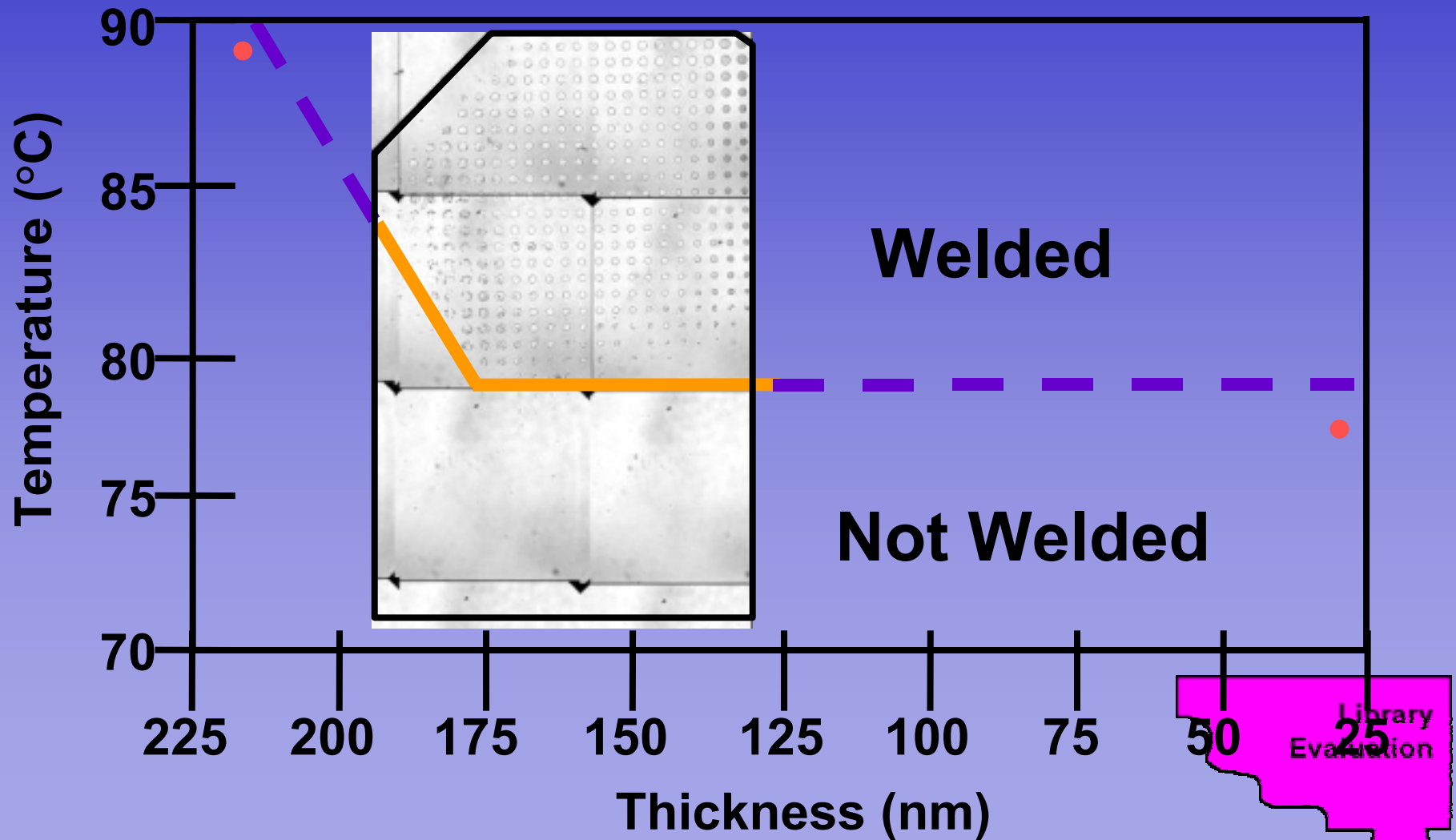
# Does the critical temperature depend on thickness?

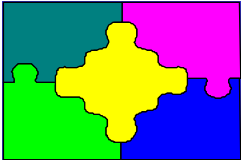
1 mm  



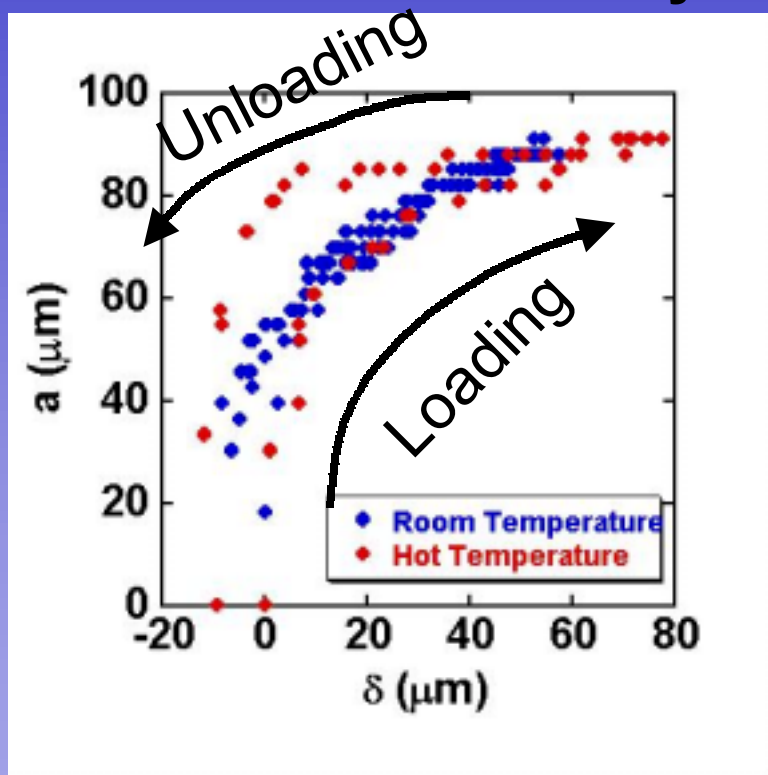
# Does the critical temperature depend on thickness?



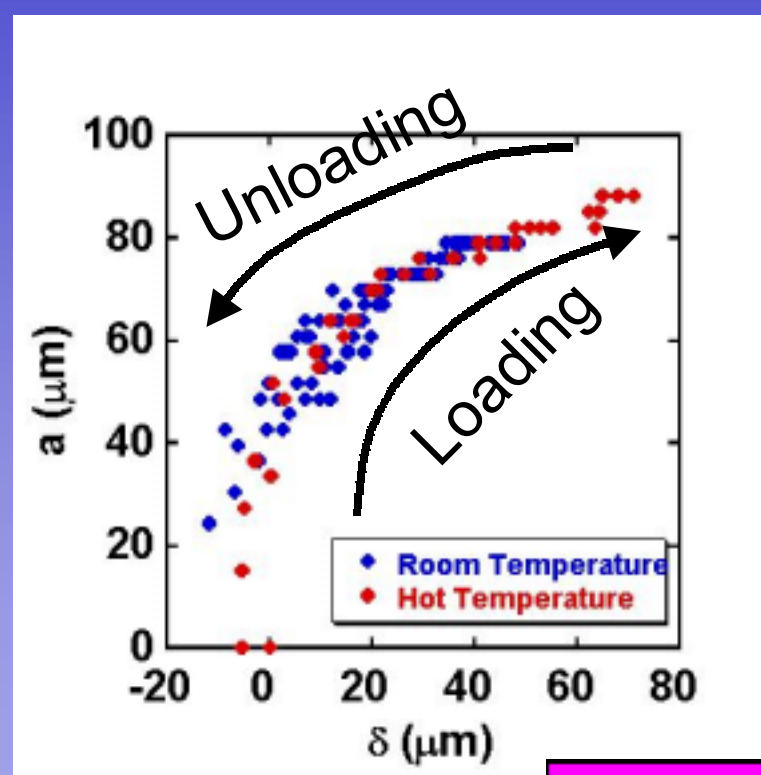


# What does the data look like?

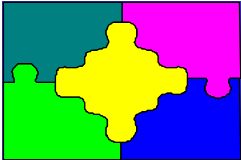
## PS/PS Contact History



## PS/PDMS Contact History



**Same Sample, Same Conditions!**



Combinatorial  
Methods Group

# Automated Analysis

## Combinatorial Adhesion Analysis

Directory Path for Input Files

c:\test\

Directory Path for Output Files

c:\test\_out\

Path for Composite Image

c:\test\_out\

Threshold Values

Minimum Value

Maximum Value



Number of Files

820

Time of First Image

550.183

Pixel Conversion

0.5971

E (Pa)

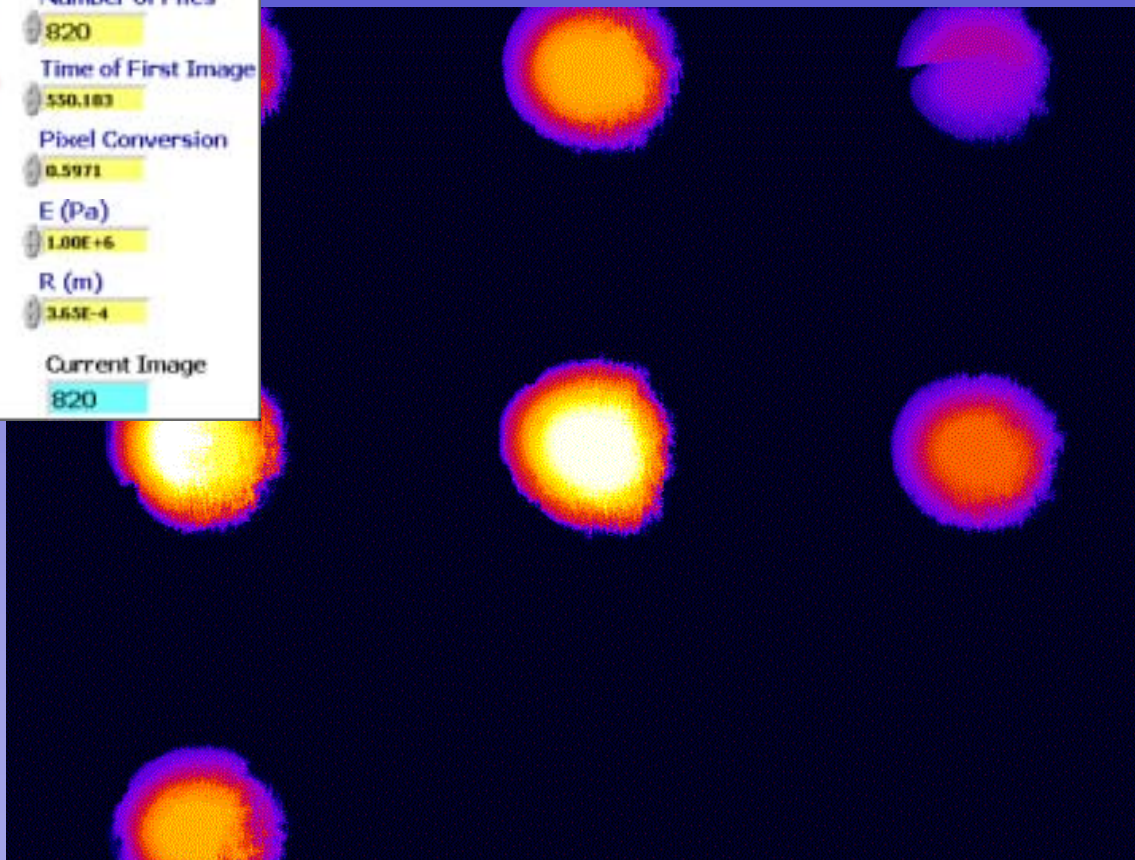
1.00E+6

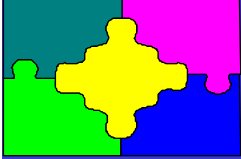
R (m)

3.65E-4

Current Image

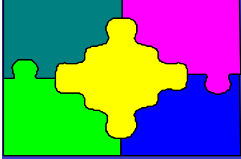
820





# What are the main points?

- Multilens contact reflects classical JKR results
- Combinatorial methods are powerful for studying polymer adhesion
  - e.g. 1600 JKR tests within the time of one conventional test
- Thickness of glassy polymer affects welding temperature
- Adhesion maps provide quick assessment of interfacial properties



Combinatorial  
Methods Group

# Acknowledgements

- National Research Council Research Associateship Program
- Many helpful discussions with:
  - Ken Shull
  - Amit Sehgal
  - Kate Beers
  - A. Paul Smith