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Dynamic Wetting Behavior of Complex Liquids on Rough Surfaces

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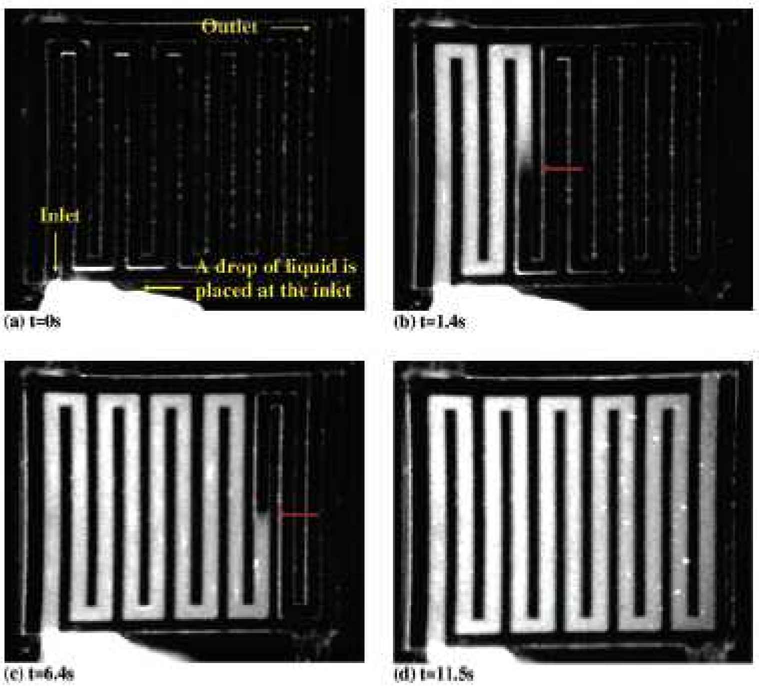
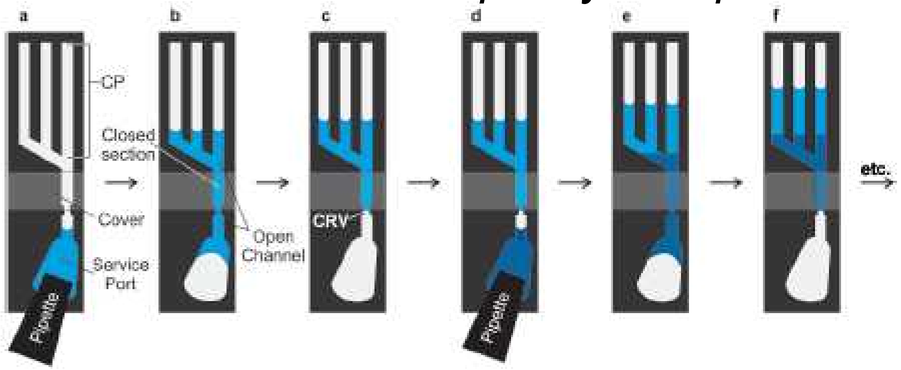
The Importance of Wetting Dynamics

Nanoliter Viscometer



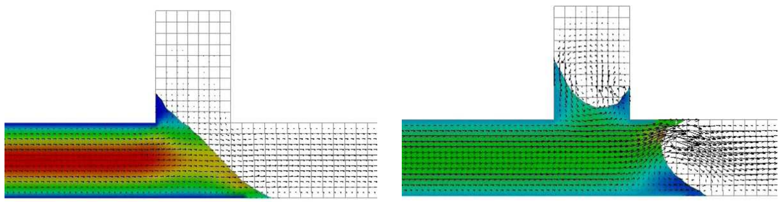
N. Srivastava, R.D. Davenport, M.A. Burns, *Anal. Chem.* **2005**, *77*, 383-392.

Microfluidic Capillary Pump



D. Juncker et al., *Anal. Chem.* **2002**, *74*, 6139-6144.

Gap Filling

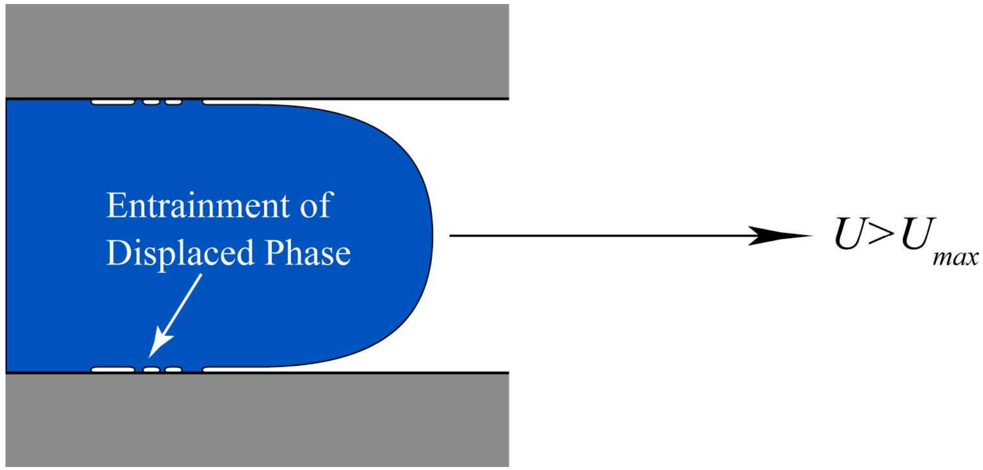


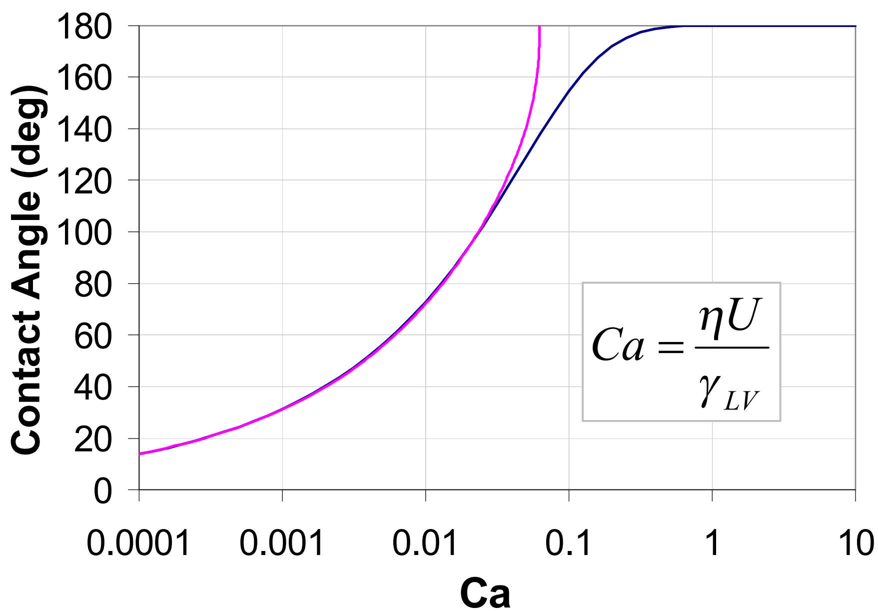
• Capillary/Surface forces can strongly impact flow behavior in small geometries

• Require an understanding of how the contact angle depends on contact line velocity

Void Formation Mechanism

Entrainment

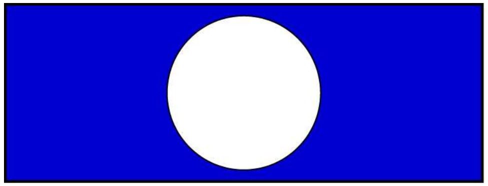




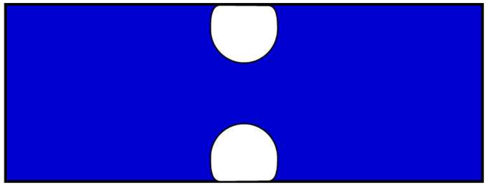
Void Formation Mechanism

Combining Advancing Fronts

$\theta < 90^\circ$



$\theta > 90^\circ$

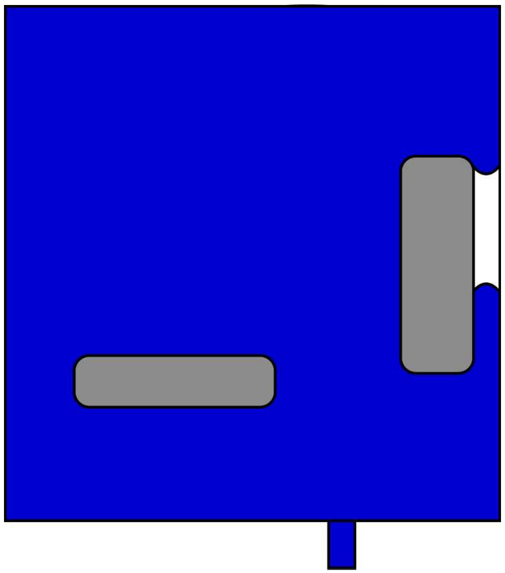


•Knowing the dependence of θ with *U* aids in predicting the shape of the advancing front

•Movable voids or surface attached voids may result depending on the interface shape (θ<90º or θ>90º)

Void Formation Mechanism

Entrapment



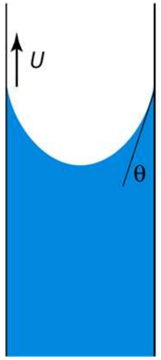
Results from multiple flow paths with different flow resistance (strongly geometry dependent)

Overview

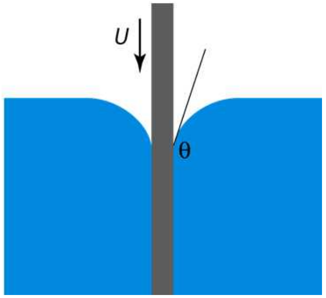
- Experimental Approaches to Measuring Dynamic Wetting
- Feed-through goniometer
  - Blake Model
  - Kinetic Blake Model
- Reactive Liquids
- Surface Roughness
- Summary

Methods to Study Dynamic Wetting

Spreading Drop



Induced Flow in Capillary

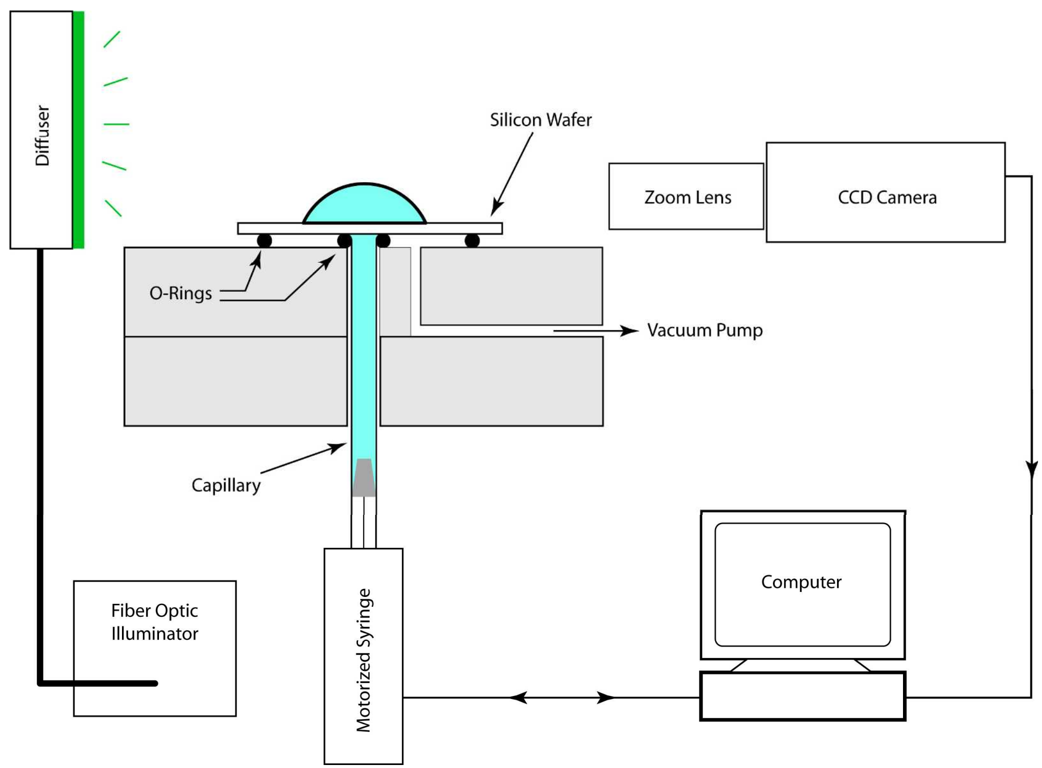


Immersion

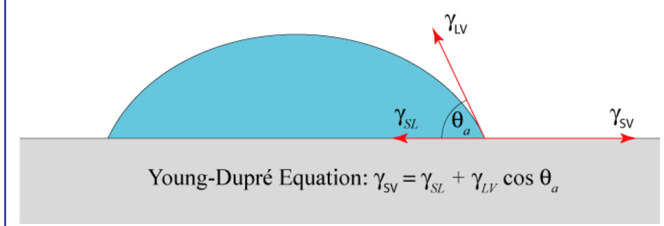
Spontaneous Wetting

Forced Wetting

Feed-Through Goniometer



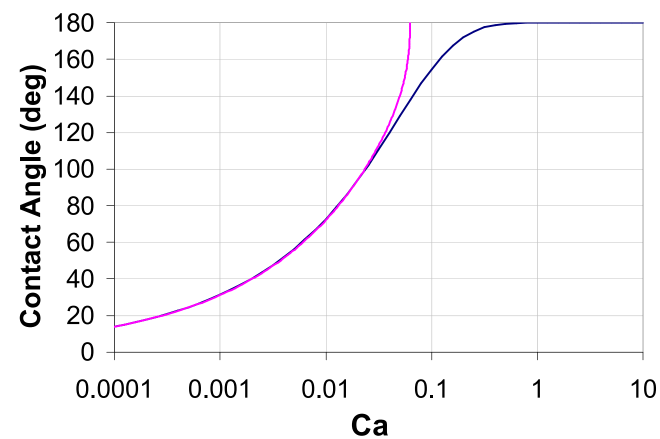
Amirfazli, Kwok, Gaydos, Neumann, J. Colloid Interface Sci. 205 (1998) 1.



$S \equiv \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$

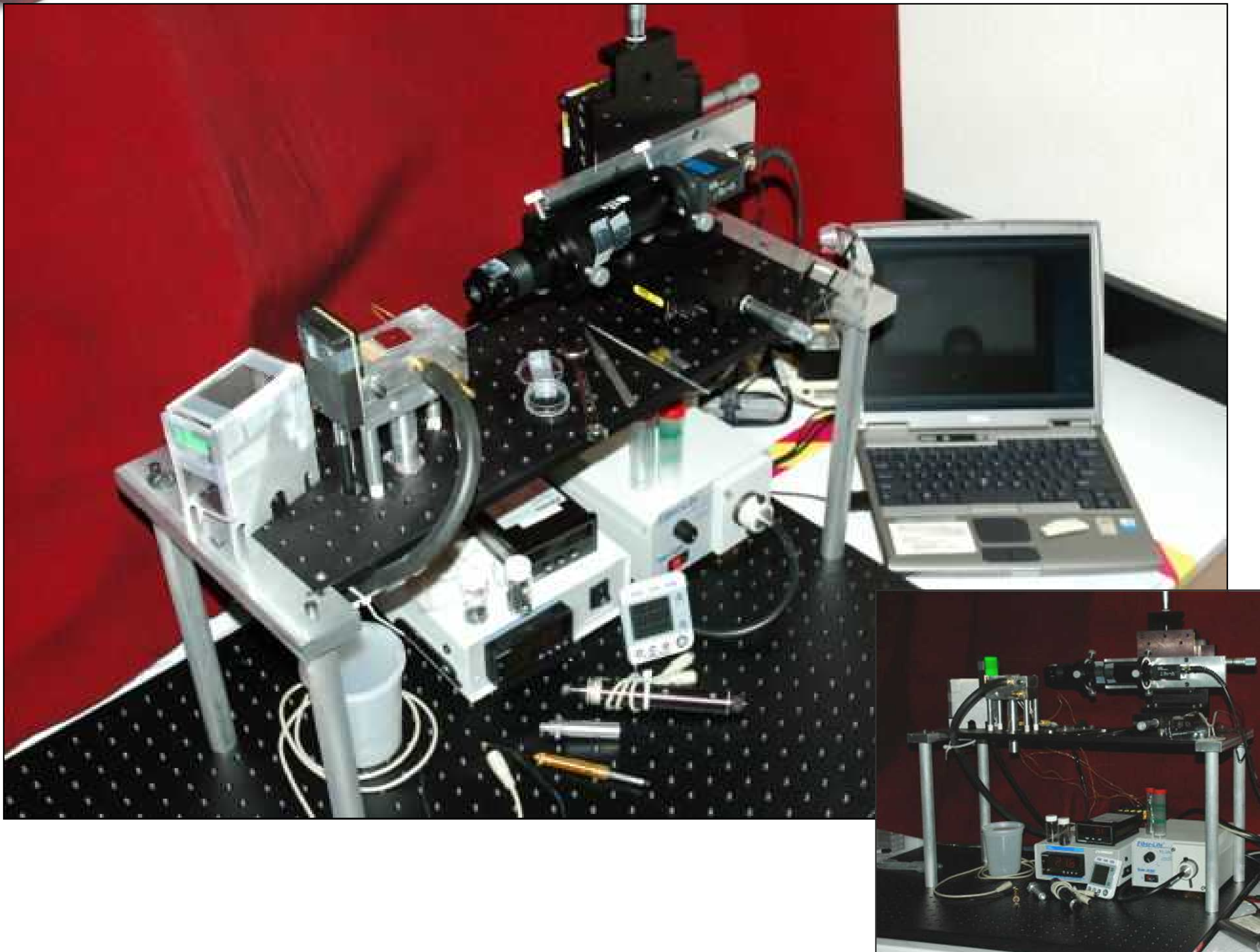
$S > 0$ **Complete Wetting** $\left(\theta_a = 0^\circ\right)$

$S \le 0$ **Partial Wetting** $\left(\theta_a > 0^\circ\right)$

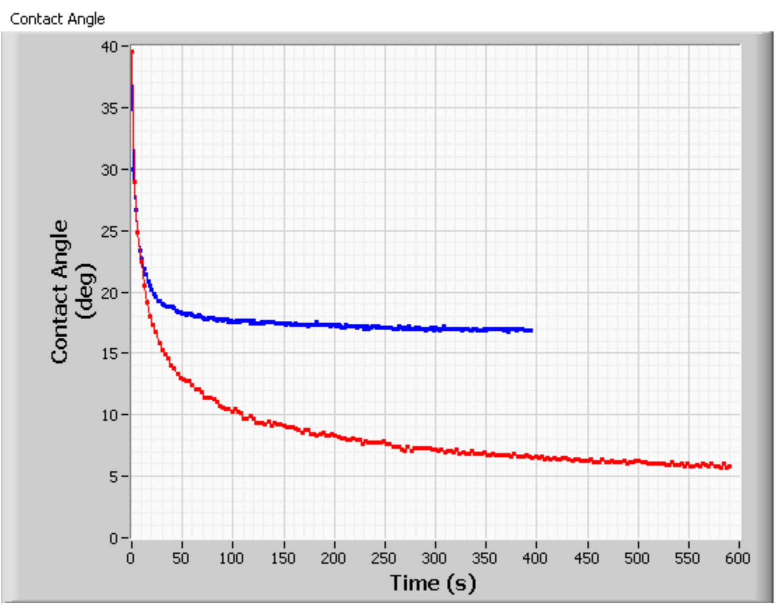


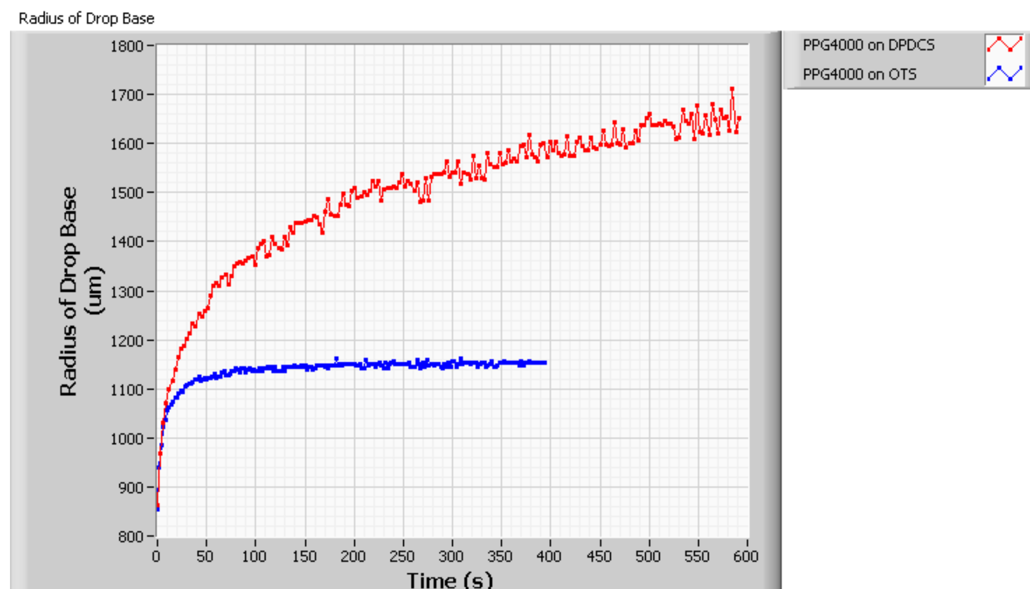
- Analyze dynamics of spontaneous spreading
- Continuously inject liquid to achieve "high" velocities
- Stop flow and let sessile drop relax to obtain "low" velocities

Feed-through Goniometer Setup



Wetting Experiment Results





Wetting Models

- Molecular-Kinetic Model (Full Non-linear Blake)

T.J. Blake, J. De Coninck *Adv. Colloid Int. Sci.* **2002**, *96*, 21-36.

Adhesion to Substrate

$$U = \frac{2kT\lambda}{\eta v_L} \exp\left[\frac{-\gamma_{LV}(1+\cos\theta_\infty)}{nkT}\right] \sinh\left[\frac{\gamma_{LV}(\cos\theta_\infty - \cos\theta)}{2nkT}\right]$$

Viscosity

Molecular-Kinetic

Group terms

Solve for $\cos\theta$

$$U = A\sinh\left[\frac{\cos\theta_\infty - \cos\theta}{B}\right]$$

$$\cos\theta = \cos\theta_\infty - B\sinh^{-1}\left[\frac{U}{A}\right]$$

$$\cos\theta_\infty = a_0 + a_1 t_{cure}$$

$$B = a_2 + a_3 t_{cure}$$

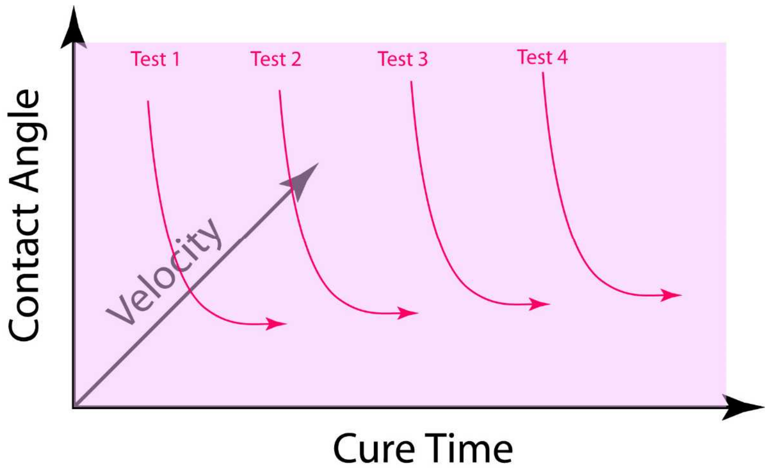
$$A = a_4 + a_5 t_{cure}$$

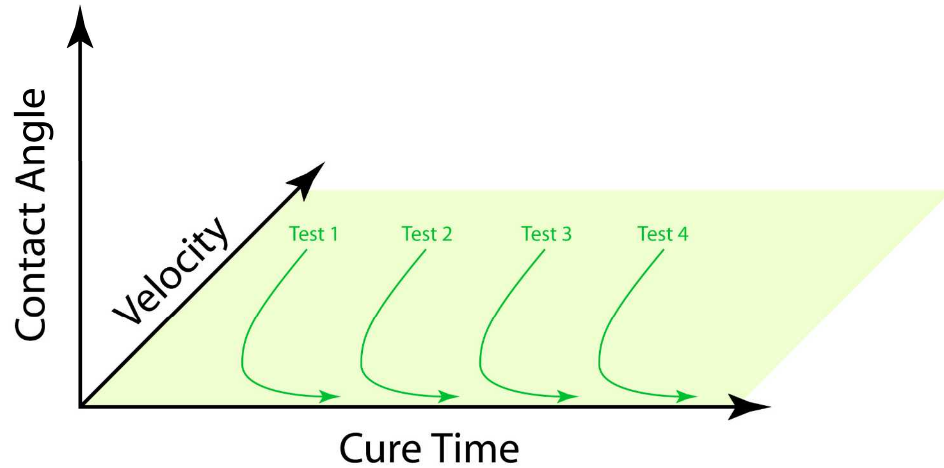
"Curing" model empirically uses a linear dependence on cure time, t_{cure} (6 unknowns)

"No Cure" model has 3 parameters

$$a_1 = a_3 = a_5 = 0$$

Dynamic Wetting Measurements on Reactive Systems





- Velocity is indirectly controlled in wetting experiment with pump rate
- Each experiment measures the contact angle and velocity as a function of cure time
- To obtain contact angle-velocity relationship as a function of cure time, multiple tests are conducted at different cure times with additional substrates
- Perform nonlinear regression over a 2D domain to determine model parameters

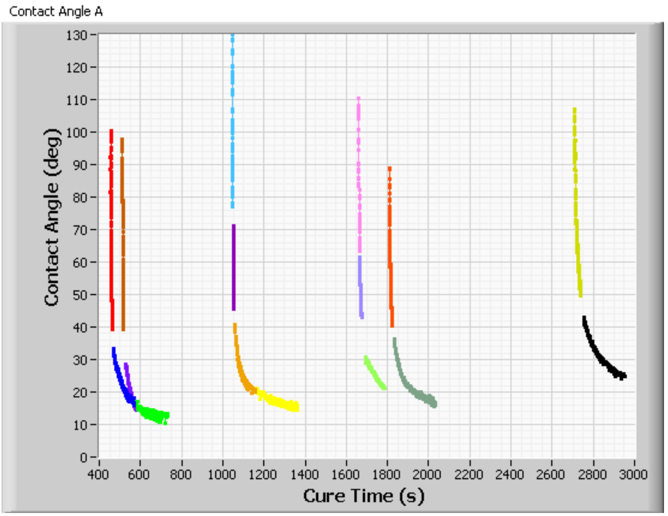
Dynamic Wetting on Reactive Systems

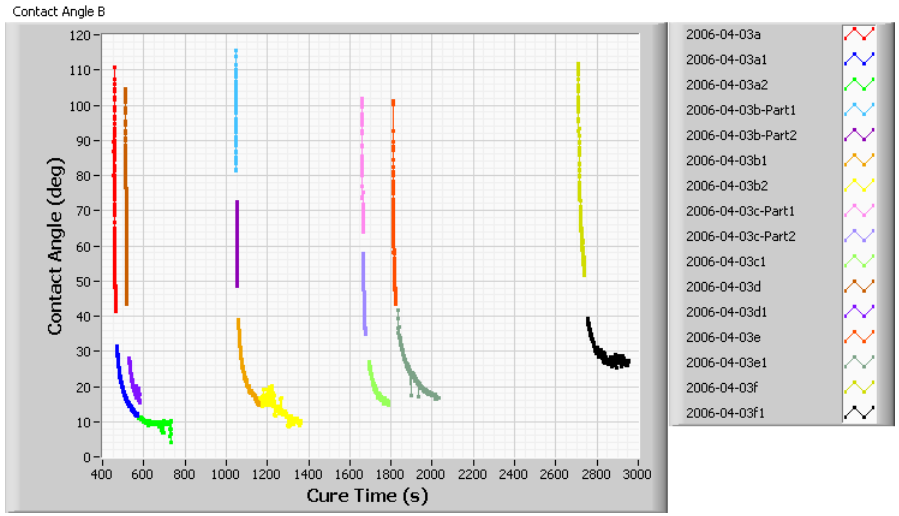
Sylgard 184 with 5 wt.% Accelerator on Aluminum at 35°C

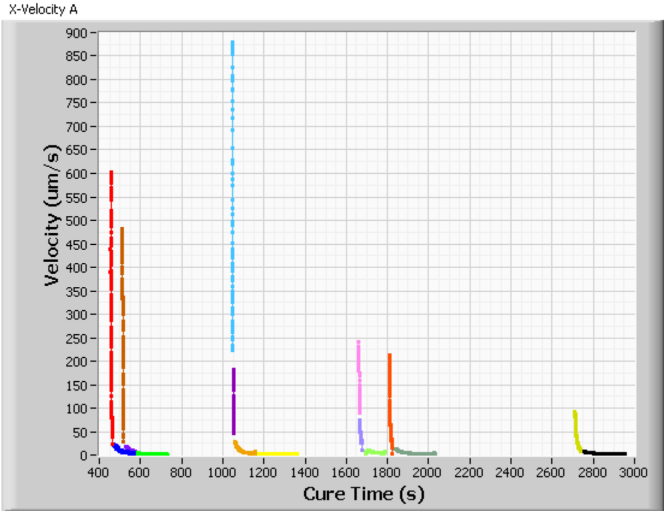
Raw Data Extracted from Images from Multiple Tests

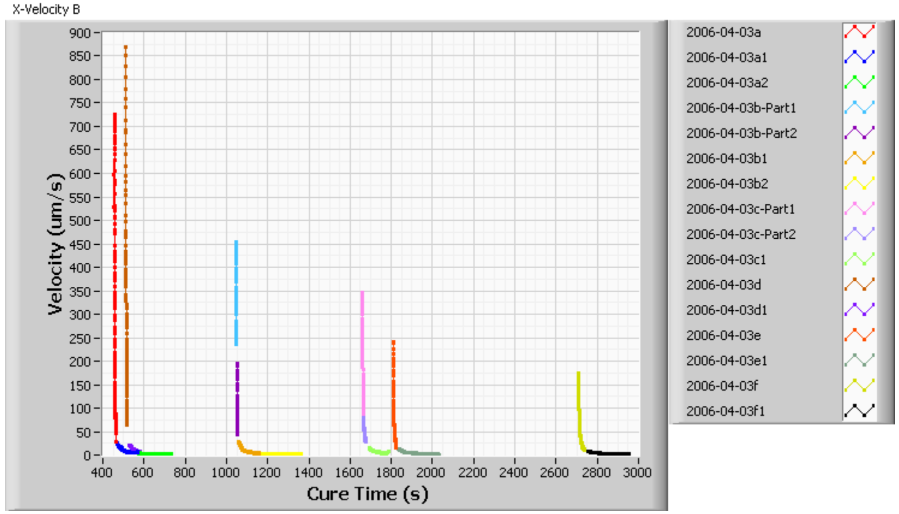
Left Contact Line

Right Contact Line





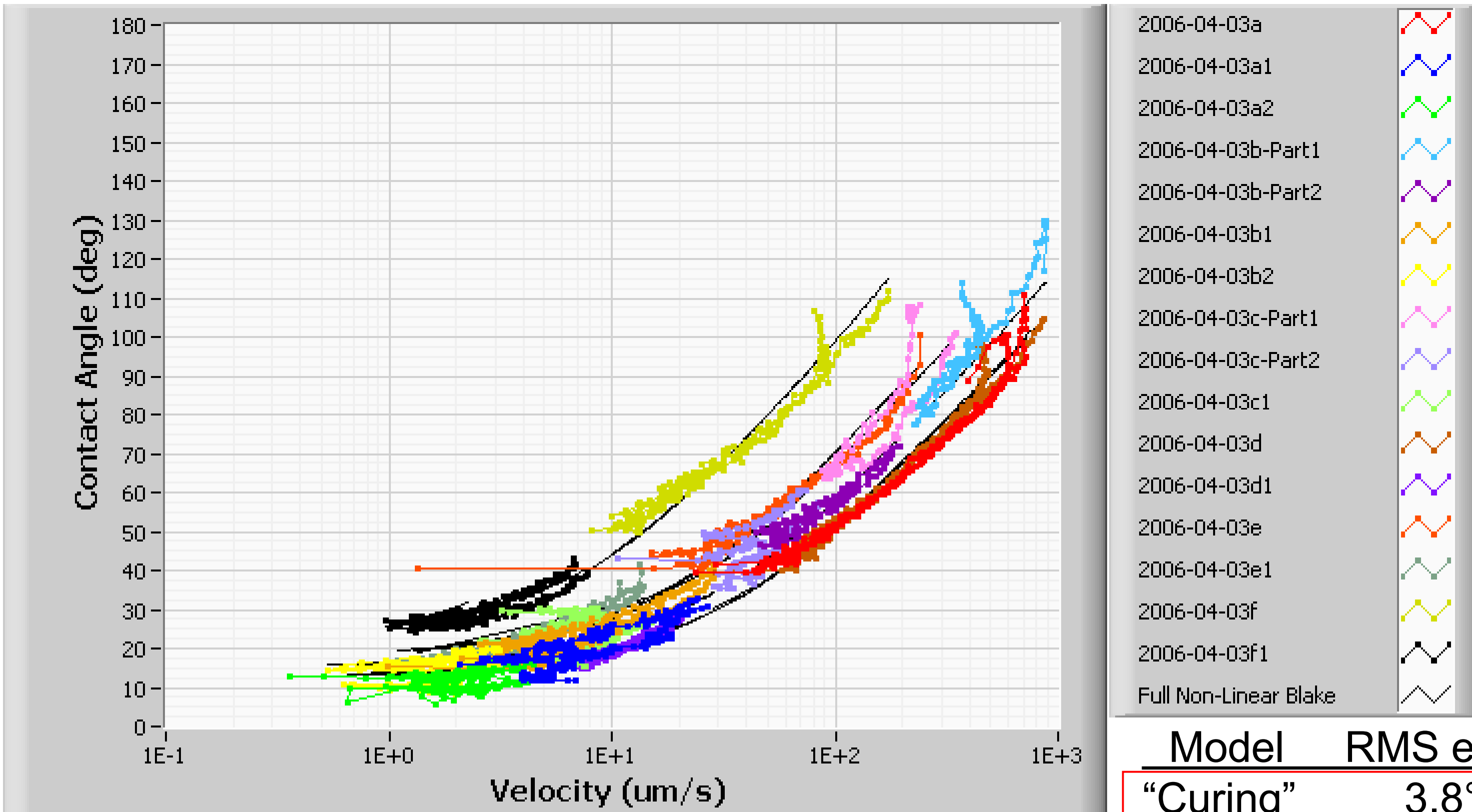




Dynamic Wetting on Reactive Systems

Sylgard 184 with 5 wt.% Accelerator on Aluminum at 35°C

Angle vs. Velocity for both Left and Right Three Phase Contact Lines

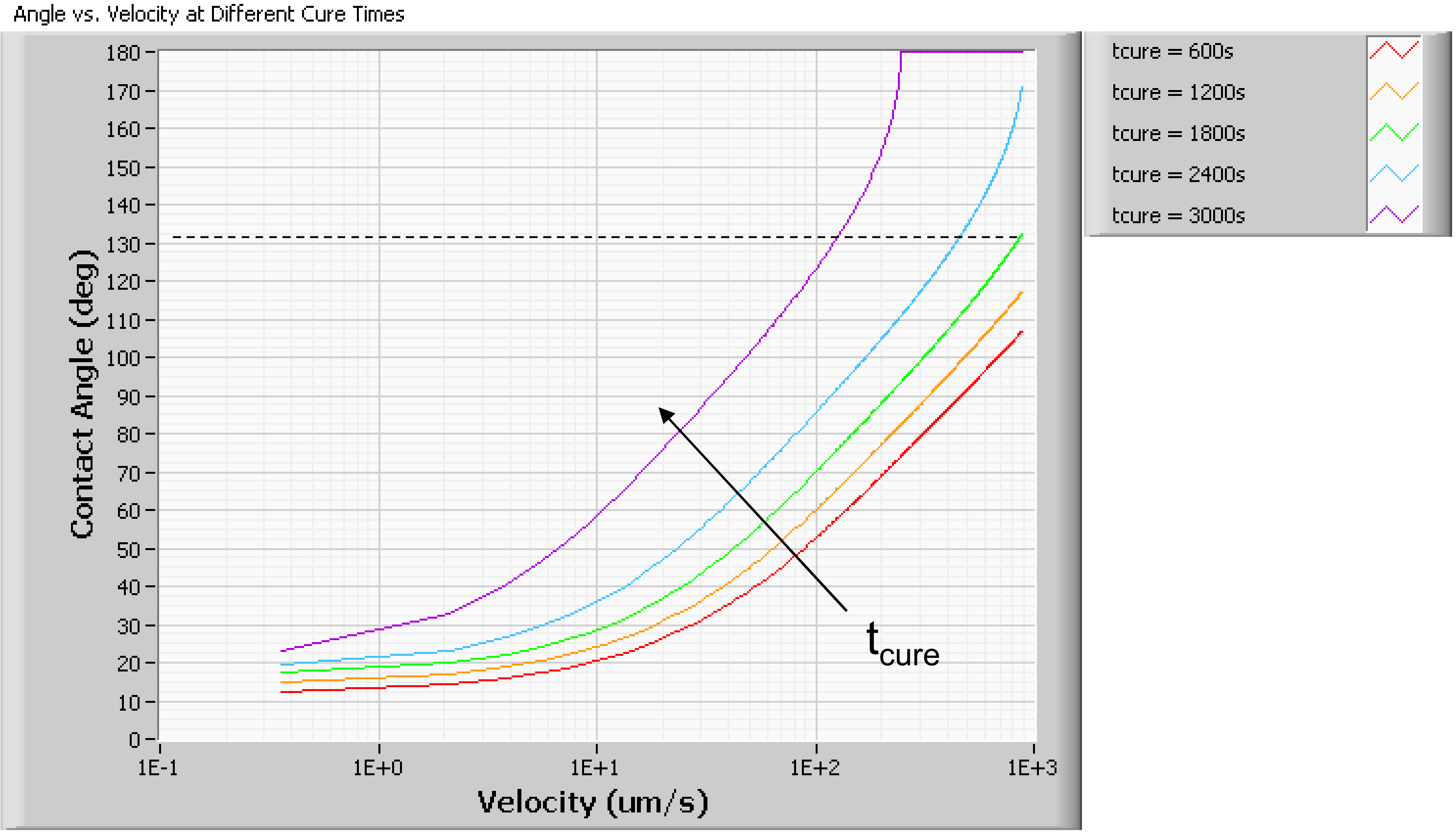


Model	RMS error
"Curing"	3.8°
"No Cure"	10.0°

- **Select "best model" – only select curing model if *much better than* no cure model**
- **Interpretation is complicated since reaction is occurring in each test – data cannot be taken at constant cure time**
- **Model Predictions can be used to illustrate response at constant cure time**

Dynamic Wetting on Reactive Systems

Sylgard 184 with 5 wt.% Accelerator on Aluminum at 35°C

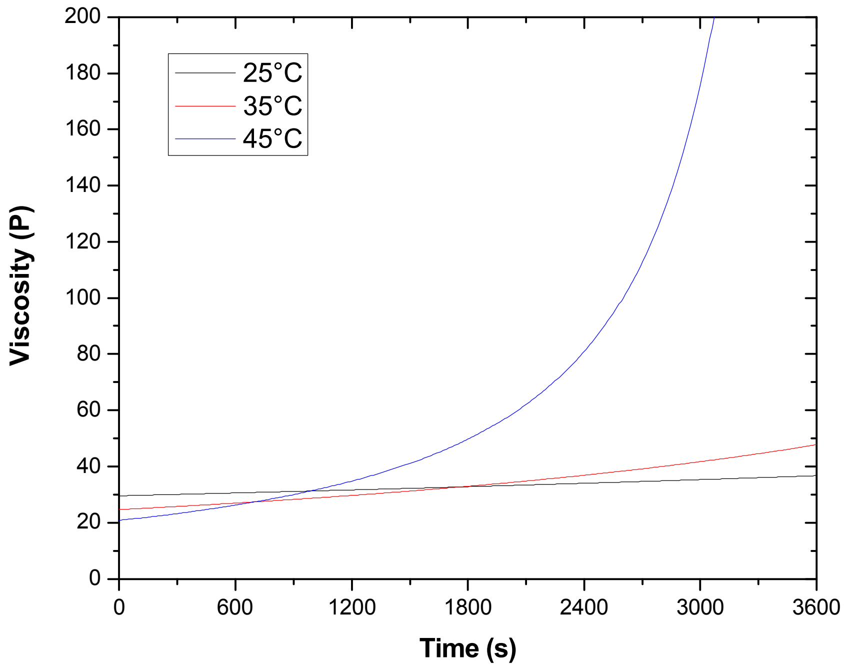


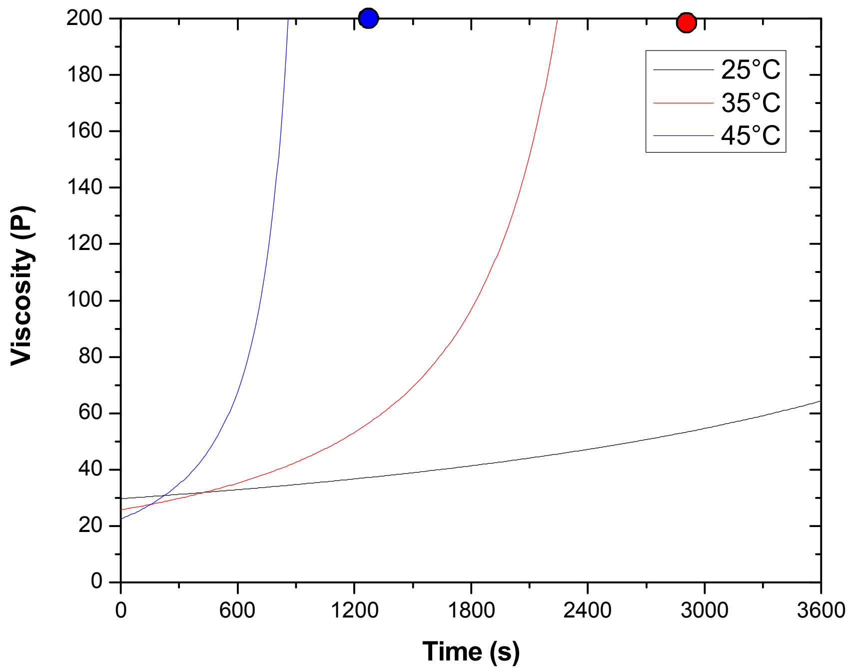
Sylgard 184 Time-Dependent Viscosity

90.9 wt.% Elastomer Base

9.1 wt.% Curing Agent

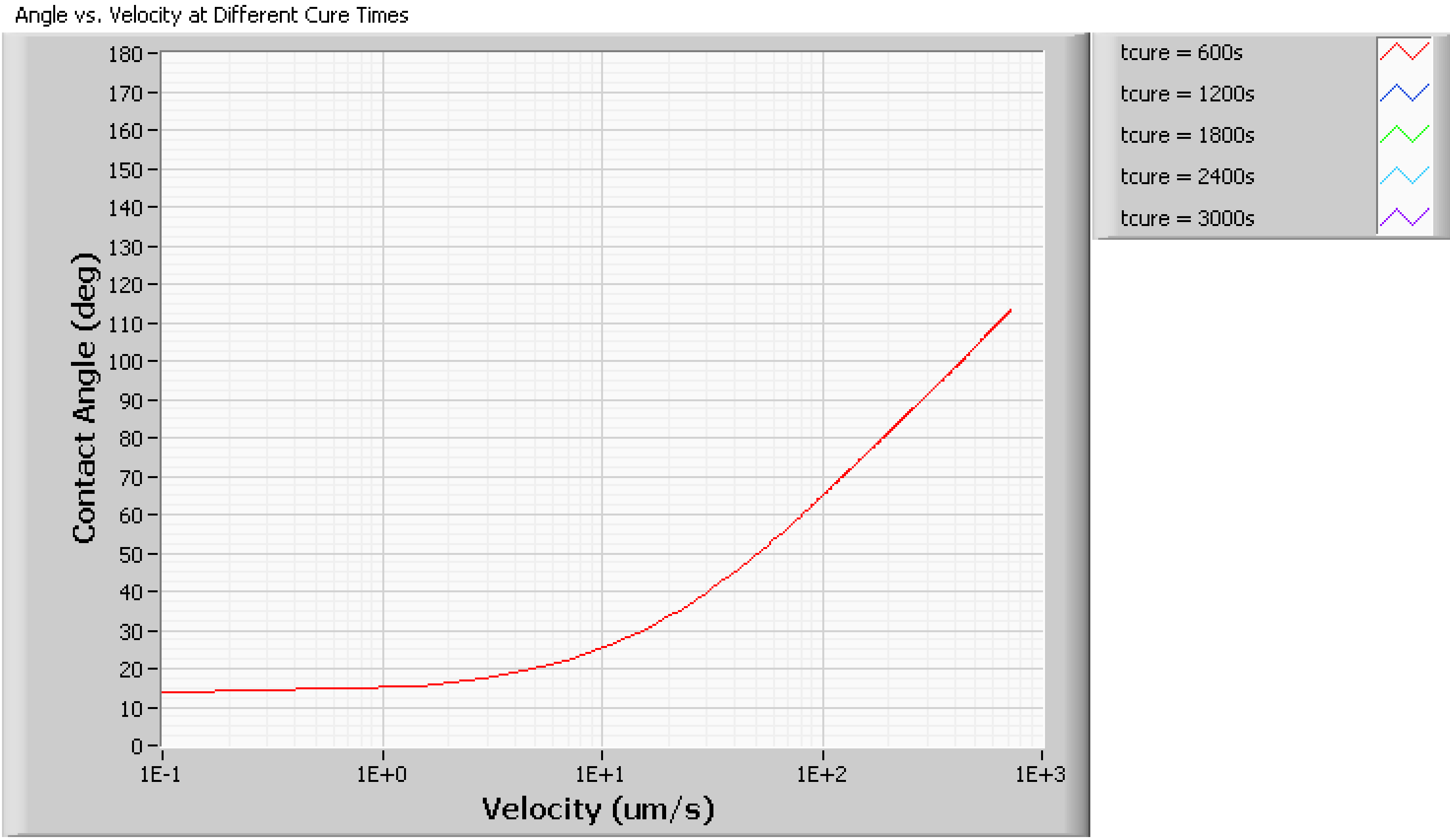
86.4 wt.% Elastomer Base
4.5 wt.% Accelerator
9.1 wt.% Curing Agent





Sylgard 184 Wetting on Aluminum with Mirror Finish

No Accelerator in Part A; T= 25°C



ror

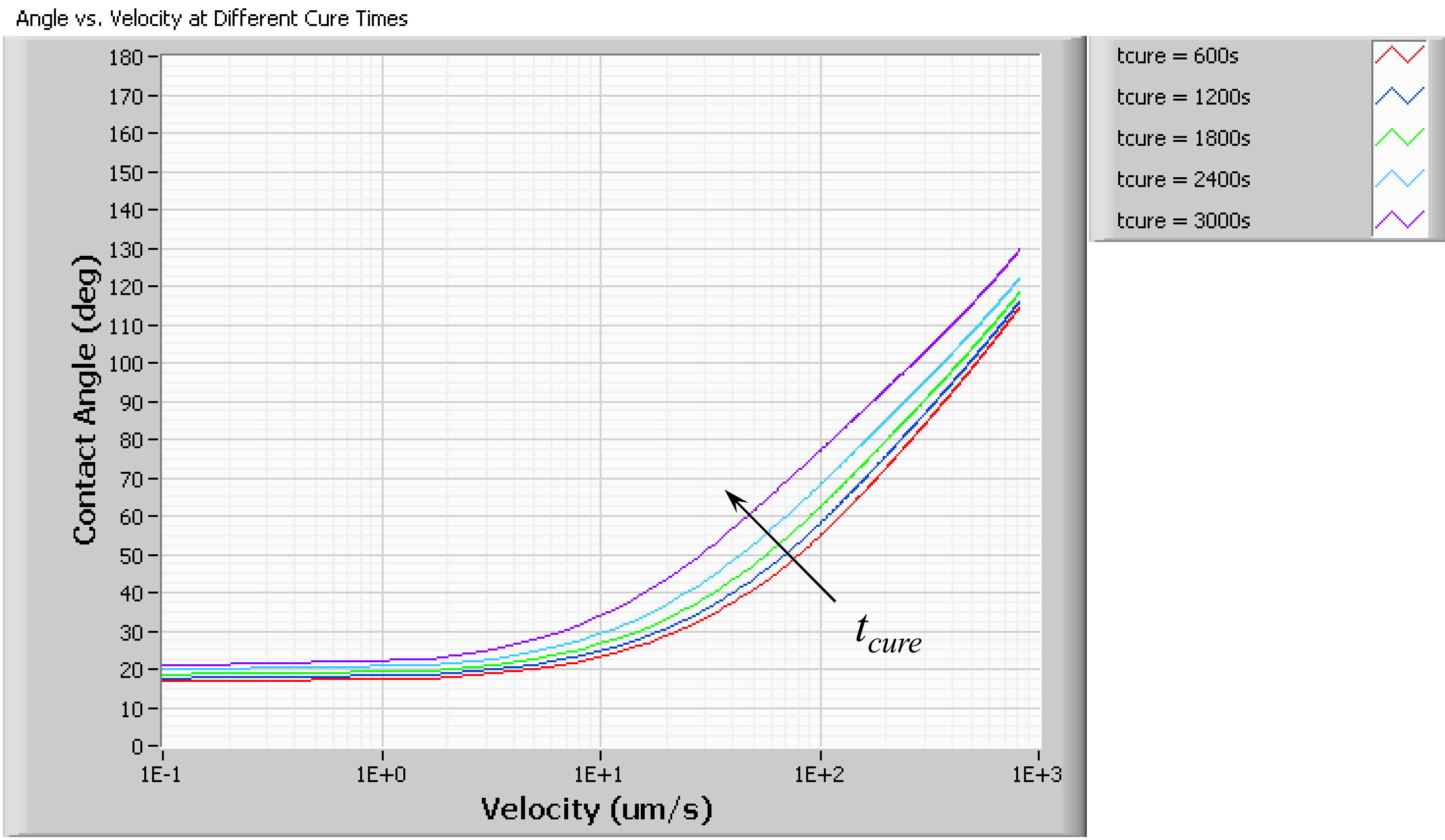
$$\cos\theta_\infty = 0.974 \left(\theta_\infty = 13.1^\circ\right)$$

$$B = 0.434$$

$$A = 61.1$$

Sylgard 184 Wetting on Aluminum with Mirror Finish

No Accelerator in Part A; T= 35°C



ror

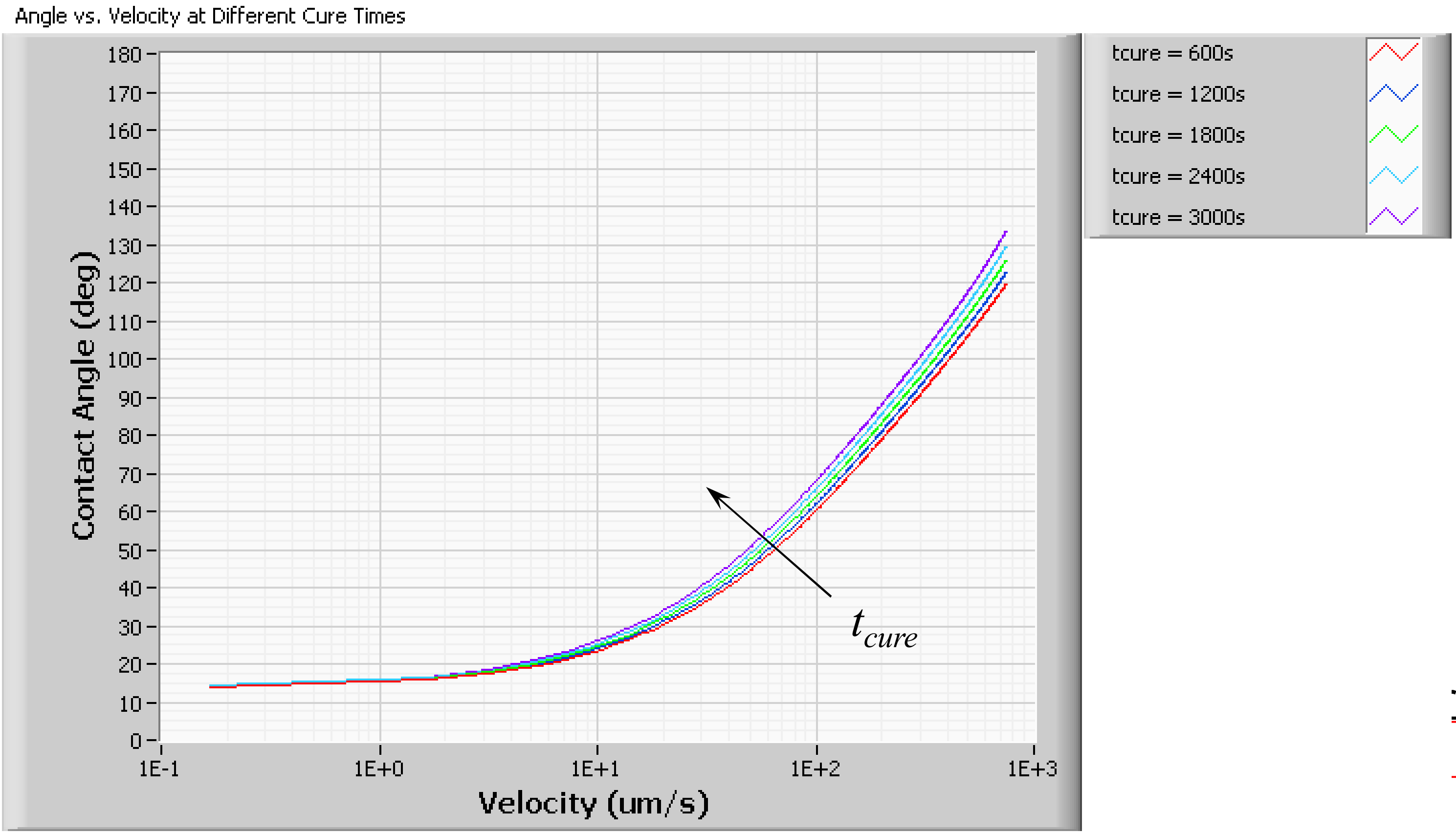
$$\cos\theta_\infty = 0.965 - \left(7.29\times10^{-6}\right)\cdot t_{cure} \qquad \left(\theta_\infty(300s) = 15.7^\circ\right)$$

$$B = 0.573 - \left(5.26\times10^{-5}\right)\cdot t_{cure}$$

$$A = 154 - 0.0390\cdot t_{cure}$$

Sylgard 184 Wetting on Aluminum with Mirror Finish

5wt.% Accelerator in Part A; T= 25°C



ror

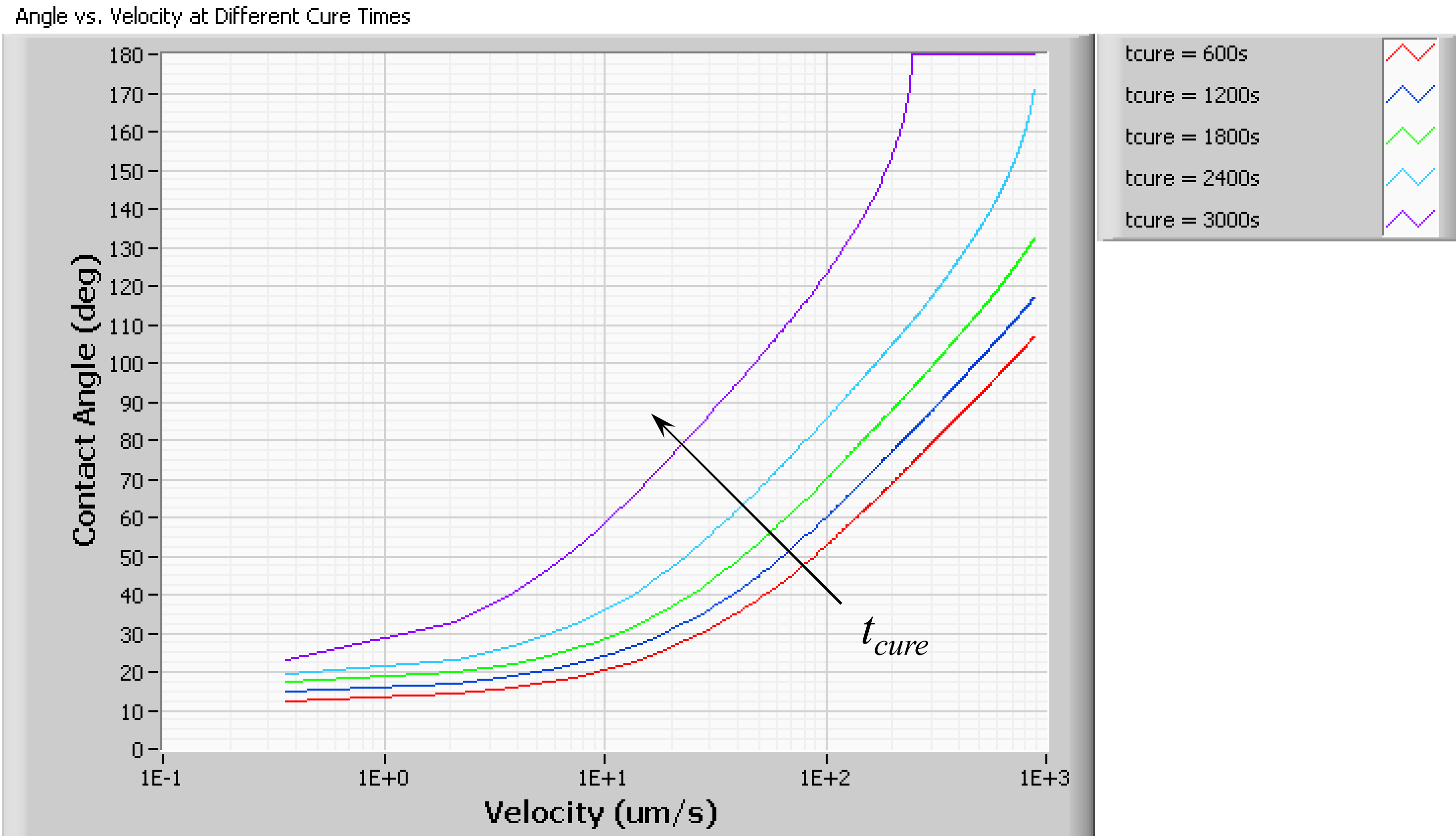
$$\cos\theta_\infty = 0.971 - \left(2.45\times10^{-7}\right)\cdot t_{cure} \qquad \left(\theta_\infty\left(300s\right) = 13.8^\circ\right)$$

$$B = 0.538 + \left(9.10\times10^{-6}\right)\cdot t_{cure}$$

$$A = 107 - \left(9.14\times10^{-3}\right)\cdot t_{cure}$$

Sylgard 184 Wetting on Aluminum with Mirror Finish

5wt.% Accelerator in Part A; T= 35°C



ror

“No Cure” 10.0°

$$\cos\theta_\infty = 0.989 - \left(1.71\times10^{-5}\right)\cdot t_{cure} \qquad \left(\theta_\infty(300s) = 10.3^\circ\right)$$

$$B = 0.444 + \left(2.23\times10^{-5}\right)\cdot t_{cure}$$

$$A = 136 - \left(4.16\times10^{-2}\right)\cdot t_{cure}$$

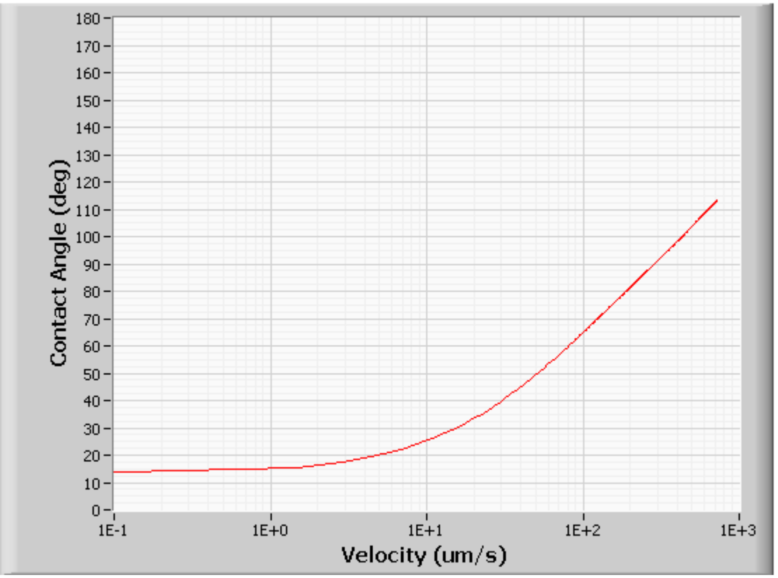
Comparison of Curing Temperature and Accelerator

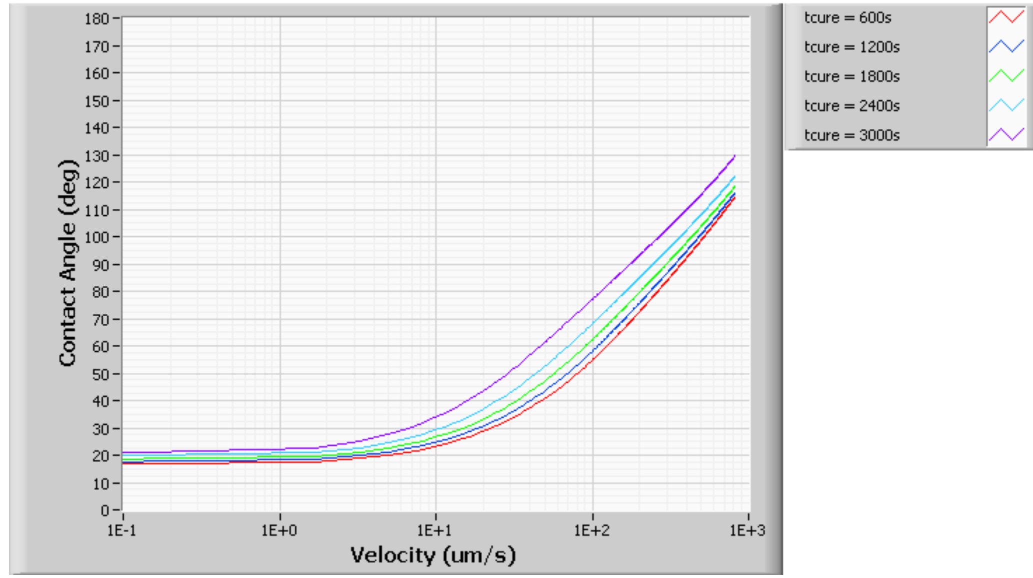
Aluminum with Mirror Finish

T = 25°C

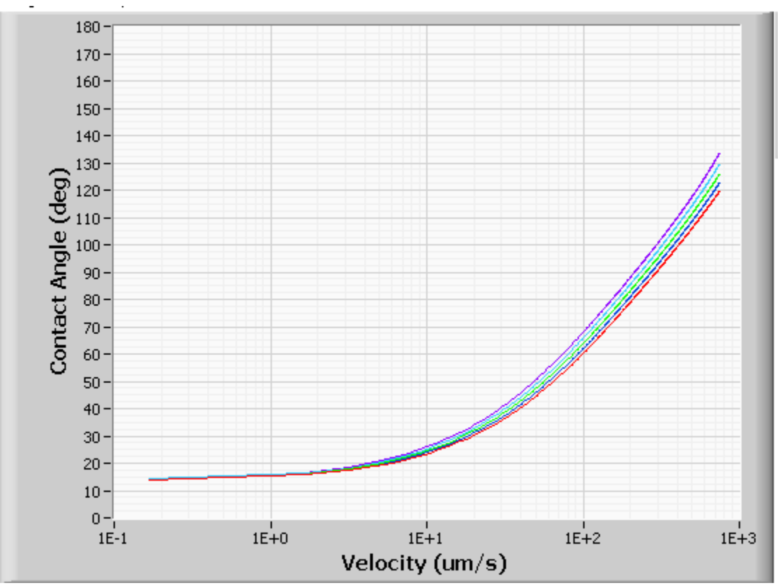
T = 35°C

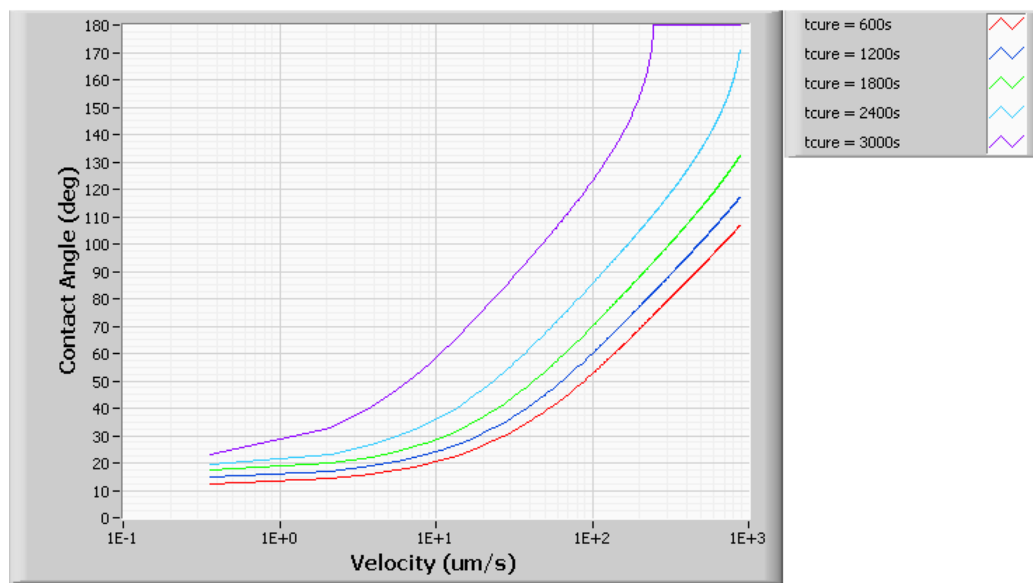
No Accelerator





5wt.% Accelerator in Part A

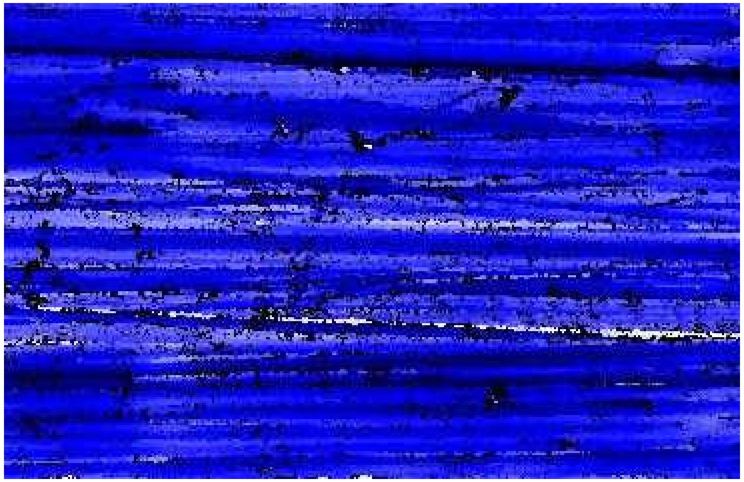




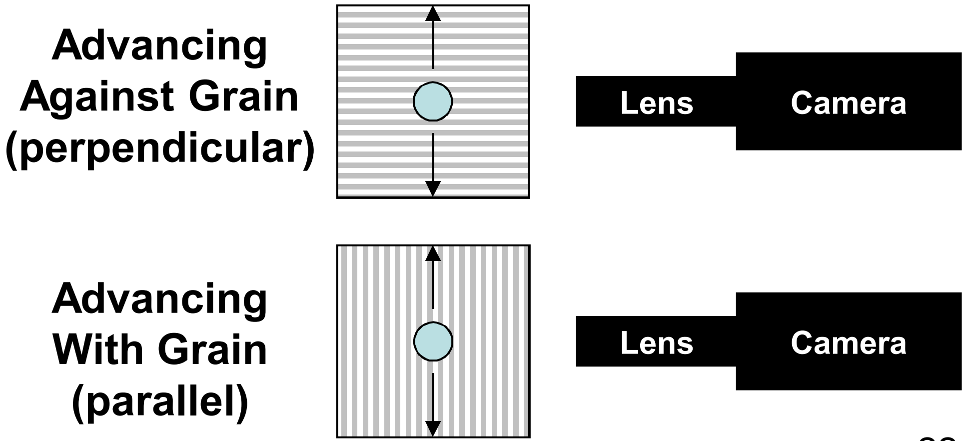
Effect of Surface Roughness on Dynamic Wetting

- Machined aluminum surfaces with varying degrees of roughness - roughness is anisotropic. (16 to 250 μ-inch)
- Measure dynamic wetting of UCON 75-H-9500 fluid at 25ºC
  - rand. copolymer with 75wt.% ethylene oxide and 25wt.% propylene oxide; μ = 4300 cP; γ = 37.0 mN/m

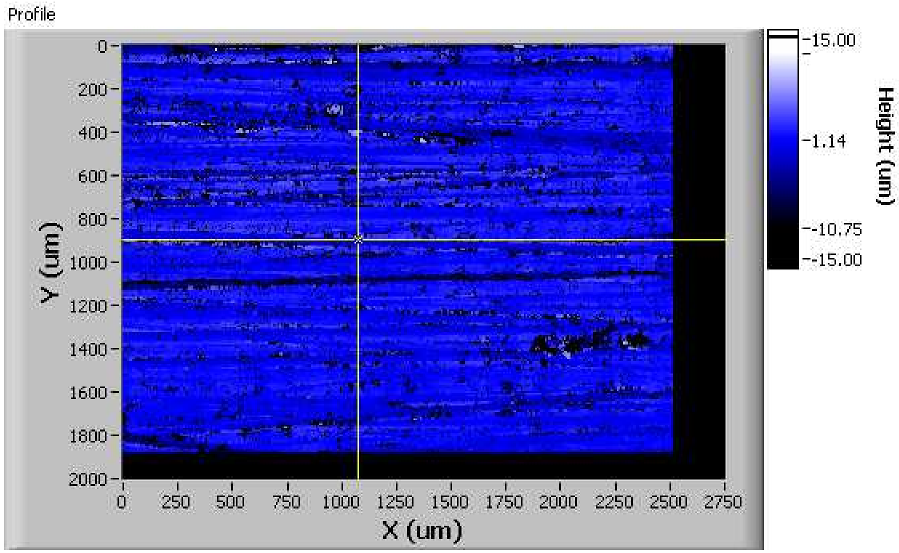
WYKO Optical Profilometer

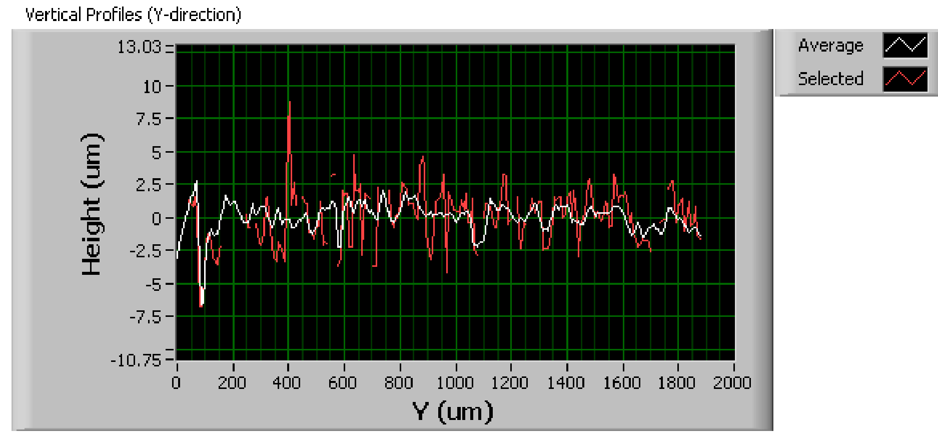


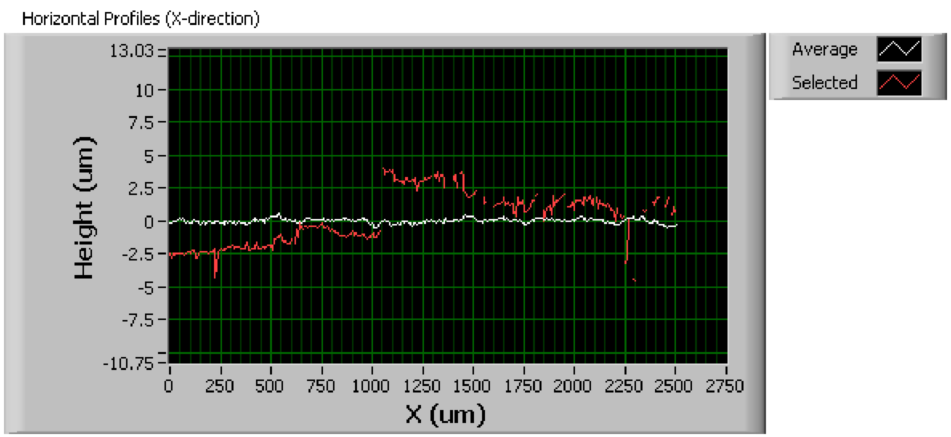
TOP VIEW



Measuring Anisotropic Surface Roughness







$$\mu = \frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} z_{ij}$$

$$R_q = \sqrt{\frac{\sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \left(z_{ij} - \mu\right)^2}{N_x N_y - 1}}$$

$$Y_j = \frac{1}{N_x} \sum_{i=1}^{N_x} z_{ij}$$

$$R_{qy} = \sqrt{\frac{\sum_{j=1}^{N_y} \left(Y_j - \mu\right)^2}{N_y - 1}}$$

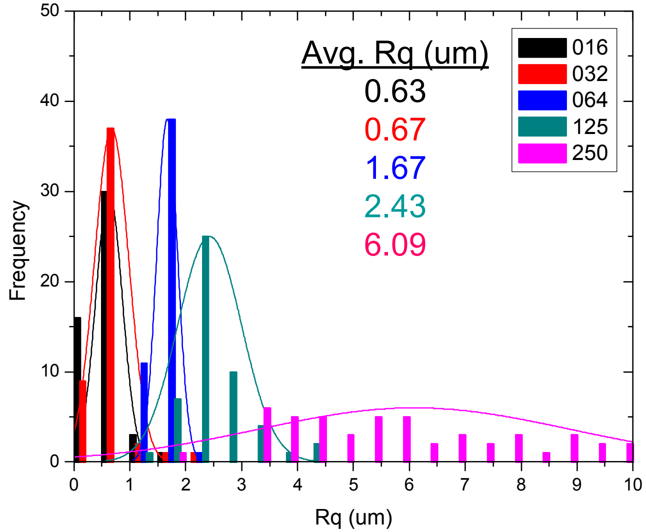
$$X_i = \frac{1}{N_y} \sum_{j=1}^{N_y} z_{ij}$$

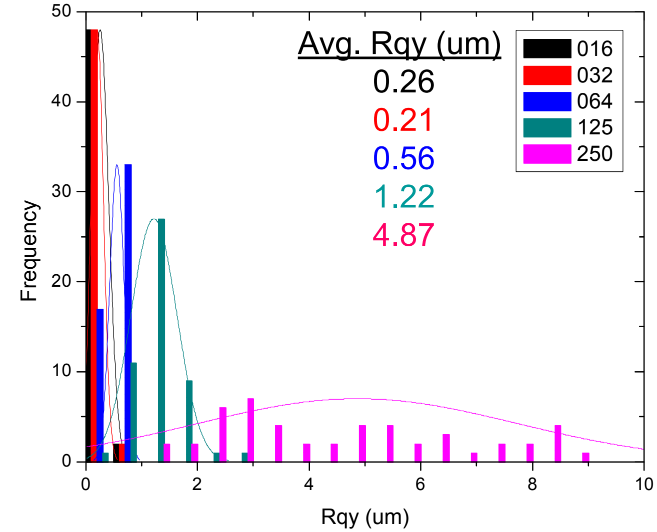
$$R_{qx} = \sqrt{\frac{\sum_{i=1}^{N_x} \left(X_i - \mu\right)^2}{N_x - 1}}$$

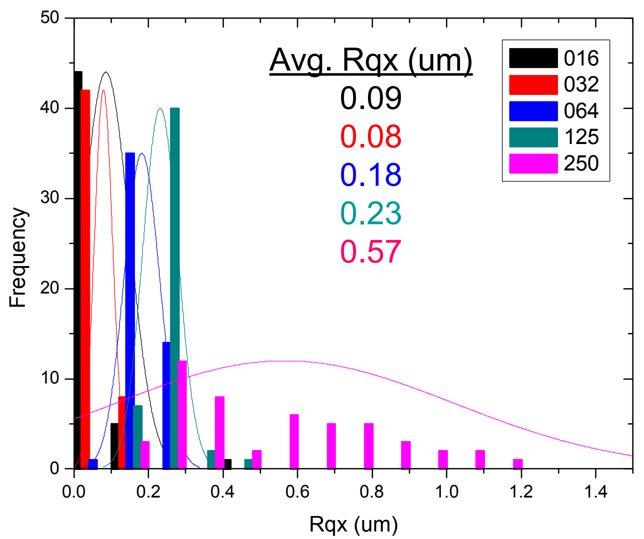
Roughness Ratio

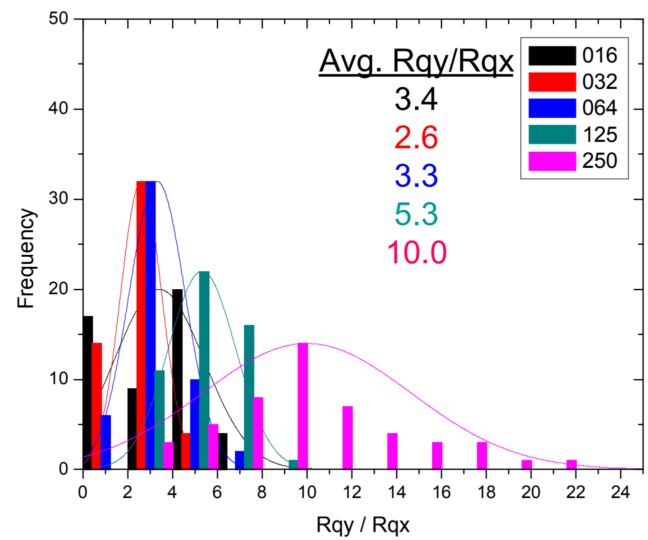
$$\frac{R_{qy}}{R_{qx}}$$

Roughness Statistics for Al Samples

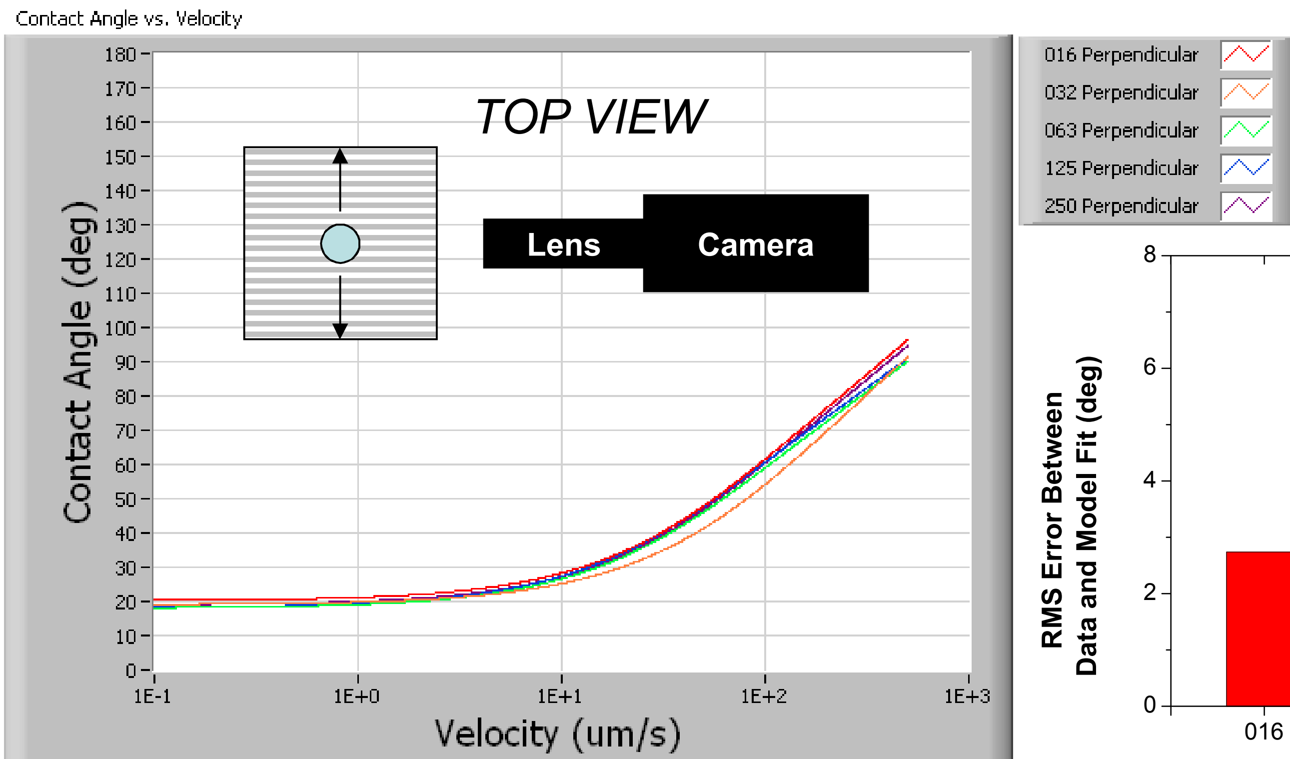


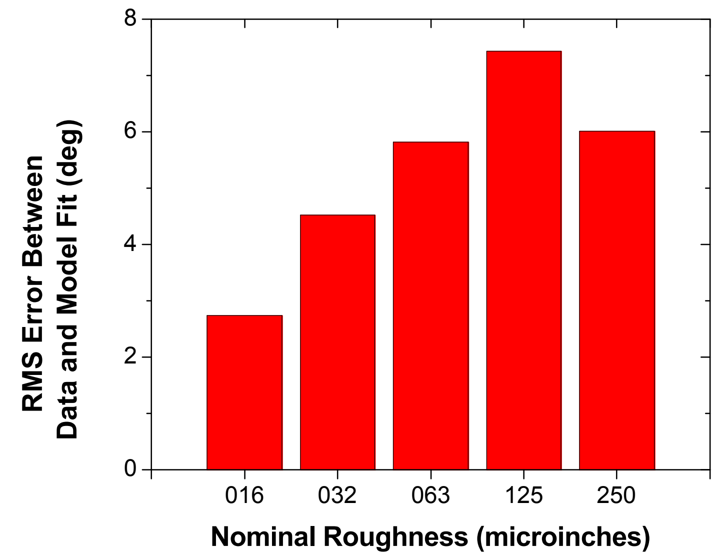






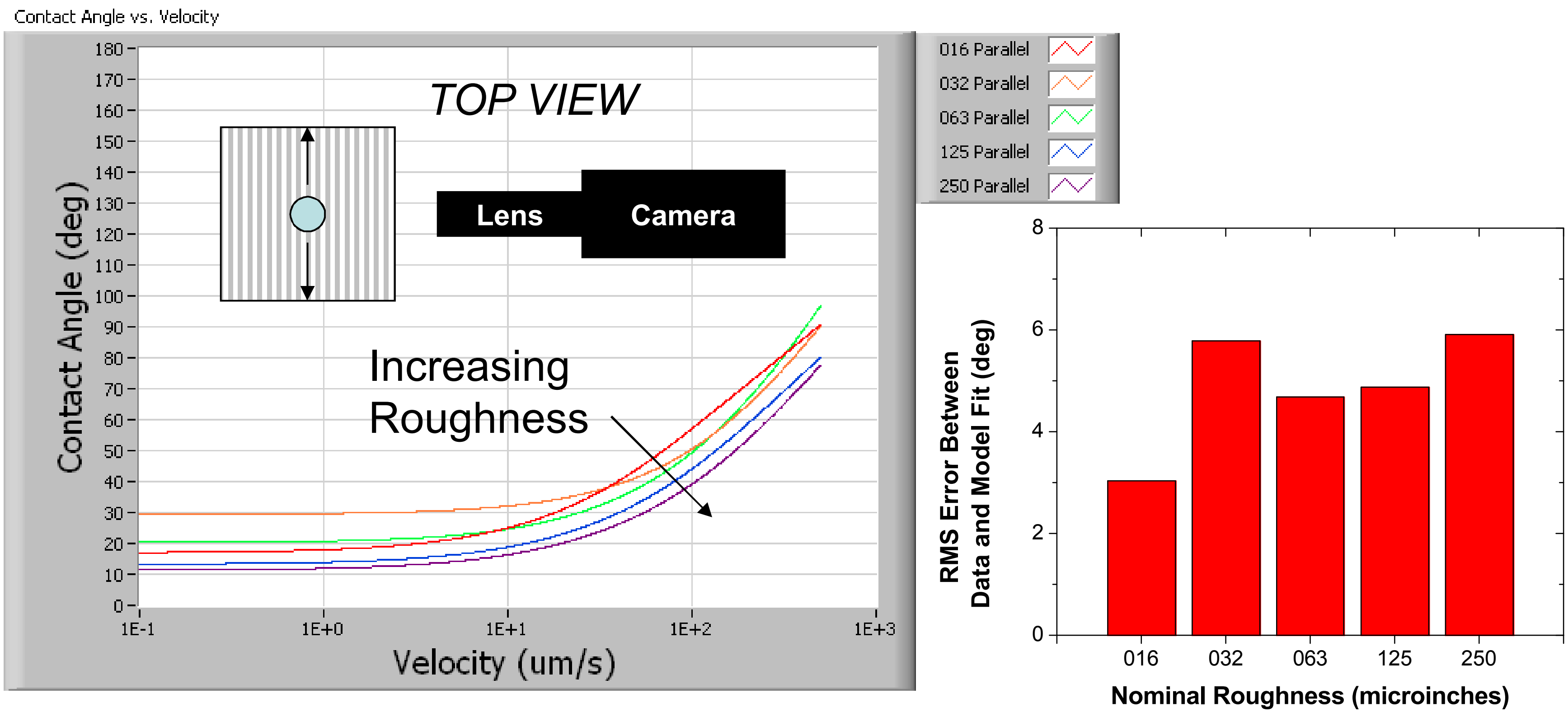
Liquid Advancing Against Grain
(Perpendicular)





- "Jumpy" motion of contact line above 16 μ-inch (410nm)
- Despite increased "jumping" with increasing perpendicular roughness, average motion is not affected

Liquid Advancing Against Grain
(Parallel)



- Enhanced motion observed when grooves are parallel to fluid motion (more pronounced with higher RR)

Summary

- Altered Blake model to account for time-dependent liquids
- Examined a crosslinking silicone elastomer (Sylgard 184) and as it cured, the dynamic contact angle depended more strongly on velocity
- Liquid motion perpendicular to the roughness direction was not smooth yet when averaged, showed no roughness dependence
- Rougher surfaces exhibited a reduced resistance to liquid motion when the liquid is moving in the roughness direction
- Able to characterize the dynamic wetting of liquids and surfaces that are encountered in practice

Acknowledgements

Tom Dimiduk

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