Improving Adhesive Bonding of Composites Through Surface Characterization

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May 19, 2010

The Joint Advanced Materials and Structures Center of Excellence

Improving Adhesive Bonding of Composites

- Motivation and Key Issues
  - Adhesive bonding is being used for primary composite structure in commercial transport aircraft manufacture and repair- surface preparation is a critical step
  - Good bonds are produced but questions remain:
    - What are appropriate techniques to inspect surfaces?
    - What are key factors for making a good/poor bond?
    - How to predict material and surface preparation compatibility?
- Objective
  - Further understand the requirements for surface preparation to produce strong primary structural composite bonds with different substrates and adhesives

Variables that affect contact angle measurements on peel ply surfaces

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VARIABLES THAT AFFECT CONTACT ANGLE MEASUREMENTS ON PEEL PLY SURFACEs

- Motivation and Key Issues
  - Most important step for bonding is SURFACE PREPARATION!!
  - Inspect the surface prior to bonding to ensure proper surface preparation
- Objective
  - Develop QA technique for surface preparation
- Approach
  - Investigate variables that affect contact angle measurements
  - Verify technique on intentionally contaminate surfaces

FAA Sponsored Project Information

- Principal Investigators & Researchers
  - Brian D. Flinn (PI)
  - Ashley Tracey (new PhD student, UW-MSE)
  - Jeffery Saterwhite (MS 2009 UW-MSE)
- FAA Technical Monitor
  - David Westlund
- Other FAA Personnel Involved
  - Larry Ilcewicz
- Industry Participation
  - Toray Composites
  - Henkel International
  - Precision Fabrics & Richmond Aerospace & Airtech International
  - The Boeing Company (Kay Blohowiak, Peter Van Voast, and William Grace)

Outline

- Surface energy and bonding
- Effect of time to measure contact angle on measurement
- Effect of peel ply orientation on contact angle measurement
- Detection of Si contamination
- Conclusions

Surface Energy to Probe Surfaces

- Why use surface energy to probe the surface preparation method applied to the composite for bonding?
  - One requirement of adhesion is the adhesive must wet the substrate
    - This is controlled by surface energy

Low surface energy

High surface energy

Surface Energy

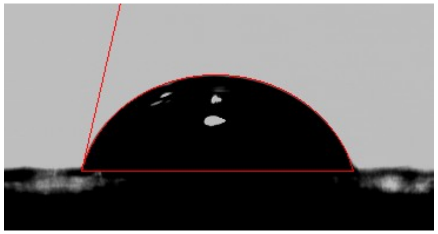
- Surface energy is a complex property composed of many components
  - Owen Wendt model - breaks the surface energy into polar and dispersive components

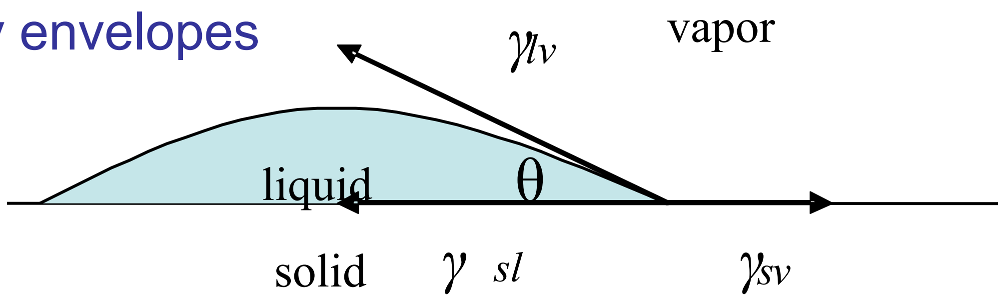
$$\gamma_{Total} = \gamma_{Polar} + \gamma_{Dispersive}$$

- Use this approach to probe the surface to determine if we can detect variations, or contamination that correlate with bond quality

Methodology

- Using a goniometer, the contact angle of a 1 μL drop of fluid is measured
  - Four fluids, 10 drops per fluid were evaluated on each surface
  - Average contact angle and standard deviation were calculated to determine surface energies and generate wettability envelopes





- Complete wetting when θ approaches zero
- Contaminants usually lower the solid’s surface energy (increase θ)
- Surface preparations try to increase the solid’s surface energy and clean off contaminants

Calculation of Surface Energy

- **To calculate the surface energy using, the following equation was used:**

$$\frac{\gamma_{lv}(\cos\theta + 1)}{2\sqrt{\gamma_{lv}^{d}}} = \sqrt{\gamma_{sv}^{p}}\left(\sqrt{\frac{\gamma_{lv}^{p}}{\gamma_{lv}^{d}}}\right) + \sqrt{\gamma_{sv}^{d}}$$

  - γ_{lv} is the total surface energy between the liquid and the vapor,
  - γ^{p}_{lv} is the polar component of the surface energy between the liquid and vapor, γ^{d}_{lv} is the dispersive component of the surface energy between the liquid and the vapor,
  - γ^{p}_{sv} is the polar component of the surface energy between the solid and the vapor,
  - γ^{d}_{sv} is the dispersive component of the surface energy between the solid and vapor, and
  - θ is the average contact angle.

Calculation of Surface Energy

- From equation (1), the following equations were used to plot the data:

$$\frac{\gamma_{lv}(\cos\theta + 1)}{2\sqrt{\gamma_{lv}^{d}}} \quad (2) \qquad\qquad \sqrt{\frac{\gamma_{lv}^{p}}{\gamma_{lv}^{d}}} \quad (3)$$

  – Where (2) is the y-coordinate and (3) is the x-coordinate
  – From this plot (Kaelble plot), the polar and dispersive components of the surface energy are determined as follows:
    - Polar component = b^2 (b = y-intercept of plot)
    - Dispersive component = m^2 (m = slope of plot)
- By inputting these polar and dispersive components of the surface energy of the composite into the computer program BKCWet v 1.1, wettability plots were generated.

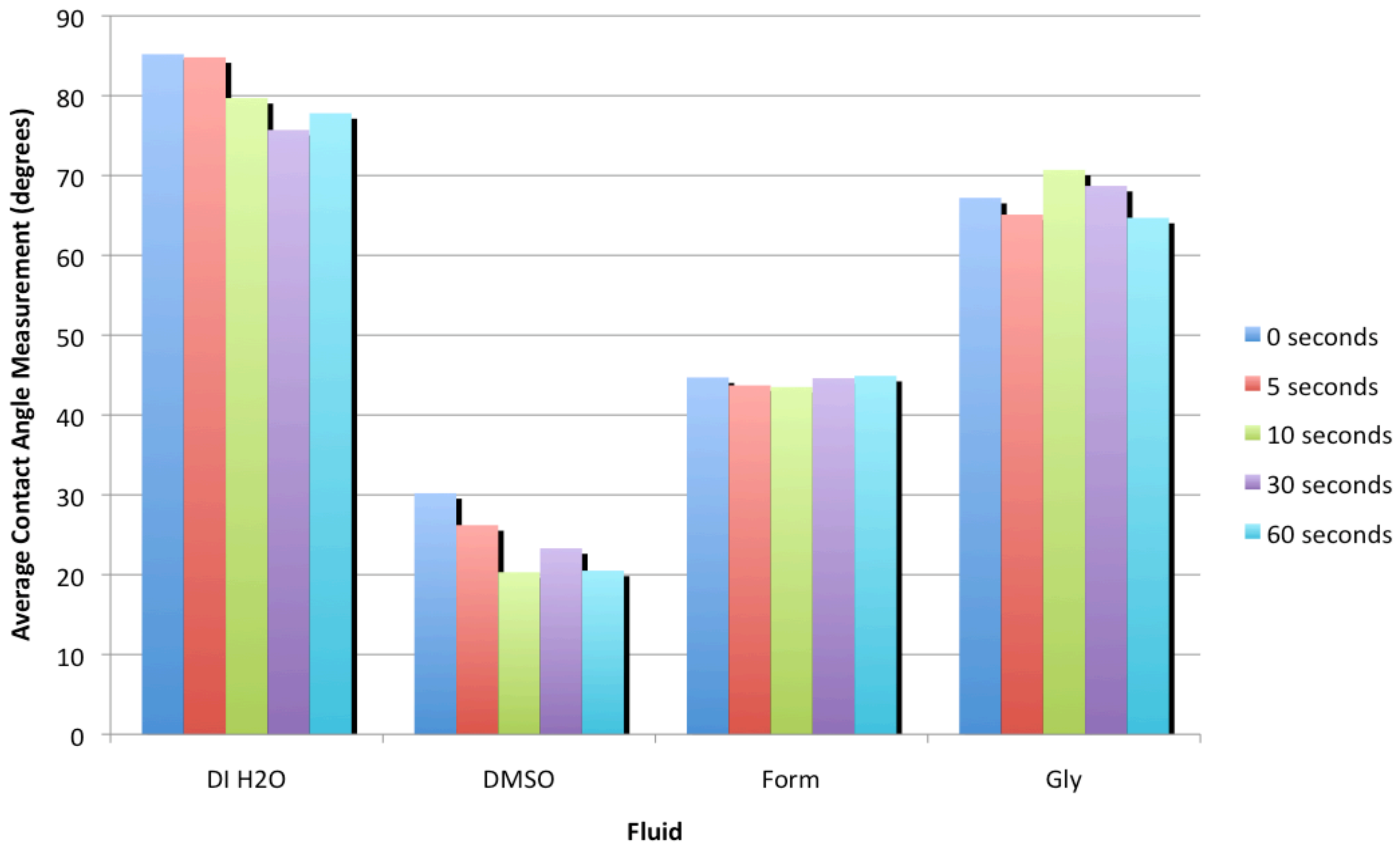
Materials

- Toray 3900/T800 unidirectional laminates
- Precision Fabric Group 60001 polyester peel ply
- Autoclave cure of composite (max 176.7 °C, 0.6 MPa)
- Peel ply removed and contact angles measured within 1 hour
- Fluids used for contact angle analysis:
  - De-ionized water (DI water)
  - Dimethlysufoxide (DMSO)
  - Ethylene Glycol (EG)
  - Glycerol (Gly)
  - Formamide (Form)

Time to Measure Contact Angle

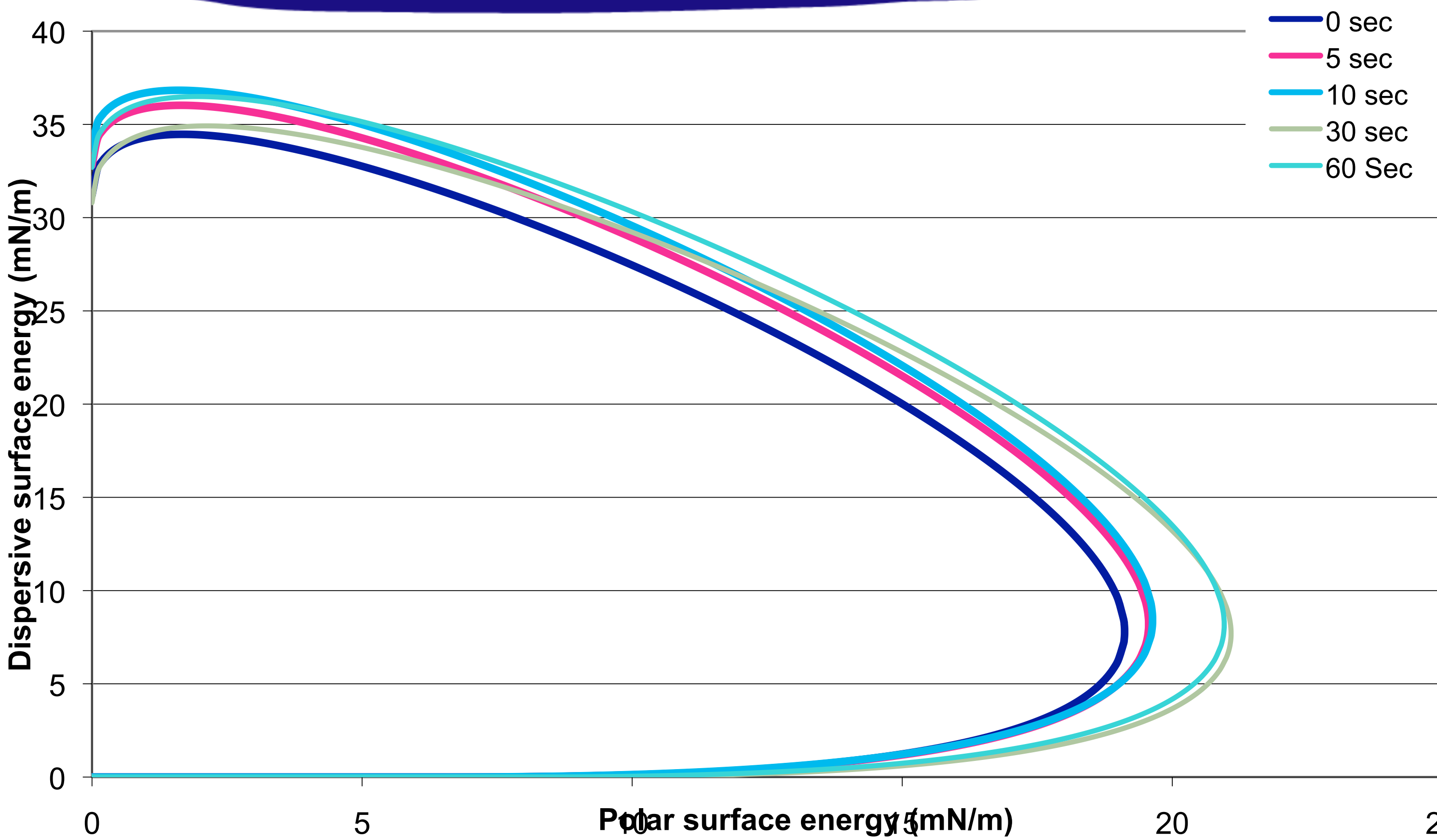
- Does the time at which the contact angle is measured after application of the liquid droplet to the solid surface effect the measurement?
  - Measure contact angles at 0+, 5, 10, 30 and 60 second
  - 4 different fluids

Effect of Time to Measure on Contact Angle (CA)



- DI H_2O and DMSO contact angles decrease with increasing time

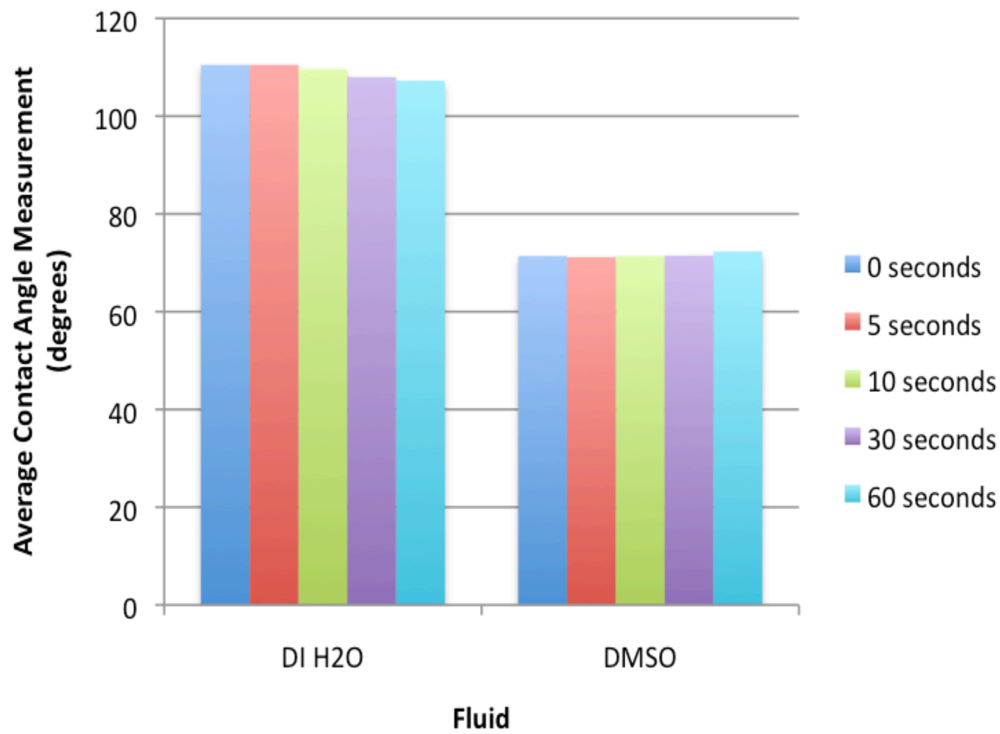
Wettability Envelopes



- **Wettability envelopes increase with increasing time (contact angle decreases with time)**

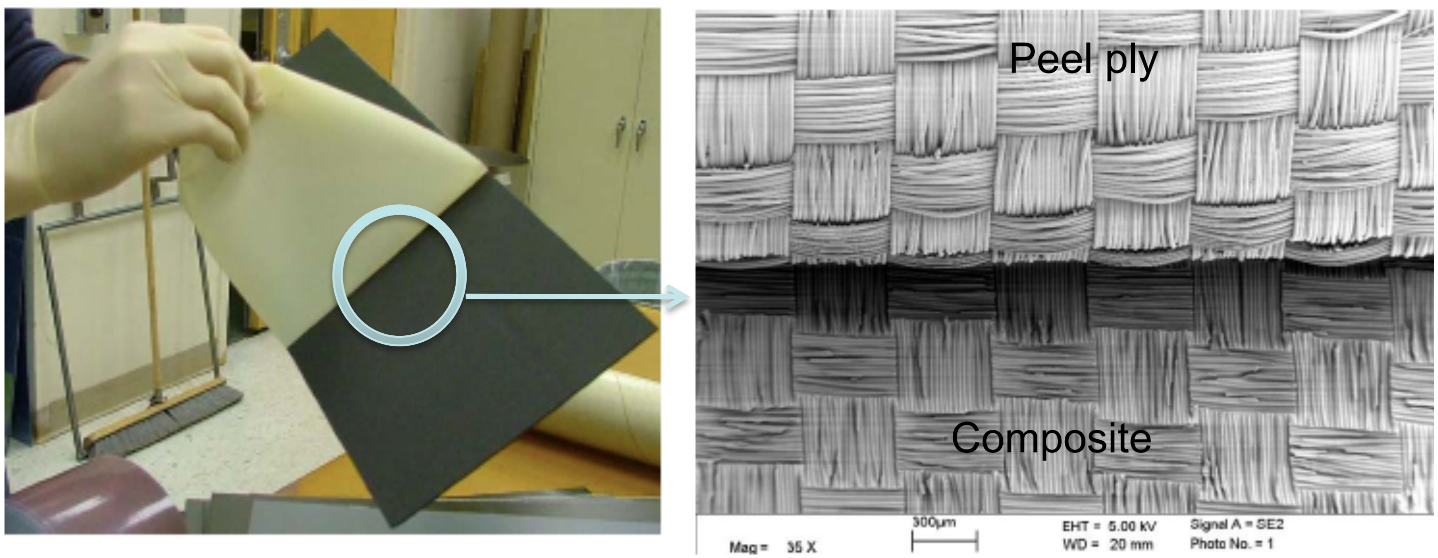
Effect of Time on CA

- To determine if this was a viscosity effect, contact angles using DI H_2O and DMSO were measured on release film, an inert and smooth surface
- Results show no time dependence and thus viscosity effects are dismissed as a possibility for this affect
- Possibly due to adsorption of fluid onto surface



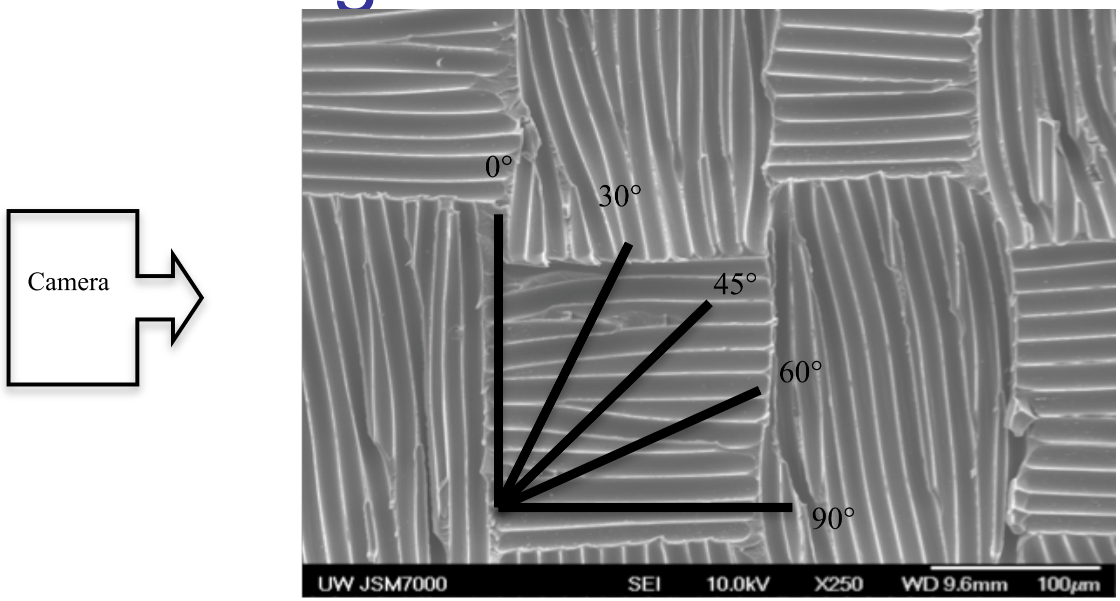
Peel Ply Texture Orientation

- Effect of surface texture left in epoxy resin after peel ply removal

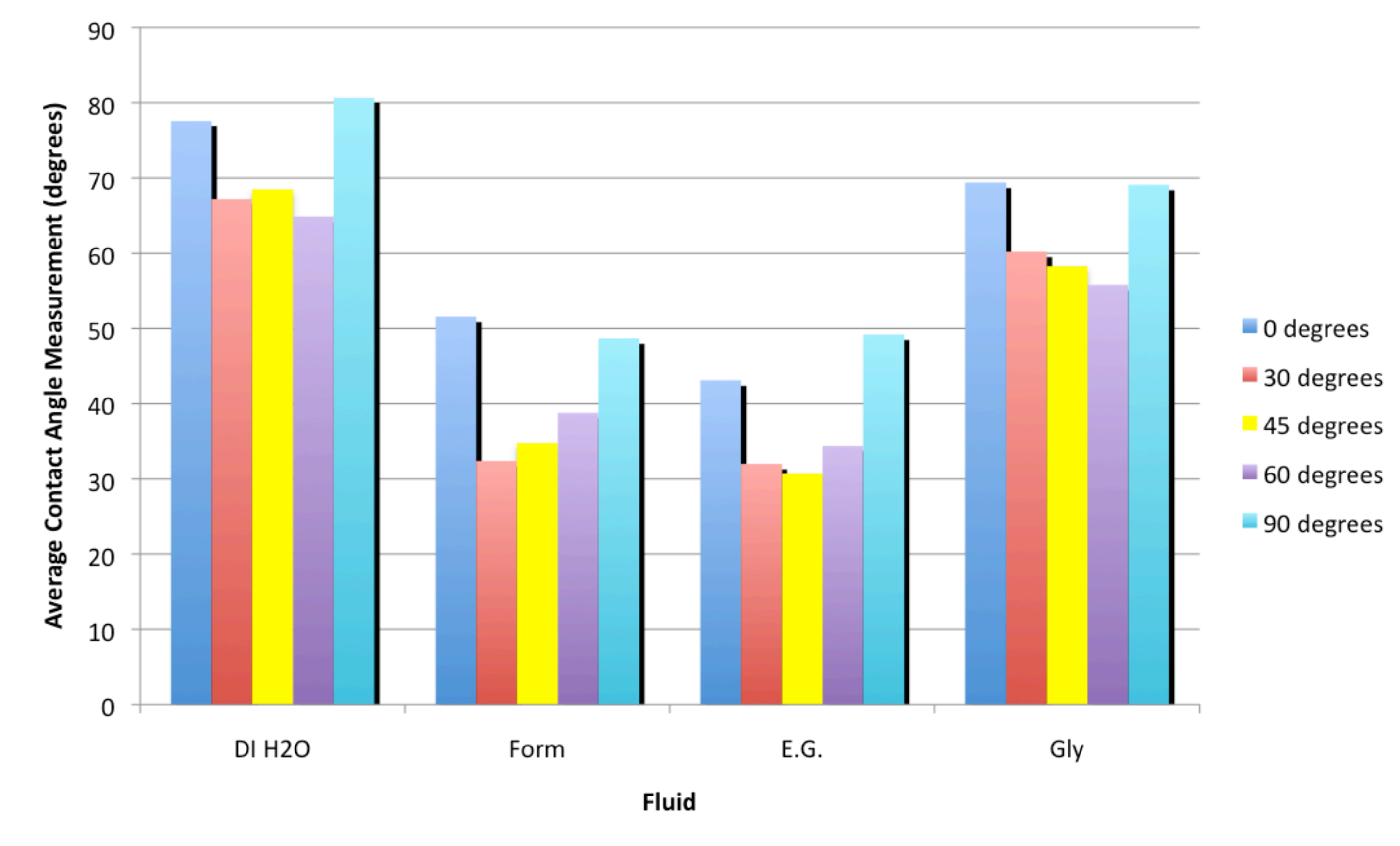


Peel Ply Texture Orientation

- Peel ply angle is defined as the angle at with the peel ply texture is oriented with respect to the goniometer camera

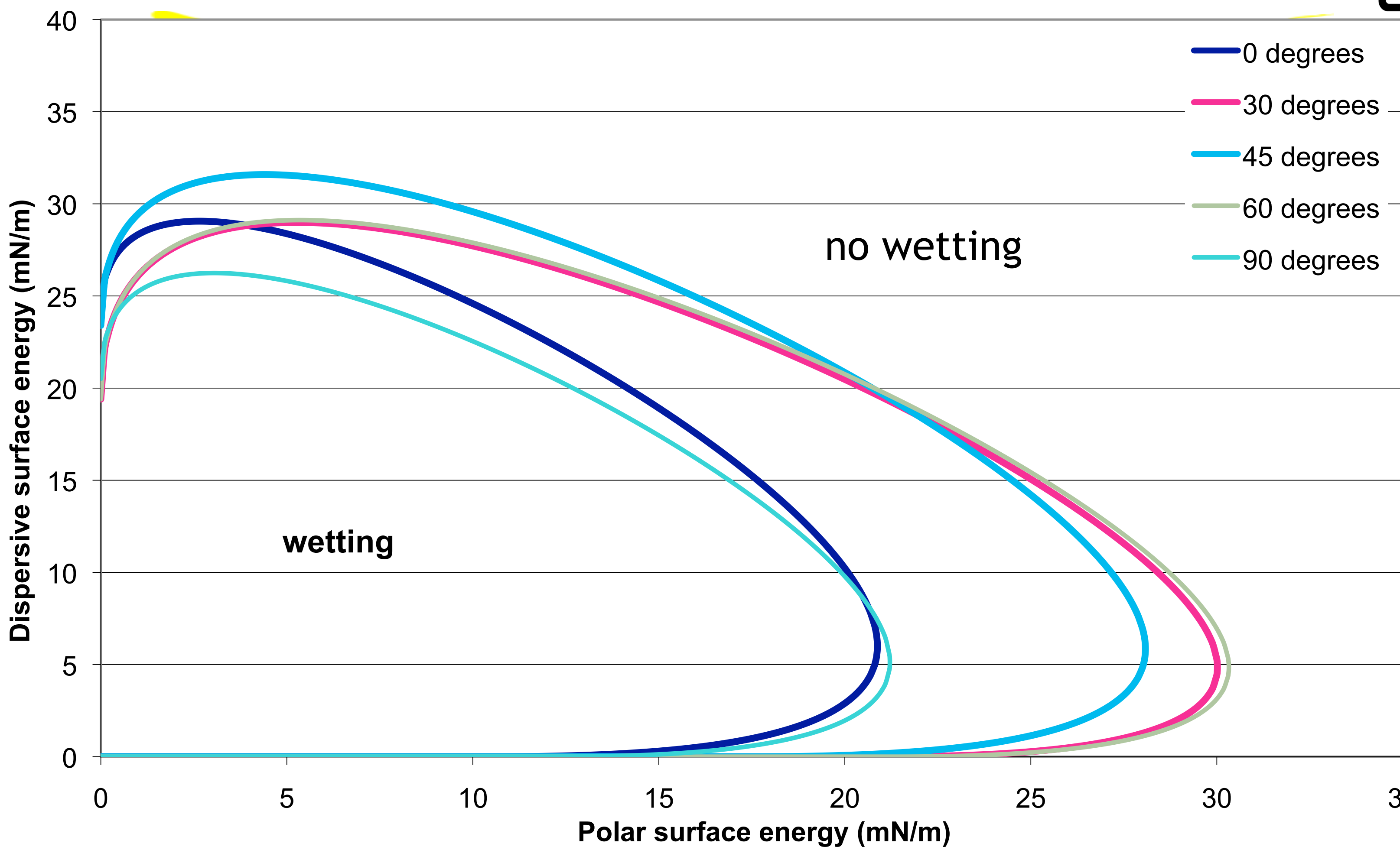


Effect of Peel Ply Texture Orientation on Contact Angle



- Peel ply orientation affects contact angle measurement
  - Contact angles measured at 0 and 90 degrees are greatest

Orientation Affect on Wettability

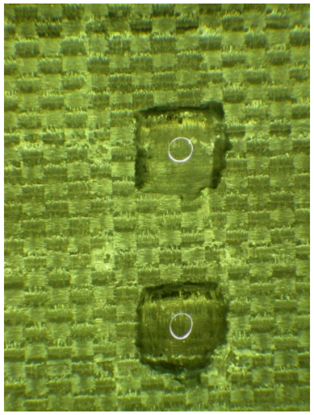
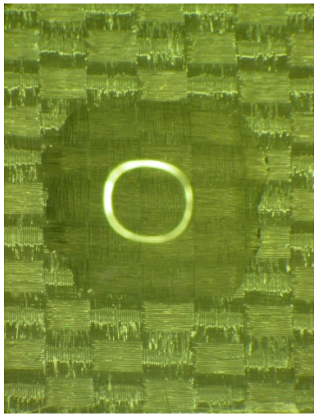
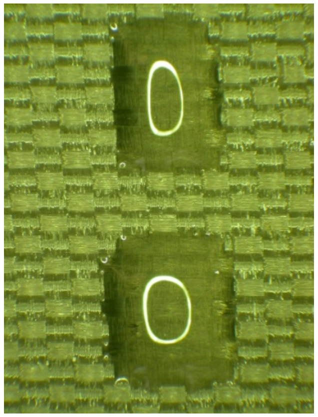
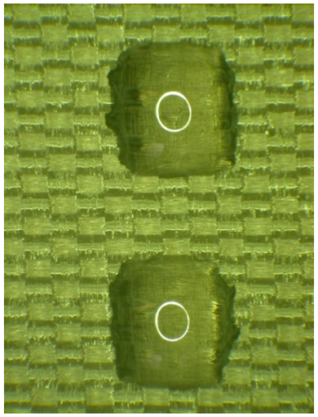


30 and 60 Orientation produced similar wettability envelopes

0 and 90 Orientation produced similar wettability envelopes

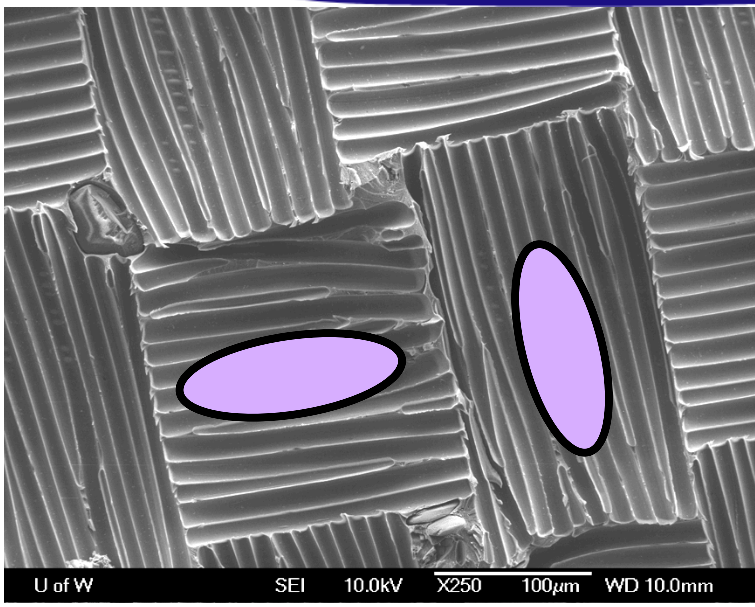
Evaluation of Peel Ply Texture and its Affect on Contact Angle

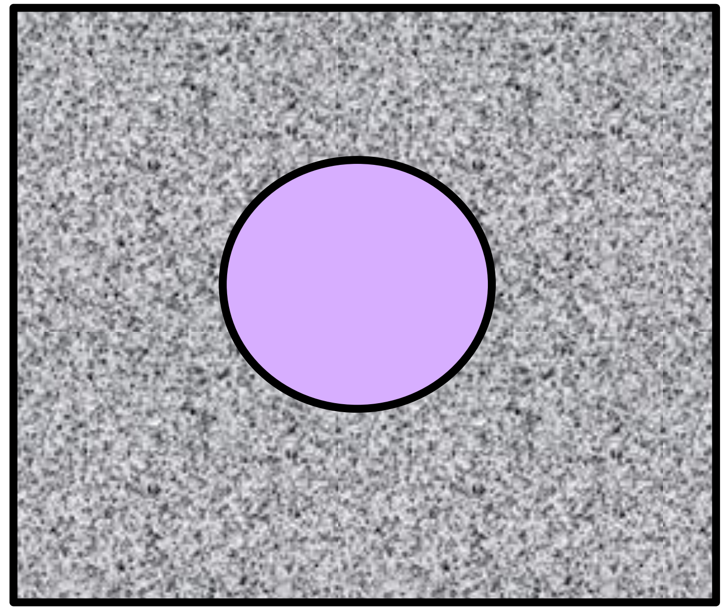
- Difference in contact angle at differing orientations of the substrate is due to the texture left in the resin upon peel ply removal
  - The fluids form non-circular drops on the substrate

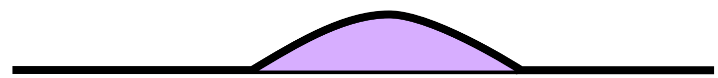





Top down pictures from right to left of formamide, DI water, ethylene glycol, and glycerol drops (note: white circles on each drop are a reflection of light)

Peel Ply Texture



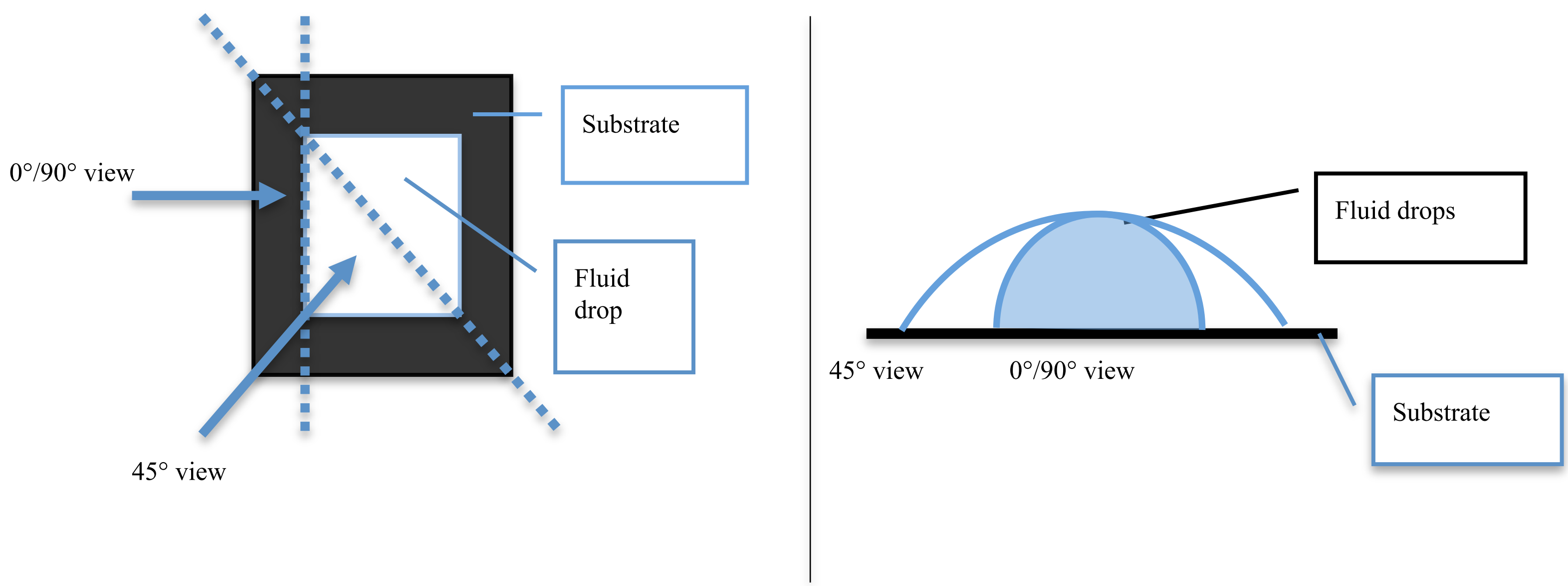




- Peel ply texture affects the shape of the fluid drop

Peel Ply Texture Affects Drop Shape

- The non-circular drops resulted in differing contact angle measurements at different orientations

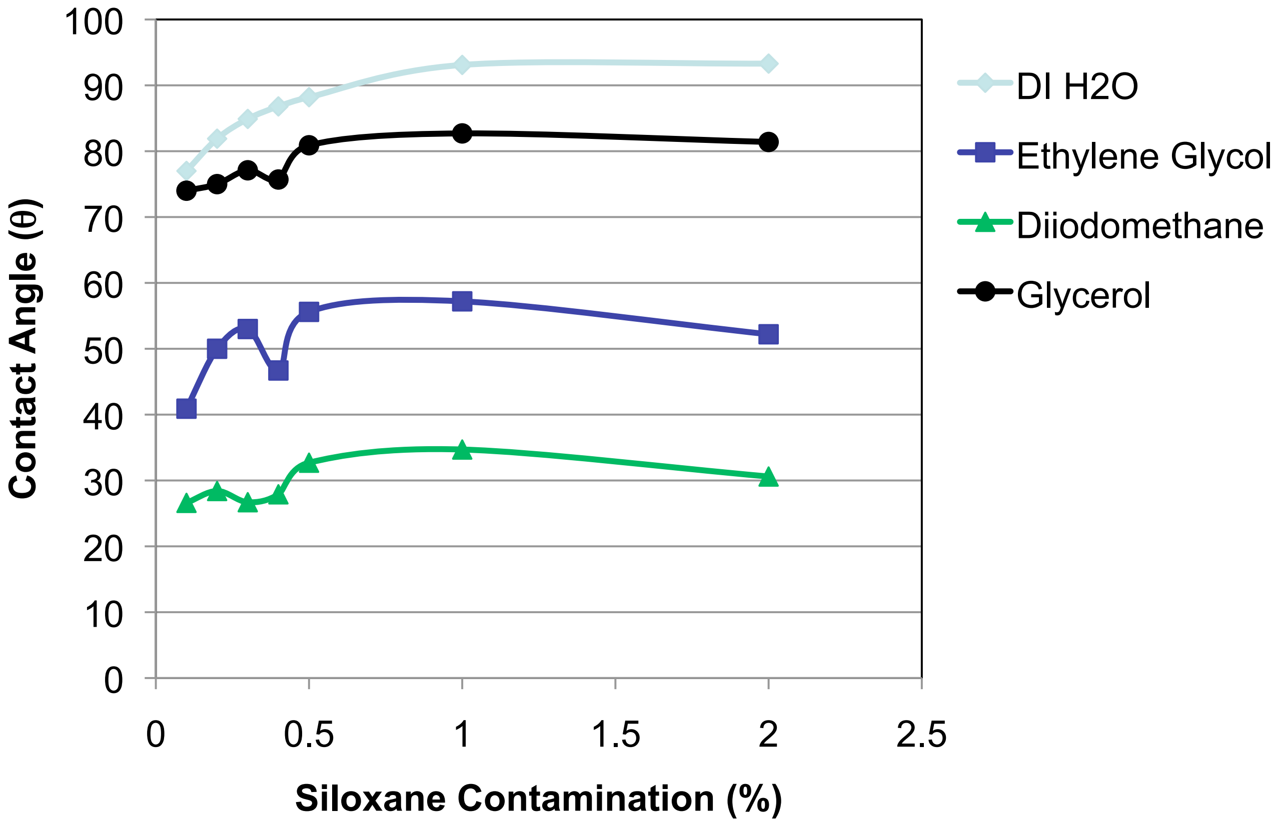


Detection of Si Contamination

How sensitive is the CA method to contamination?

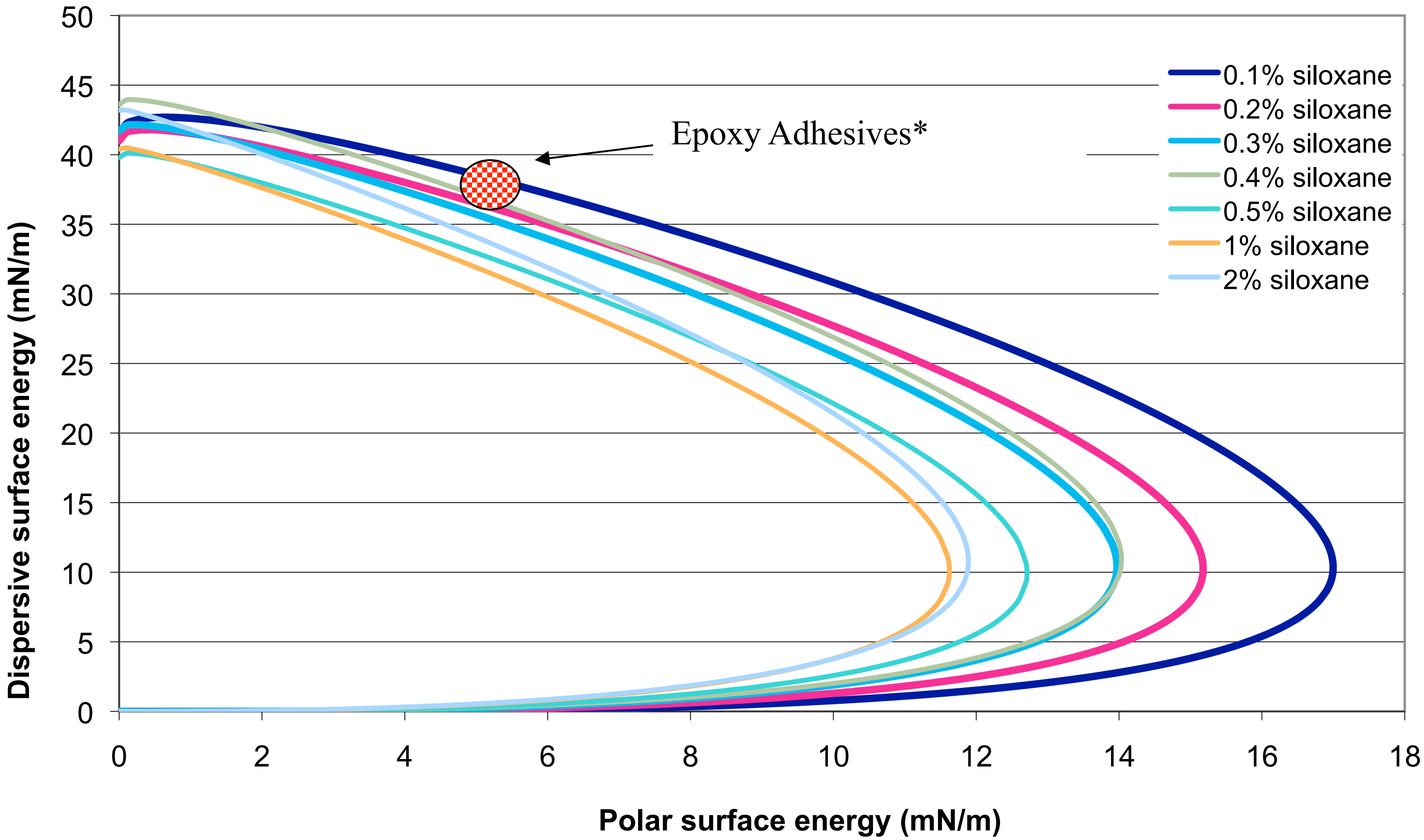
- Controlled amount of siloxane added to peel plies to produce intentionally contaminated CFRP surfaces for evaluation
  - Contact Angle (4 fluids)
  - Surface Energy and Wettability
  - Bond Quality (G_{IC} and fracture mode)

Contact Angle vs. Si

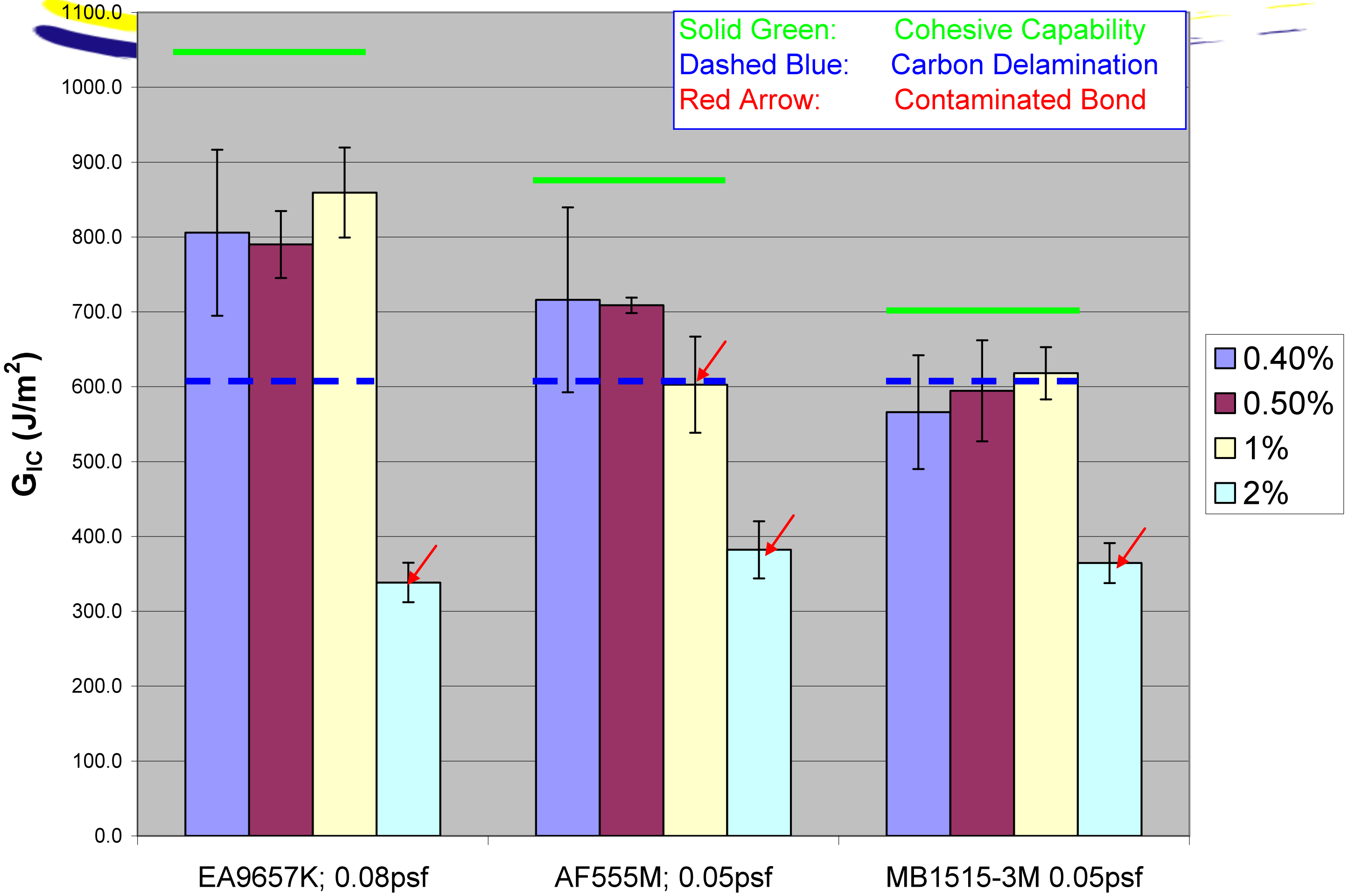


- **Contact Angle Increases with Increasing Si**

Wettability Envelopes



- **Wettability envelopes decreased with increasing Si**



Contamination decreased bond toughness

- Correlates with surface energy and wettability envelopes

Work In Progress…

- Investigation of Other Experimental Variables
- Modeling of Texture affect
- Advancing/Receding Contact Angle Measurement
- Other Surface Energy Measurement Techniques
- Effect of CA fluids on bonding
- Other Contaminates? (input requested)
- Identification of Preferred Fluids

Conclusions

- Time to measure contact angle has an affect on the measurement
  - Some fluids more sensitive
- Surface texture can results in non spherical drops
  - results in change in the measured contact angle
- CA, wettability and bond quality correlated with % Si
- Use of multiple fluids and wettability envelopes recommended
- Potential QA technique for surface preperation

A Look Forward

- Benefit to Aviation
  - Better understanding of peel ply surface prep.
  - Guide development of QA methods for surface prep.
  - Greater confidence in adhesive bonds
- Future needs
  - Surface energy (wetting) vs. bond quality model
  - Surface energy at cure temperature
  - QA method to ensure proper surface for bonding
  - Applicability to other composite and adhesive systems
  - Model to guide bonding based on characterization, surface prep. and material properties

Acknowledgements

- FAA, JAMS, AMTAS
- Boeing Company
- Precision Fabric Group
- Richmond Fabrics
- Airtech International
- Prof. Mark Tuttle (UW)

Surface Preparation

- Crucial for proper adhesion in composites
- Several methods
  - Peel ply (as tooled)
  - Abrasion (Sanding or grit blasting)
- Surface preparation influences surface energy and the wettability of a surface, also prevents/removes contamination
- A high energy surface promotes intimate contact between the surface and the adhesive

QUESTIONS ?
COMMENTS?
SUGGESTIONS?