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# Improving Adhesive Bonding of Composites Through Surface Characterization

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University of Washington

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# Improving Adhesive Bonding Through Surface Characterization

- 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 quality assurance (QA) techniques for surface preparation
- Approach
  - Investigate surface preparations, process variables

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# 2013-2014 FAA Sponsored Project Information

- Principal Investigators & Researchers
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  - David Pate (MS graduate, UW-MSE)
  - Jonathan T. Morasch (undergraduate, UW-ME)
  - Nina Gerber (undergraduate, UW-MSE)
- FAA Technical Monitor
  - Curt Davies
- Other FAA Personnel Involved
  - Larry Ilcewicz
- Industry Participation
  - Toray Composites
  - Precision Fabrics, Richmond Aerospace & Airtech International
  - The Boeing Company (Marc Piehl, Kay Blohowiak, Will Grace, Tony Belcher, Pete VanVoast, Liz Castro, John Osborne)

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# 2013-2014 Statement of Work

| | Surface Characterization/QA Technique | | | |
|---|---|---|---|---|
| | Contact Angle (CA) | | FTIR | |
| | Goniometer | Surface Analyst | DATR | Diffuse Reflectance |
| Cure Temp and Dwell Time | ✔ | ✔ | --- | In progress |
| Peel Ply Preparation Material | ✔ | ✔ | ✔ | ✔ |
| Si Contaminants | ✔ | ✔ | ✔ (Boeing) | |
| Peel Ply Orientation | ✔ | ✔ No effect | N/A | In progress |
| Peel Ply + Abrasion | ✔ | | --- | ✔ |
| Scarfed/Sanded Surfaces | ✔ | TBD | --- | ✔ |
| Effect of Measurement on Bonding Surface | ✔ | TBD | TBD | N/A |
| Sandpaper Type | ✔ | | --- | In progress |
| Peel Ply + Plasma Treatment | ✔ | | --- | ✔ |

**✔ = work completed** **--- = not of focus, diffuse reflectance for rough surfaces**

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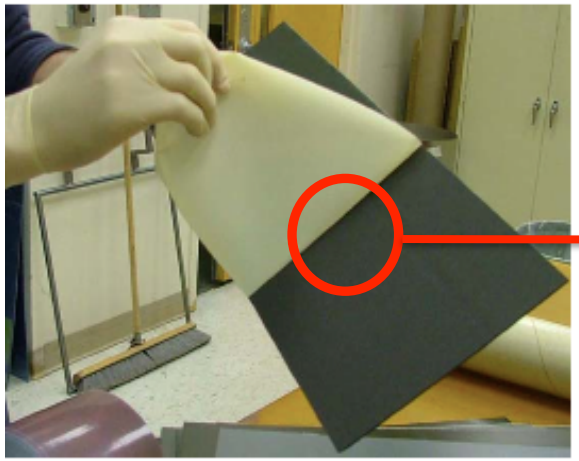
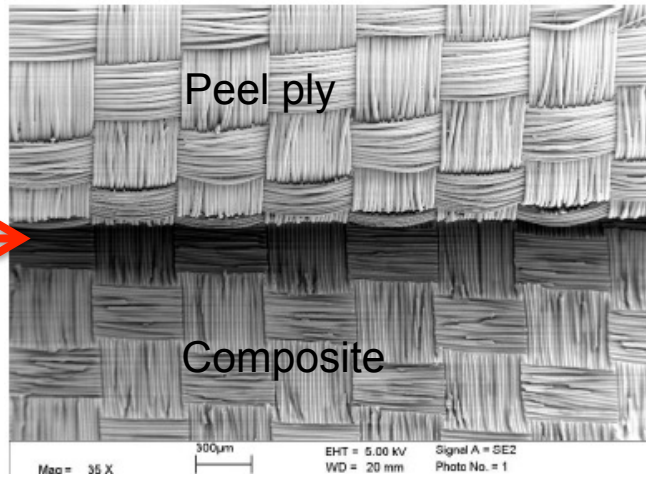
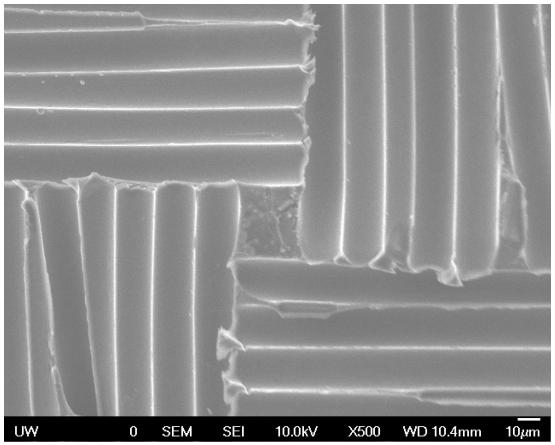
# Peel Ply Surface Preparation

- Polymer fabric, last layer applied to composite before cure, removed directly before bonding
- Produces repeatable and consistent surfaces
- Provides surface roughness → roughness influences CA measurements and surface energy [1-3]
- Can prevent contamination
- Materials system specific[4-7]
  - ➢ Improve mechanical considerations, some chemical alterations lead to poor bonds



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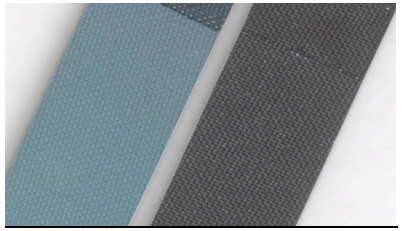
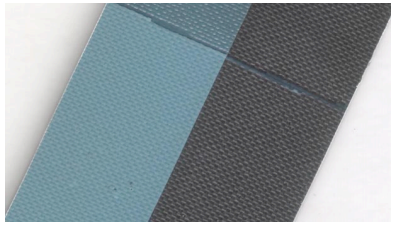
# Peel Ply Surface Preparation

- Materials system specific[4-7]
  - Difference in bond quality (failure mode, Mode I strain energy release rate ($G_{IC}$)) with use of different peel ply materials[5]

| | Polyester Prepared | Nylon Prepared | SRB Prepared |
|---|---|---|---|
| |  |  |  |
| Failure Mode | Cohesive | Adhesion | Adhesion |
| $G_{IC}$ | 4.6±0.20 in-lbf/in$^2$ | 0.70±0.09 in-lbf/in$^2$ | < 0.54 in-lbf/in$^2$ |

- Peel ply: mechanical and chemical alterations to surface

➢ Can atmospheric pressure plasma treatment change chemistry of peel ply surface and activate it?

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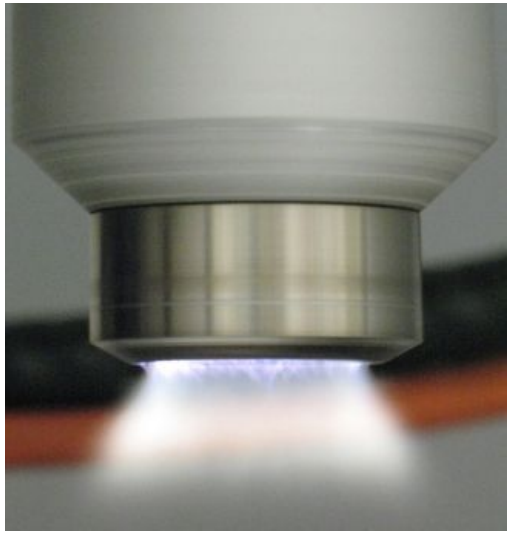
# Atmospheric Pressure Plasma Treatment

- Partially ionized gas: unbound electrons, electrically charged ions, neutral atoms and molecules[8,9]
- Chemically active[8]
- Advantages
  - Can be automated → reduce process variability and increase reliability and processing rates[10]
  - No vacuum system[8] → more versatile, no part size limit



[10]

# Experimental Overview

**Investigate the effect of plasma treatment on bond quality and surface characterization measurements of peel ply prepared composites**

- Atmospheric pressure plasma treat nylon peel ply prepared composites
  - high plasma (slower raster speed)
  - low plasma (faster raster speed)
- Characterize surfaces with various analysis techniques and relate to bond quality
  - Analysis methods: CA, FTIR, X-ray photoelectron spectroscopy (XPS)
  - Bond quality: double cantilever beam (DCB) test

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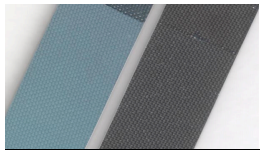
# Materials

- Toray T800/3900 unidirectional laminates
- Surface Preparation
  - Precision Fabrics Group (PFG) 52006 nylon peel ply
  - Atmospheric pressure plasma treatment: PlasmaTreat system with single flume jet, 0.5 in plasma head to sample distance, 50% raster pass overlap with rotating flume
    1. no plasma (**control**) →
    2. 1 in/s plasma treatment (**high**)
    3. 6 in/s plasma treatment (**low**)



- Adhesive Bonding
  - MetlBond 1515-3M film adhesive (0.0325 psf)
  - Fluorinated ethylene propylene (FEP) release film crack starter

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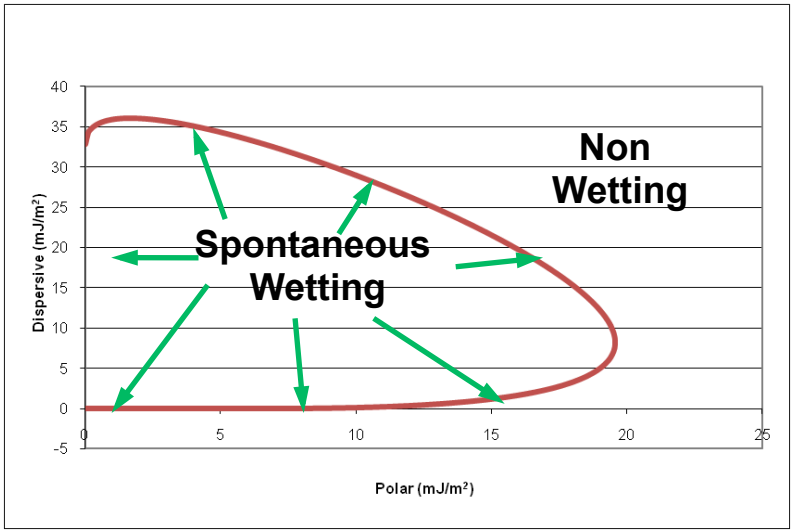
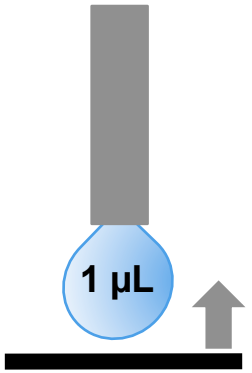
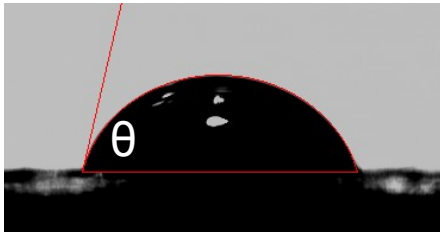
# Contact Angle Methodology – Surface Energy

- Adhesive must wet substrate – controlled by surface energy
- Surface energy calculated from Owens-Wendt model $(\gamma_{tot} = \gamma^p + \gamma^d)$[11-13]
  - Four fluids: deionized water (DI $H_2O$), diiodomethane (DIM), ethylene glycol (EG), and glycerol (GLY)
- Wettability envelopes: 2D representation of surface energy[14]



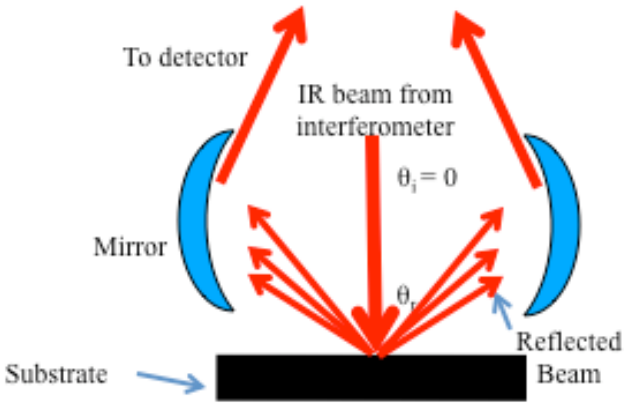

Drop application: dispense drop, raise surface




Side-view of drop as viewed from goniometer camera

# FTIR Methodology – Surface Chemistry

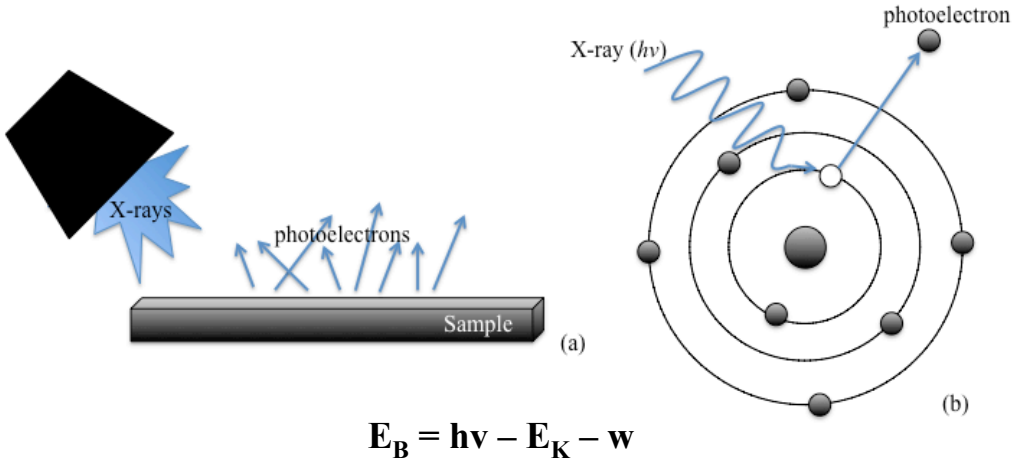
- Diffuse reflectance FTIR for rough surfaces
  - Chemical information from 1-10 μm[15]
- Mid-IR data range (4000-650 $cm^{-1}$)
- 90 scans with 16 $cm^{-1}$ resolution
- 7 spectra averaged per sample
- GRAMS IQ software used for principal component analysis (PCA) of spectra



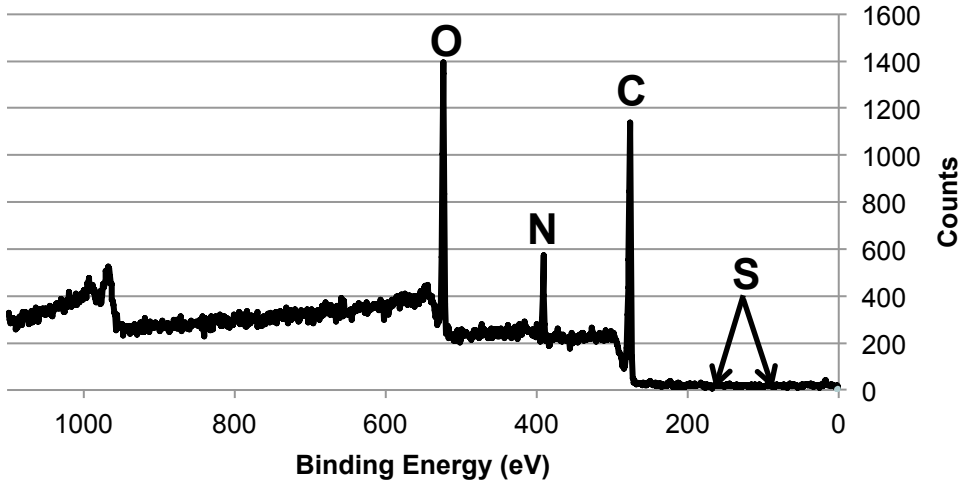

An IR beam path for diffuse reflectance

# XPS Methodology – Surface Chemistry

- Surface (2-5 nm) chemistry
- Three survey scans
  - Composition – atomic percentages
  - Linear fit
- One high-resolution carbon scan
  - Fit C 1s peak with multiple peaks → carbon chemical states




$$E_B = hv - E_K - w$$

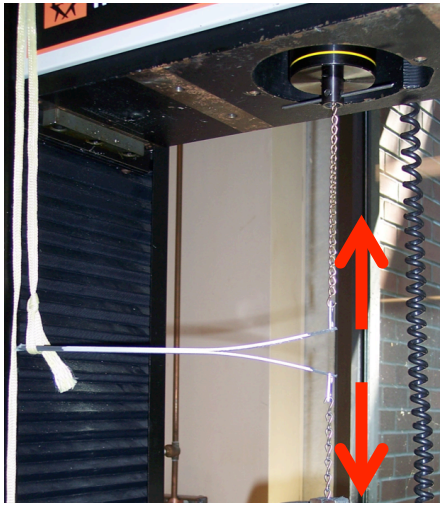


# DCB Testing – Bond Quality

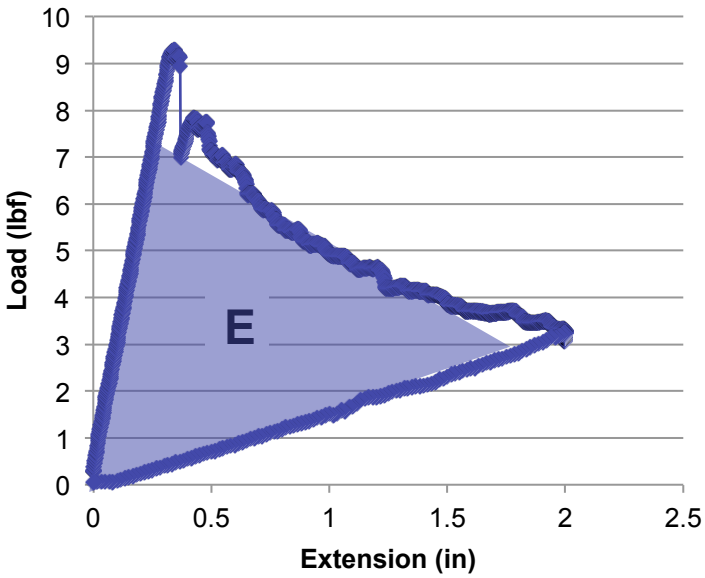
- Mode I strain energy release rate ($G_{IC}$) and failure mode
- 7-8 samples per condition
- Area method for $G_{IC}$ calculations
  - E: area of curve
  - A: crack length
  - B: specimen width

$$G_{IC} = \frac{E}{A \times B}$$

- Bondline thickness measurements to ensure consistency



DCB Test




| Sample | Maximum (mil) | Minimum (mil) | Range (mil) | Average (mil) | Standard Deviation (mil) |
|---|---|---|---|---|---|
| control | 7.55 | 4.70 | 2.84 | 5.84 | 0.47 |
| low | 5.65 | 4.01 | 1.64 | 4.93 | 0.38 |
| high | 7.00 | 3.57 | 3.43 | 5.10 | 0.63 |

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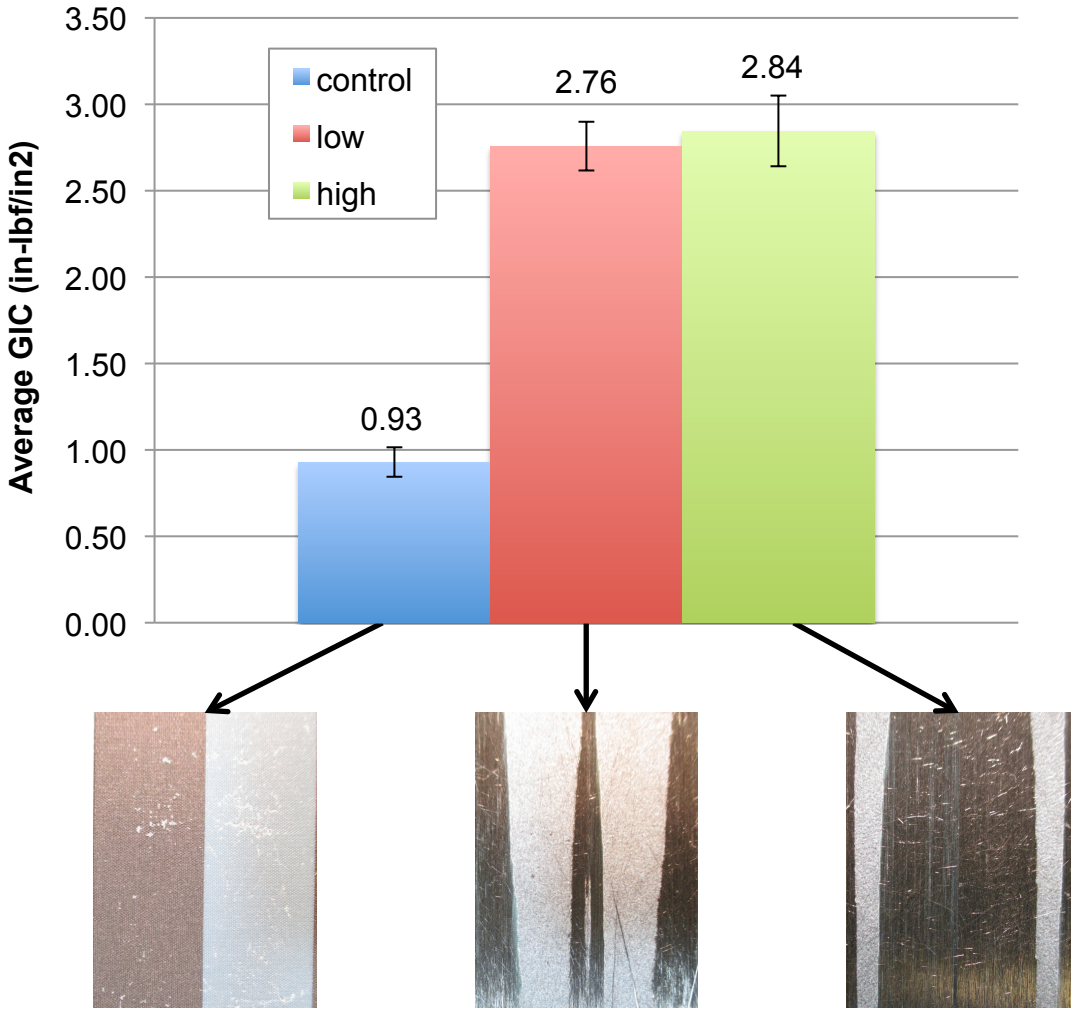
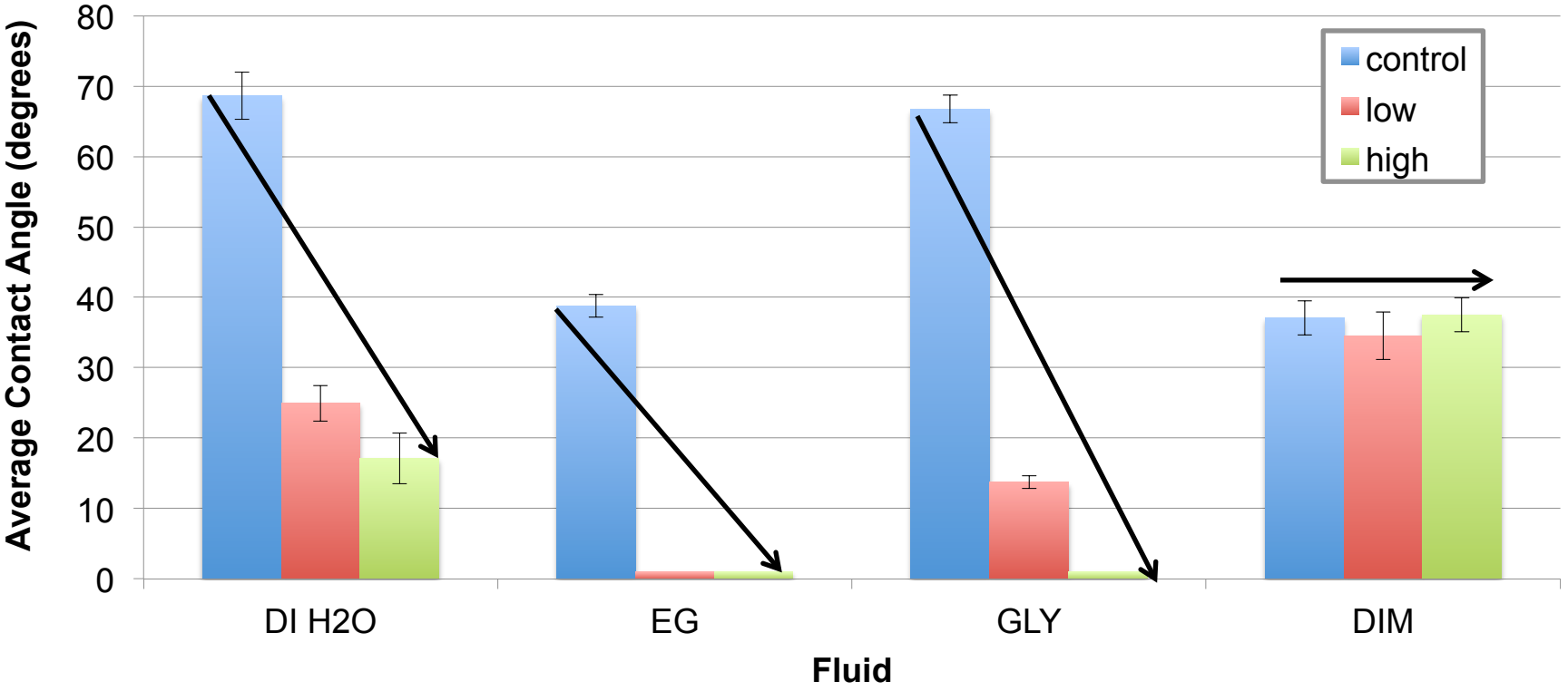
# $G_{IC}$ Measurements




- 3-fold increase in $G_{IC}$ for plasma treated samples compared to control
- Failure modes correspond to fracture energies

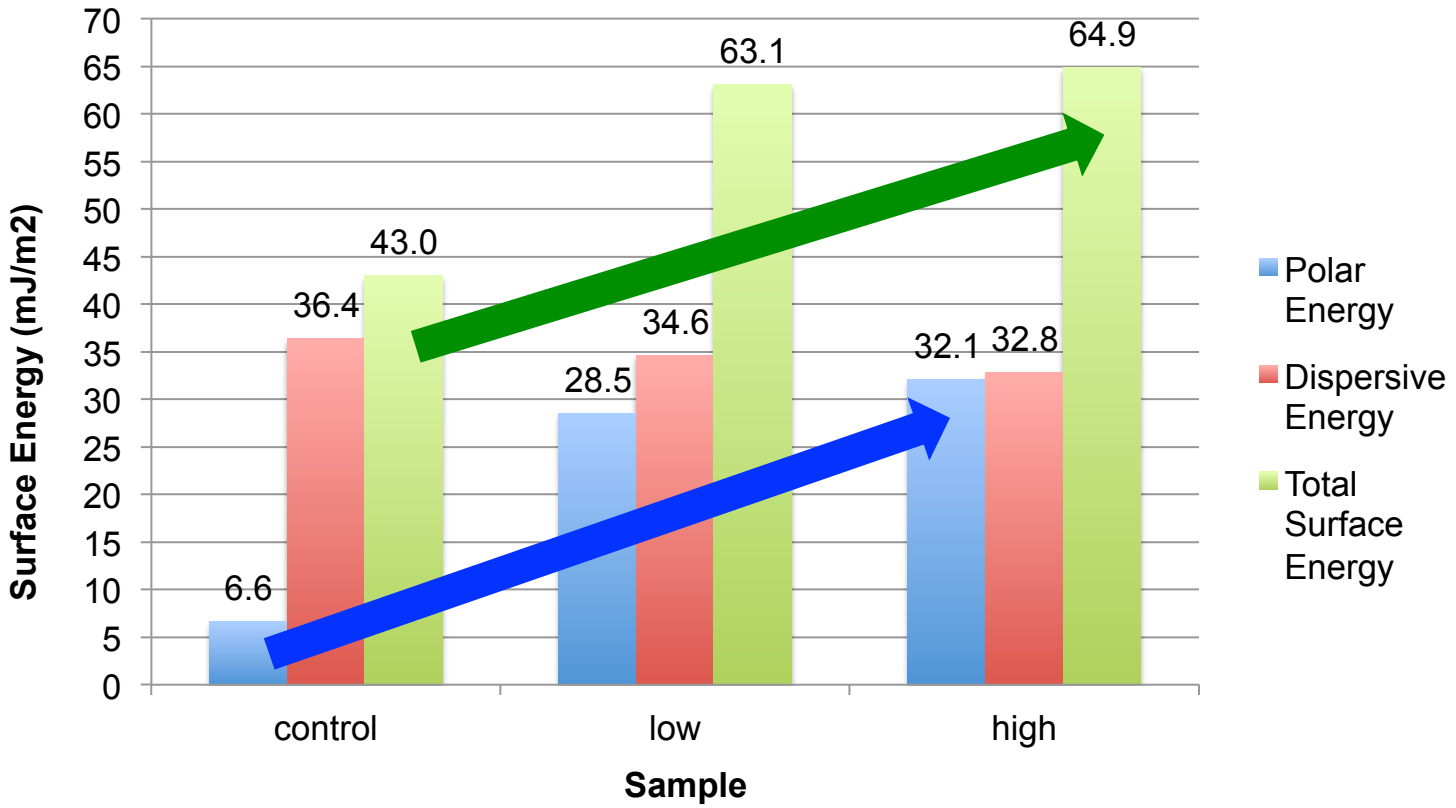
# Contact Angle Measurements




- Plasma changed polar character of surface
  - Polar fluids wet more on plasma treated surfaces

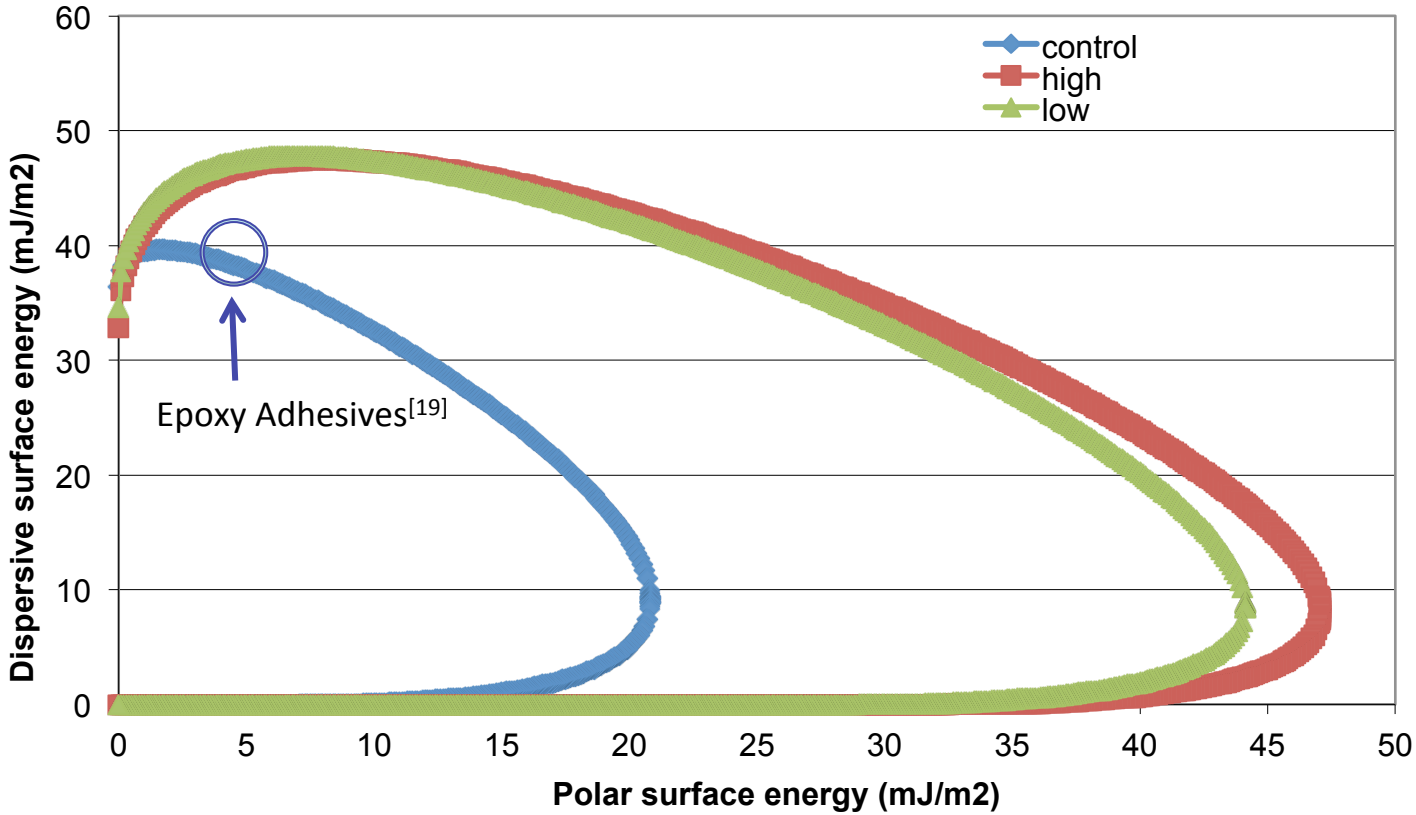
# Surface Energy

$$\gamma_{tot} = \gamma^p + \gamma^d$$



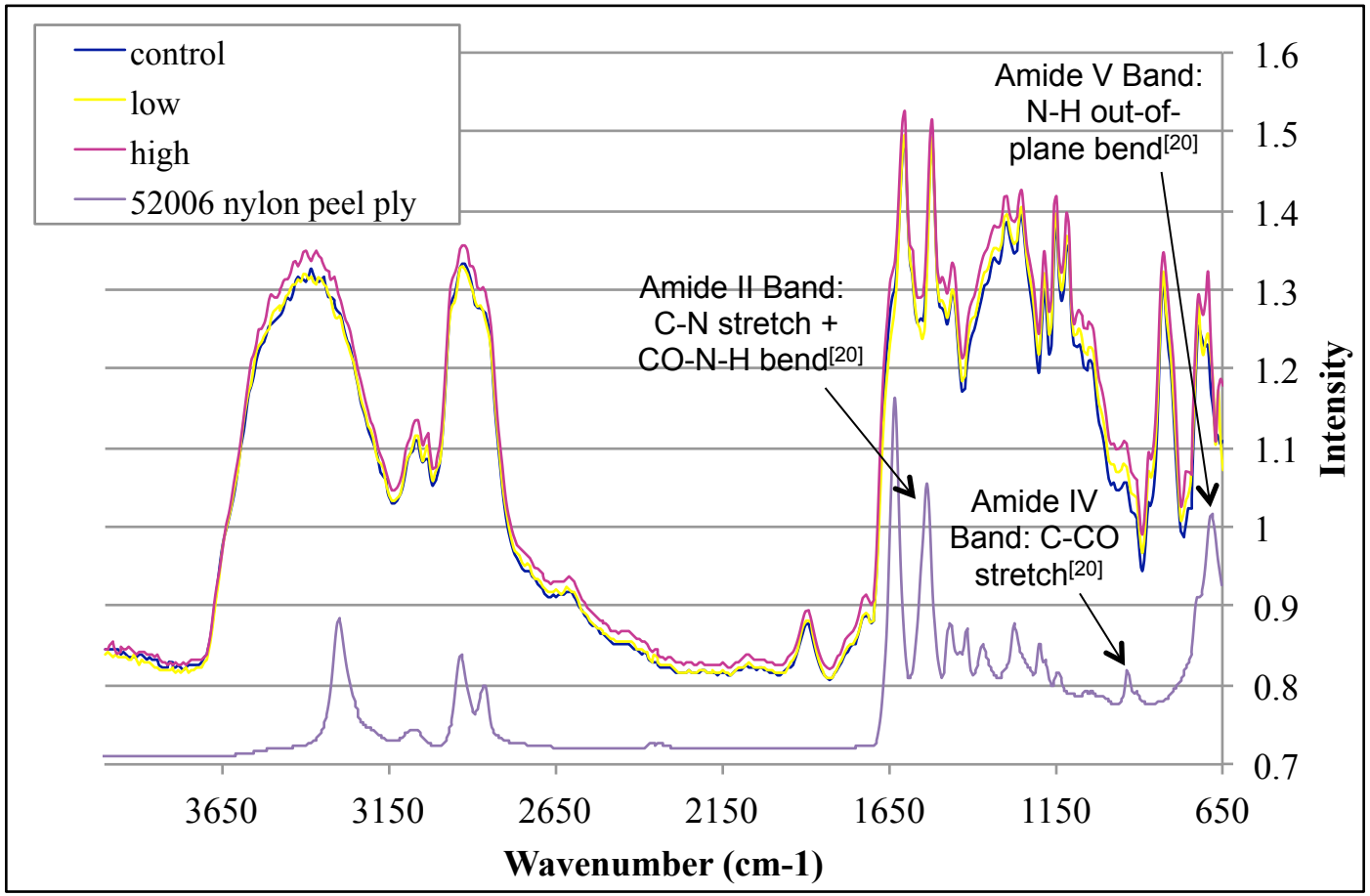

- Significant increase in polar (and total) surface energy
  - Polar groups promote adhesion[16-18]
- Very little change in dispersive surface energy

# Wettability Envelopes




- Significant change in surface energy shown by wettability envelopes
  - Could help explain difference in bonding

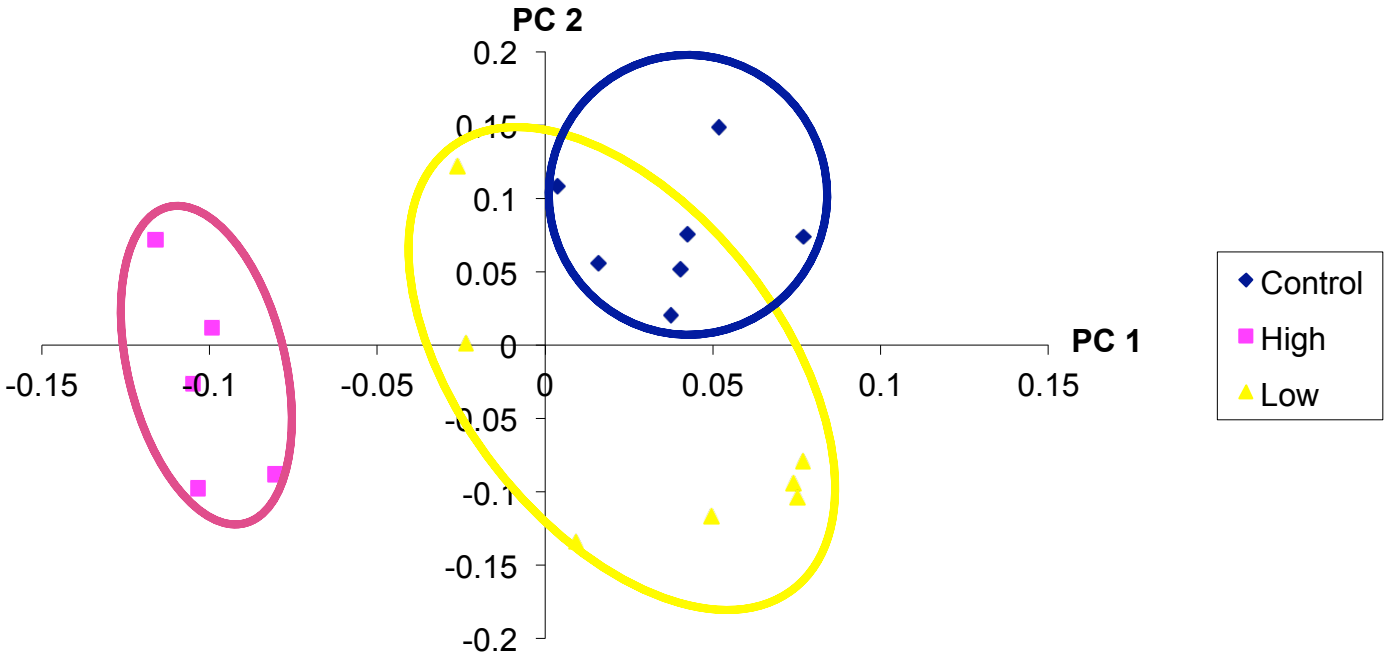
# FTIR Spectra




- No obvious nylon peaks on composite surfaces or changing peaks in those locations
  - Due to sampling depth (up to 10 μm) vs. depth of plasma treatment (few nm)?

➢ PCA to detect differences?

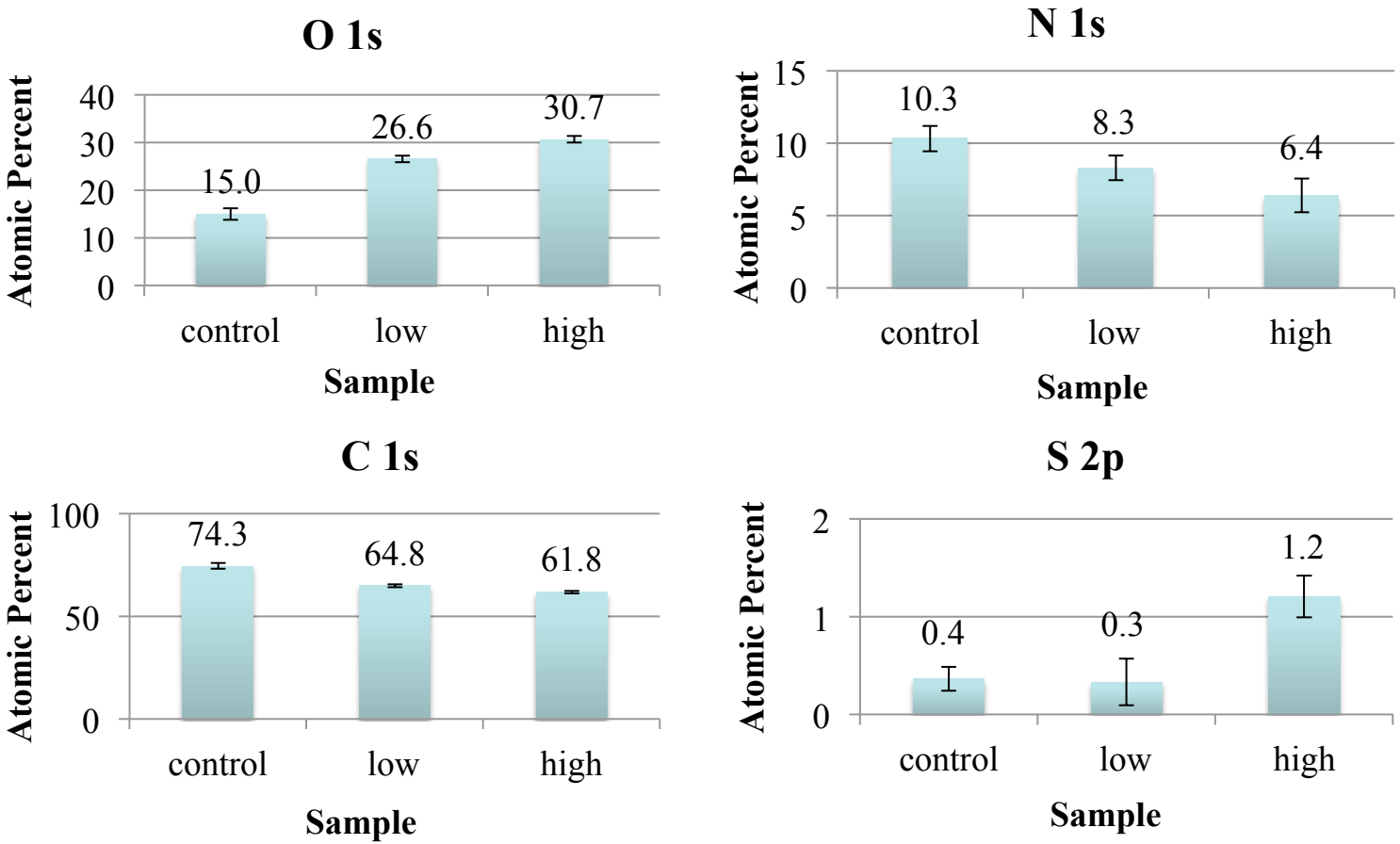
# PCA – Preliminary Results




- High samples and control samples identified as different
- Low samples not significantly different from high or control
- Differences could be due to polar groups on surface or other factors (reflectivity, roughness)

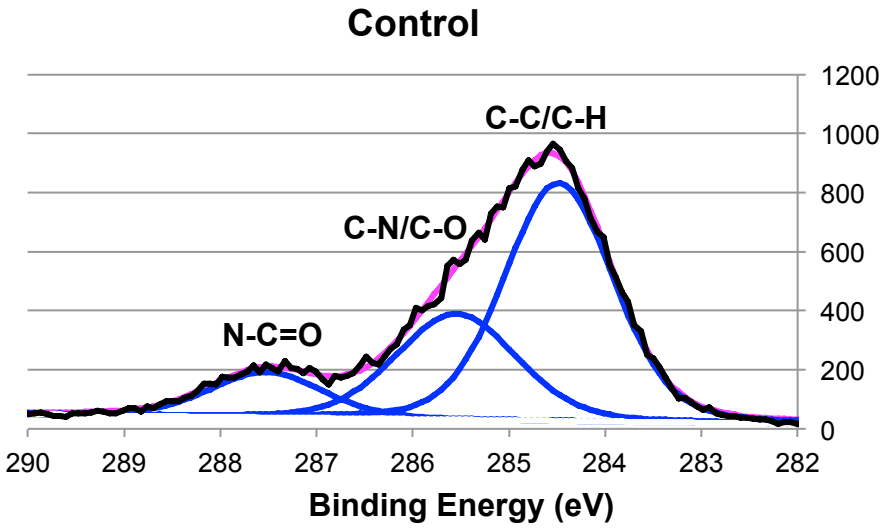
➢ XPS to understand chemical differences

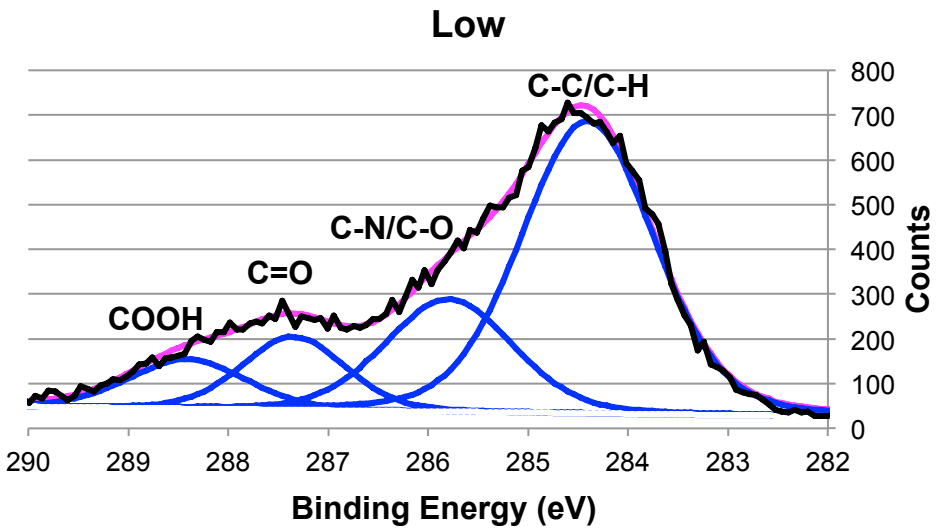
# XPS Measurements – Survey Scans

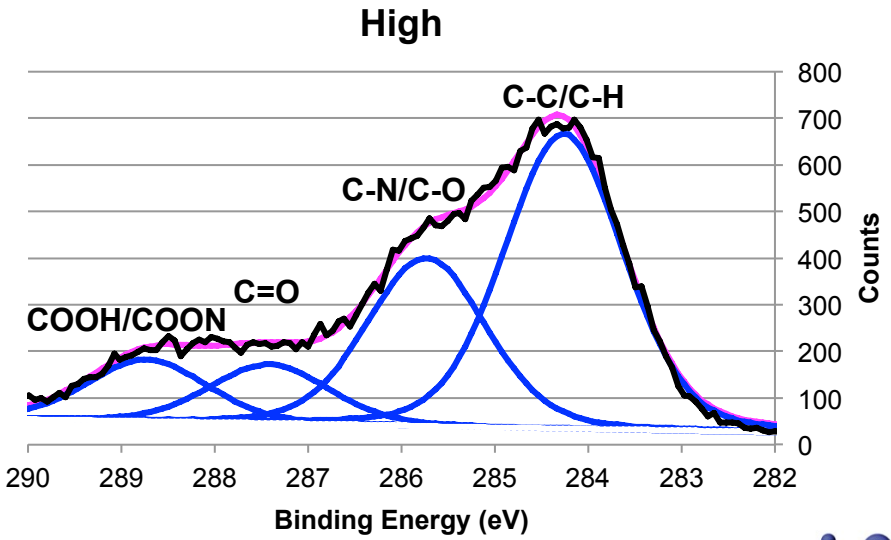



- Plasma increased oxygen significantly
- Carbon and nitrogen decreased on plasma treated surfaces
- Sulfur from proprietary tougheners in matrix, curing agent?

# XPS Measurements – High-Resolution Spectra




- Amide groups on control surfaces
  - From nylon peel ply
- No nylon groups on plasma treated surfaces
- Oxygen containing functional groups after plasma treatment
  - Polar groups promote adhesion[16-18]
  - Carboxyl groups bond with epoxy adhesive during cure?[21]

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# Summary of Key Results

- DCB measurements
  - **3-fold increase of $G_{IC}$ for plasma treated samples**
  - Cohesive/interlaminar failure for plasma treated samples, adhesion failure for controls
- Contact angle and surface energy
  - Plasma increased polar character of surface
  - **Improvements in surface energy and wettability envelopes may contribute to why MetlBond 1515-3M does not adhere to PFG 52006 nylon peel ply prepared Toray 3900/T800**
- FTIR measurements
  - Some differences detected with PCA
- XPS measurements
  - Clear differences in C, N, and O content on all samples
  - **N-C=O on controls, COOH on plasma treated samples**
- **DCB measurements correlate well to CA and XPS**

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# Future Work

- Plasma treatment variables:
  - Different plasma treatment raster speeds
    - Is there a plasma treatment threshold?
  - Time exposure to controlled environment
    - Bonding sites eliminated with time?
    - Times: directly after treatment, 8 hrs, 24 hrs, 72 hrs, 1 wk, 2 wks, 1 mo
- Other variables:
  - Abrasive material type (3M 255P 180 grit, Merit 180 grit, 3M Scotch Brite)
- Durability of bonded composites
  - Hot/wet testing
  - Thermal cycling

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# Looking Forward

- Benefit to Aviation
  - Guide development of QA methods for surface preparation
  - Greater confidence in adhesive bonds
- Future needs
  - Application to other composite/surface prep/adhesive systems
  - Model to guide bonding based on characterization, surface preparation and material properties
  - QA methods to ensure proper surface for bonding

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- Airtech International
- UW MSE
  - Tucker Howie, PhD
- Prof. Mark Tuttle, UW ME

Questions and comments are strongly encouraged.

Thank you.