A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

Improving Adhesive Bonding of Composites Through Surface Characterization

Ashley Tracey, Brian Flinn
David Pate, Jonathan Morasch, Nina Gerber
Materials Science and Engineering
University of Washington

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

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

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	✔
Peel Ply + Abrasion	✔		---	✔
Scarfed/Sanded Surfaces	✔	TBD	---	✔
Effect of Measurement on Bonding Surface	✔	TBD	TBD	N/A
Sandpaper Type	✔		---	✔
Peel Ply + Plasma Treatment	✔	TBD	---	✔

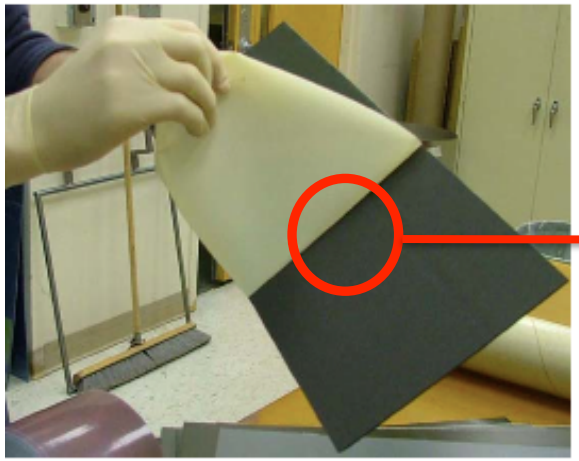
✔ = work completed --- = not of focus, diffuse reflectance for rough surfaces

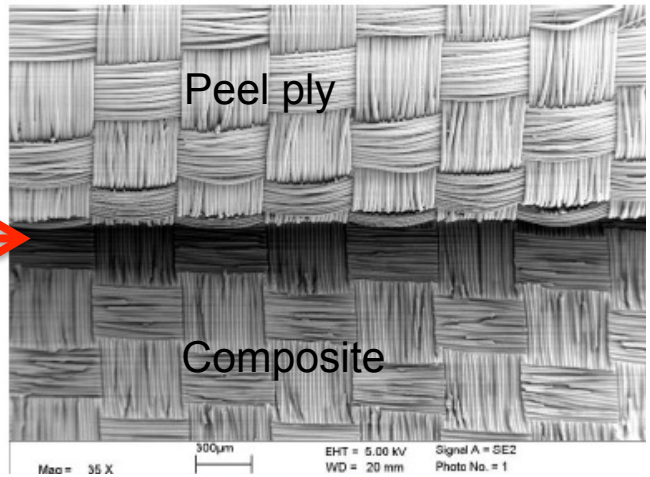
JAMS Joint Advanced Materials & Structures Center of Excellence

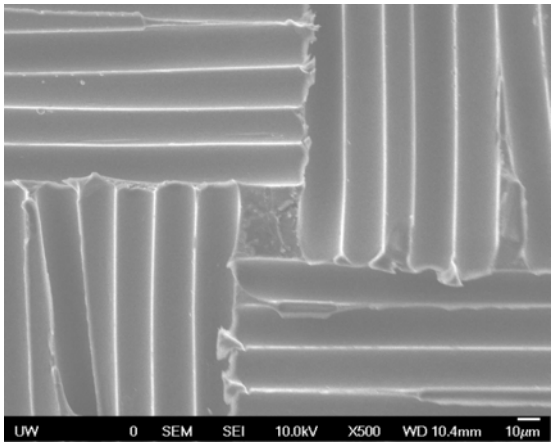
A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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 can lead to poor bonds





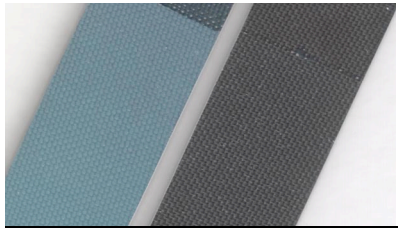
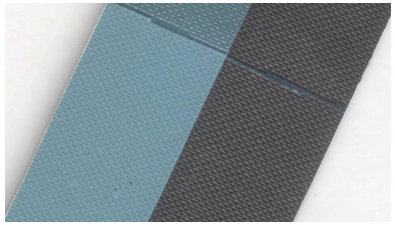


JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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

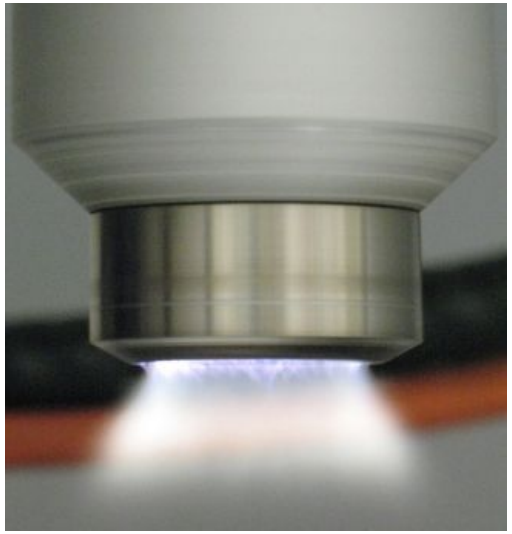
➢ Can atmospheric pressure plasma treatment change chemistry of peel ply surface and activate it?

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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

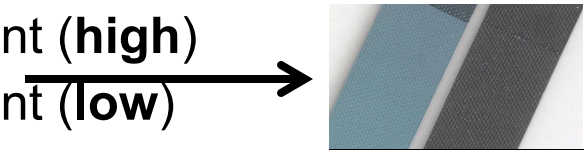
- Atmospheric pressure plasma treat nylon peel ply prepared composites
  - high plasma (slower raster speed)
  - low plasma (faster raster speed)
  - Out time (time after plasma treatment before bonding
- Characterize surfaces with various analysis techniques and relate to bond quality
  - Analysis methods: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

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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**)
    4. Out time up to 30 days



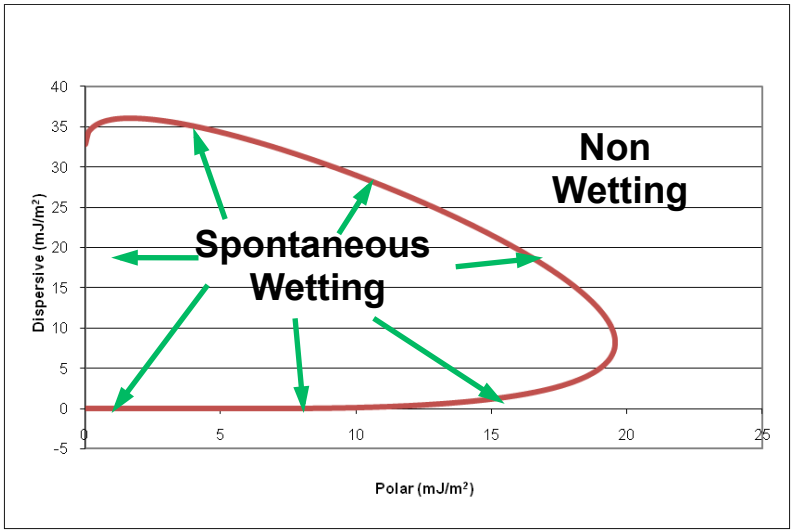
- Adhesive Bonding
  - MetlBond 1515-3M film adhesive (0.0325 psf)
  - Fluorinated ethylene propylene (FEP) release film crack starter

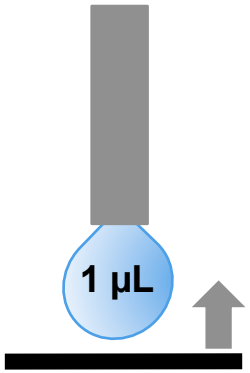
JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

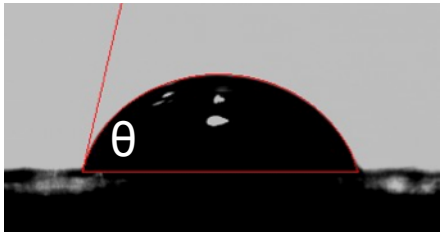
Contact Angle Methodology – Surface Energy

- 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



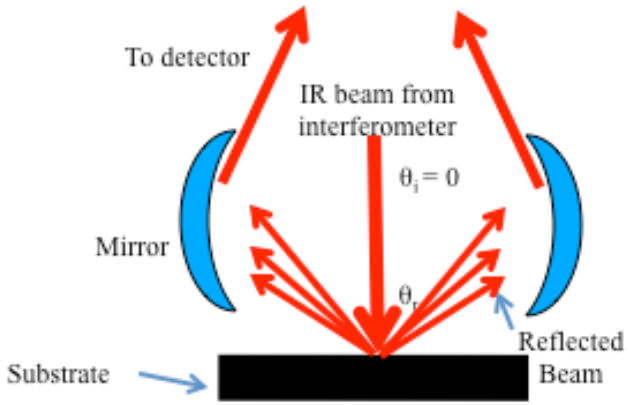
Side-view of drop as viewed from goniometer camera

JAMS Joint Advanced Materials & Structures Center of Excellence

AMTAS A Center of Excellence — Advanced Materials in Transport Aircraft Structures

FTIR Methodology – Surface Chemistry

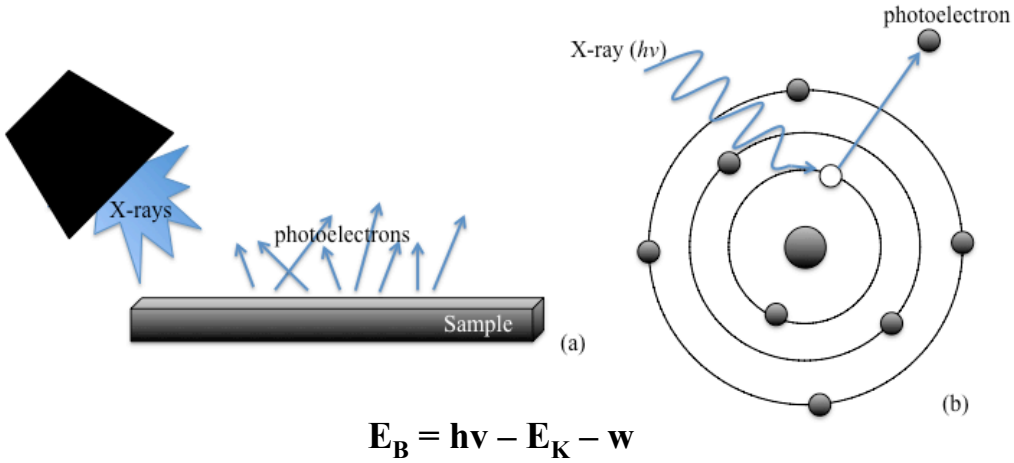
- Diffuse reflectance FTIR for rough surfaces
  - Chemical information from 1-10 μm[15]
- Mid-IR data range (4000-650 cm^{-1})
- 90 scans with 16 cm^{-1} resolution
- 7 spectra averaged per sample
- GRAMS IQ software used for principal component analysis (PCA) of spectra



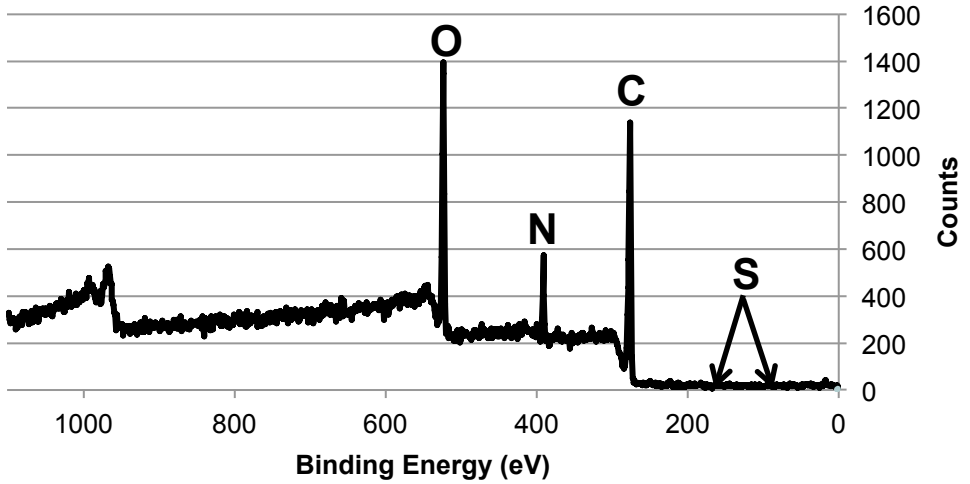
An IR beam path for diffuse reflectance

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



$$E_B = hv - E_K - w$$



JAMS Joint Advanced Materials & Structures Center of Excellence

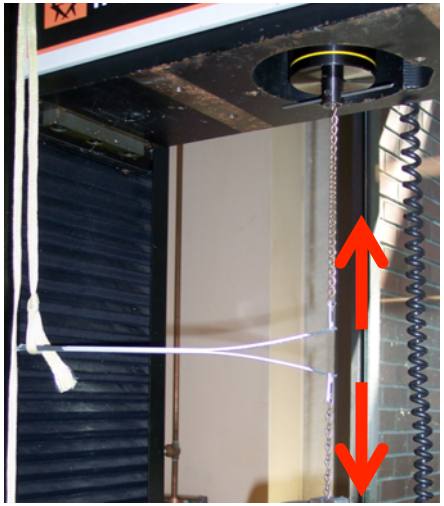
AMTAS A Center of Excellence Advanced Materials in Transport Aircraft Structures

DCB Testing – Bond Quality

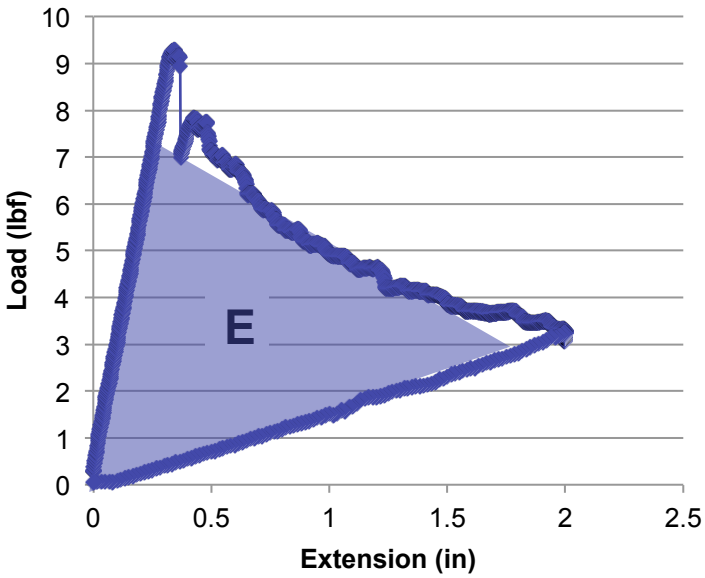
- Mode I strain energy release rate (G_{IC}) and failure mode
- 7-8 samples per condition
- Area method for G_{IC} calculations
  - E: area of curve
  - A: crack length
  - B: specimen width

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

- Bondline thickness measurements to ensure consistency



DCB Test

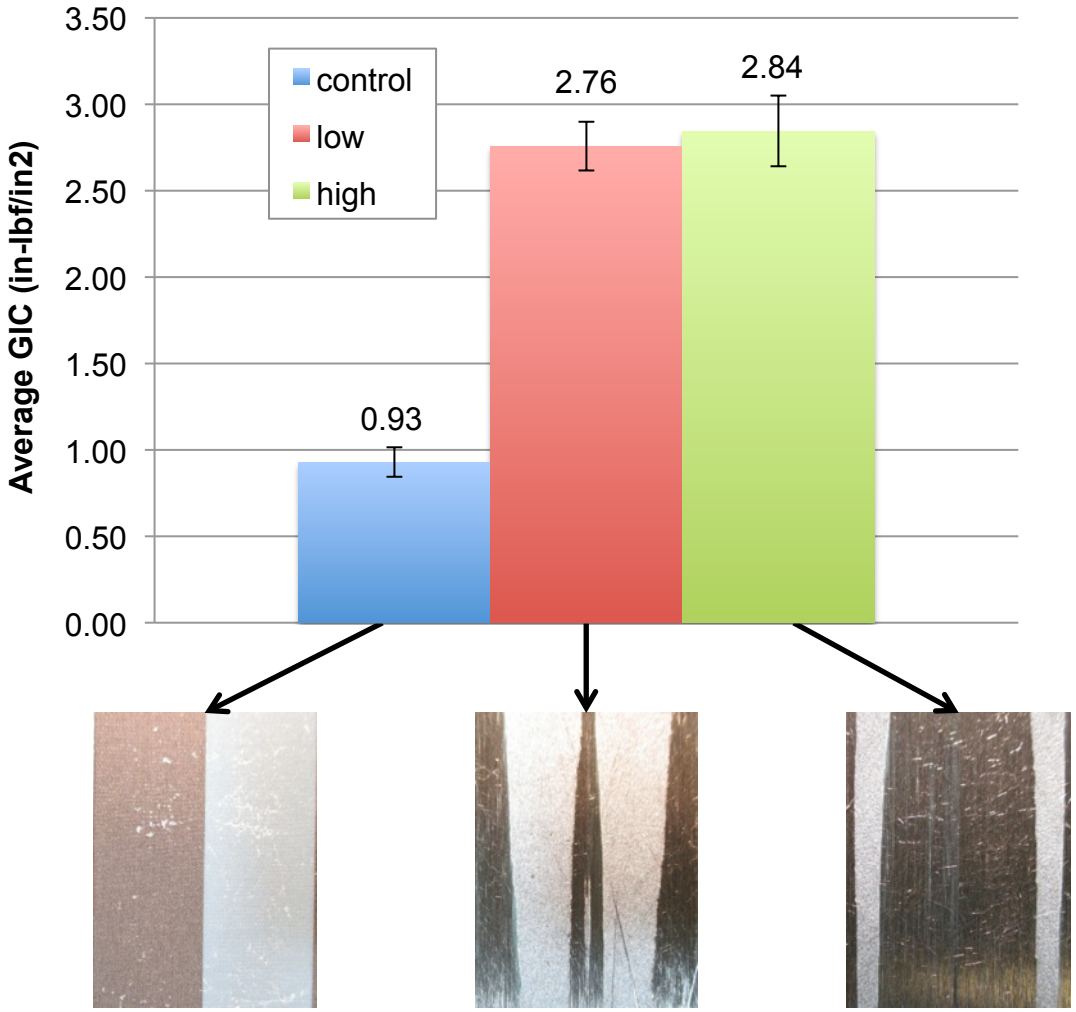


Sample	Maximum (mil)	Minimum (mil)	Range (mil)	Average (mil)	Standard Deviation (mil)
control	7.55	4.70	2.84	5.84	0.47
low	5.65	4.01	1.64	4.93	0.38
high	7.00	3.57	3.43	5.10	0.63

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

DCB Results

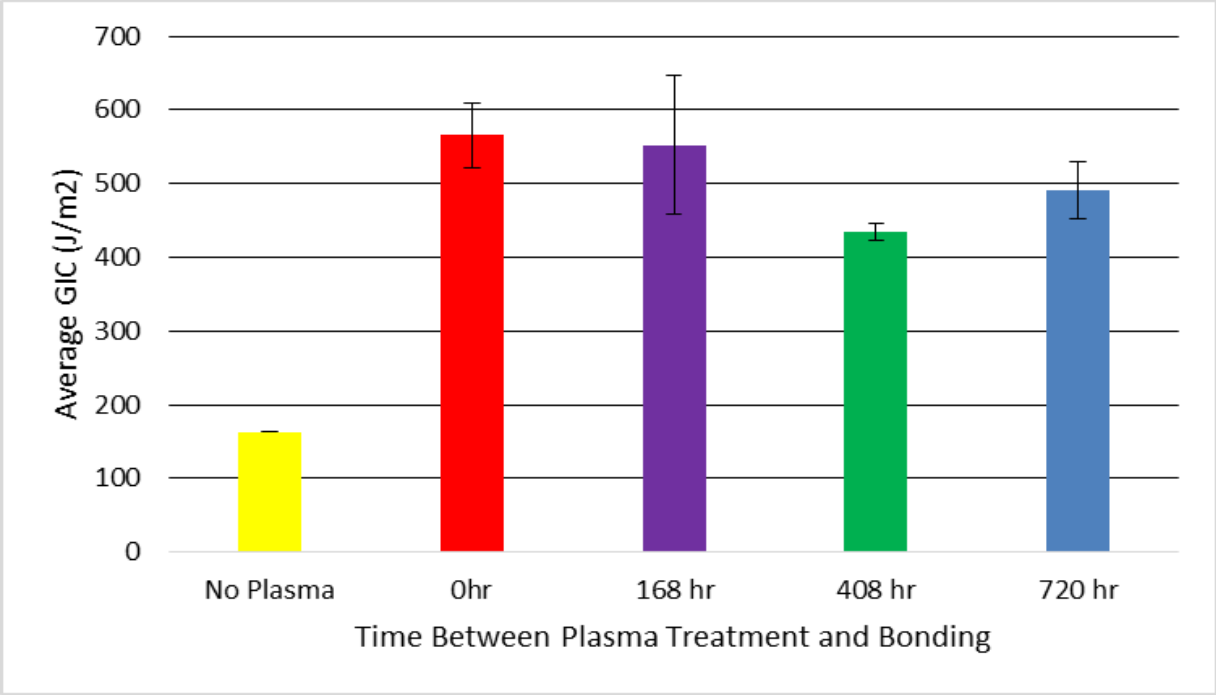


- 3-fold increase in G_{IC} for plasma treated samples compared to control
- Failure modes correspond to fracture energies

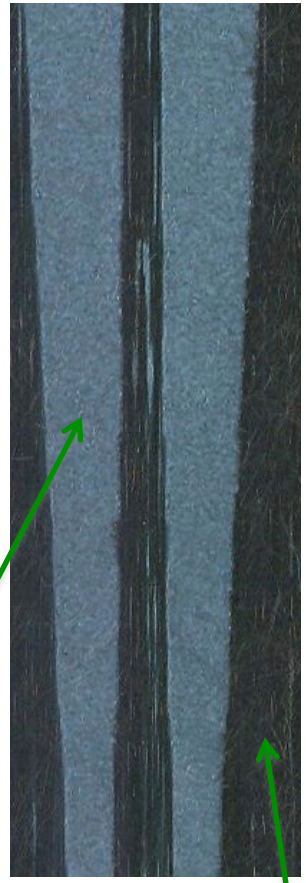
JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

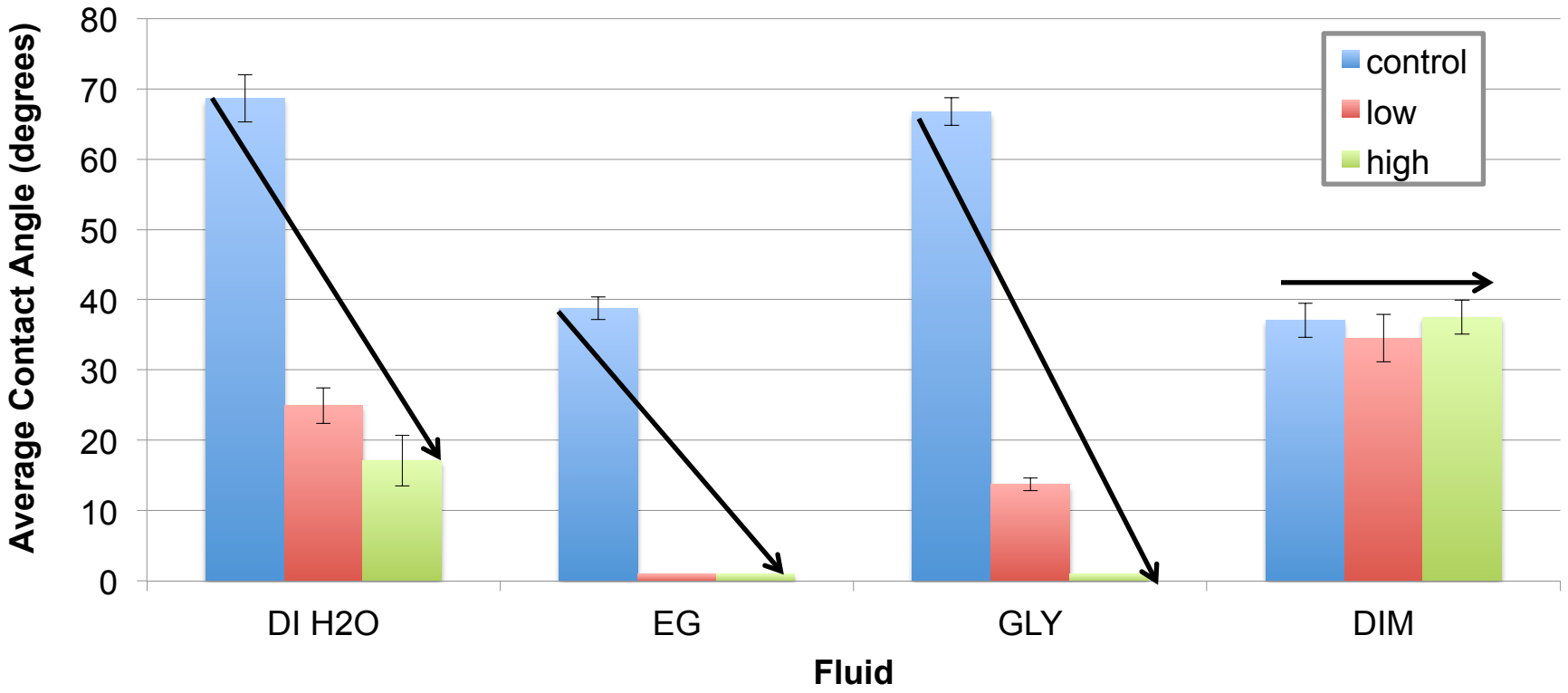
DCB Results-Out Time



- G_{IC} values decreased slightly after 408 and 720 hour ambient exposure
- Differences correspond with surface characterization
- All values within acceptable range



Contact Angle Measurements



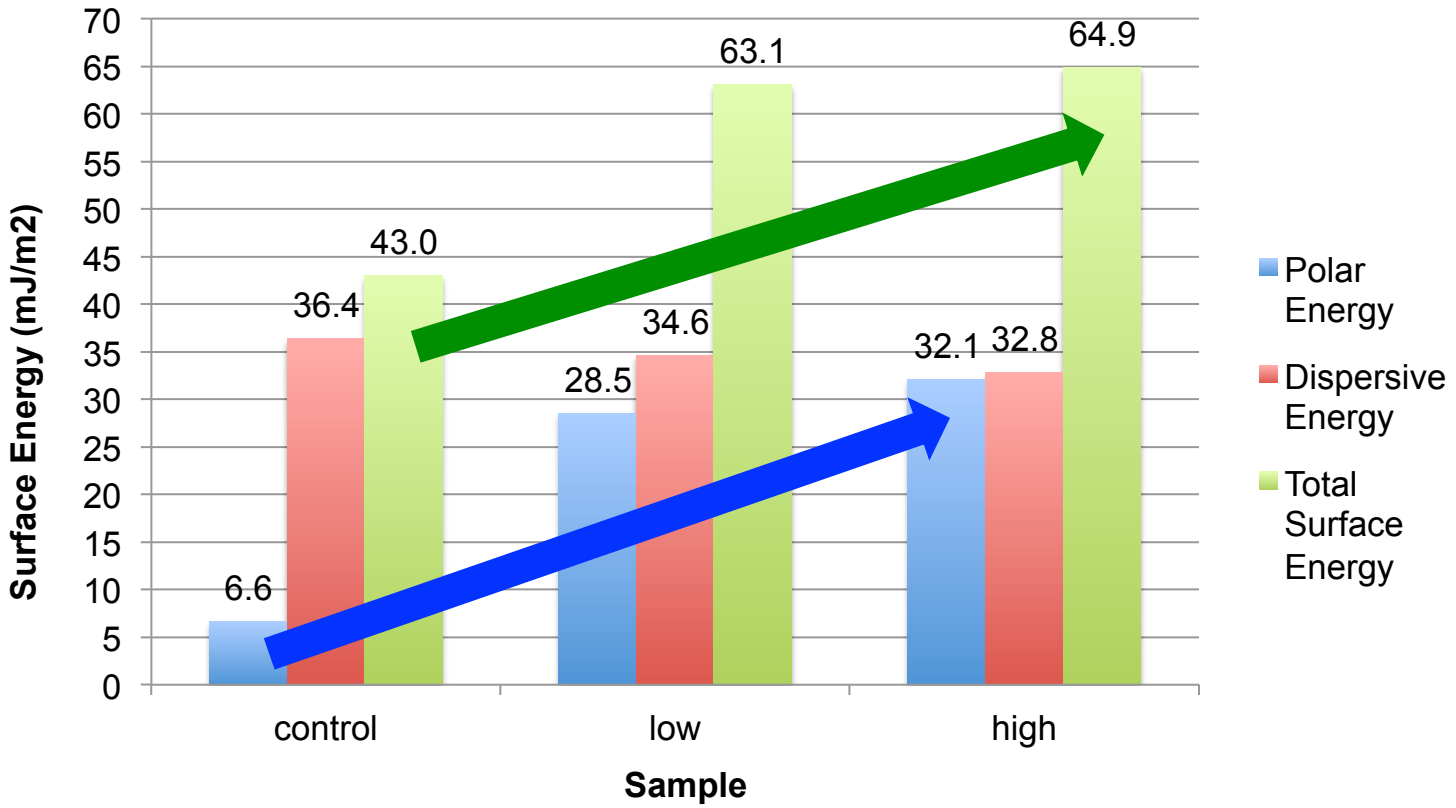
- Plasma changed polar character of surface
  - Polar fluids wet more on plasma treated surfaces

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Surface Energy

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

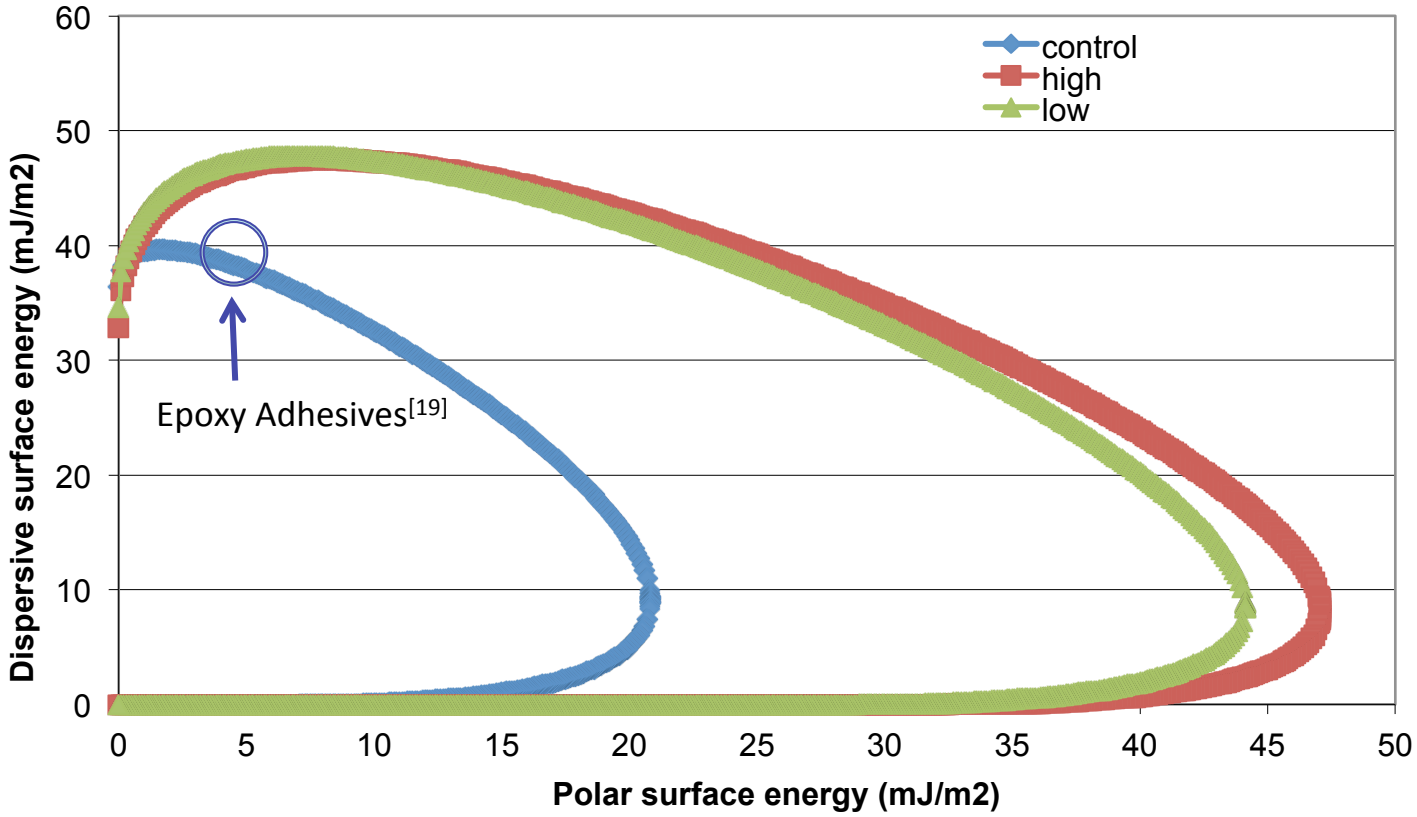


- Significant increase in polar (and total) surface energy
  - Polar groups promote adhesion[16-18]
- Very little change in dispersive surface energy

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

Wettability Envelopes

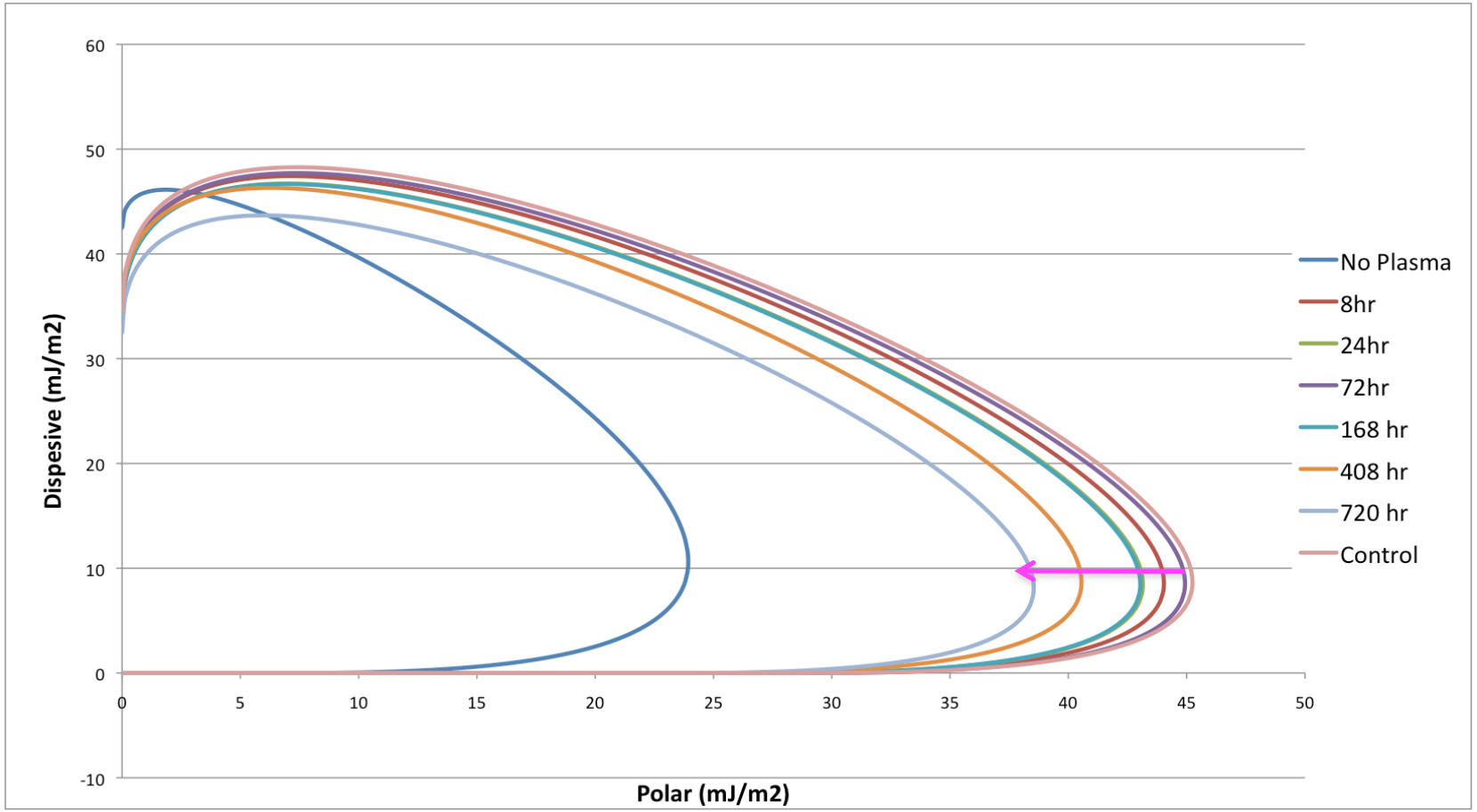


- Significant increase in surface energy shown by wettability envelopes
  - Could help explain difference in bonding

JAMS Joint Advanced Materials & Structures Center of Excellence

AMTAS A Center of Excellence Advanced Materials in Transport Aircraft Structures

Wettability Envelopes-Out Time

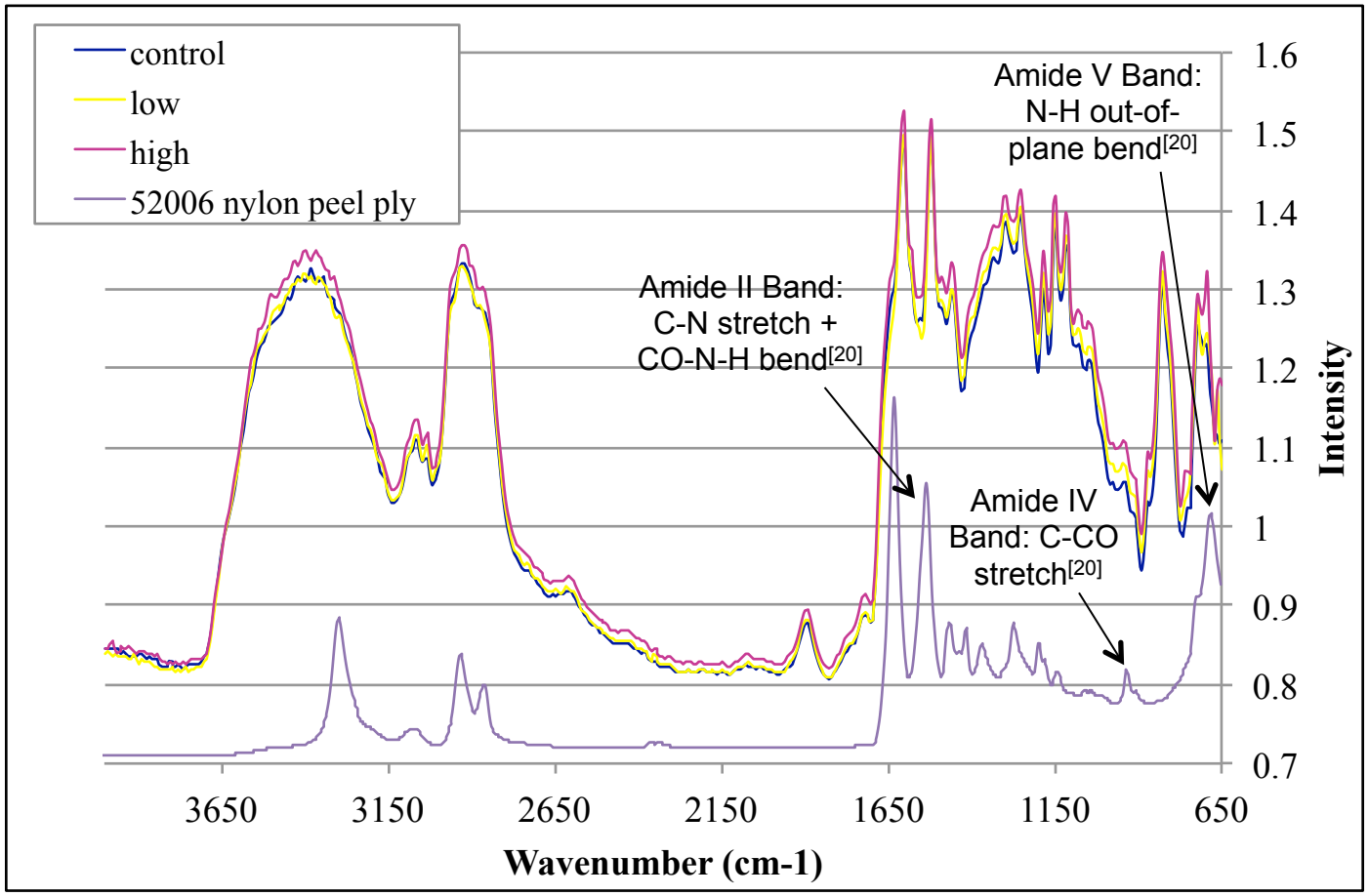


- Decreasing surface energy → smaller wettability envelope
- After 30 days, still much larger than control

JAMS JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

FTIR Spectra



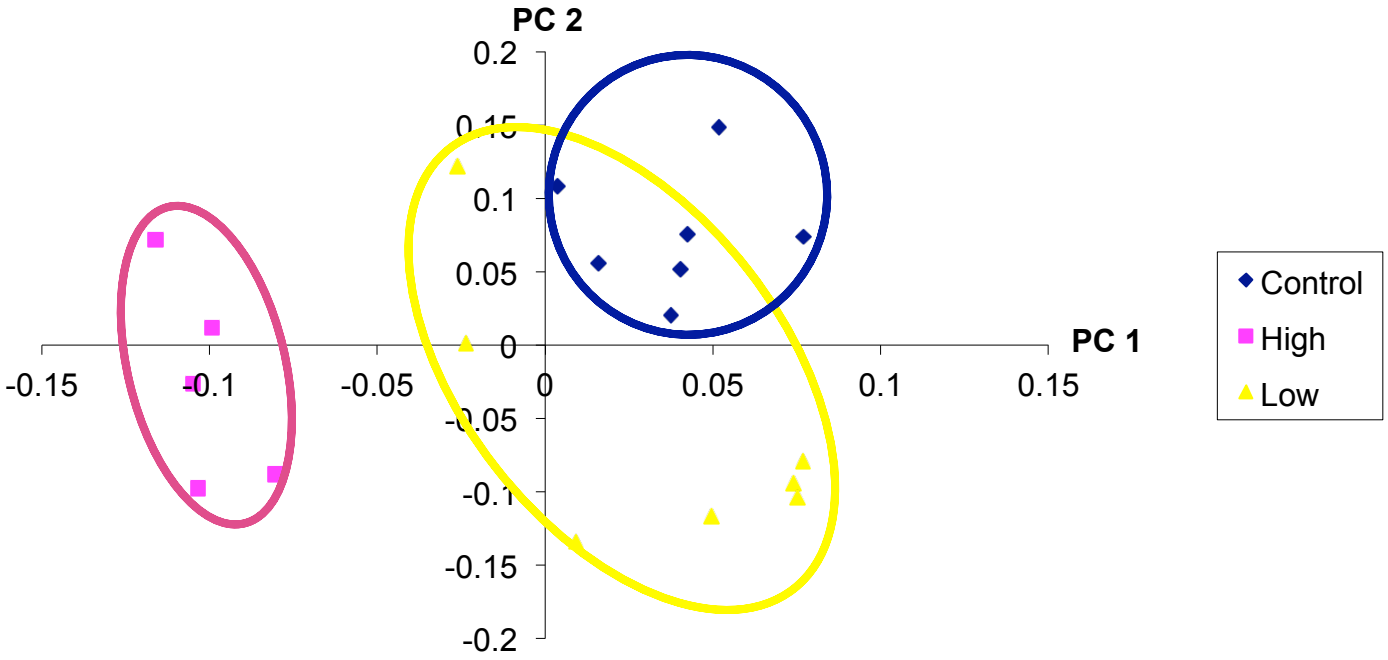
- No obvious nylon peaks on composite surfaces or changing peaks in those locations
  - Due to sampling depth (up to 10 μm) vs. depth of plasma treatment (few nm)?

➢ PCA to detect differences?

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

FTIR PCA – Preliminary Results



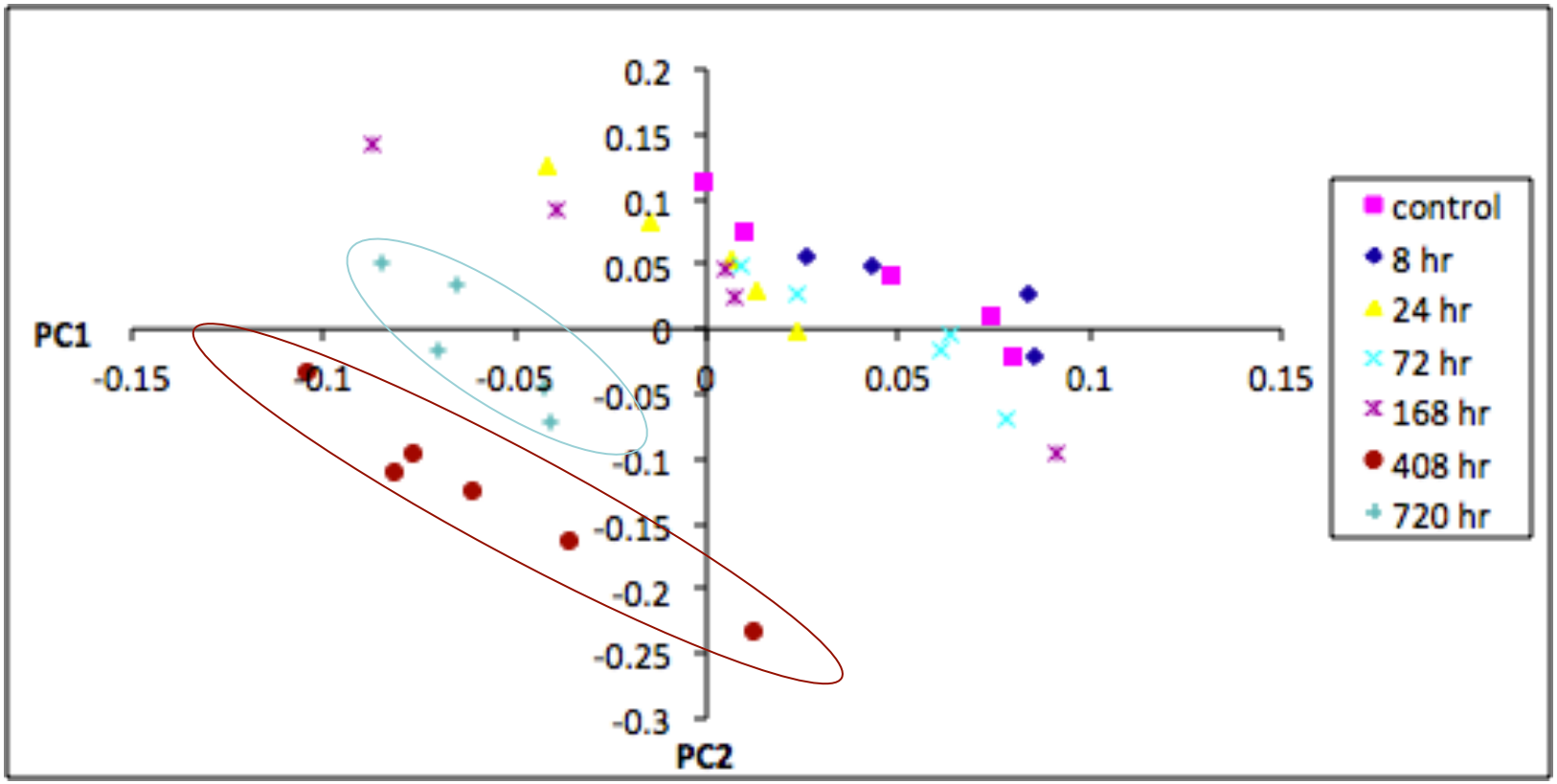
- Clusters observed
- Low samples overlap with control samples
- Differences could be due to polar groups on surface or other factors (reflectivity, roughness)

➢ XPS to understand chemical differences

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

FTIR PCA - Out Time

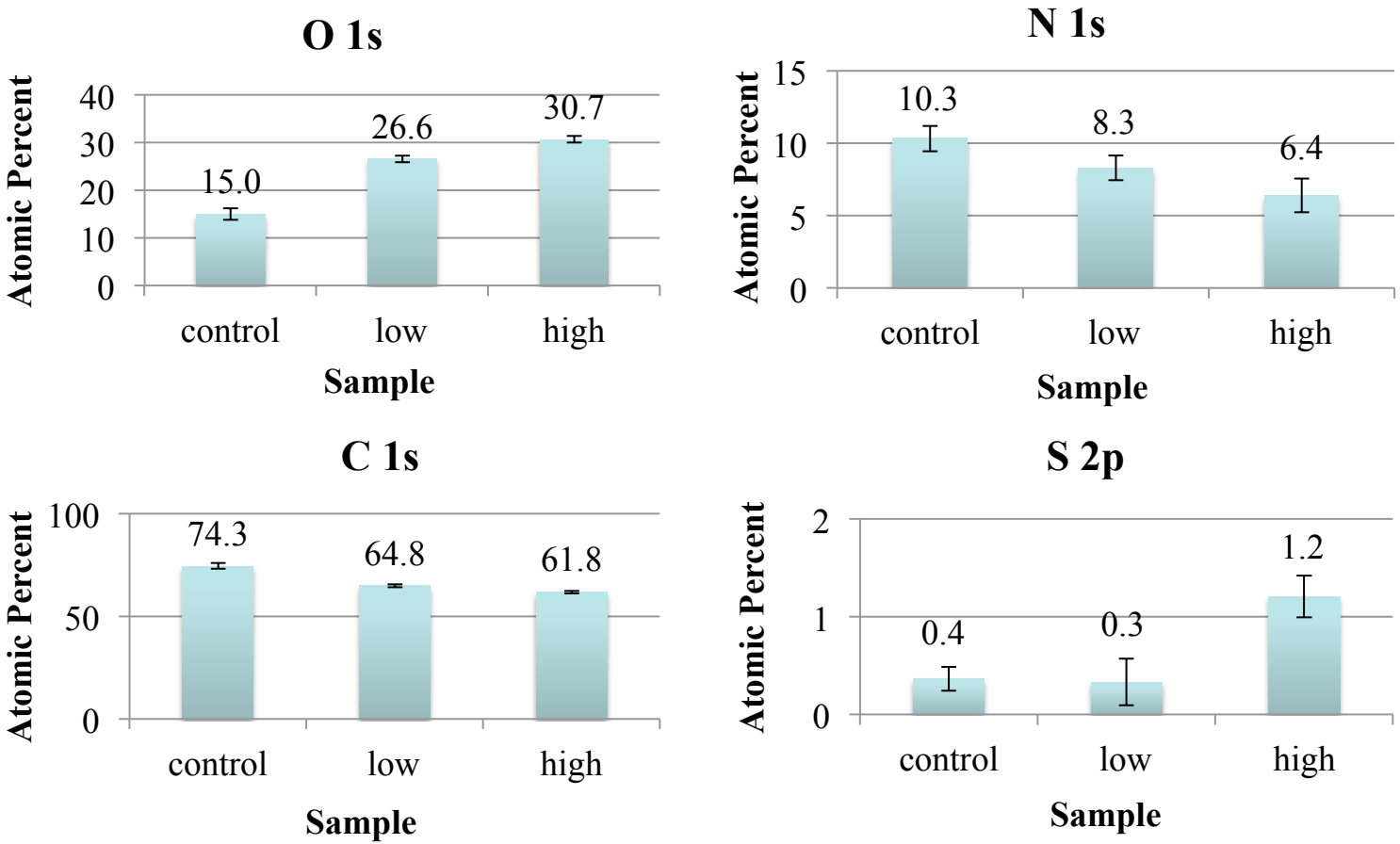


- Data for 408 and 720 hour samples differ from remainder
- Roughly correlates with contact angle trend

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

XPS Measurements – Survey Scans

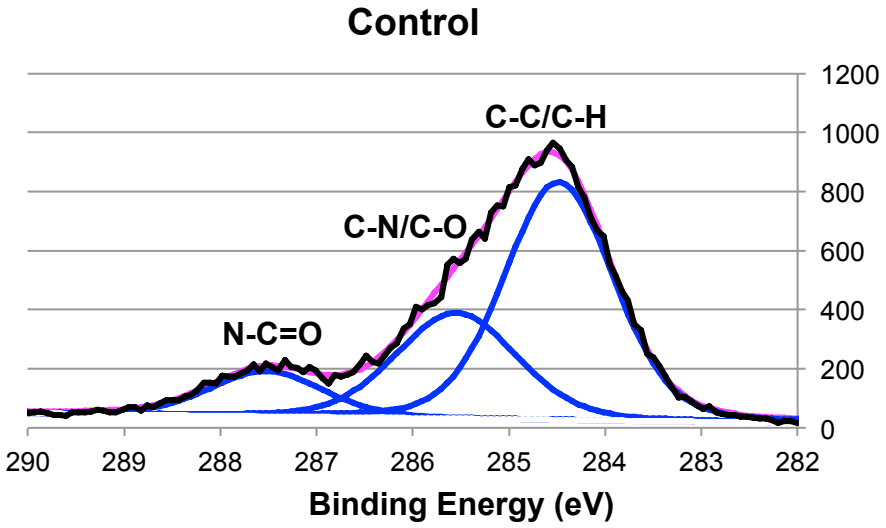


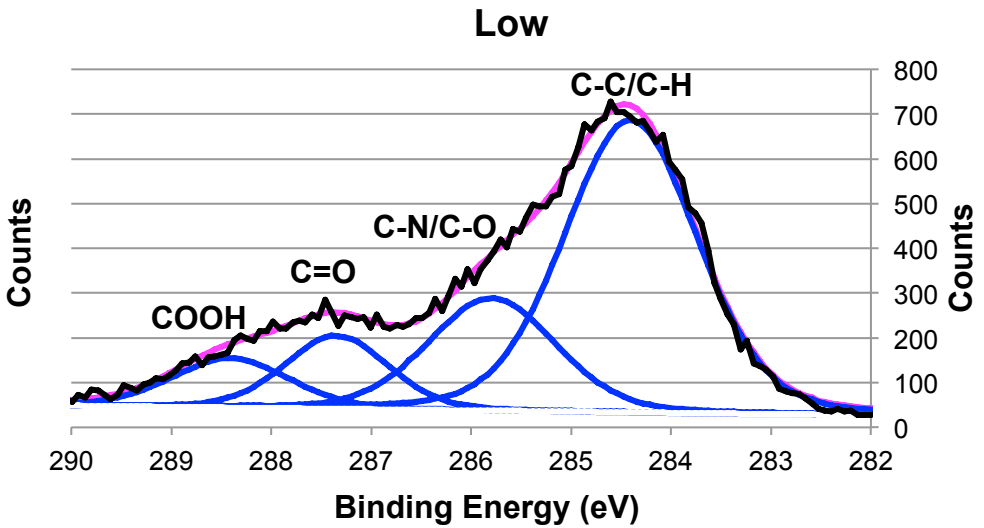
- Plasma increased oxygen significantly
- Carbon and nitrogen decreased on plasma treated surfaces
- Sulfur from proprietary tougheners in matrix, curing agent?

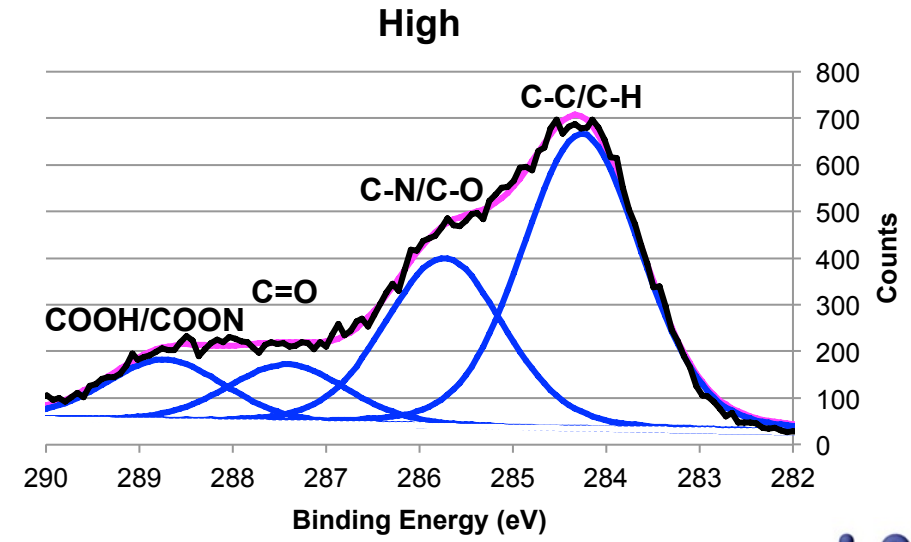
JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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]

JAMS Joint Advanced Materials & Structures Center of Excellence

AMTAS A Center of Excellence — Advanced Materials in Transport Aircraft Structures

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
  - **Strong bond formed up to 30 days after plasma treatment**
- Contact angle and surface energy
  - Plasma increased surface energy, notable polar component
  - Slight decrease in surface energy over time (30 days)
- FTIR measurements
  - Some differences detected with PCA, potential for QA
- 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**
- **Similar results in other systems (250 F cure and paste)**

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Conclusions

- Plasma treatment turned a bad surface prep. good (reversed the curse of the nylon peel ply!)
  - Surface energy
  - Surface chemistry
  - Fracture energy
  - Failure mode
- Strong bonds produced up to 30 days after plasma
  - Acceptable surface chemistry, fracture energy and failure mode
- Surface chemistry measurements have potential for QA

Plasma treatment is a robust surface preparation process for bonding purposes

JAMS Joint Advanced Materials & Structures Center of Excellence

A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

Ongoing and Future Work

- Plasma treatment variables:
  - Different plasma treatment raster speeds
    - Is there a plasma treatment threshold?
  - Other material systems
- Durability of bonded composites
  - Hot/wet testing
  - Thermal cycling

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Ongoing and Future Work 2014-15

- Amine Blush in Paste Adhesives
  - Amine rich surface can form under certain conditions
  - Can lead to weak/poor bonds with paste adhesive
  - ➢ Can amine blush be detected
  - ➢ How much amine blush is acceptable
  - ➢ Working with GA partners (Epic, Cessna)
- Accelerated Aging of Bonds
- Bonded repair of aged aircraft
- Durability of bonded composites
  - Hot/wet testing
  - Thermal cycling

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

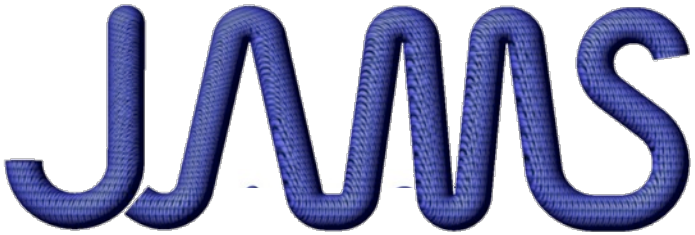
A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures

Acknowledgements

- FAA, JAMS, AMTAS
- Boeing Company
  - Tony Belcher and Kay Blohowiak
- Precision Fabrics Group
- Airtech International
- UW MSE
- Prof. Mark Tuttle, UW ME

Questions and comments are strongly encouraged.

Thank you.



References

1. H. J. Busscher, A. W. J. Van Pelt, P. de Boer, H. P. de Jong, and J. Arends, *Coll. and Surf.*, vol. 9, 1984.
2. Y. H. Mori, G. M. van de Ven, and S. G. Mason, *Coll. and Surf.*, vol. 4, 1982.
3. J. F, Oliver, C. Huh, and S. G. Mason, "Coll. and Surf.," vol. 1, 1980.
4. L. J. Hart-Smith, G. Redmond, and M. J. Davis, "The Curse of the Nylon Peel Ply," in *41st SAMPE International Syposium and Exhibition*, 1996.
5. M. Phariss and B. Flinn, "The Effect of Peel-Ply Surface Preparation Variables on Bond Quality," in *DOT/FAA/(AR)-06/28*, 2006.
6. B. D. Flinn and C. W. Hickmott, "Effect of Surface Preparation Technique on Bond Quality of AGATE Composite Laminates," in *SAMPE 2009*, Baltimore, MD.
7. B. D. Flinn, B. K. Cark, J. Satterwhite, and P. J. Van Voast, "Influence of Peel Ply Type on Adhesive Bonding of Composites," in *SAMPE 2007*, Baltimore, MD, 2007.
8. R. A. Wolf, *Atmospheric Pressure Plasma for Surface Modification*. Hoboken: Wiley, 2012.
9. Alexander Fridman and Lawrence A. Kennedy, *Plasma Physics and Engineering*, 2nd ed. Boca Raton, FL: CRC Press, 2011.
10. M. A. (Tony) Belcher, K. L. Krieg, P. J. Van Voast, and K. Y. Blohowiak, "Nonchemical Surface Treatments Using Atmospheric Plasma Systems for Structural Adhesive Bonding," in *SAMPE 2013*, Long Beach, CA, 2013.
11. R. Bossi, R. Carlsen, F. J. Boerio, and G. Dillingham, "Composite Surface Preparation QA for Bonding," in *SAMPE 2005*, Long Beach, 2005.
12. D. K. Owens and R. C. Wendt, "Estimation of the Surface Free Energy of Polymers," *Journ. of Appl. Poly. Sci.*, vol. 13, pp. 1741-47, 1969.
13. C. Rulison, "So You Want to Measure Surface Energy?," in *Technical Note #306*, 1999.
14. M. Tuttle, WET v 1.0, 2005, personally distributed executable for generating wetting envelopes.
15. B. C. Smith, *Fundamentals of Fourier Transform Infrared Spectroscopy*. Boca Raton, FL: CRC Press, Inc., 1996.
16. Encinas, N., Oakley, B. R., Belcher, M. A., Blohowiak, K. Y., Dillingham, R. G., Abenojar, J., and Martinez, M. A. Surface modification of aircraft used composties for adhesive bonding. *International Journal of Adhesion & Adhesives* ((in press)).
17. Encinas, N., Diaz-Benito, B., Abenojar, J., and Martinez, M. A. *Surf. Coat. Technol.*, 205 (2010), 396-402.
18. Encinas, N., Abenojar, J., and Martinez, M. A. *International Journal of Adhesion & Adhesives*, 33 (2012), 1-6.
19. A. V. Pocius, *Adhesion and Adhesives Technology, An Introduction*, 2nd ed. Cincinnati, OH: Hanser Gardner Publications, Inc., 2002.
20. E. M. Enlow, J. L. Kennedy, A. A. Nieuwland, J. E. Kendrix, and S. L. Morgan, "Discrimination of Nylon Polymers Using Attenuated Total Reflection Mid-Infrared Spectra and Multivariate Statistical Techniques," *Applied Spectroscopy*, vol. 59, no. 8, 2005.
21. R. J. Zaldivar, J. Nokes, G. L. Steckel, H. I. Kim, and B. A. Morgan, "The Effect of Atmospheric Plasma Treatment on the Chemistry, Morphology and Resultant Bonding Behavior of a Pan-Based Carbon Fiber-Reinforced Epoxy Composite," *Journal of Composite Materials*, vol. 44, no. 2, pp. 137-56, 2010.

JAMS
JOINT ADVANCED MATERIALS & STRUCTURES CENTER OF EXCELLENCE

A Center of Excellence
AMTAS
Advanced Materials in Transport Aircraft Structures