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Improving Adhesive Bonding of Composites Through Surface Characterization

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Improving Adhesive Bonding of Composites

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- FAA Technical Monitor
  - Curtis Davies and David Westlund
- Other FAA Personnel
  - Larry Illecwicz
  - Cindy Ashforth
- Industry Participation
  - Epic Aircraft
  - The Boeing Company
  - Textron

Two projects will presented today

1. Amine Blush in Epoxy Paste Adhesives
   - Characterization of Bondline
     - Effect of bonding environment on bond quality

2. Surface Characterization using Inverse Gas Chromatography (IGC) Methods
   - Characterization of Adherend Surfaces
     - Effect of surface preparation on bond quality

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Amine Blush in Epoxy Paste Adhesives

- Project Background
- Test Methods and Design
- Current Results
- Upcoming Work

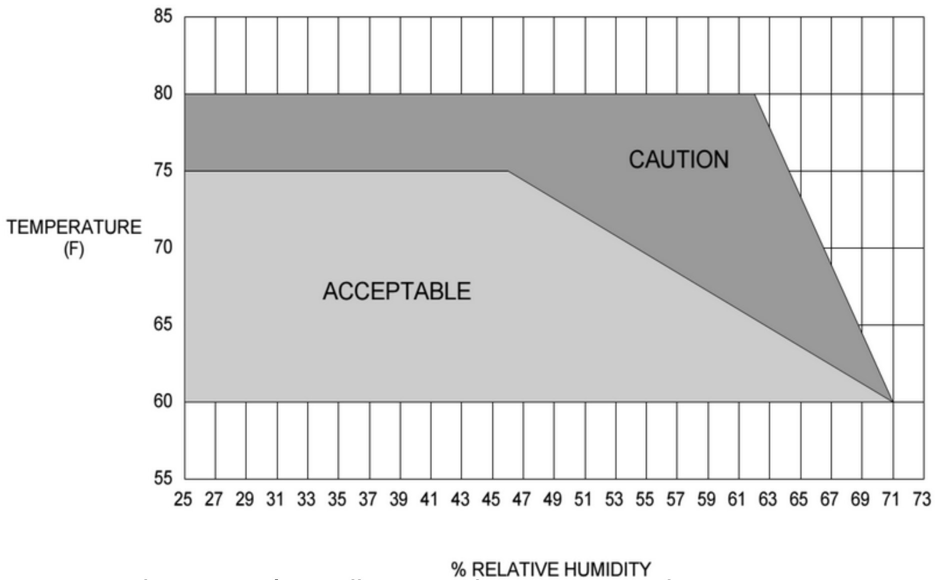
Motivation and Key Issues

- Bond failures have been attributed to amine blush
  - Cessna incident (2010)

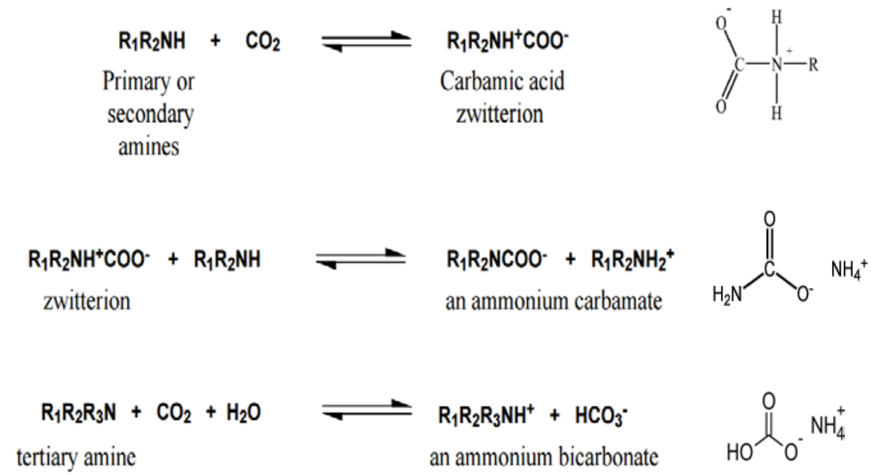
- What are the conditions for blush formation?
- What are the effects on bond quality?
- Investigate blush NDI methods

Amine Blush Formation

- Bloom - Amine component diffuses to the surface creating greasy, tacky layer.
- Blush - The amine rich layer reacts with the atmosphere, turns powdery and white
- The bloom/blush process degrades the overall quality of the desired epoxy-amine crosslink reaction.



Environmental Bonding Requirements per Cirrus SR22T SRM



Amine Blush Chemical Reactions

Assumed Critical Factors:

Temperature, humidity, exposure time, and CO_2

Project Outline

1. Expose epoxy paste bonds to a range of environmental conditions and analyze the effect on bond strength.

2. Perform FTIR analysis on traveler coupons to determine if blush formation can be detected and quantified.

3. Relate the mechanical response of the bond relative to any measured blush formation.

Project Test Plan

1. Adhesive: Henkel Loctite EA 9360
   - Two part epoxy – amine system

2. Experimental Exposure Variables
   - Temperature (60 – 90 F)
   - Humidity (50 – 85 %RH)
   - CO_2 (500 – 5000 ppm)
   - A & B component exposure time (0 – 3 weeks)
   - Bondline exposure time (20 – 50 min)
   - 2^{5-1} Factorial DOE

3. Test Methods
   - FTIR – Amine Blush Measurement
   - T-Peel – Bond Quality Measurement
   - DCB – Bond Quality (In progress)

Exposed Amine Component (Left)
Environmental Conditioning Chamber (Right)

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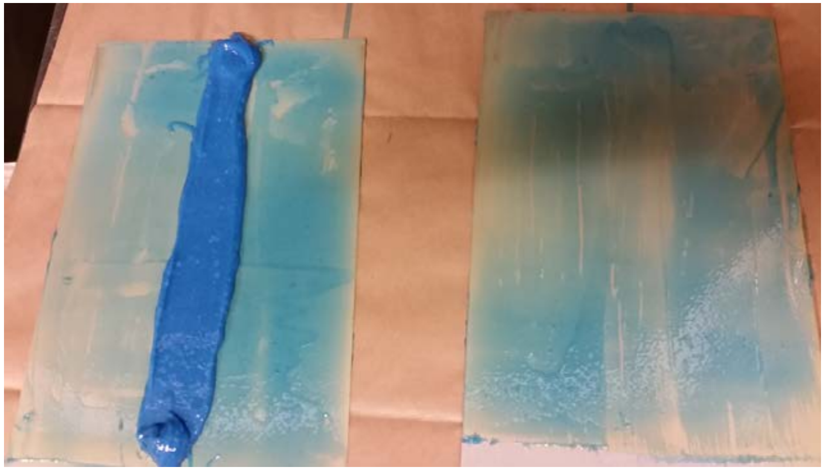
Specimen Exposure & Bonding Procedure

- Mix parts A and B
- "Wet out" both substrates (apply a thin layer of adhesive)
- Apply adhesive mound to center of one substrate
- Expose w/ traveler surface per DOE conditions.
- Place bond rods and crack starter on one substrate
- Tape substrates together
- Place in hot press

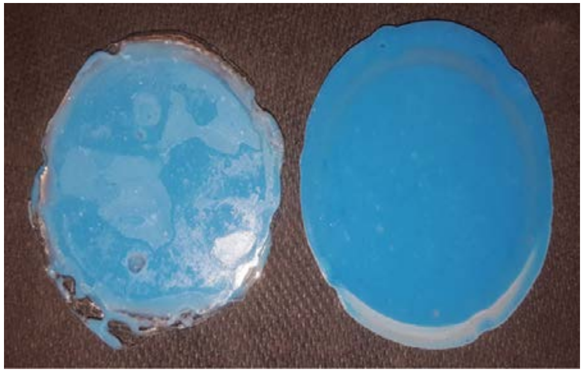


T-Peel Bonding Procedure

FTIR Witness Coupon

FTIR Analysis

- Testing with benchtop ATR FTIR
  - Samples exposed alongside mechanical samples
  - Samples closed out after designated exposure time
- Establishment of quantification procedures
- Comparisons to reference literature



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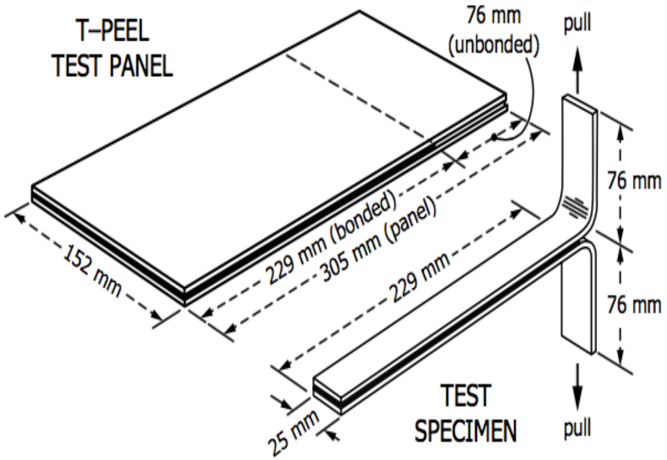
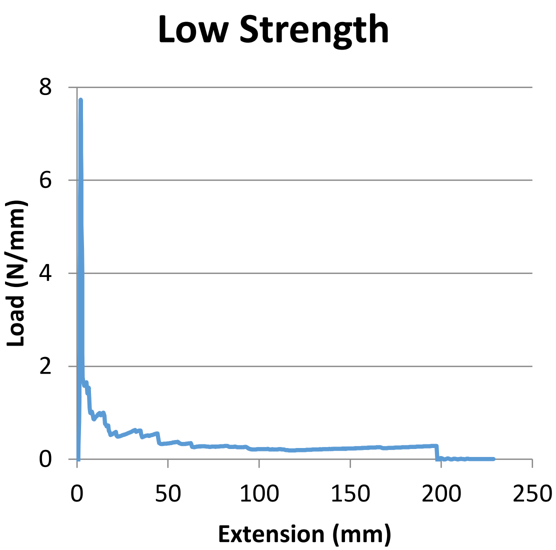
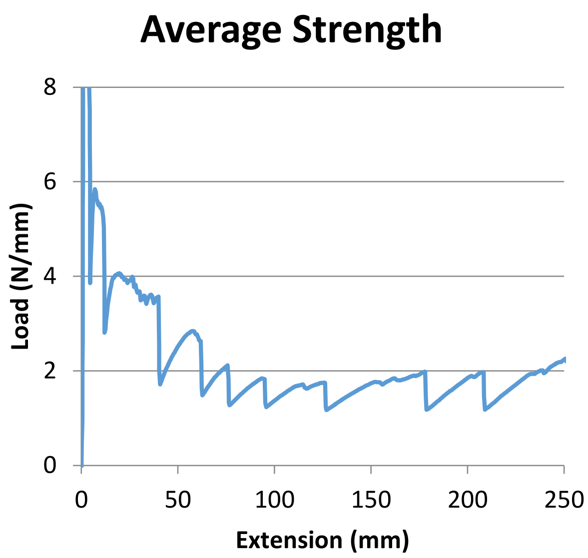
T-Peel Test – ASTM D1876

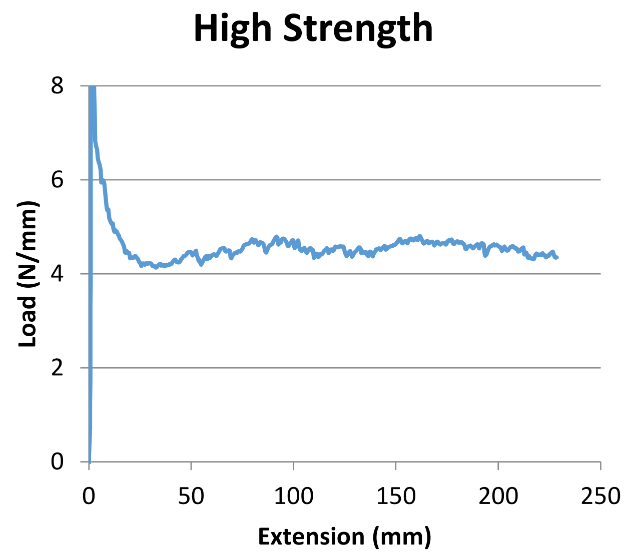


- Aluminum substrates (primed)
- Bond does not extend full length of substrates
- After bonding, non-bonded substrate ends bent to a 90º angle
- Ideal failure is mode I - cohesive

T-Peel Test Results







Temperature :	(+) 90 °F	(+) 90°F	(–) 60 °F
Relative Humidity:	(+) 85 %RH	(+) 85%RH	(–) 50 %RH
ppm CO_2:	(+) 5000 ppm	(–) 500 ppm	(–) 500 ppm
Bondline Exp Time:	(+) 50 min	(–) 20 min	(–) 20min
A/B Exposure:	(–) 1 day	(–) 1day	(–) 1day
	Run 1	Run 13	Run 16

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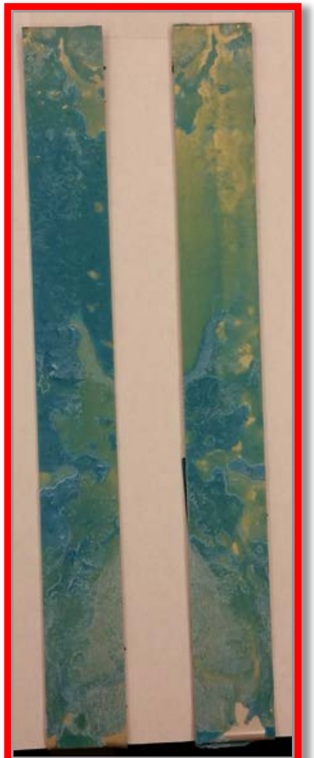
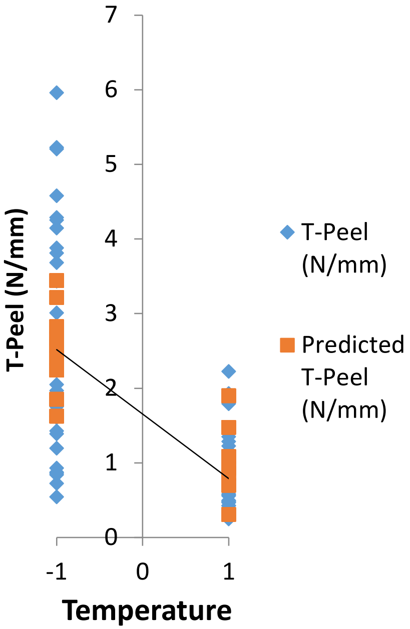
T-Peel Test Result – Failure Mode

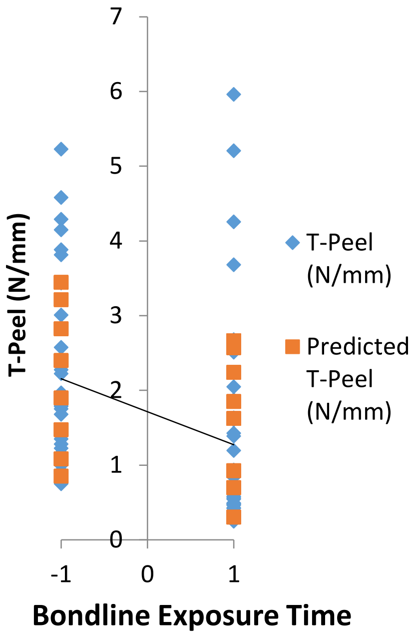
- Fracture surfaces from low to high strength (left to right)

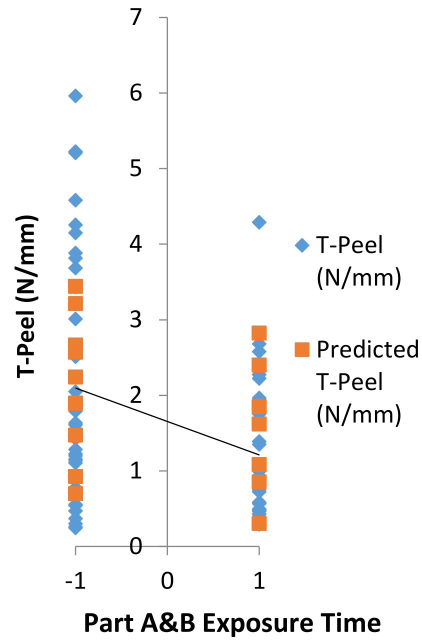



	Low Strength	Avg Strength	High Strength	Control Samples:
Temperature :	(+) 90 °F	(–) 60°F	(–) 60 °F	• No environmental exposure
Relative Humidity:	(+) 85 %RH	(–) 50%RH	(–) 50 %RH	
ppm CO_2:	(+) 5000 ppm	(–) 500 ppm	(–) 500 ppm	
Bondline Exp Time:	(+) 50 min	(+) 50 min	(–) 20min	
A/B Exposure:	(–) 1 day	(+) 3 weeks	(–) 1day	
Avg T-Peel:	0.32 N/mm	1.62 N/mm	4.24 N/mm	7.41 N/mm

Mechanical Testing Results

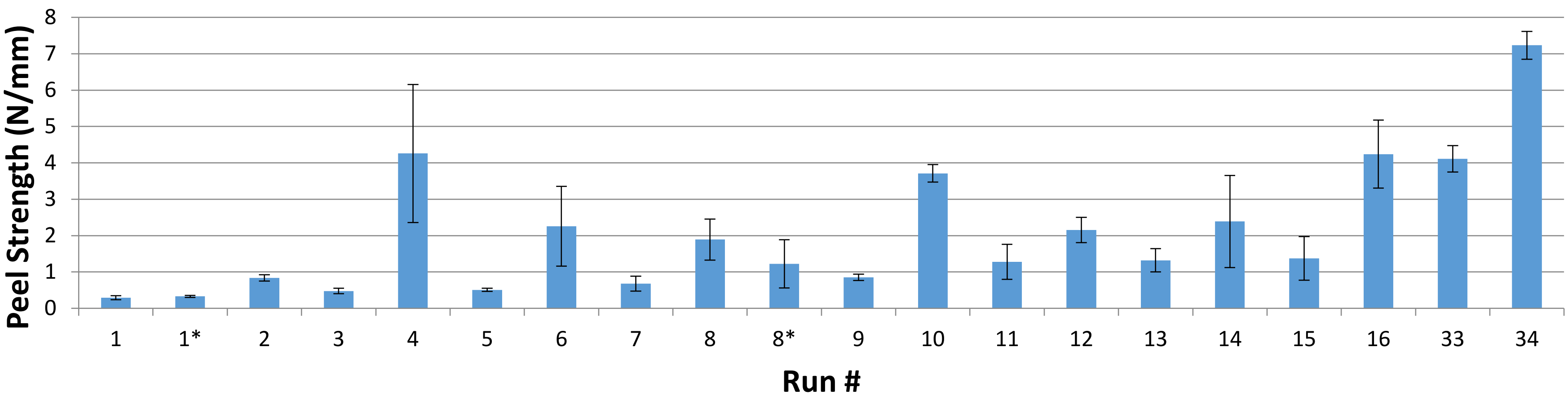






Main Factor Effects:

- **Temperature (-1.64 N/mm)**
- **Bondline Exposure Time (-0.87 N/mm)**
- **Part A/B Exposure Time (-0.72 N/mm)**



Mechanical Testing Results

1. Temperature was strongest factor for decrease in strength
2. Other significant negative factors:
   - Bondline Time Exposure
   - Part A&B Time Exposure
3. CO_2 had no measureable effect on t-peel strength
4. Humidity (50-85%) had no measurable effect on t-peel strength.
5. Combination effects are being analyzed.

Regression Statistics	
Multiple R	0.759
R Square	0.576
Adjusted R Square	0.543
Standard Error	0.942
Observations	70

Average Value (1.71 N/mm)

Main Effects

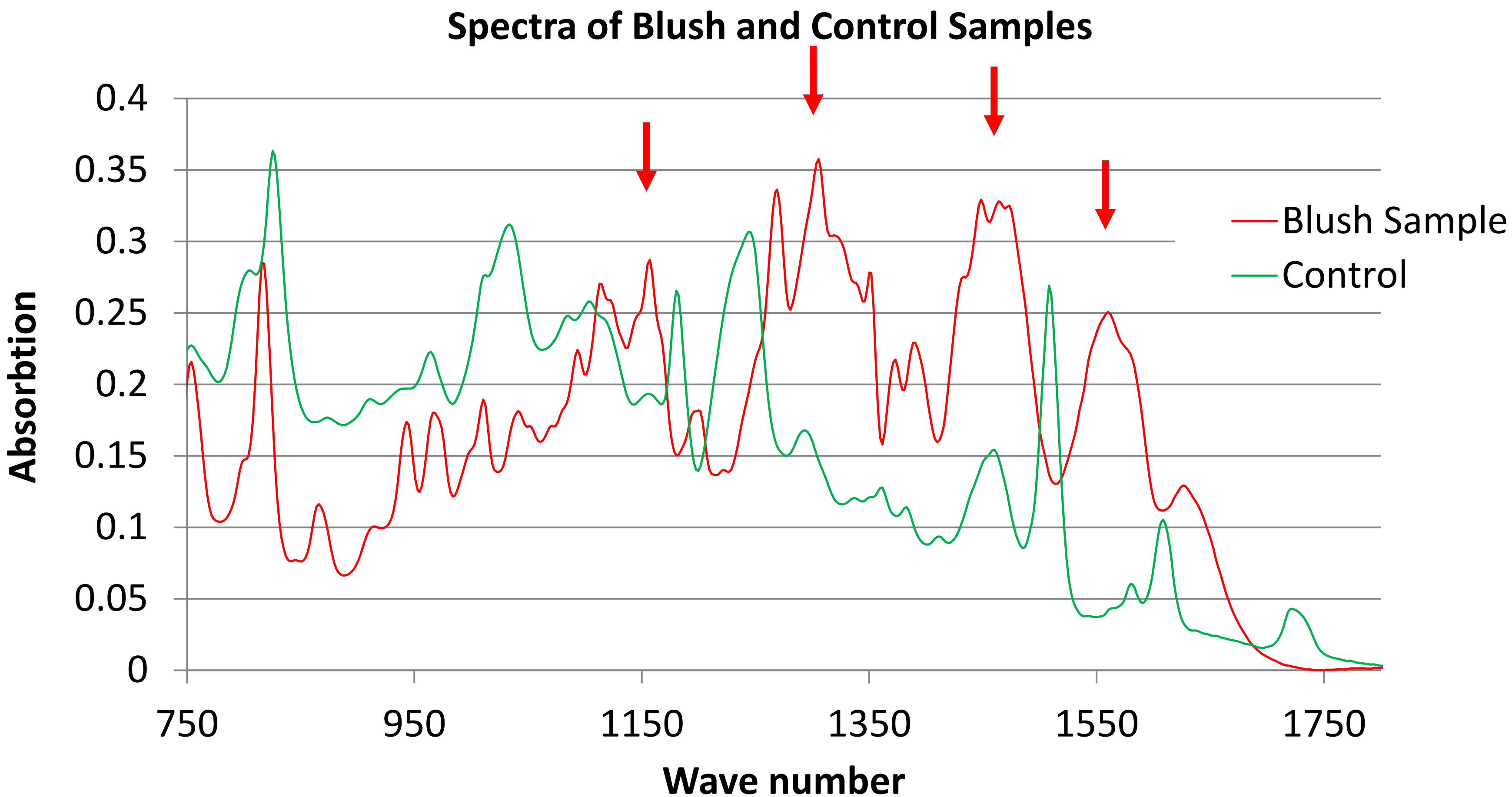
- **Temperature (-1.64 N/mm)**
- **Bondline Exposure (-0.87 N/mm)**
- **Part A/B Exposure (-0.72 N/mm)**

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	5	77.150	15.430	17.383	**7.80E-11**
Residual	64	56.809	0.888		
Total	69	133.959			

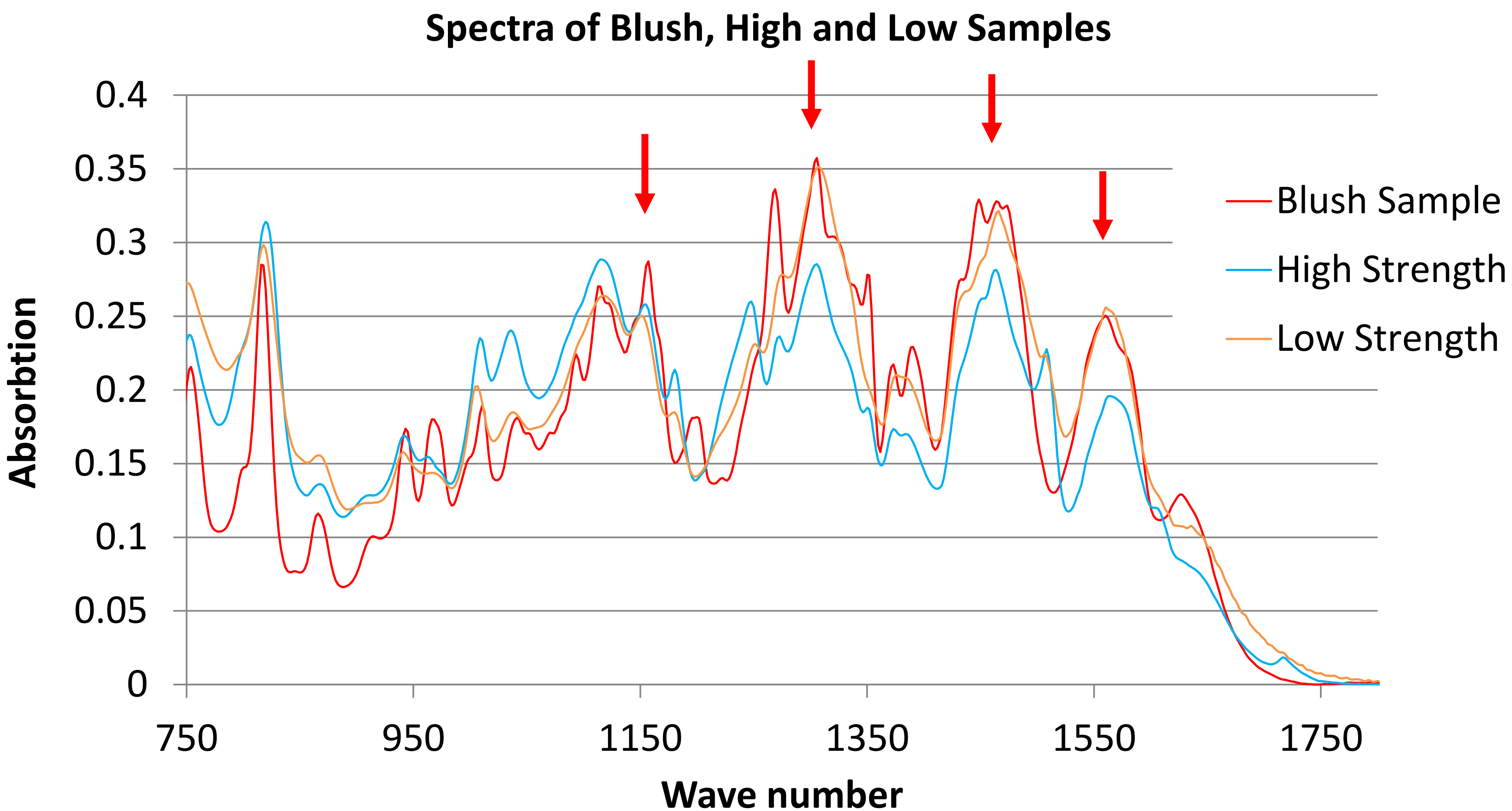
	Coefficients	*Standard Error*	*t Stat*	*P-value*
Intercept	**1.713**	0.114	15.036	1.11E-22
Temp	**-0.821**	0.114	-7.189	8.67E-10
Humidity	-0.163	0.114	-1.427	0.158
CO2	0.048	0.114	0.424	0.673
Mixed Exposure	**-0.437**	0.114	-3.837	2.88E-04
Part A&B Exposure	**-0.359**	0.114	-3.140	0.003

FTIR Results



- **Notable difference between control and exposed samples**

FTIR Results



- **Minor differences between low and high strength samples.**

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Summary

- T-Peel results show effects of exposure conditions.
  - No significant effect of humidity or CO_2
  - DOE Main Factor Effects:
    - Temperature (-1.64 N/mm)
    - Bondline Exposure Time (-0.87 N/mm)
    - Part A/B Exposure Time (-0.72 N/mm)

- FTIR detected presence of amine blush after exposure.
  - No blush detected on control samples.
  - Blush detected on exposed samples.
  - The current FTIR analysis technique has not yielded any significant correlation to T-Peel strength

Discussion

- How can we correlate FTIR measurements to mechanical properties?
  - Can FTIR Traveler coupons represent bondline?
    - Direct measurement of fracture surface.
    - Measure FTIR before and after cure.
  - Blush Thickness
    - FTIR detection may not reflect the amount (thickness) of blush.
    - May be detecting thin layers that are not detrimental to bond quality.
  - Bonding Procedure
    - Adhesive squeeze out may break up thin layers of blush

Looking forward- Amine Blush

- Benefit to Aviation
  - Understand conditions that can create weak bonds
  - Safer, more reliable bonds

- Future needs
  - Models that correlate chemical characterization with mechanical bond performance
  - QA methods to detect amine blush
  - Methods to mitigate amine blush

Surface Characterization using Inverse Gas Chromatography (IGC) Methods

- Motivation & Key Issues
- Introduction
- Experimentation
- Results
  - Contact Angle Measurements
  - IGC Measurements
- Conclusions/Discussions
- 2017 FAA Research Proposal Objectives/Future Work

MOTIVATION AND KEY ISSUES

- Most important step for bonding is surface preparation
- Inspect the surface prior to bonding to ensure proper surface preparation for high bond qualities
- Common surface energy measurement methods useful, but doesn't provide all answers
- Investigating new method to be able to discern between:
  - High and low energy site profiles/distributions
  - Different surface preparation techniques
  - Matrix and peel ply interactions during cure

MEASURING SURFACE ENERGY

– **Contact angle measurements is a preferred method**

Contact Angle	Inverse Gas Chromatography
Flat, smooth samples	powders, nano particles, films, semi-solids
Homogenous data	Heterogeneous data
Ambient test conditions	Varying test conditions
Quick Test Time: complete in minutes to hours	Long Test Time: complete in hours to days
Inexpensive, portable	Expensive, non-portable

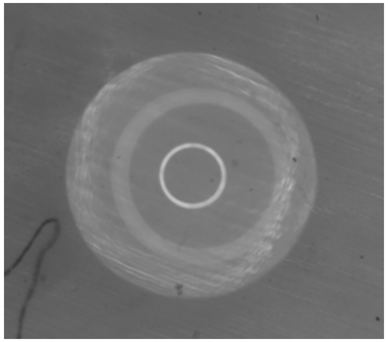
Objective:

Investigate Inverse Gas Chromatography as a reliable, repeatable method to characterize various surface preparation methods with high fidelity

IGC VS. CONTACT ANGLE

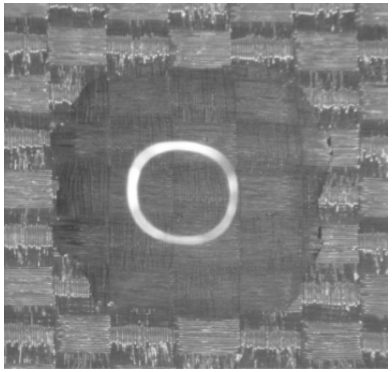
Contact Angle (CA)

- Small drops (1 ml) of 3-5 known liquids placed on surface
- Surface energy calculated over small area (order of mm2)
- Can be affected by surface texture (non-circular drops)
- Quick, inexpensive, can be portable



Inverse Gas Chromatography (IGC)

- 8-10 Known gases flow over surface
- Larger area sampled (2”X8”)
- More information obtained (higher fidelity data)
- Distribution of surface energy
- Greater sensitivity to subtle changes
- Expensive equipment, skilled operator



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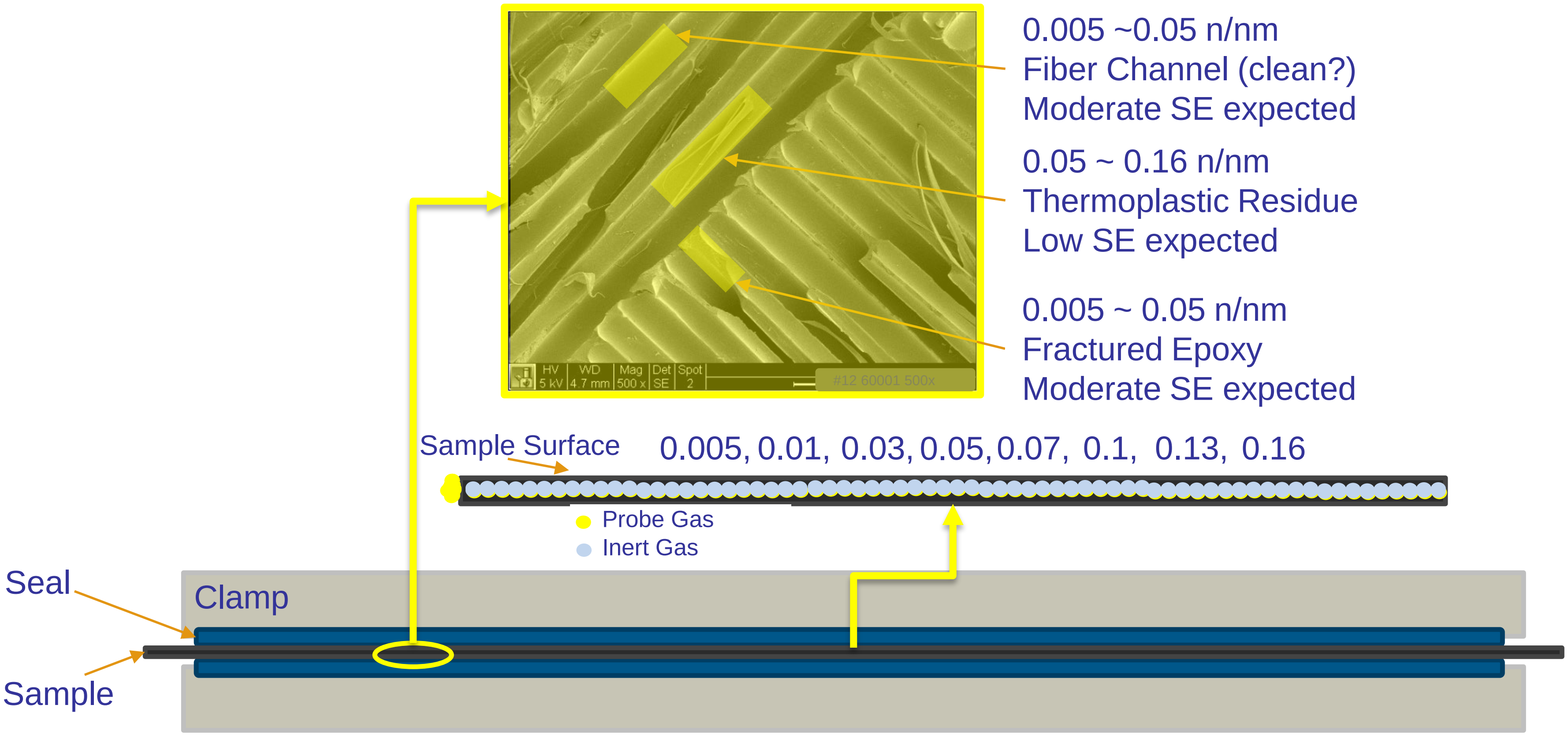
IGC METHODOLOGY

Variable	Description
Probe Gases	Undecane, Decane, Nonane, Heptane, Dichloromethane, Ethyl Acetate, Acetonitrile, Acetone
Targeted Fractional Surface Coverage	0.005, 0.01, 0.03, 0.05, 0.07, 0.1, 0.13, 0.16 n/nm



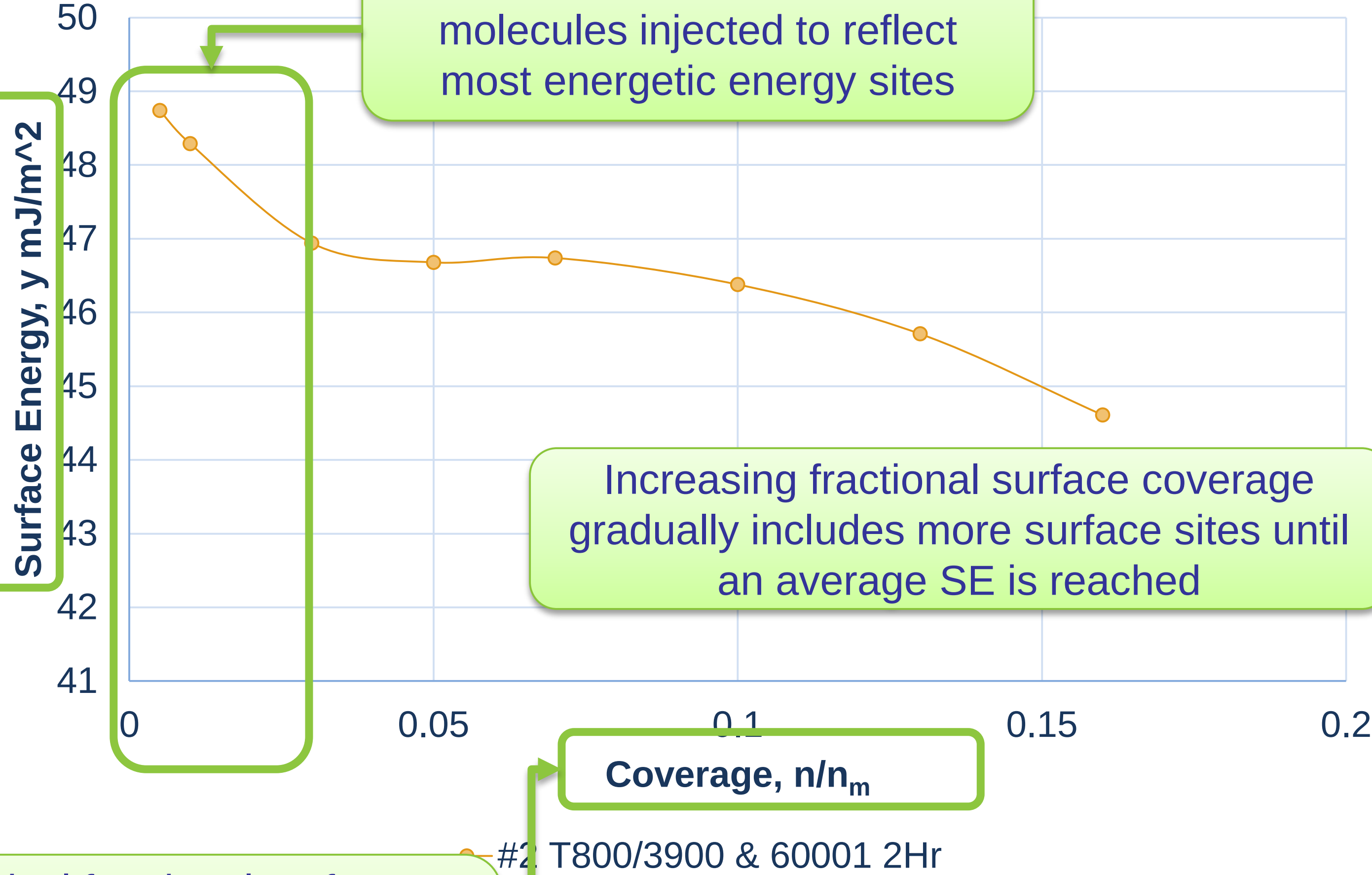
Retention time → retention volume → surface energy

→ Thermodynamic work adhesion and cohesion

IGC Surface Energy Profiles

Total Surface Energy

Infinite dilution – small number of molecules injected to reflect most energetic energy sites



Increasing fractional surface coverage gradually includes more surface sites until an average SE is reached

Theoretical fractional surface coverage of the monolayer with ratio of injected moles to moles required to cover the surface

PILOT STUDY EXPERIMENTATION

Test Specimens:

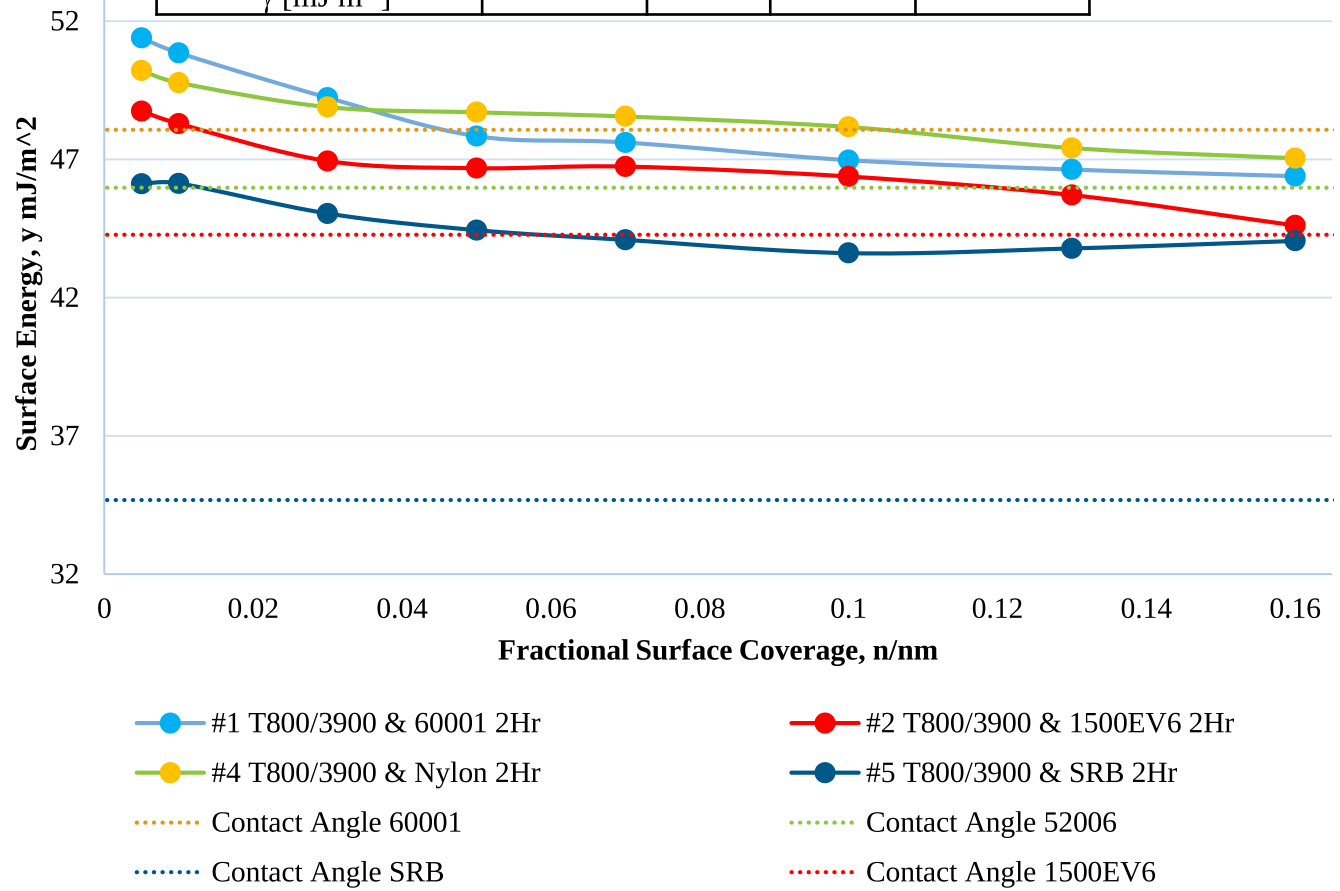
Variable	Description
Prepregs	Toray's 3900/T800 6K
	Cytec Solvay's Cycom 970/T300 3K HyE 970/PWC
Peel Plies Surface Preparation	Precision Fabrics Group's Polyester Peel Ply 60001
	Precision Fabrics Group's Nylon Peel Ply 52006
	Precision Fabrics Group's Super Release Blue (SRB) Peel Ply
	DIATEX 1500EV6 Polyester Peel Ply
	Henkel EA9895 0.033psf Wet Peel Ply (WPP)
	Cytec Solvay MXB-7668
	Fluorinated Ethylene Propylene (FEP) Release ply
Cure Holds	2hr cure hold, 176 °C (350 °F), 85 psi
	6hr cure hold, 176 °C (350 °F), 85 psi

Panel ID#	Adherend (Fabric, Prepreg)	Peel Ply	Cure Dwell
1	3900/T800	60001 Polyester	2hr
2	3900/T800	DIATEX 1500EV6 Polyester	2hr
4	3900/T800	52006 Nylon	2hr
5	3900/T800	SRB	2hr
6	3900/T800	60001 Polyester	6hr
7	3900/T800	DIATEX 1500EV6 Polyester	6hr
11	3900/T800	FEP*	2hr
12	970/T300	60001 Polyester	2hr
13	970/T300	DIATEX 1500EV6 Polyester	2hr
14	970/T300	EA9895 Wet PP	2hr
15	970/T300	MXB-7668	2hr
16	970/T300	60001 Polyester	6hr
17	970/T300	DIATEX 1500EV6 Polyester	6hr
19	970/T300	MXB-7668	6hr
22	970/T300	FEP*	2hr

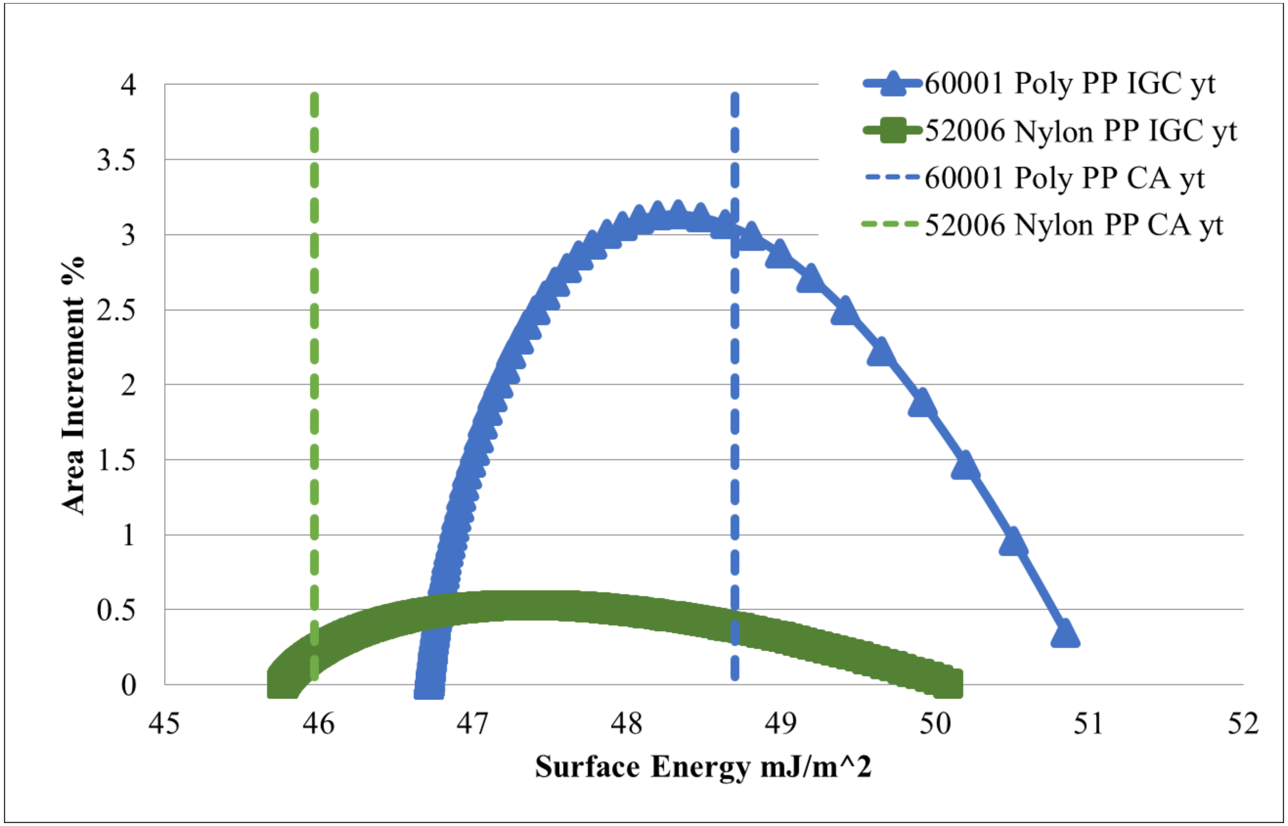
IGC AND CA COMPARISON

	60001 Polyester	52006 Nylon	Diatex Poly 1500EV6	Super Release Blue (SRB
IGC highest energy site γ [mJ m^{-2}]	51.39	50.21	48.78	46.11
IGC Average SE γ [mJ m^{-2}]	46.63	47.04	44.61	43.61
CA SE Measurement γ [mJ m^{-2}]	48.03	45.97	44.27	34.68

- Heterogeneity of SE
- Suggests contact angle is not panel's average surface energy



IGC AND CA COMPARISON



1. Nylon and Polyester have significantly different distributions according to IGC
2. Contact angle is controlled by complex wetting phenomena
3. Contact angle correlation to the IGC data is different for each peel ply type

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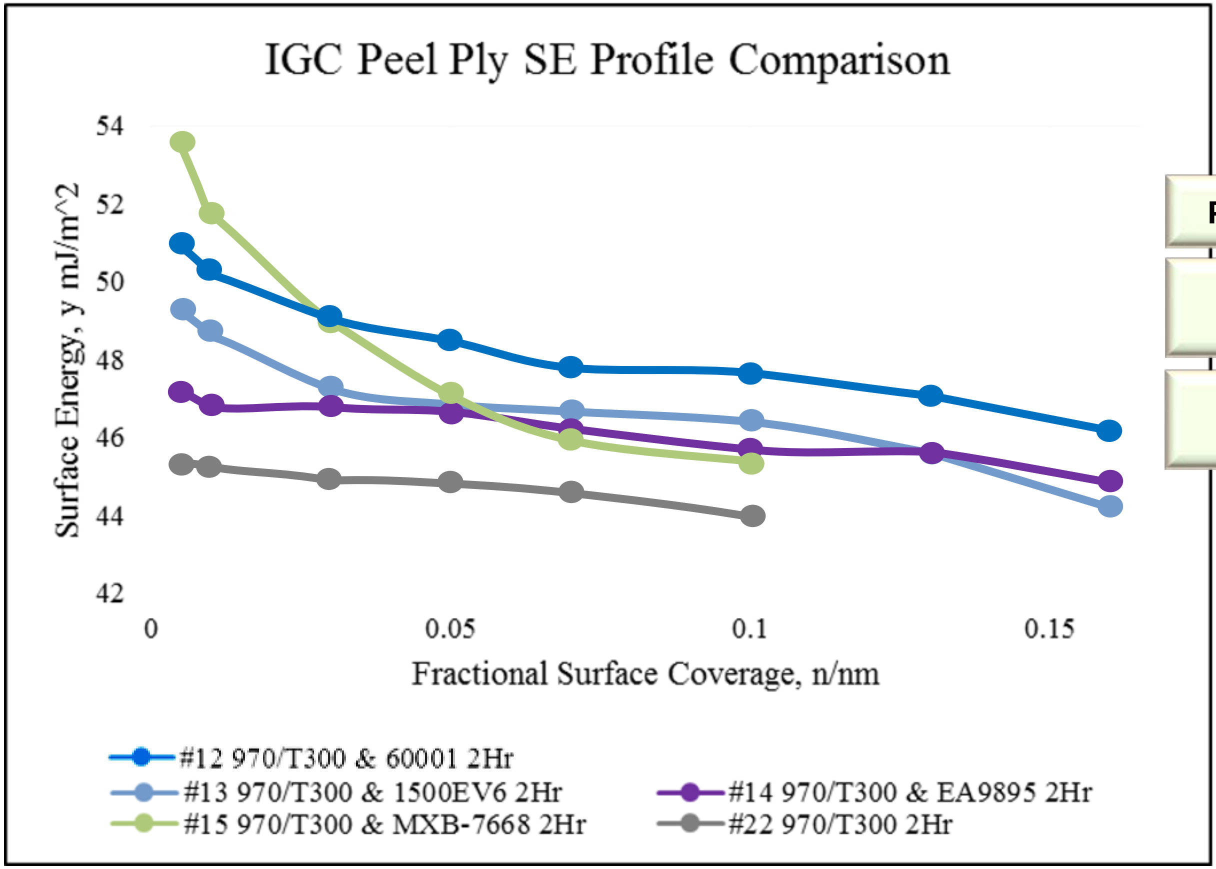
IGC Peel Ply Comparison



Polyester Comparison

MXB Fiberglass Comparison

9598 Wet PP Comparison

- Fiberglass fiber transfer → wide range of SE
- Working to compare the Wet PP Se to CA measurements

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Pilot Study Conclusions/Discussion

- Contact angle measurements result in a single value of surface energy (γ_{CA}) while IGC is able to show the distribution of surface energy values on a heterogeneous surface
- γ_{CA} is within γ_{IGC} measured value ranges, but γ_{CA} does not necessarily represent the average surface energy
- Different interactions between fluids (contact angle) and gases (IGC) with textured surfaces may lead to differences in γ_{CA} and γ_{IGC}
- IGC trends suggest there may be additional variables that affect the bonding surface

Pilot study motivates further understanding of the IGC method and its relation to bond quality.

Current Work

- Understand the advance models of wetting versus gas interactions
- Characterize additional surface preparation methods with IGC

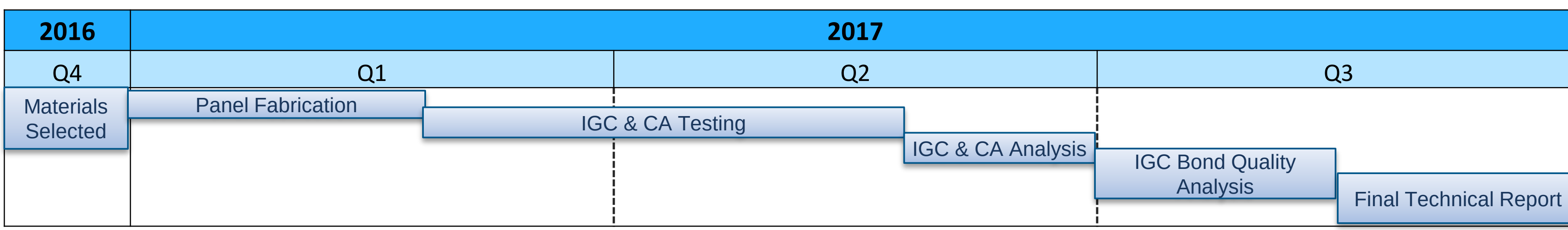
Priority Testing

- Relate surface preparation to bond quality types
- Additional statistical data and material coupon testing for a more complete representation of the bonding surface
    - X-ray photoelectron spectroscopy (XPS)
    - Scanning electron microscopy (SEM)
    - Double cantilever beam (DCB)

Although IGC is able to provide more information on surface energies related to various surface preparations techniques, other components contributing to the quality of the bonding surface need to be investigated.

Current Work

- Surface Preparation Methods (in order of research priority)
  - Plasma Treated
  - Grit Blasted
  - Orbital Sanding
- Surface Energy Testing
  - IGC
  - Advanced Contact Angle Measurements
    - Static, advancing and receding



Status Update 3/23: Plasma panel testing is in-progress

Current Work

Panel #	Substrate	Surface Prep	Cure Dwell	Comments
1	Toray's 3900/T800 Unidirectional Prepreg	60001	2	Baseline for plasma treatment
2	Toray's 3900/T800 Fabric Prepreg	60001	2	Baseline for plasma treatment
3, 4, 5	Toray's 3900/T800 Unidirectional Prepreg	60001 & Plasma Treated	2	3 panels for 3 separate IGC runs
6, 7, 8	Toray's 3900/T800 Fabric Prepreg	60001 & Plasma Treated	2	3 panels for 3 separate IGC runs
9	Toray's 3900/T800 Unidirectional Prepreg	FEP	2	Baseline for sanding and grit blasting
10	Toray's 3900/T800 Fabric Prepreg	FEP	2	Baseline for sanding and grit blasting
11, 12, 13	Toray's 3900/T800 Unidirectional Prepreg	FEP & Grit Blasted	2	3 panels for 3 separate IGC runs
14, 15, 16	Toray's 3900/T800 Fabric Prepreg	FEP & Grit Blasted	2	3 panels for 3 separate IGC runs
17, 18, 19	Toray's 3900/T800 Unidirectional Prepreg	FEP & Orbital Sanded	2	3 panels for 3 separate IGC runs
20, 21, 22	Toray's 3900/T800 Fabric Prepreg	FEP & Orbital Sanded	2	3 panels for 3 separate IGC runs
23, 24, 25	Toray's 3900/T800 Fabric Prepreg	60001 & Plasma Treated	6	Contingency testing if time/funding permits

Priority Testing (panels 1–8)

Looking Forward

Surface Characterization using iGC Methods

- Benefit to Aviation
  - Better understanding of surface prep.
  - Guide development of QA methods for surface prep.
  - Greater confidence in adhesive bonds
- Future needs
  - Surface energy (wetting) vs. bond quality
  - 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

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- Airtech International
- UW MSE

Questions?

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DOE Test Matrix

Factor	Control	Low Level (-1)	High Level (+1)
Temperature (A)	-	15.6°C (60°F)	32.2°C (90°F)
Humidity (B)	-	50%RH	85%RH
CO_2 (C)	-	500ppm	5000ppm
Mixed Exposure Time (D)	> 5min*	20min	50min
Part A & B Exposure Time (E)	> 1hr*	>1hr*	3 weeks**

* - ambient conditions

** - 65%RH 75°F

Measured Response
FTIR Peak Shift
T-Peel (ASTM D1876)

DOE: 2^5-1 Reduced Factorial

E=-ABCD

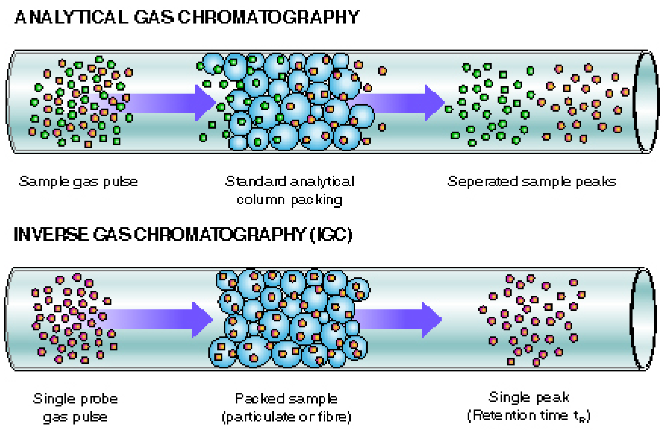
20 Runs

Potential Areas to Explore

1. Bonding procedure
   - Mound vs even spread
   - Using vacuum to reduce voids
2. Quantifying exposure of parts A and B
3. FTIR Measurement Procedures.
   - Direct measurement before cure
   - Direct measurement of fracture.
   - Use thinner surface samples to match bondline.
   - Apply chemometric analysis to analyze changes in spectra.
4. Is it more important to establish amine blush factors or reflect industrial production?

IGC Overview

- Technique to characterize physicochemical properties of materials
- Carrier gas transports probe molecule (adsorptive) over composite material (absorbent)
- Retention time → retention volume → surface energy
  → Thermodynamic work adhesion and cohesion
- Ideal for powders, fibers, nano particles, granules,
  films, semi-solids
- Provides surface heterogeneity data




iGC Film Shell


iGC equipment

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