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Improving Adhesive Bonding of Composites Through Surface Characterization

Brian Flinn, Rita Johnson, Marc Staiger,
Erik Engstrom

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Improving Adhesive Bonding of Composites

- Principal Investigator and Researchers
  - Brian Flinn (PI)
  - Rita Johnson UW MSE/Boeing
  - Marc Seiger (UW MSE)
  - Erik Engstrom (UW MSE)
- FAA Technical Monitor
  - Curtis Davis
- Other FAA Personnel
  - Larry Illecwicz
  - Cindy Ashforth
- Industry Participation
  - Epic Aircraft
  - The Boeing Company
  - Textron

Two projects will presented today

1. Surface Characterization using Inverse Gas Chromatography (iGC) Methods

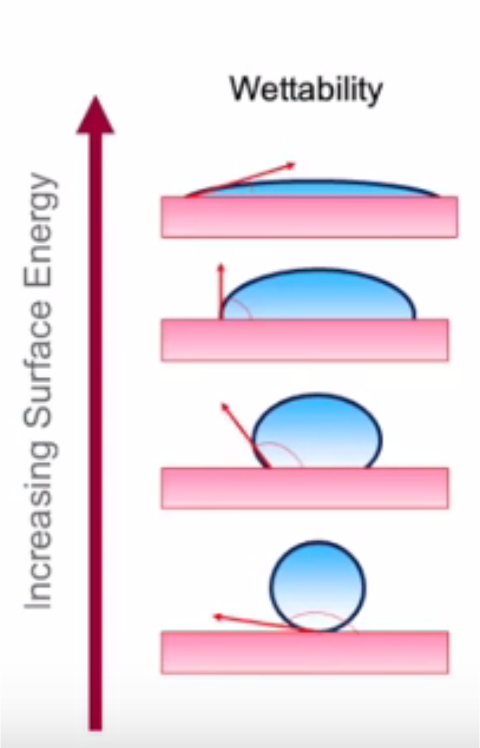
2. Amine Blush in Epoxy Paste Adhesives

Surface Characterization using iGC Methods

- 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
  - Compare with Contact Angle Data

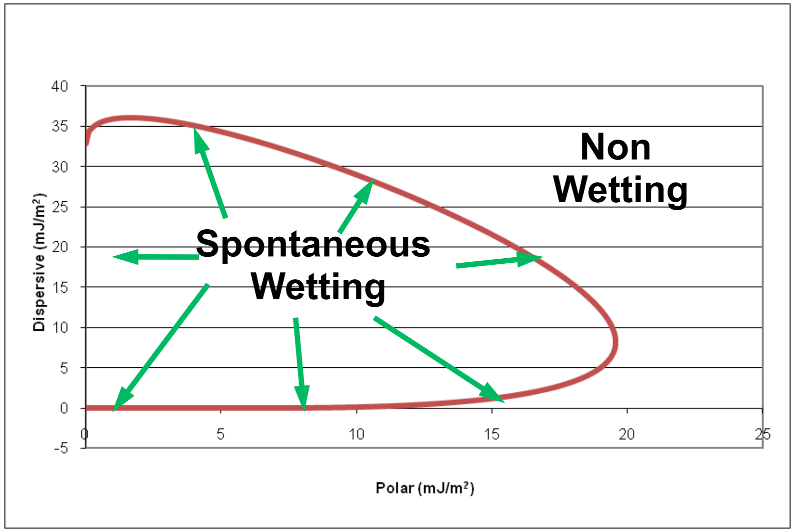
Surface Energy Review

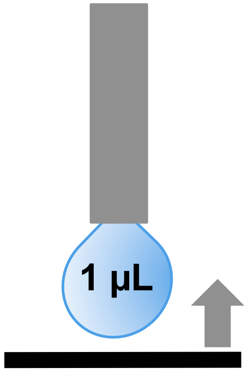
- SE → thermodynamic adhesion and cohesion
- Affects wettability of a material
  - Ability of liquid to spread over surface-required for bonding



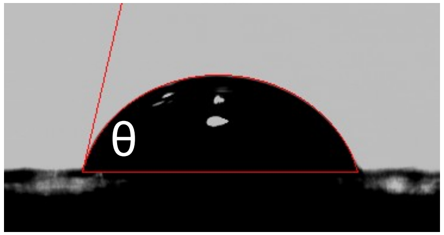
Contact Angle Methodology – Surface Energy

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





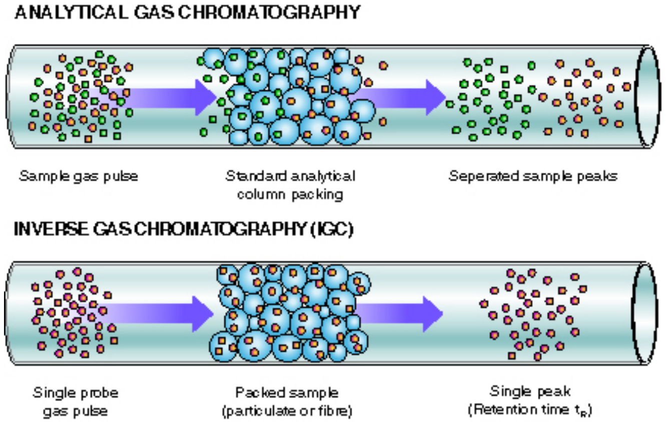
Drop application: dispense drop, raise surface

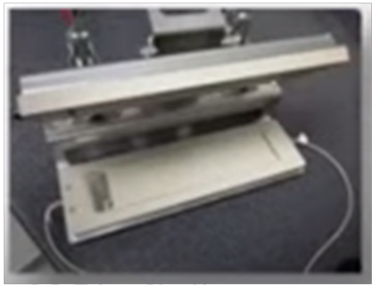


Side-view of drop as viewed from goniometer camera

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

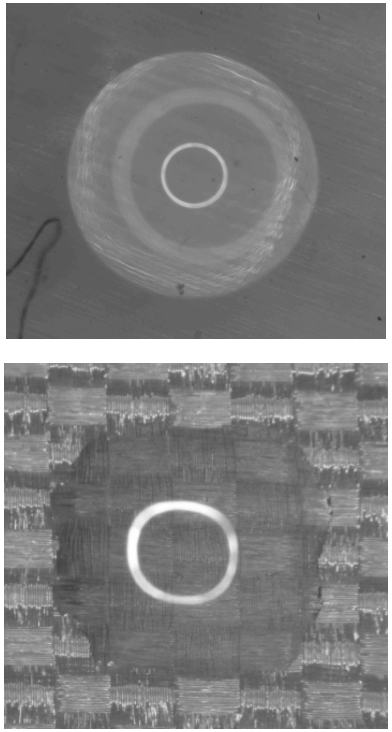



iGC Film Shell


iGC equipment

Surface Energy: iGC vs. Contact Angle (CA)

- Contact Angle (CA)
  - Small drops (1 ml) of 3-5 known liquids placed on surface
  - “Average” surface energy calculated over small area
  - Can be affected by surface texture (non-circular drops)
  - Quick, inexpensive, can be portable
- Inverse Gas Chromotography (iGC)
  - 8-10 Known gases flow over surface (1”X10”)
  - More information obtained (higher fidelity data)
    - Distribution of surface energy
    - Larger area sampled
    - Greater sensitivity to subtle changes
  - Expensive equipment, skilled operator

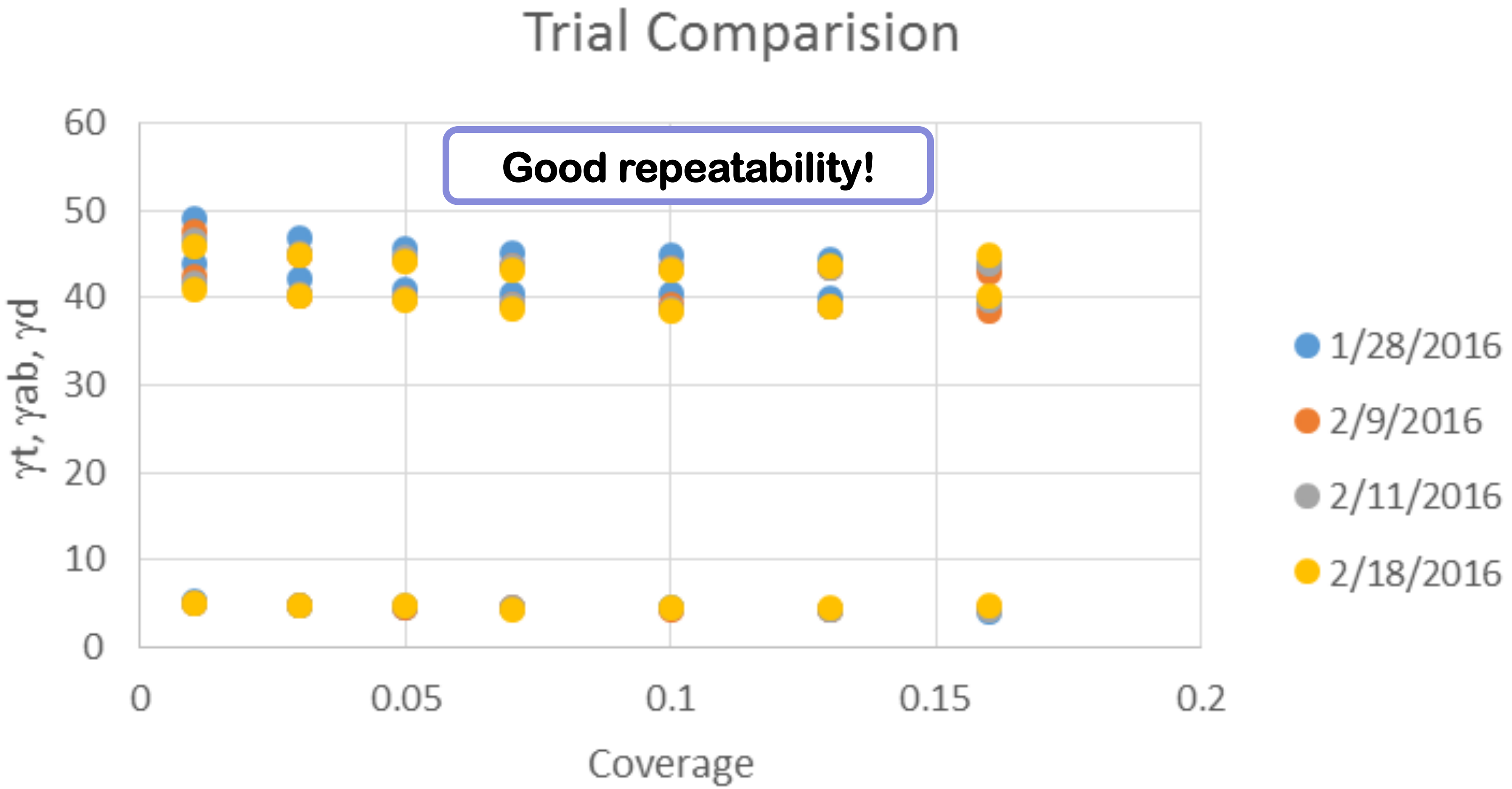


Experimental Overview

- Large volume of contact angle data, surface energies and bond quality from previous years
  - Surface Preparations (peel ply, abrasion, plasma)
  - Adherends (250 F and 350 F cure epoxies)
  - Adhesives (paste and film)

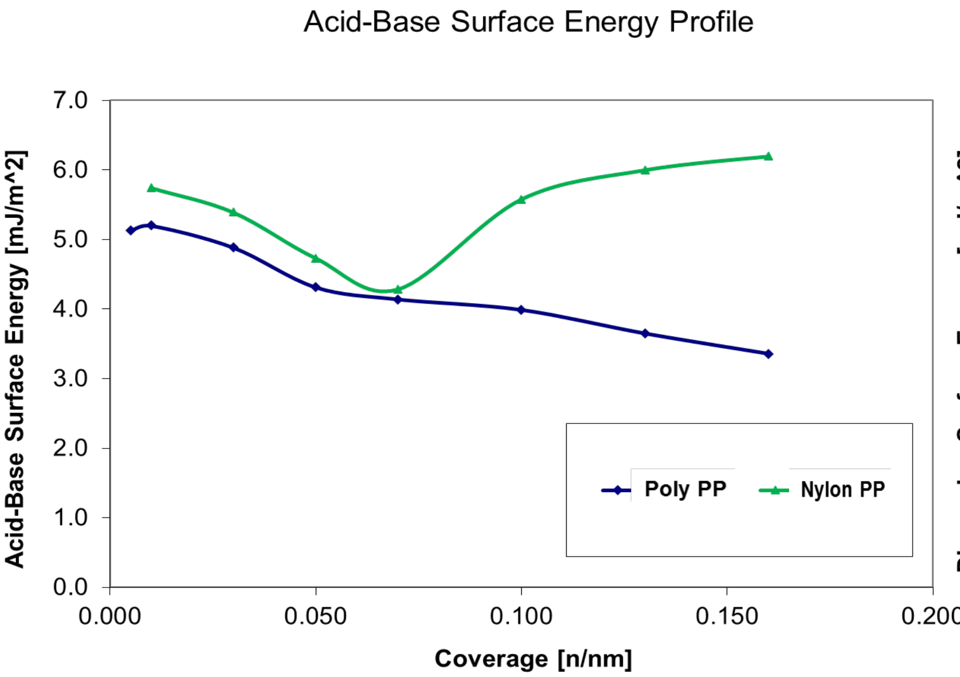
- Repeat measurements using iGC
- Compare surface energies iGC vs CA
- Validate iGC method
- Explore unknowns and bonding mysteries

Repeatability:
Polyester Peel Ply Trial Comparison

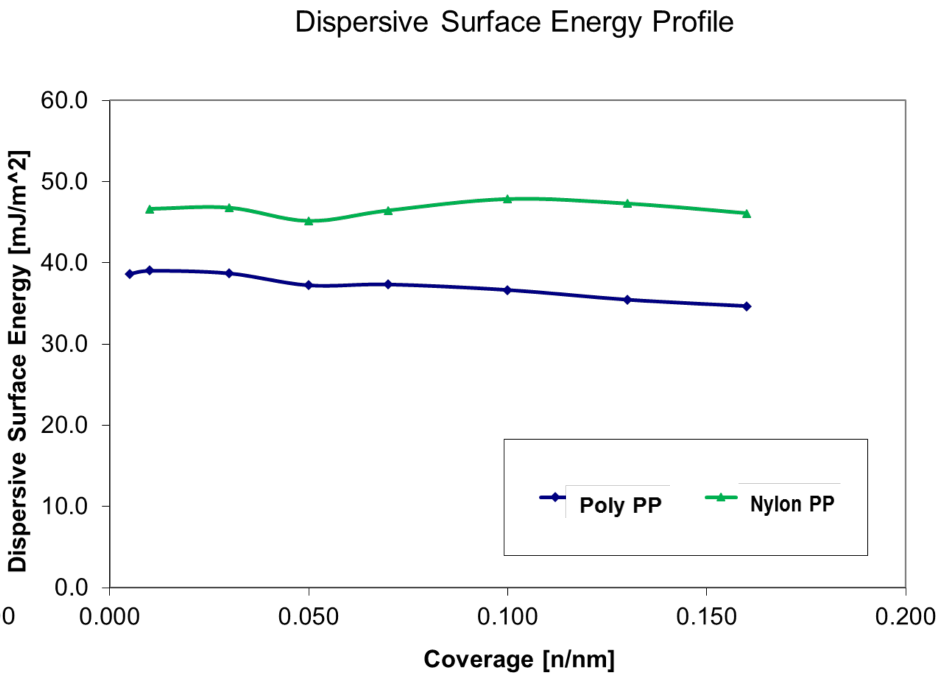


Good repeatability!

Peel Ply Comparison: Nylon vs Polyester

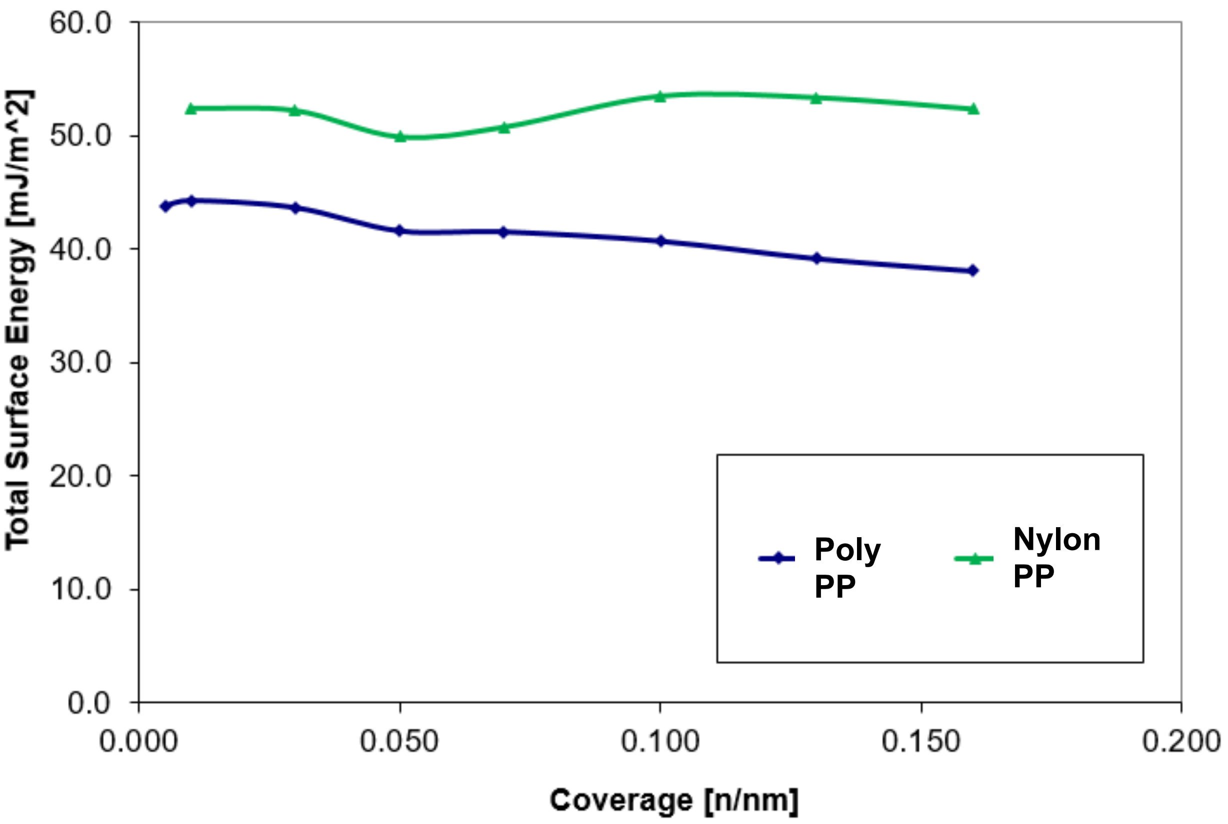


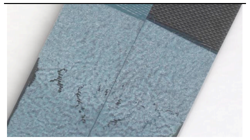
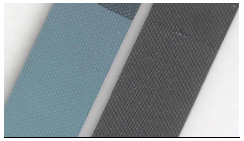
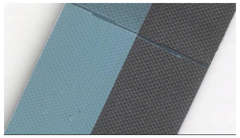
Acid-Base Surface Energy Profile



Dispersive Surface Energy Profile

Peel Ply Comparison: Nylon vs Polyester



	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

CA Peel Ply Comparison: Nylon vs Polyester

Substrate - Peel ply *	γ_d	γ_p	γ_{tot}
Cytec970 – 60001 polyester	55.5	1.7	57.2
Cytec970 – 51789 nylon	22.0	25.8	47.8
Cytec970 – EA9895 polyester/epoxy	40.4	8.6	49.0
Cytec970 – nylon/epoxy	20.1	23.9	44.0
Toray 3631 – 60001 polyester	53.8	1.2	55.0
Toray 3631 – 51789 nylon	22.8	19.8	42.6
Toray 3631 – EA9895 polyester/epoxy	57.4	0.9	58.3
Toray 3631 – nylon/epoxy	16.5	27.8	44.3
(Adhesive) 3M AF555 uncured	*31.6*	*8.9*	*40.5*
(Adhesive) Cytec MB1515-3 uncured	*29.7*	*3.1*	*32.8*

Similar to results from contact angle measurements as iGC

Next Steps:

- Compare polyester peel ply data with contact angle measurements
- Begin test matrix with various surface preparation methods.

Panel/Test #	Adherend (Fabric)	Peel Ply	Cure Dwell	Post Cure Surf Prep
1	BMS8-276	BMS8-308 Type III	2hr	N/A
2	BMS8-276	BMS8-308 Type IV	2hr	N/A
3	BMS8-276	BMS8-308 Type IV	2hr	Plasma
4	BMS8-276	Nylon	2hr	N/A
5	BMS8-276	SRB	2hr	N/A
6	BMS8-276	BMS8-308 Type III	6hr	N/A
7	BMS8-276	BMS8-308 Type IV	6hr	N/A
8	BMS8-276	BMS8-308 Type IV	6hr	Plasma
9	BMS8-276	N/A	2hr	Orbital Sand of Tool Side
10	BMS8-276	N/A	2hr	Grit Blast of Tool Side
11	BMS8-276	N/A	2hr	N/A
12	BMS8-256	BMS8-308 Type III	2hr	N/A
13	BMS8-256	BMS8-308 Type IV	2hr	N/A
14	BMS8-256	BMS8-403 Class 1	2hr	N/A
15	BMS8-256	BMS8-139	2hr	N/A
16	BMS8-256	BMS8-308 Type III	6hr	N/A
17	BMS8-256	BMS8-308 Type IV	6hr	N/A
18	BMS8-256	BMS8-403 Class 1	6hr	N/A
19	BMS8-256	BMS8-139	6hr	N/A
20	BMS8-256	N/A	2hr	Orbital Sand of Tool Side
21	BMS8-256	N/A	2hr	Grit Blast of Tool Side
22	BMS8-256	N/A	2hr	N/A

Looking Forward

Surface Characterization using iGC Methods

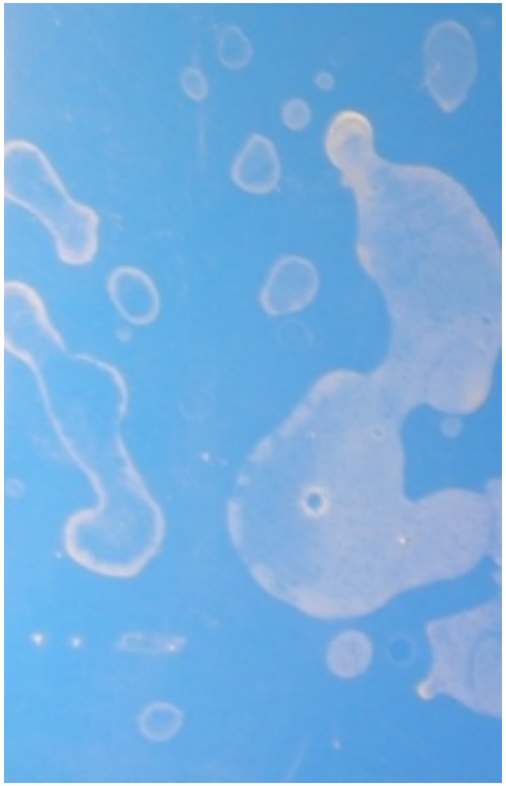
- Benefit to Aviation
  - Better understanding of surface prep.
  - Guide development of QA methods for surface prep.
  - Greater confidence in adhesive bonds
- Future needs
  - Surface energy (wetting) vs. bond quality
  - Surface energy at cure temperature
  - QA method to ensure proper surface for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

Amine Blush in Epoxy Adhesives

- Motivation and Key Issues
  - Amine blush causes poor quality bonds
  - How to detect and quantify amine blush/bloom
- Objective
  - Develop QA techniques for paste adhesives
- Approach
  - Identify key parameters for amine blush/bloom
  - Characterize adhesive surface after various exposures
  - Quantify amine blush/bloom
  - Create QA strategies to mitigate formation

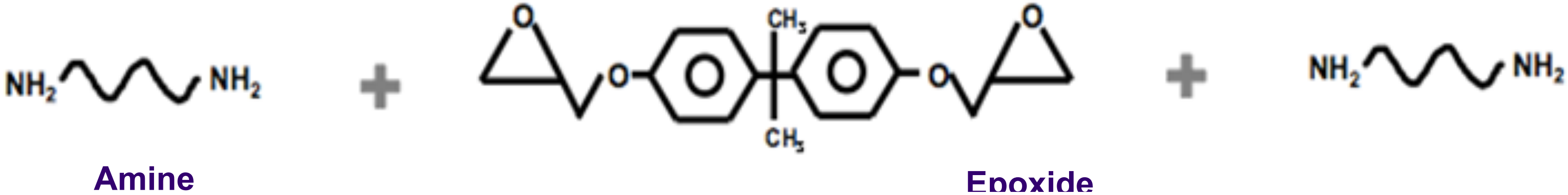
Amine Blush and Amine Bloom

- Present in epoxy-amine adhesive systems
  - Surface is greasy
  - Then turns powdery and white
  - Causes poor adhesion
- Formation of carbamates and carbonates
- Critical Parameters
  - Out time
  - Temperature
  - Relative Humidity
  - Atmospheric CO_2



Amine blush in Loctite 9360

Amine Cured Epoxy - Chemistry



Epoxy/amine adhesive reaction

Amine Blush Formation

Can form on surface of uncured epoxies - moisture and CO_2

1. Primary + Secondary Amines react on surface:

   $CO_2 + H_2O \rightarrow H_2CO_3$

2. Ammonium Carbamate + Tertiary Amines:

   $H_2CO_3 + \sim RNH2 \rightarrow \sim RNHCOOH + H_2O$

3. Ammonium Bicarbonate:

   $\sim RNHCOOH + RNH_2 \rightarrow RNH_3^{+-}OCONHR$

Amine blush in Loctite 9360

Causes:

- Incomplete cure
- Surface tackiness
- Poor surface adhesion

Experimental Overview

Investigate the effect of amine blush on bonding and corroborate with surface characterization

- Condition specimens & witness coupons:
  - Humidity: 35% (Low), 80% (High)
  - Temperature: 65°F (Low), 90°F (High)
  - Out Time: 30 mins (Low), 60 mins (High)
- Measure Bond Quality
  - Lap Shear (ASTM D3165)→ shear strength
  - Dual Cantilever Beam (DCB) (ASTM D5228)→ fracture toughness
- Identify and quantify amine blush via FTIR
  - Witness coupons

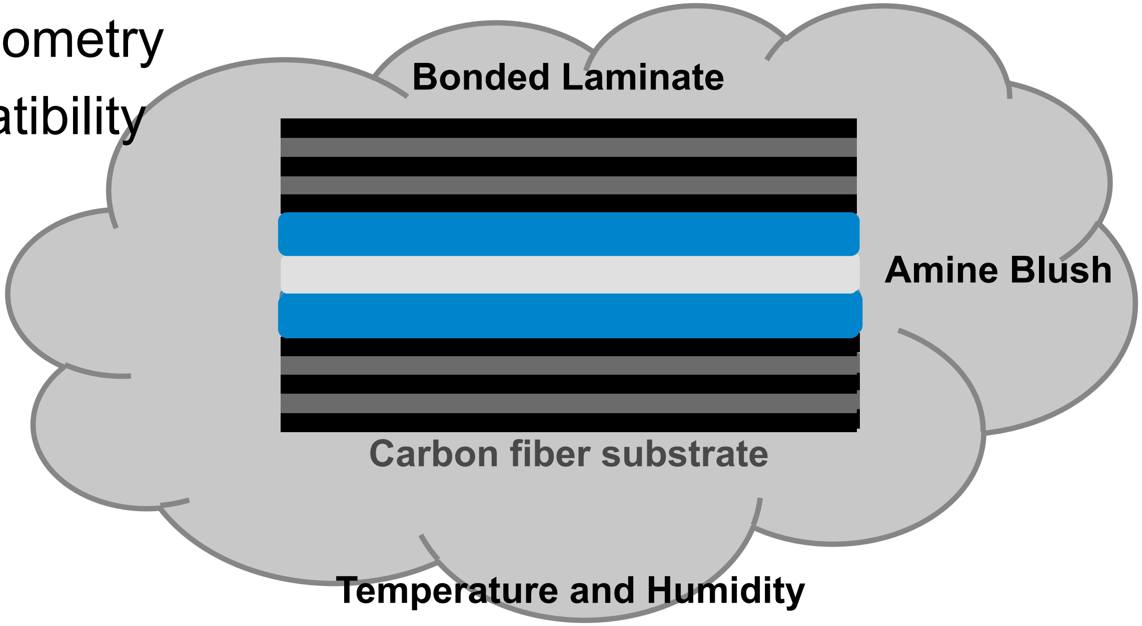
Materials and Methods

- Toray T800/3090 Laminates
  - Lap shear: 0°/+45°/-45°/0°
  - DCB: unidirectional
- Surface preparation
  - Mechanical abrasion
  - Solvent wipe and flash off
- Bonding
  - Loctite 9360 adhesive
  - Apply adhesive on both adherends
  - Exposed to controlled atmospheres (T & RH)
  - Bagged and cured 25 psi, 90 F
  - Bondline thickness 0.020-0.030”

Amine Blush Production

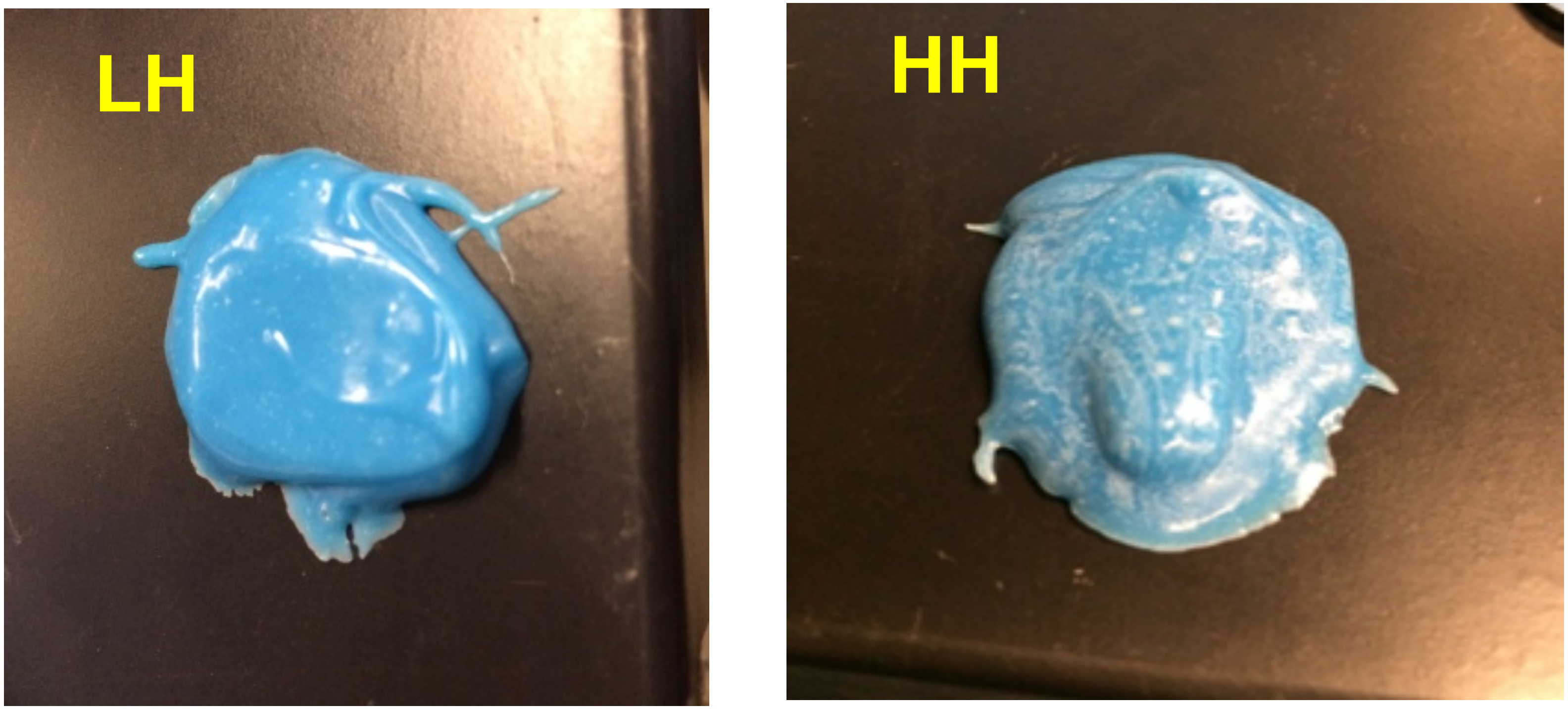
- Intrinsic Factors
  - Amine content
  - Dilutes
  - Gel time
  - Stoichiometry
  - Compatibility

- Testable Factors
  - Temperature
  - Humidity
  - Out time



Amine blush production on bonded laminate

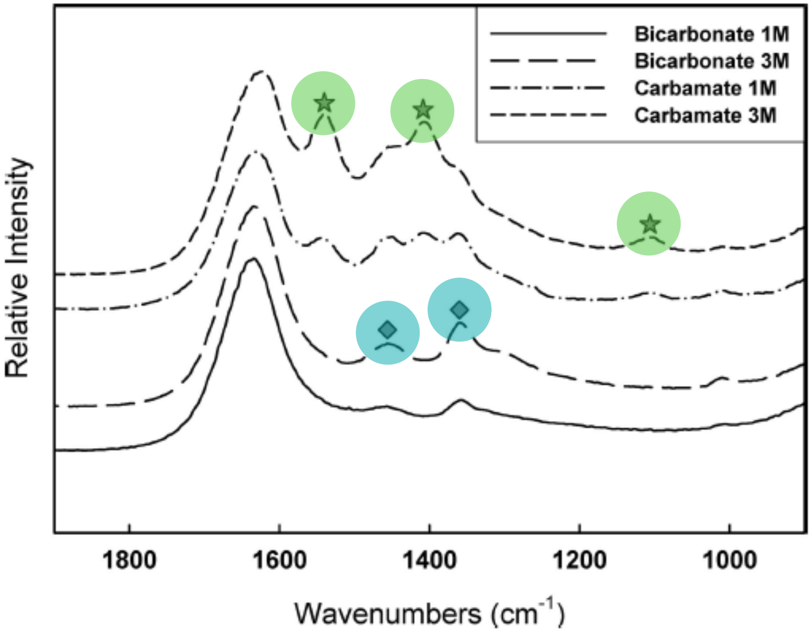
Visual Test Results- Amine Blush



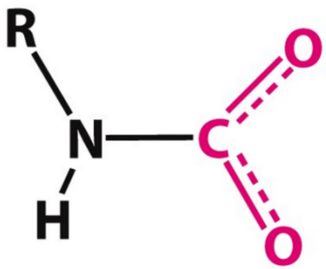
Henkel EA 9360

Detecting Amine Blush-FTIR

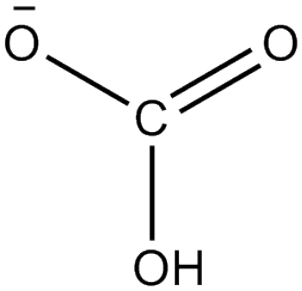
- Carbamate ☆
  - 1100 cm^{-1} C=O symmetric stretching
  - 1400 cm^{-1} C-N stretching
  - 1550 cm^{-1} C=O asymmetric stretching
- Bicarbonate ◊
  - 1350 cm^{-1} C-O symmetric stretching
  - 1450 cm^{-1} asymmetric stretching



FTIR Spectra of carbamate and bicarbonate

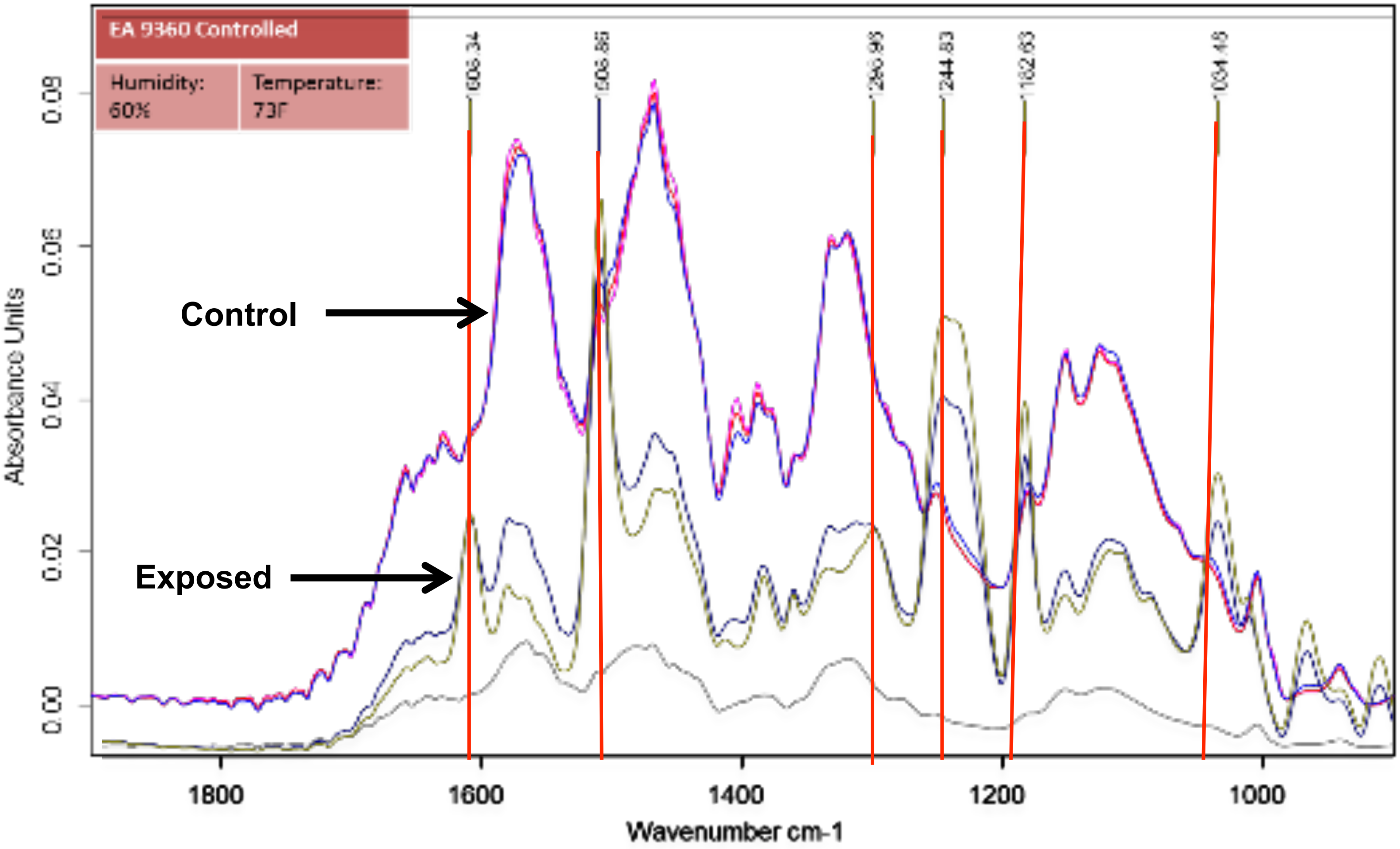


Carbamate



Bicarbonate

FTIR Results-Humidity Exposure



- **Carbamate and carbonate peaks develop with exposure**

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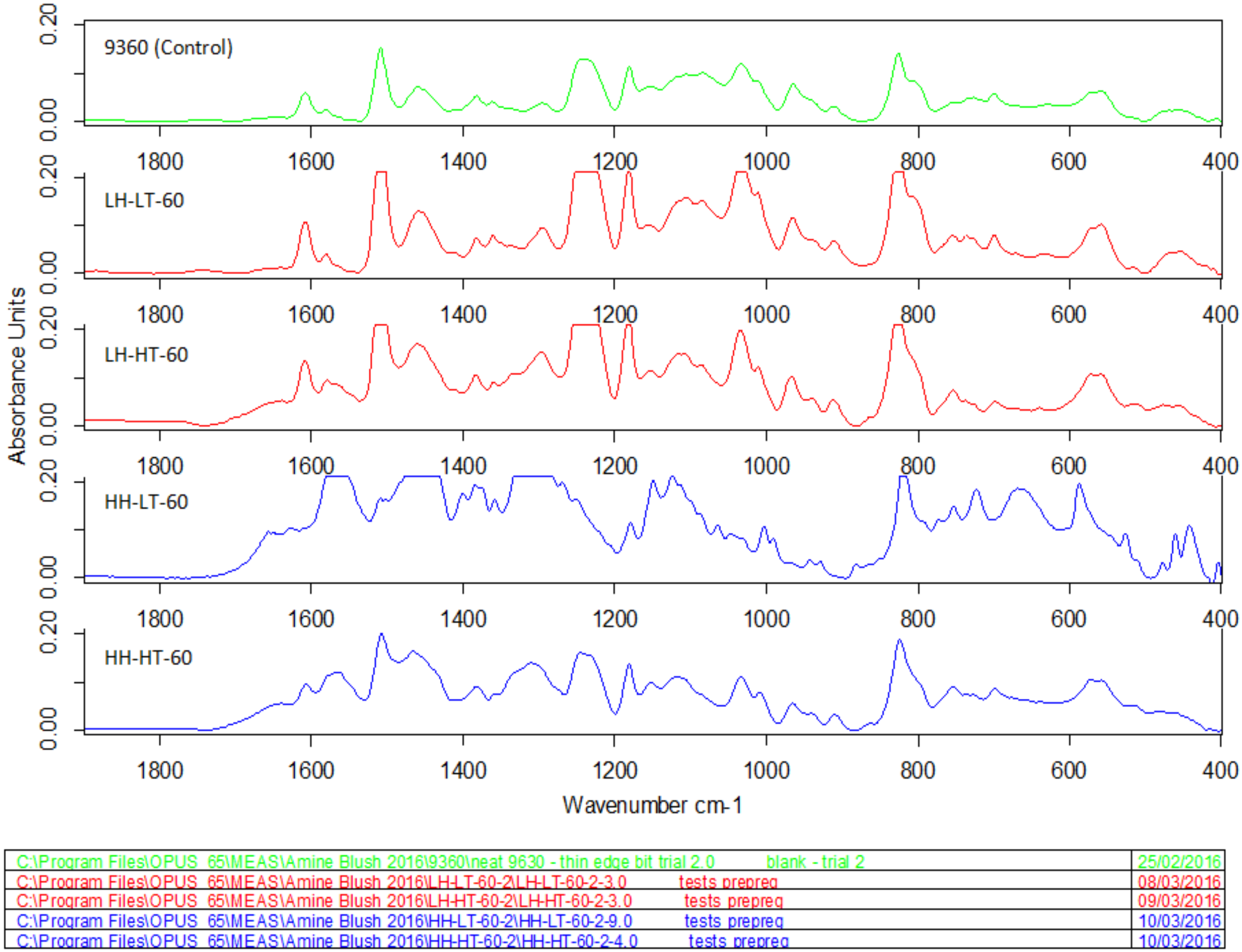
FITR Results

- Spectra from the control matches well with LH-LT.
- As Temp and %RH increase the specrta show a shift at the 1330, 1450 and 1550cm-1 absorbance.
- Evidence of carbamate and amine groups on the surface.
- Spectral difference correlates with the difference in surface gloss



C:\Program Files\OPUS_65\MEAS\Amine Blush 2016\9360\neat 9630 - thin edge bit trial 2.0	blank - trial 2	25/02/2016
C:\Program Files\OPUS_65\MEAS\Amine Blush 2016\LH-LT-60-2\LH-LT-60-2-3.0	tests prepreg	08/03/2016
C:\Program Files\OPUS_65\MEAS\Amine Blush 2016\LH-HT-60-2\LH-HT-60-2-3.0	tests prepreg	09/03/2016
C:\Program Files\OPUS_65\MEAS\Amine Blush 2016\HH-LT-60-2\HH-LT-60-2-9.0	tests prepreg	10/03/2016
C:\Program Files\OPUS_65\MEAS\Amine Blush 2016\HH-HT-60-2\HH-HT-60-2-4.0	tests prepreg	10/03/2016

Sample ID:

HT - High Temp (90F)

LT - Low Temperature (65F)

LH - Low Humidity (65%RH)

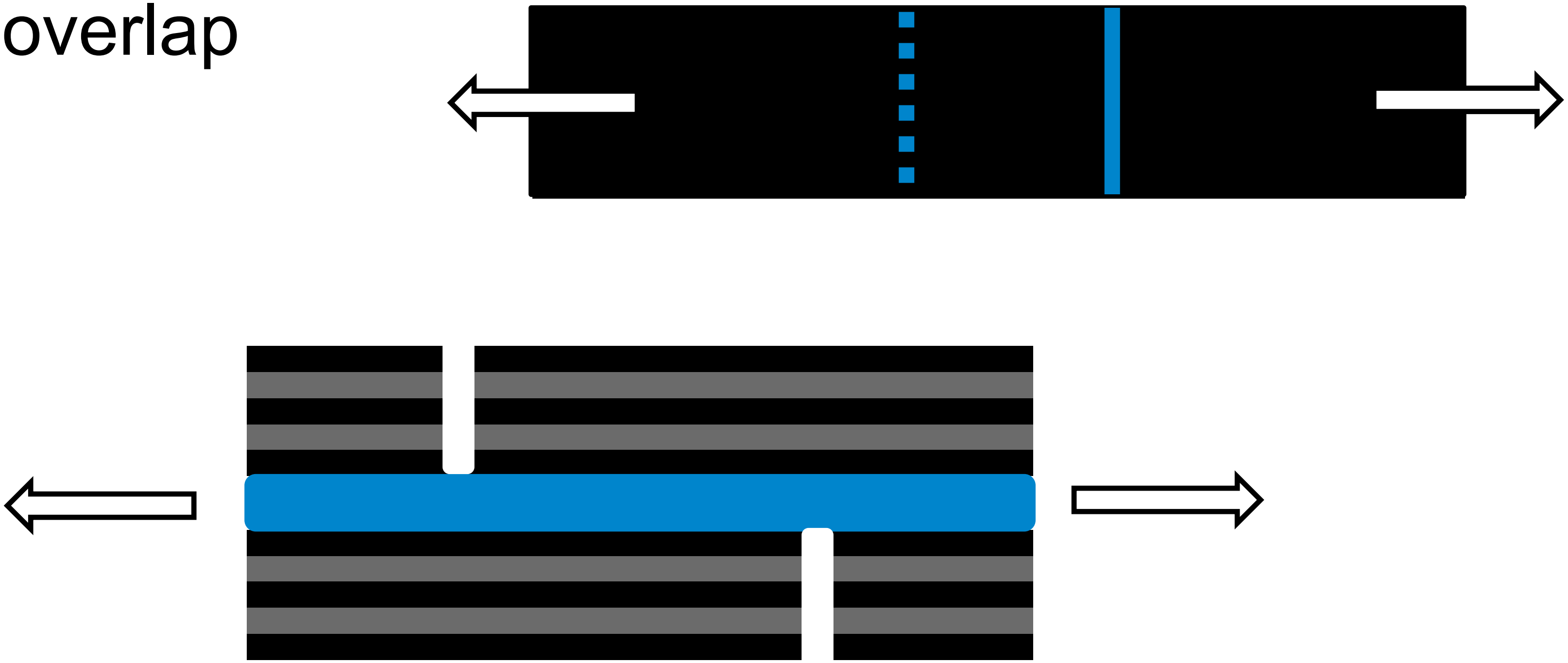
HH – High Humidity (80%RH)

60 – 60 min exposure

Control - No exposure

Bond Quality – Lap Shear

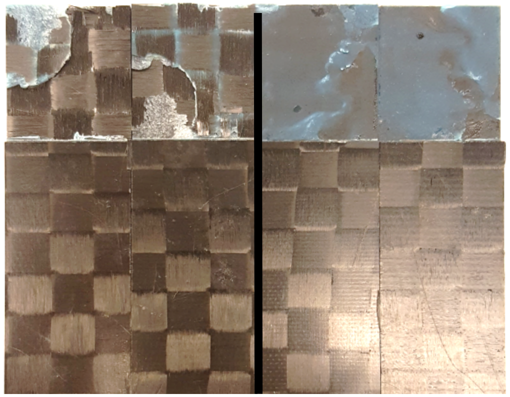
- ASTM D3165
- 10” x 1” specimen
- 1” overlap



Lap shear schematic. Top = birds eye. Bottom = profile

Preliminary Lap Shear Results

Condition			Avg. Shear Strength (psi)	Standard Deviation (psi)	Coefficient of Variation (%)
Temp (°F)	Humidity (%)	Time (min)			
65	35	30	1090.81	67.73	6.20
90	35	30	1431.17	110.84	7.74
65	**80**	**60**	**376.91**	**79.92**	**21.20**
90	80	60	1275.43	85.09	6.67

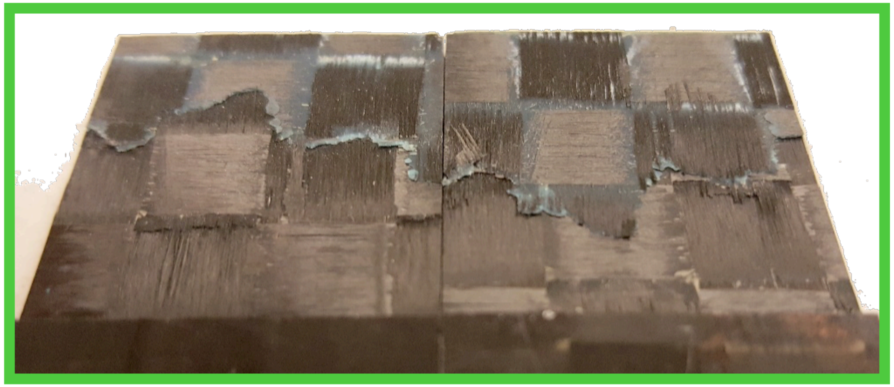


Interlaminar ave>1000psi

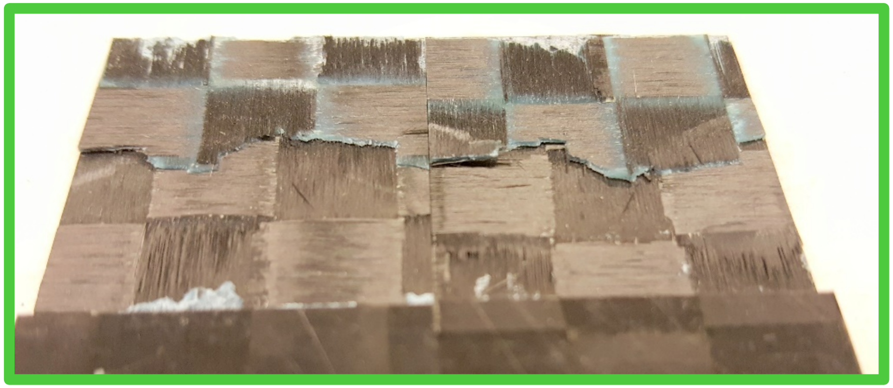
Cohesive ave= 376 psi

- Decreases shear strength by 65-75%
- Increases variability (COV)
- Amine blush changes failure mode

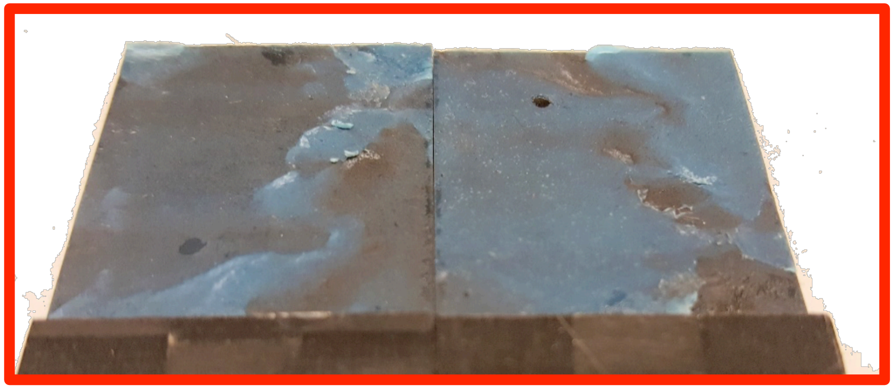
Lap Shear Results – Failure Modes



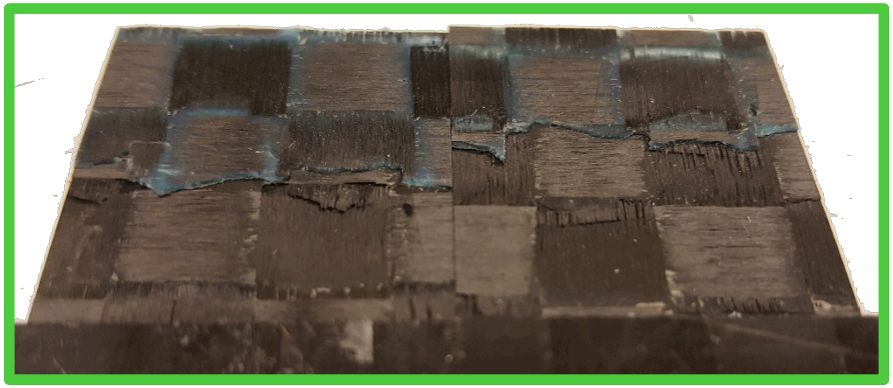
Low Temp, Low Humidity



High Temp, Low Humidity



Low Temp, High Humidity



High Temp, High Humidity

Summary of Current Results

- Humidity and out time have the largest impact on amine bloom/blush formation
- Amine blush severely decreases shear strength
- FTIR results do corroborate this pattern
- Unclear why High Humidity-High Temp samples have high strength
- Test remaining DOE conditions

Future Work

- Repeatability testing for lap shear and FTIR
- DCB testing
- Increase complexity for DOE
  - More temperatures, humidity's, out times
  - More adhesives
- Mitigation methods
- Investigate other blush detection methods
  - Dielectric spectroscopy
  - Fluorescence spectroscopy

Looking forward- Amine Blush

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

- Future needs
  - QA methods to detect amine blush
  - Methods to mitigate amine blush

Acknowledgements

- FAA, JAMS, AMTAS
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- Textron Aircraft
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- Precision Fabrics Group
- Airtech International
- UW MSE

Comments and questions are welcomed

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Contact Angle Goniometry

- Surface-specific, typically measures outermost 5 Å of a material
- The surface free energies (γ_{SV}, γ_{LV}, γ_{SL}) and the Young's contact angle (Θ_Y) are interrelated

$$\cos \Theta_Y = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$$

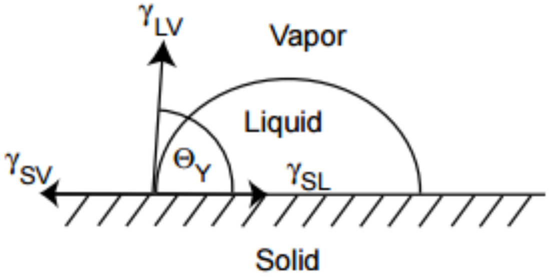

Figure 1. Graphical vector representation of sessile drop parameters: Θ_Y, Young's contact angle; γ_{SV}, solid–vapor interfacial free energy; γ_{LV}, liquid–vapor interfacial free energy; γ_{SL}, solid–liquid interfacial free energy.

- Contact angles can be converted into surface energy components using the Young-van OSS and Lewis acid-base equations

$$\gamma_L^t(1+\cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right)$$

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}}$$

Contact Angle Goniometry

- Goniometry measures polar and dispersive components for SE
- iGC measures SE with Lewis acid-base components
- Contact Angles can be compared to the iGC methods using the following values:

Liquid	γ_L	γ_L^d	γ_1^+	γ_1^-
DI Water	72.8	21.8	25.5	25.5
Ethylene Glycol	29	19	1.92	47
Glycerol	64	42	3.92	57.4
Diiodomethane	50.8	50.8	0	0
DMSO	44	36	0.5	32
Formamide	58	39	2.28	39.6

Source:

Handbook of Adhesives and Sealants: General Knowledge, Application of Adhesives, New Curing Techniques

Contact Angle Goniometry (3/3)

- Use three known contact angle measurements A, B, C with known LW, acidic and basic components to calculate SE_{solid}

$$W_{12A} = \gamma_{1A}(1+\cos\theta_A) = 2\left(\gamma_{1A}{}^{LW}\gamma_2{}^{LW}\right)^{1/2} + 2\left(\gamma_{1A}{}^{+}\gamma_2{}^{-}\right)^{1/2} + 2\left(\gamma_{1A}{}^{-}\gamma_2{}^{+}\right)^{1/2}$$

$$W_{12B} = \gamma_{1B}(1+\cos\theta_B) = 2\left(\gamma_{1B}{}^{LW}\gamma_2{}^{LW}\right)^{1/2} + 2\left(\gamma_{1B}{}^{+}\gamma_2{}^{-}\right)^{1/2} + 2\left(\gamma_{1B}{}^{-}\gamma_2{}^{+}\right)^{1/2}$$

$$W_{12C} = \gamma_{1C}(1+\cos\theta_C) = 2\left(\gamma_{1C}{}^{LW}\gamma_2{}^{LW}\right)^{1/2} + 2\left(\gamma_{1C}{}^{+}\gamma_2{}^{-}\right)^{1/2} + 2\left(\gamma_{1C}{}^{-}\gamma_2{}^{+}\right)^{1/2}$$

$$\mathbf{a} = [(\gamma_2{}^{LW})^{1/2} \quad (\gamma_2{}^{-})^{1/2} \quad (\gamma_2{}^{+})^{1/2}]$$

$$\alpha = \begin{bmatrix} \frac{(\gamma_{1A}{}^{LW})^{1/2}}{\gamma_{1A}} & \frac{(\gamma_{1A}{}^{+})^{1/2}}{\gamma_{1A}} & \frac{(\gamma_{1A}{}^{-})^{1/2}}{\gamma_{1A}} \\ \frac{(\gamma_{1B}{}^{LW})^{1/2}}{\gamma_{1B}} & \frac{(\gamma_{1B}{}^{+})^{1/2}}{\gamma_{1B}} & \frac{(\gamma_{1B}{}^{-})^{1/2}}{\gamma_{1B}} \\ \frac{(\gamma_{1C}{}^{LW})^{1/2}}{\gamma_{1C}} & \frac{(\gamma_{1C}{}^{+})^{1/2}}{\gamma_{1C}} & \frac{(\gamma_{1C}{}^{-})^{1/2}}{\gamma_{1C}} \end{bmatrix}$$

$$\beta = \begin{bmatrix} (1+\cos(\theta_A))/2 \\ (1+\cos(\theta_B))/2 \\ (1+\cos(\theta_C))/2 \end{bmatrix}$$

- The solid surface energy is given by:

$$\boxed{\mathbf{a} = \beta\,\alpha^{-1}}$$