Improving Adhesive Bonding of Composites Through Surface Characterization

(of Peel Ply Prepared Surfaces)

Brian D. Flinn and Molly Phariss
Department of Materials Science and Engineering

Improving Adhesive Bonding of Composites Through Surface Characterization

- Motivation and Key Issues
  - Peel ply surface preparation is being used for bonding primary structure on Boeing 777 and 787 and other commercial transport aircraft
  - 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 effect of peel ply surface preparation on the durability of primary structural composite bonds through surface analysis coupled with mechanical testing and fractography

Improving Adhesive Bonding of Composites Through Surface Characterization

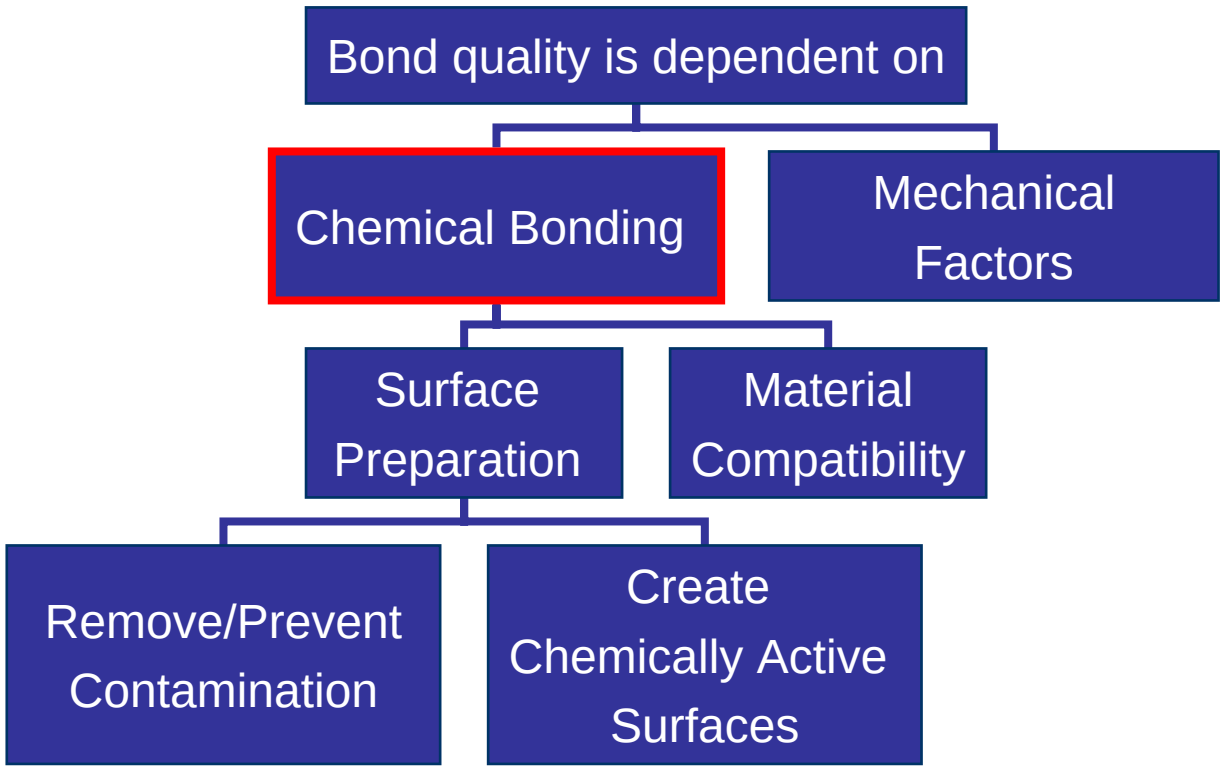
- Approach: Use Advanced Characterization Techniques To Understand The Role Of :
  - Prepreg (resin system, toughening agents, etc)
  - Adhesive (film adhesives)
  - Surface Preparation (peel ply material)

On The Surface Structure And Bond Quality

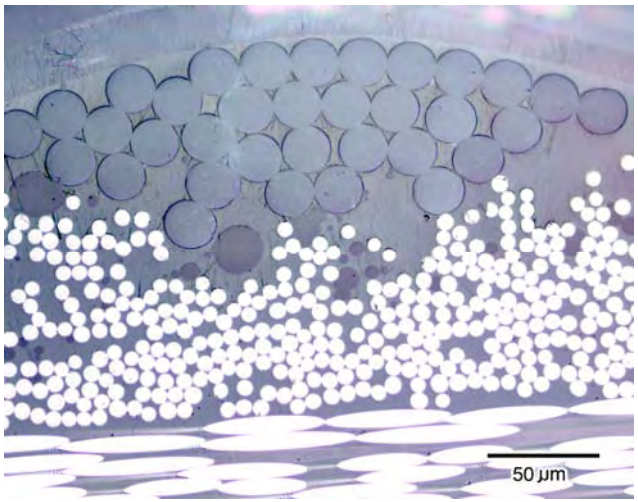
FAA Sponsored Project Information

- Principal Investigators & Researchers
  - Brian D. Flinn (PI)
  - Fumio Ohuchi (Co-PI)
  - Molly Phariss (Ph.D. Candidate, U. of Wa.)
  - Brian Clark (Masters student, U of Wa.)
- FAA Technical Monitor
  - Peter Shyprykevich (retired) and Curtis Davies
- Other FAA Personnel Involved
  - Larry Ilcewicz
- Industry Participation
  - Boeing: Peter Van Voast, William Grace, Paul Shelly
  - Precision Fabrics Group, Cytec, Toray, 3M
- JAMS Participation
  - Mark Tuttle (U. of Wa.): Wettability envelopes
  - Lloyd Smith (WaSU): Parallel study on durability

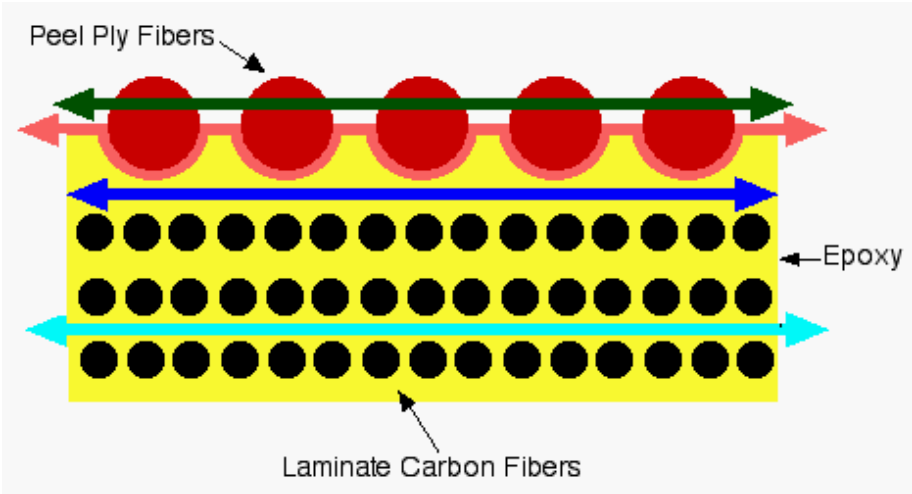
Background


Bond quality is dependent on
Chemical Bonding
Mechanical Factors
Surface Preparation
Material Compatibility
Remove/Prevent Contamination
Create Chemically Active Surfaces

Peel Ply Surface Preparation



Fracture Possibilities Upon Peel Ply Removal

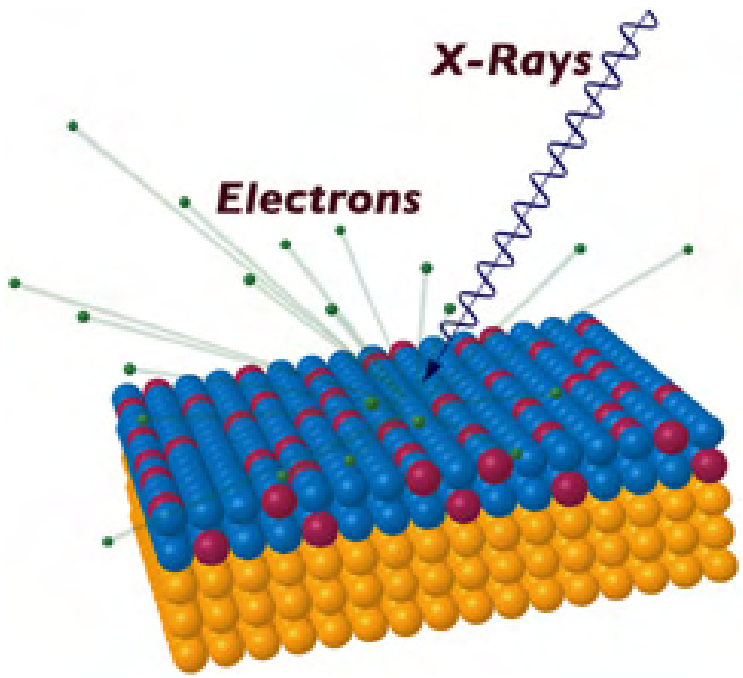


- Fracture of the epoxy between peel ply and carbon fibers
  - Fresh, chemically active, epoxy surface is created
- Interfacial fracture between the peel ply fabric fibers and the epoxy matrix
- Peel ply fiber fracture
- Interlaminar failure

Characterization and Testing

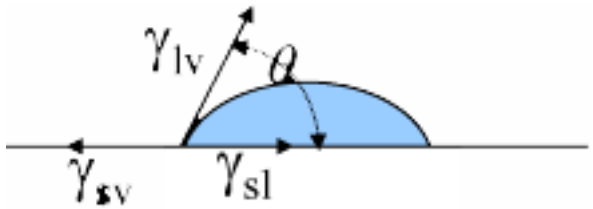
ESCA/XPS: X-Ray Photoelectron Spectroscopy

- X-Ray probes energy distribution of valence and nonbonding core electrons
- Gives chemical composition of surface (first few atomic layers)
- Peel ply removed just prior
- Survey scans and high-res scans over C (1s) peak

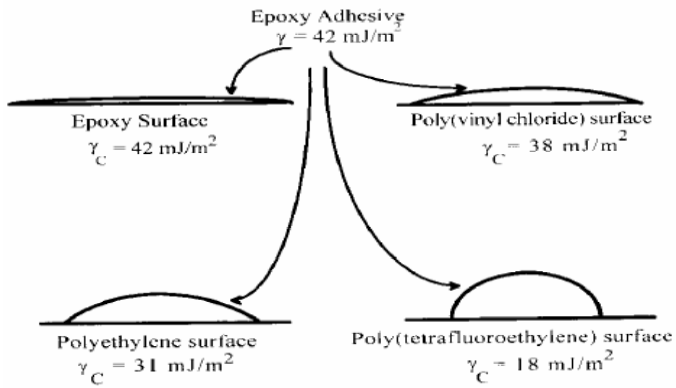


Characterization and Testing

Contact Angle Measurement

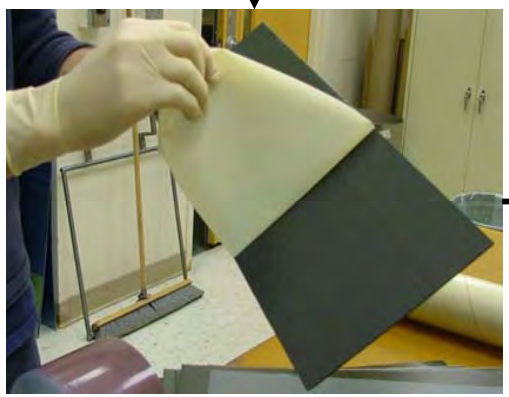


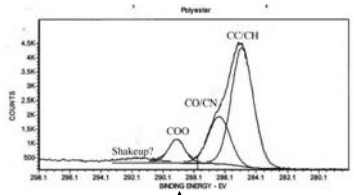
- 4 Fluids
- On laminates after peel ply removal
- On uncured film adhesives
- Kaelble plots to determine polar and dispersive surface energies $\gamma_s = \gamma_s^d + \gamma_s^p$
- Wettability envelopes calculated
  - Using WET program (M. Tuttle).

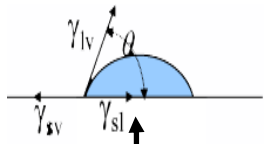


Samples were produced with standard composite processes and characterized

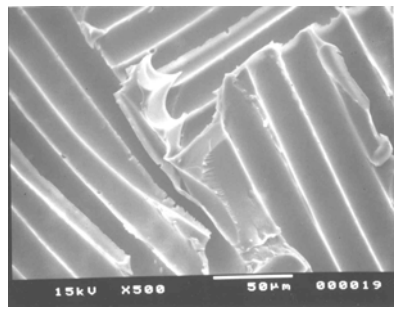
Autoclave Cure



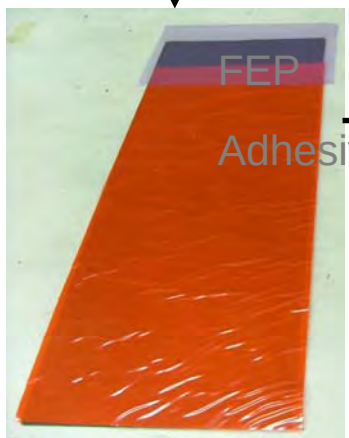




Characterization Via XPS,SEM,Contact Angle



Autoclave Cure



Peel ply removed before bonding

Bonded with film adhesive

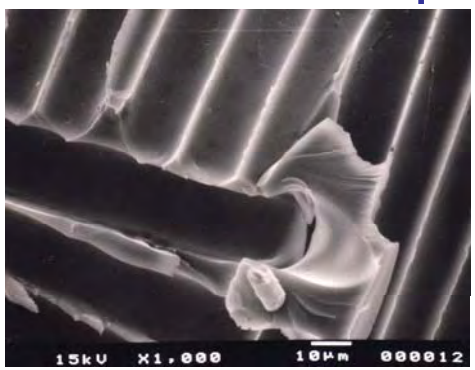
G_{IC} testing ASTM D-5528

Materials and Methods

- Test Samples produced with different:
  - Peel Plies (Nylon & Polyester)
  - Prepregs (250F & 350F cure systems)
  - Variety of Film Adhesives
- Surfaces and Bonds characterized by
  - SEM, XPS, Contact Angle (wettability)
- Laminates bonded and machined in to DCB specimens (ASTM 5573 & BSS-7273)

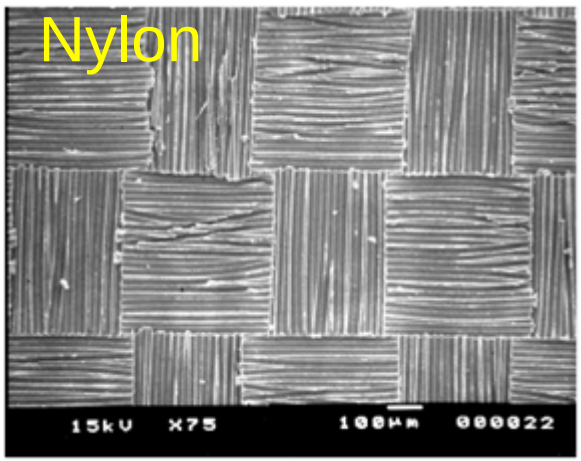
Peel Ply Surface Prep. - SEM Results

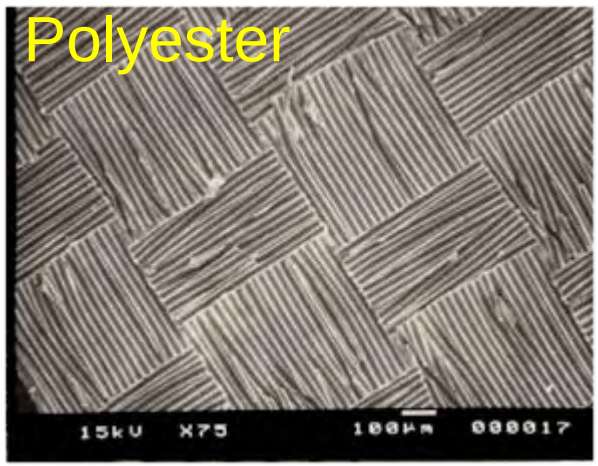
- All samples show acceptable surface on macro scale

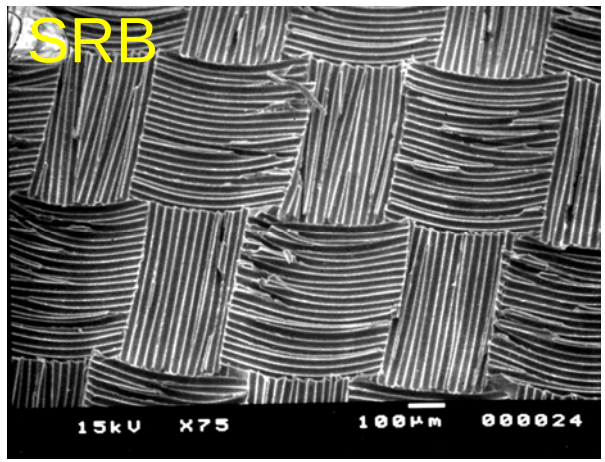


  - Interfacial fracture between the peel ply fabric fibers and the epoxy matrix
  - Limited epoxy fracture between peel ply fibers

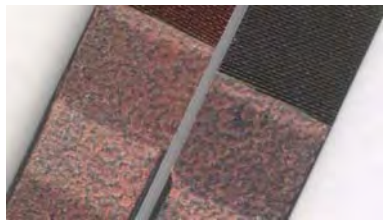
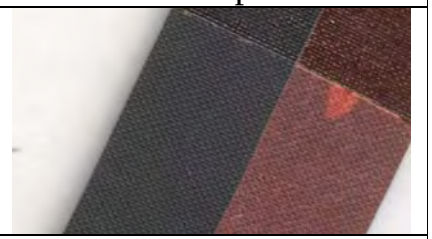
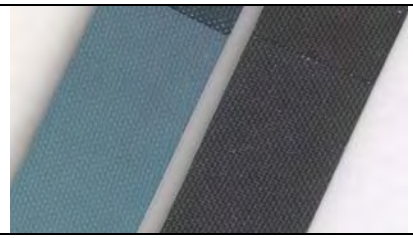
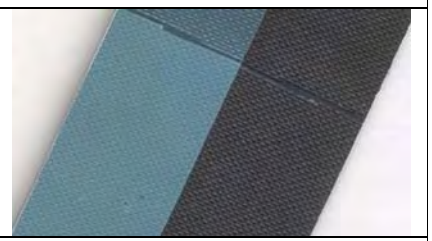
Composite surface after removal of:



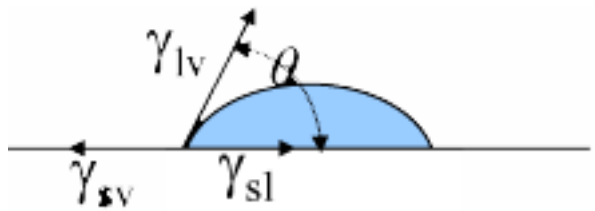




350 Cure System Results

	Polyester Prepared	Nylon Prepared	SRB Prepared
Adhesive A			
Failure Mode	Cohesive	Cohesive & Interlaminar	Adhesion
G_{IC} (J/m^2)	909.6	910.7	93.9
Adhesive B			
Failure Mode	Cohesive	Adhesion	Adhesion
G_{IC} (J/m^2)	812.3	122.1	86.0

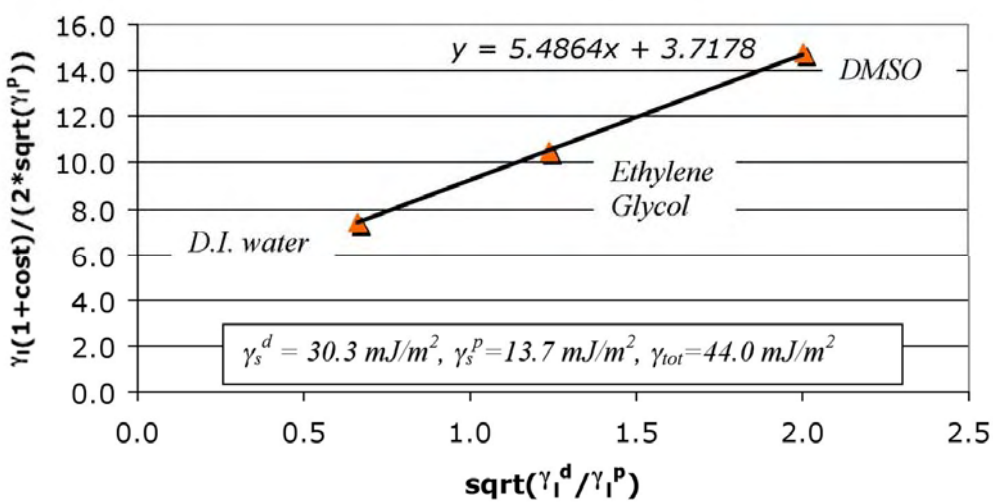
- G_{IC} and H_2O Contact Angle do not always correlate
  - G_{IC}: Polyester >>Nylon> SRB
  - Contact Angle: Nylon < Polyester<< SRB



Klaeble plots determined polar and dispersive surface energy components.

- Measured contact angles, known energies of fluids used to plot points
- Linear fit yields
  - Slope: $\sqrt{\gamma_s^d}$
  - Intercept: $\sqrt{\gamma_s^p}$

$$\gamma_s^{tot} = \gamma_s^p + \gamma_s^d$$

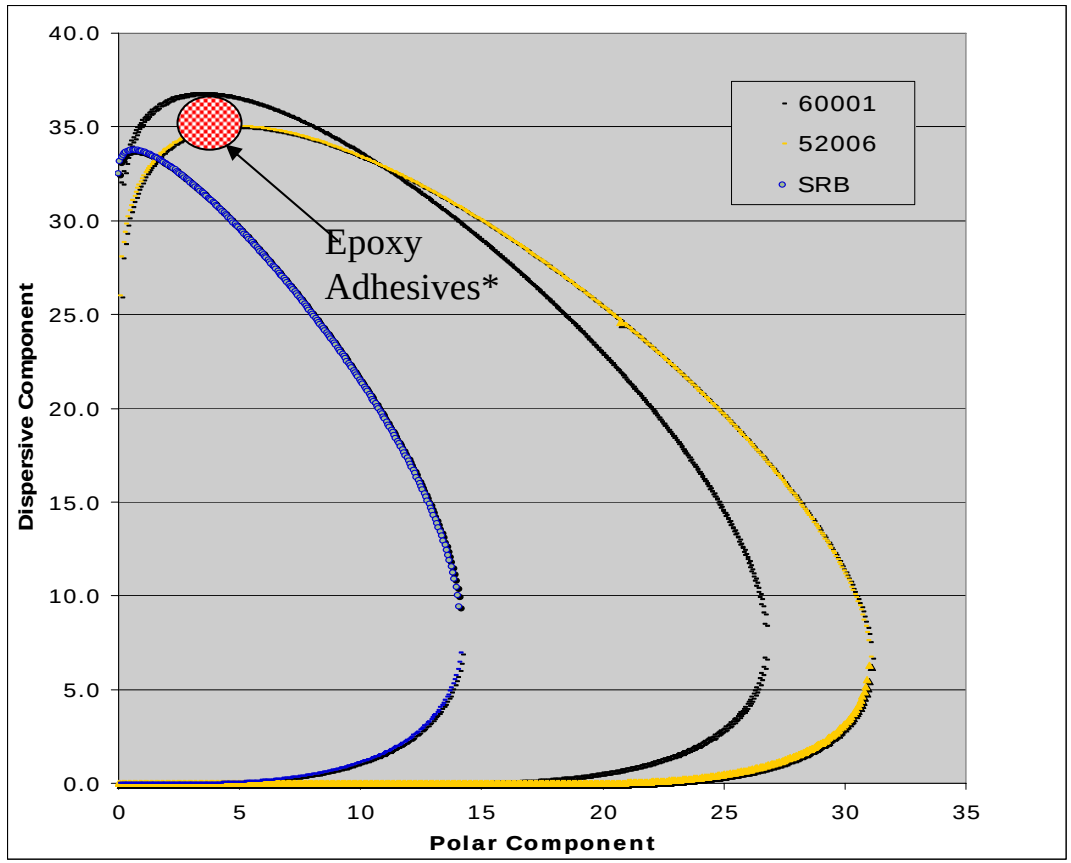


Peel Ply	γ_s^d	γ_s^p	γ_s^{total}
Nylon	25.0	20.3	45.3
Polyester	30.3	13.7	44.0

- Differences in energy components
  - Polyester ➔ greater dispersive
  - Nylon ➔ greater polar

Wettability envelopes showed the difference in the prepared surfaces.

- Fluids inside the envelope will wet spontaneously
  - Critical condition for bonding?
- Wettability envelopes a potential method to determine suitability of a surface for bonding
- Epoxy adhesives* on boundary for nylon prepared surfaces

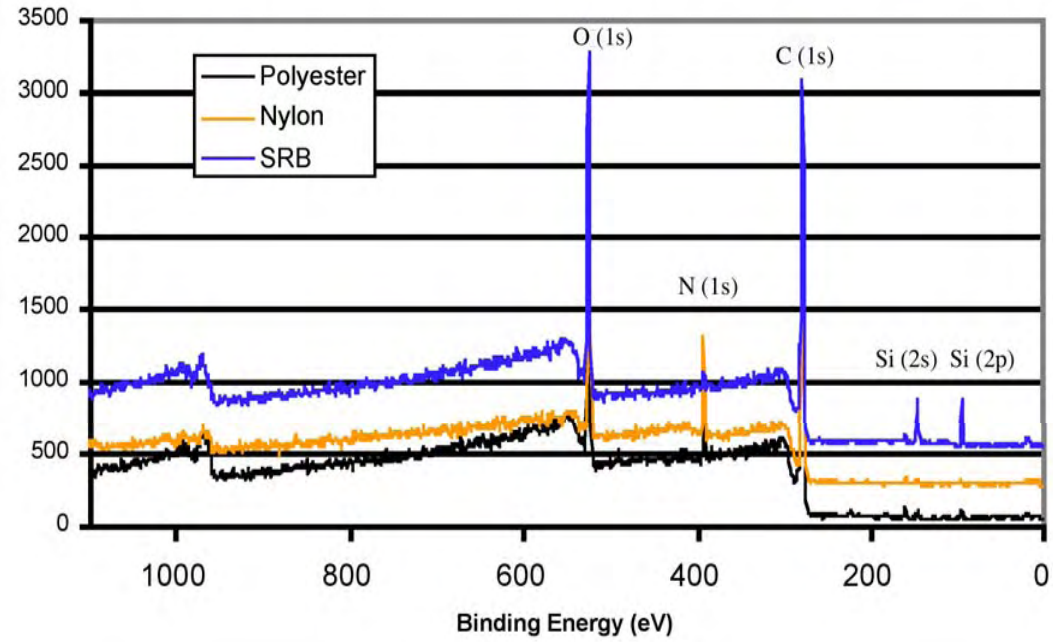


*** Literature values for aerospace epoxies**

- Curves generated using WET program (M. Tuttle)

XPS Survey Scan Results

Laminate surfaces before bonding, after peel ply removal



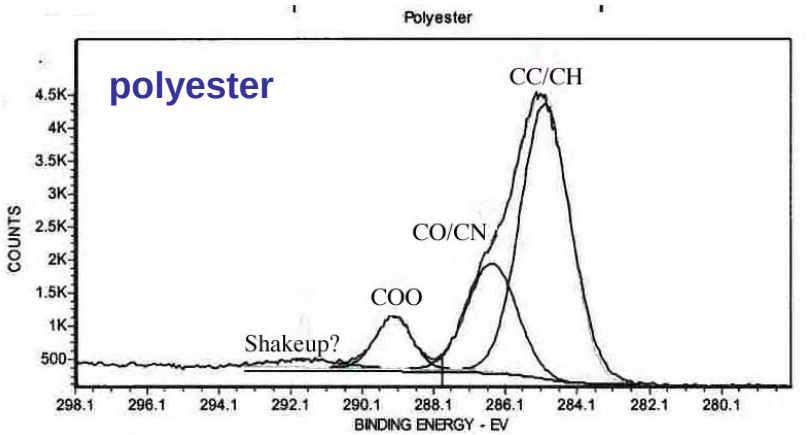
Laminate Surface Composition

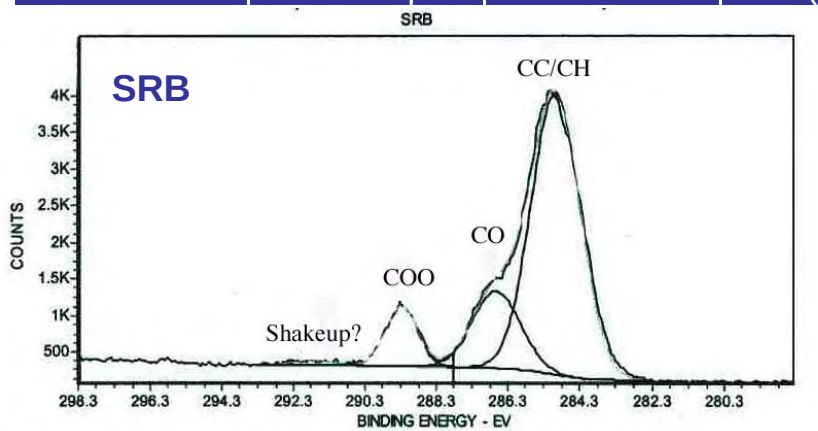
Peel Ply	%C	%O	%N	%Si
Nylon	77.5	12.6	9.8	Tr.
Polyester	75.5	21.6	1.9	Tr.
SRB	68	24.2	0.9	6.9

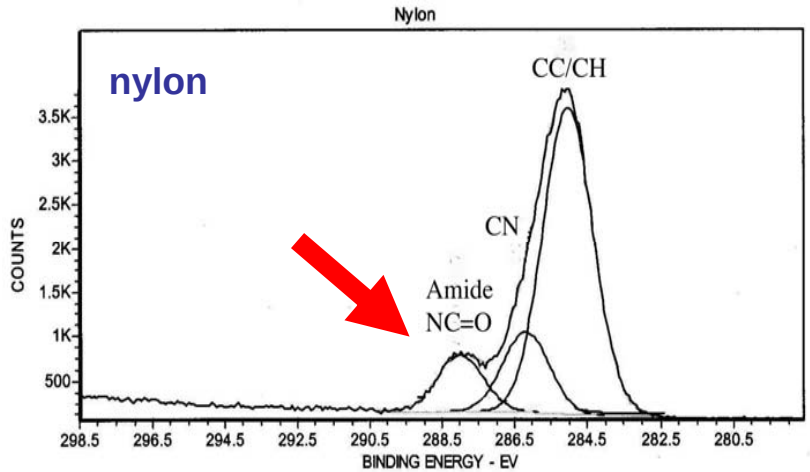
- Si explains SRB low bond quality….Siloxane coating transfers
- Amount of N on nylon peel ply prepared sample surprising

XPS High-Res Results

Peel Ply	Species	BE (eV)	%
Nylon	CC/CH	285	71
	CN	286.2	17.1
	Amide (NC=0)	288	11.9
Polyester	CC/CH	285	63.8
	CO/(CN)	286.5	24.9
	COO	289.2	8.8
	Shakeup?	291.8	2.4 (broad)
SRB	CC/CH	285	70
	CO	286.7	19.1
	COO	289.3	9.8
	Shakeup?	291.8	1.1(broad)



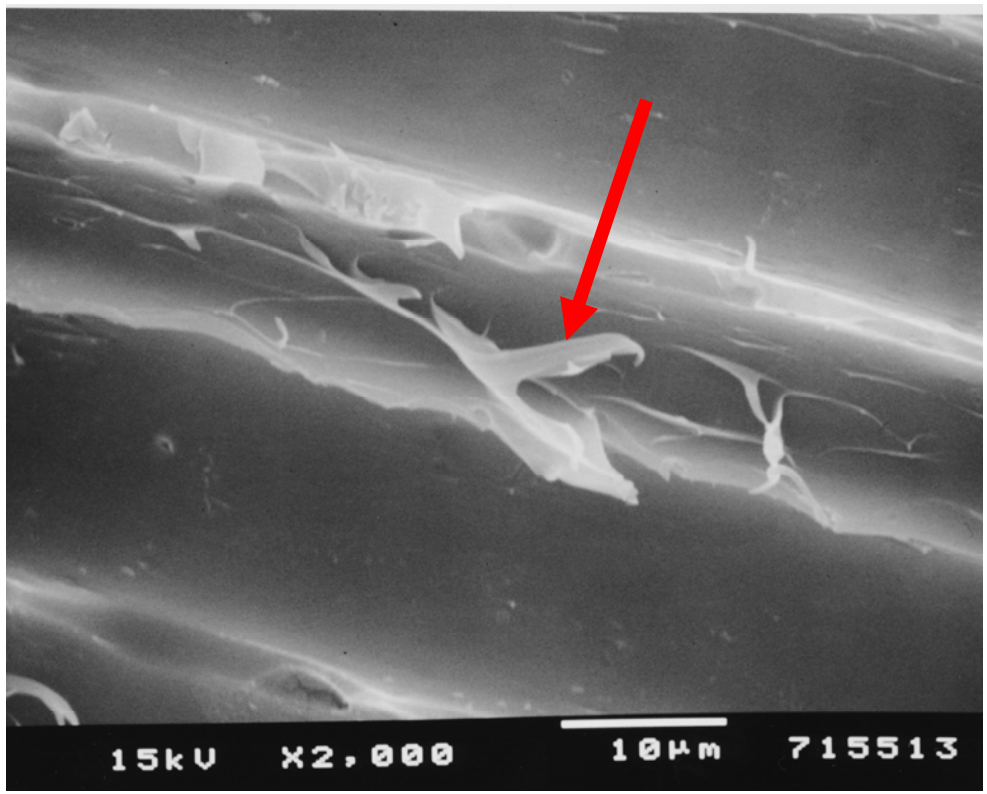




Amide detected on nylon prepared surface- nylon transfer to surface?

A Closer Look at the Laminate Surface

Laminate surface after removal of nylon peel ply



Nylon from peel ply on surface before bonding?

350F CURE SYSTEM SUMMARY

Bond Quality Depends on:

- Peel Ply Material and Adhesive
  - Polyester peel ply: high toughness bonds, cohesive failure both adhesives
  - Nylon: low toughness, adhesion failure
  - One adhesive bonded well to all surfaces
- H_20 Contact angle did not correlate well with G_{IC}
- Wettability envelopes more accurate
- XPS can provide important chemical information

250F Cure Systems

- 2 Peel Plies: Polyester 60001 and Nylon 52006
- 3 prepregs-260 ºF cure
  - HexPly® F155
  - Yokohama G7781
  - Cytec MXB7701
- 6 adhesives-260 ºF cure
  - 3M AF500; 3M AF163-2;
  - Henkel EA 9696; Henkel EA 9628
  - Cytec FM94; Cytec FMx 209
- Bond quality assessed by failure mode
  - Adhesion (poor) vs. Cohesive (good)

Peel Ply Material-250F Cure

RAT results						
updated:	3/24/2006		key:		strong bond	
spec:	BMS 8-79				mixed strong / very strong bonds	
					mixed results	
					weak bond	
Prepreg:	HexPly F155				other	
	adhesive:					
peel ply:	3M AF500	3M AF163-2	Cytec FM94	Henkel EA 9696	Cytec FMx 209	Henkel EA 9628
60001 (polyester)						
51789 (nylon)						
Prepreg:	Yokohama G7781					
	adhesive:					
peel ply:	3M AF500	3M AF163-2	Cytec FM94	Henkel EA 9696	Cytec FMx 209	Henkel EA 9628
60001 (polyester)						
51789 (nylon)						
Prepreg:	Cytec MXB7701					
	adhesive:					
peel ply:	3M AF500	3M AF163-2	Cytec FM94	Henkel EA 9696	Cytec FMx 209	Henkel EA 9628
60001 (polyester)						
51789 (nylon)						

SUMMARY

Nylon - Strong

Polyester - Weak

250F CURE SYSTEM SUMMARY

Bond Quality Depends on:

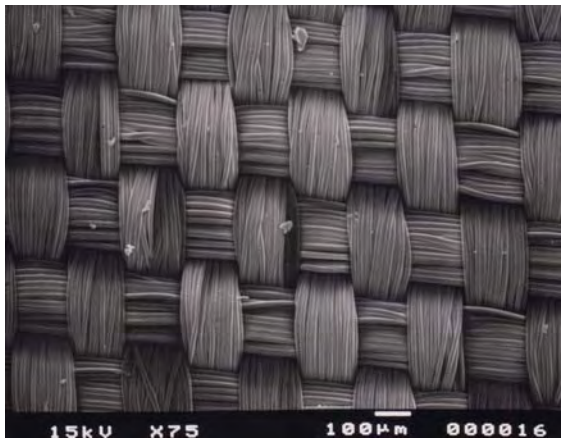
- Peel Ply Material and Adhesive
  - Nylon : high toughness bonds, cohesive failure all adhesives
  - Polyester peel ply: low toughness, adhesion failure
  - One adhesive bonded well to all surfaces
- Opposite Trend than 350 F system
  - Nylon bad, Polyester good

Effect of Peel Ply Texture

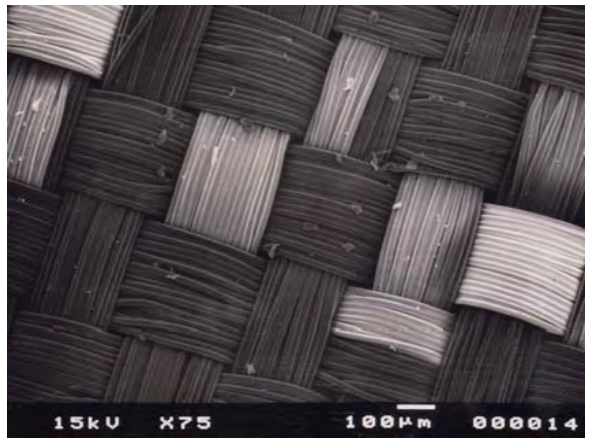
- 350F Laminates produced with 9 different peel plies
  - 4 polyester and 5 nylon peel plies
  - Surface characterization: SEM, profilometry, contact angle
  - Bond quality: Measure with G_{IC}

Material	Precision Code	Warp (ends/in.)	Fill (picks/in.)	Thickness (mil)	Comments
Polyester	60001	70	50	5-6	BMS 8-308
Polyester	60001 VLP	70	50	5-6	Calendered
Polyester	60004	120	59	4.5-5.5	
Polyester	60005	90	58	6-7	Sikorsky
Nylon 6,6	52006	160	103	4.5-5.5	Very Fine
Nylon 6,6	52008	101	82	4-5	
Nylon 6,6	50000	60	50	6.5-7.5	Twill weave
Nylon 6,6	40000	76	51	7.5-8.5	
Nylon 6,6	41661	60	50	6.5-7.5	

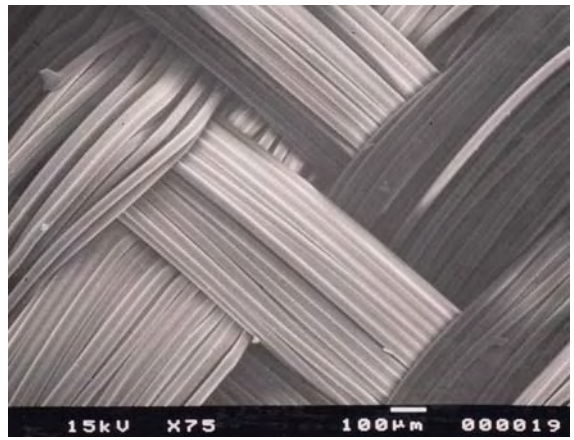
SEM's of As-Received Peel Plies



Fine 160 x103
(PF 52006)



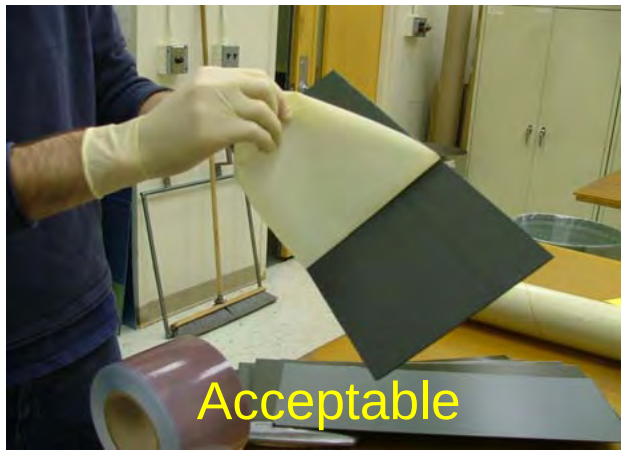
Medium 101 x 82
(PF 52008)

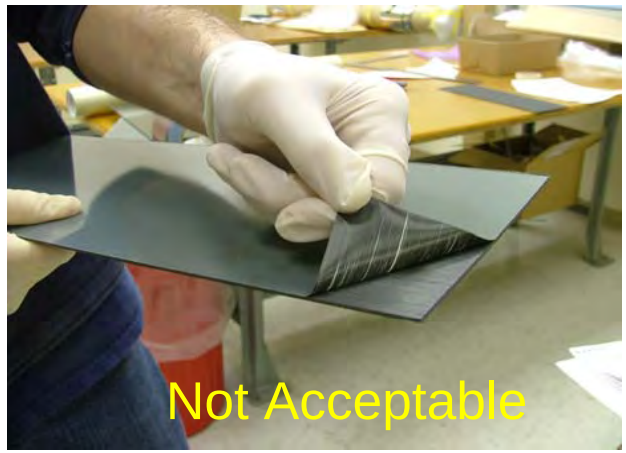


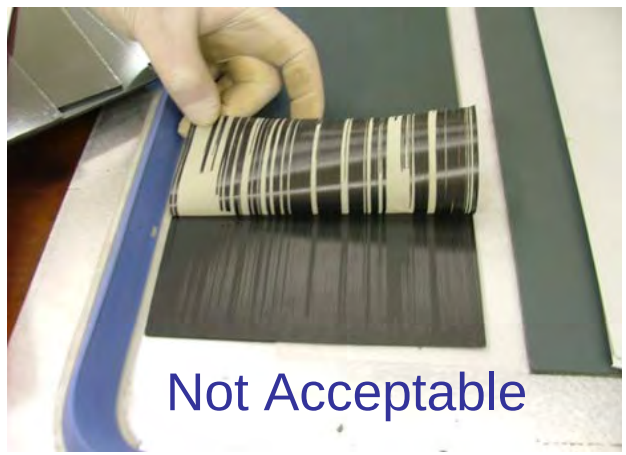
Coarse 60 x 50
(PF 52000)

- Different weaves, deniers, filament diameters will produce different surfaces

Peel Ply Removal (?)





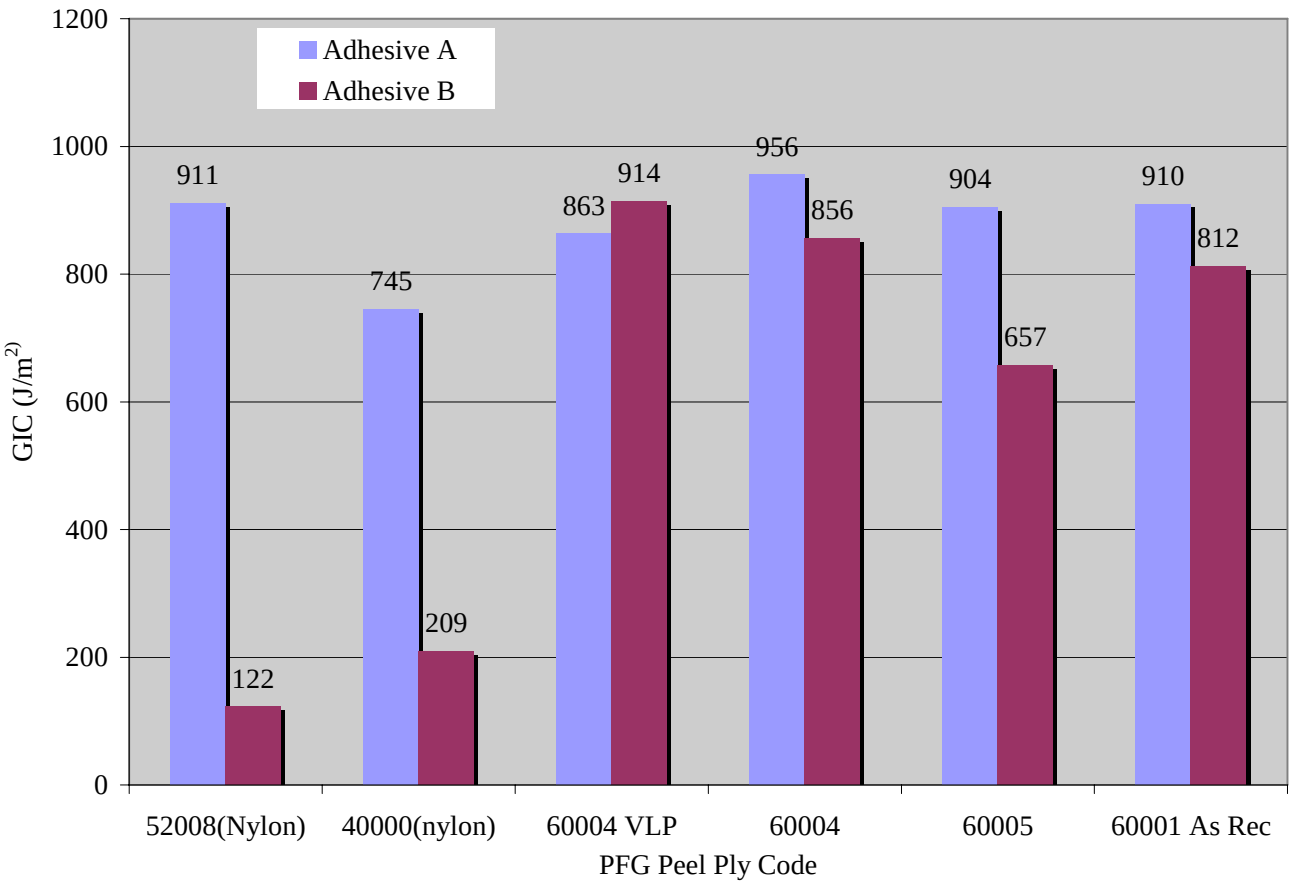


Effect Peel Ply Texture

- All polyester peel plies successfully removed
- Nylon peel plies were more difficult to remove
  - Fine weaves were removed without damage
  - Coarse weaves have not been removed without damage to laminate (3 attempts, different technicians)

Material	Code	Warp (ends/in)	Fill (ends/in)
Nylon 6,6	52006	160	103
Nylon 6,6	52008	101	82
Nylon 6,6	50000	60	50
Nylon 6,6	40000	76	51
Nylon 6,6	41661	60	50

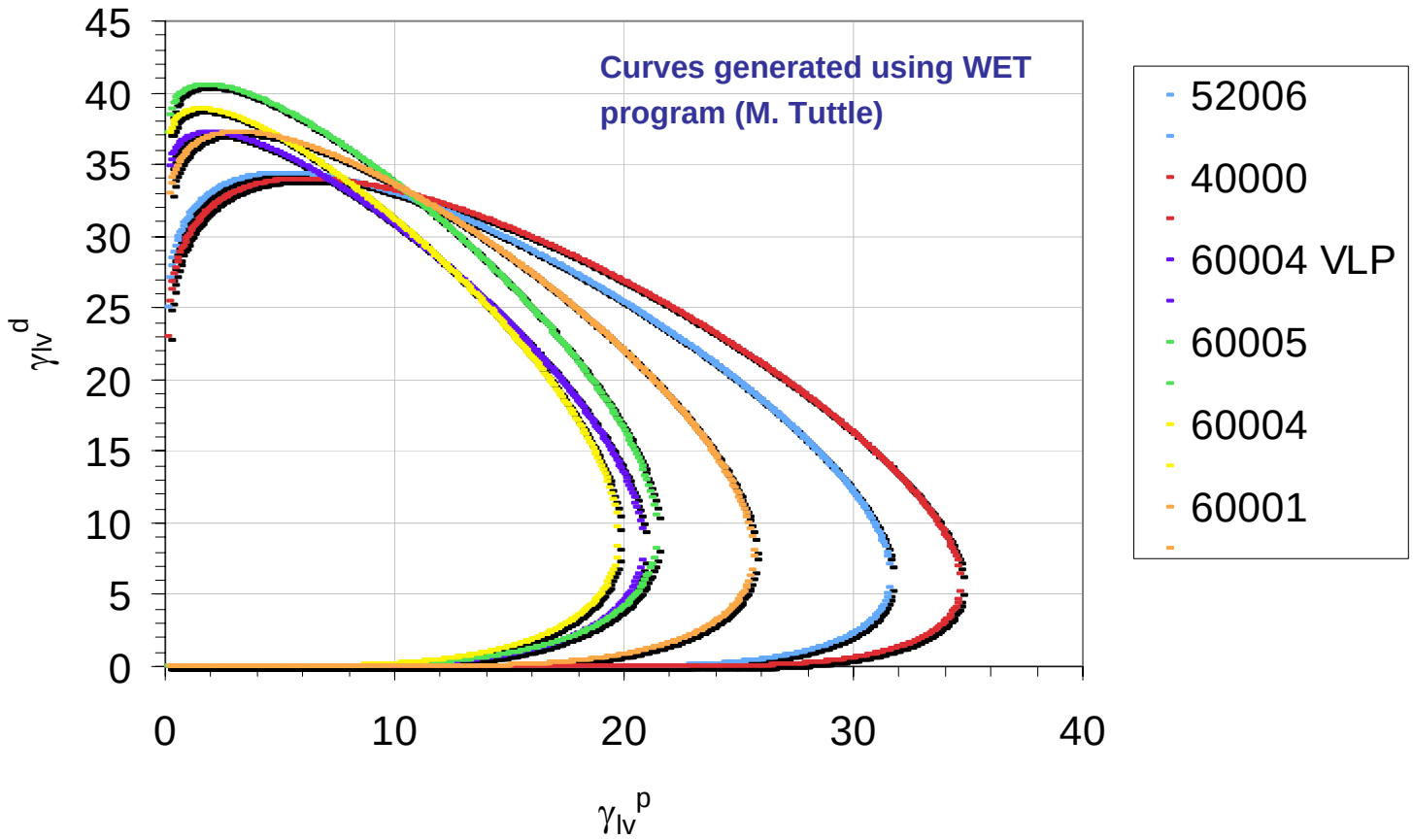
Effect of Peel Ply Texture



- Peel ply texture does not seem to affect bond quality

Effect Peel Ply Texture

- Wettability Envelopes



Peel Ply Texture Summary

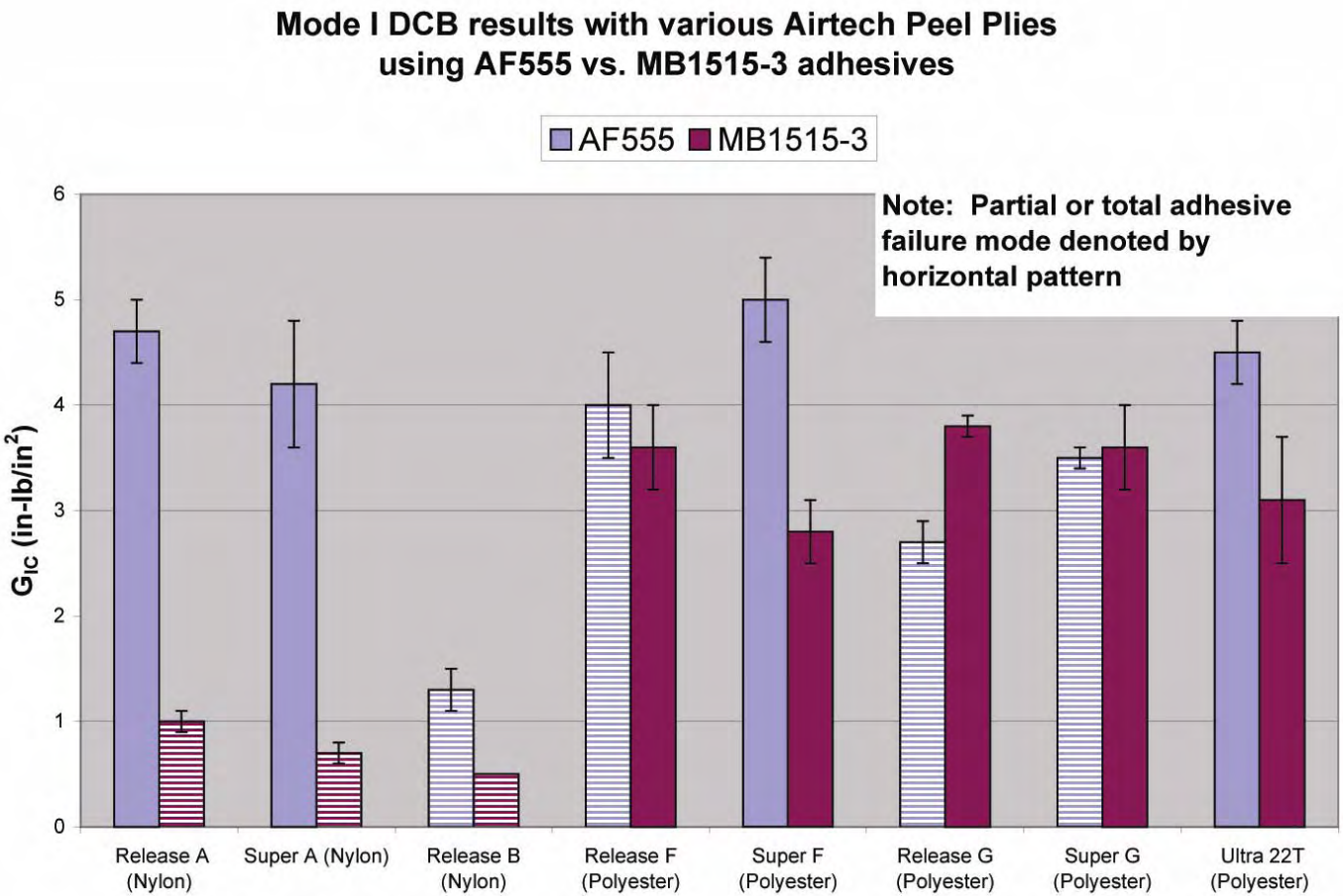
Material and 350F system

- Polyester peel plies easier to remove, bond better
- Nylon peel plies more difficult to remove
  - Coarser peel plies could not be removed without damaging laminate
- Similar trends in wettability envelopes
  - Nylon greater polar component
  - Polyester greater dispersive
- Texture does not have significant effect on G_{IC}

Effect of Peel Ply Source

- Many Polyester and Nylon Peel Plies Available
- Why Might There Be a Difference?
  - Different fiber source-impurities, MW, properties
  - Different weaves
  - Different processing-scouring and heat setting
  - Different quality control
- Measure G_{IC} and Characterize Surfaces

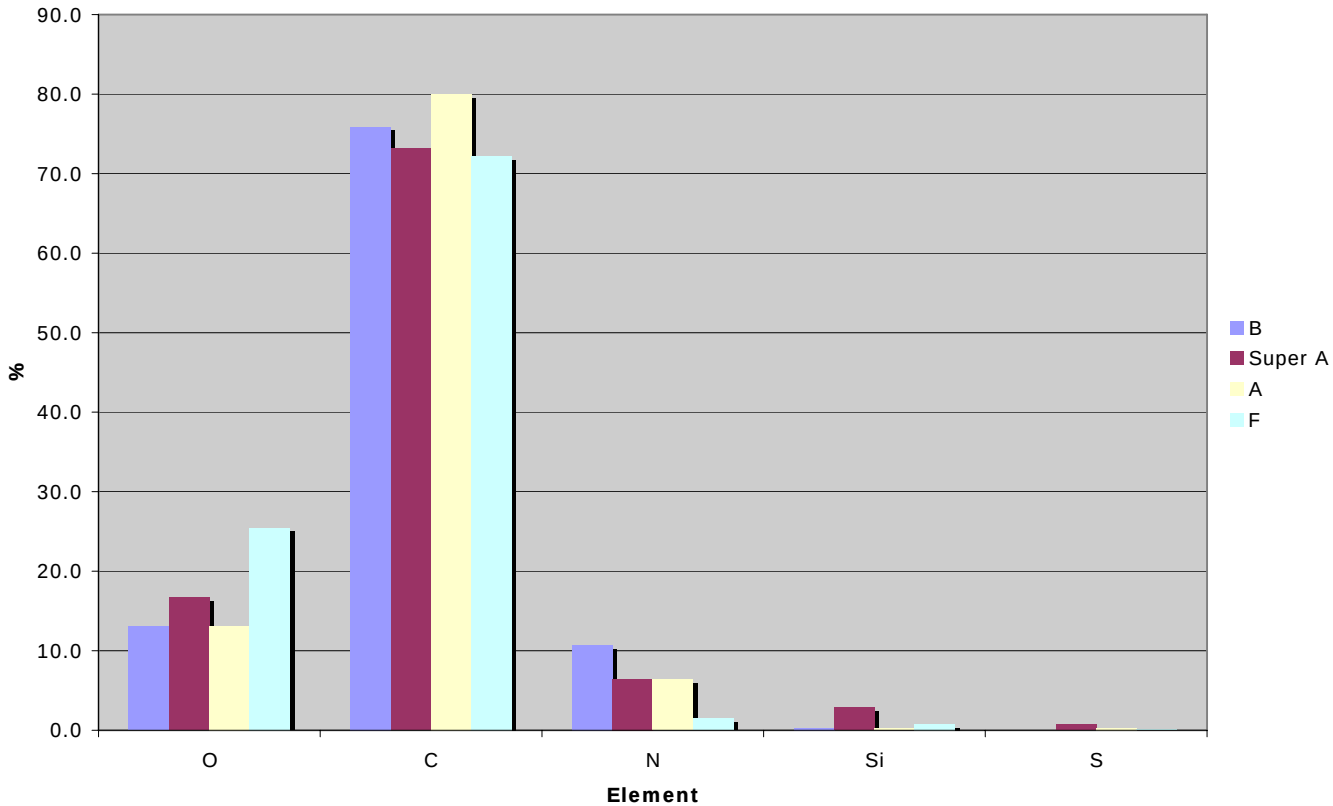
Peel Ply Material Source



- **Adhesion failure on some surfaces with polyester peel plies!**

Peel Ply Material Source

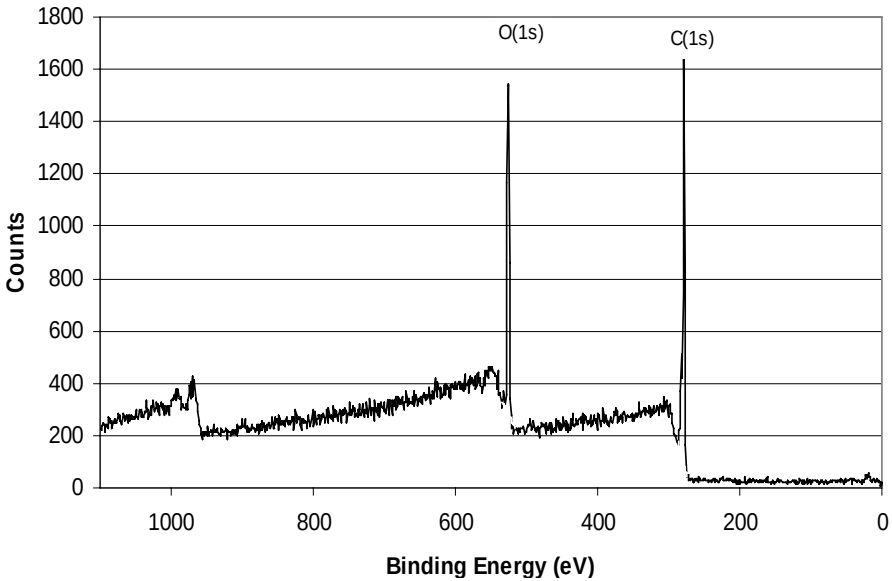
- XPS on Laminates Cured with Different Airtech peel plies



- **Peel ply "F" has highest oxygen content**
- **Peel Ply "F" closest match to Precision 60001**

Peel Ply Material Source

XPS on:
As received Airtech and PFG polyester peel plies
Laminates Cured with Airtech and PFG polyester peel plies



Typical compositional scan

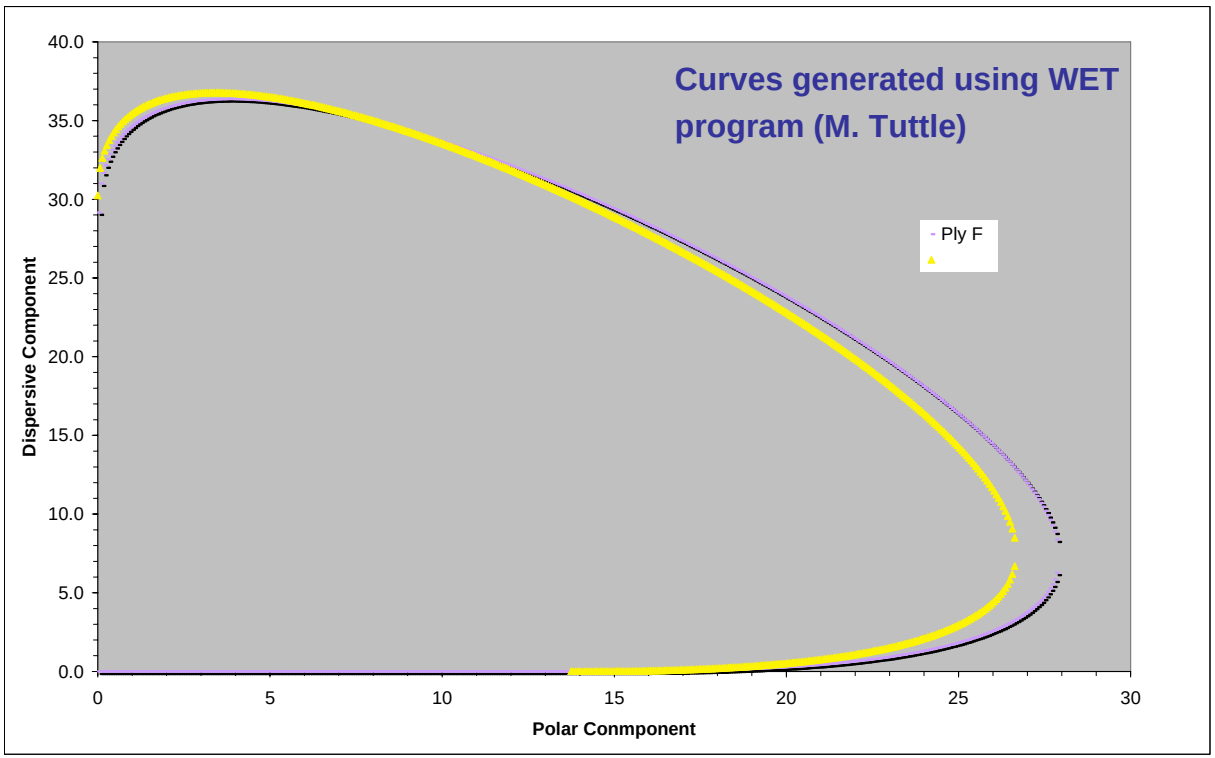
Peel Ply	Ply		C	O	N	
	60001	Mean	73.5	26.5	0.0	
		Stand Dev	0.9	1.0	0.0	
	Ply F	Mean	73.4	26.3	0.3	
		Stand Dev	0.6	0.4	0.1	
Laminate			C	O	N	S
	60001	Mean	74.8	22.5	1.8	
		Stand Dev	0.8	1.0	0.1	
	Ply F	Mean	73.2	24.1	1.5	1.1
		Stand Dev	1.3	0.9	0.2	0.6

Summary of composition scans

Peel Ply "F" close match to Precision 60001

Peel Ply Material Source

- Wetting Envelopes on Laminates Cured with Different Peel Plies



- **Peel ply “F” and “60001” have similar wettability envelopes**

Peel Ply Material Source

- Slight differences in peel ply can be important
- For Polyester 60001 and Ply F
  - Different failure modes and energies
    - 900 J/m^2 vs. 700 J/m^2
  - Similar Surface Chemistry
- More research needed to understand fundamentals of peel ply surface preparation

Conclusions

- Bonding Depends on
  - Prepreg system
  - Peel Ply Material
  - Adhesive
- Characterization Techniques (XPS, SEM and Wettability) provide useful information to help understand bonding requirements

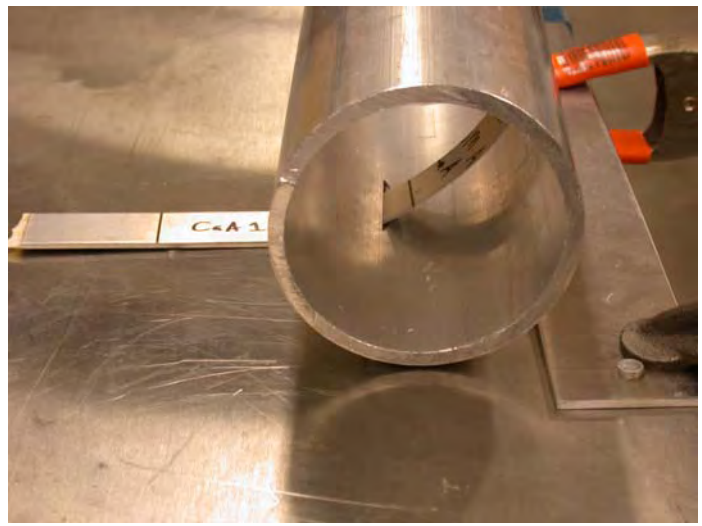
A Look Forward

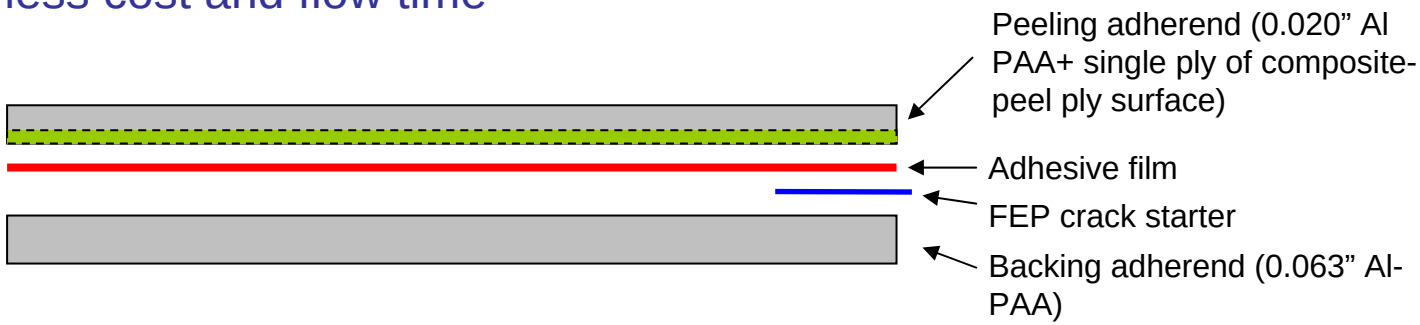
- Benefit to Aviation
  - Better understanding of peel ply surface prep.
  - Guide development of QA methods for surface prep.
  - Greater confidence in adhesive bonds

- Future needs
  - Contact angle (wetting) vs. bond quality
  - Peel ply-resin interactions
  - Applicability to other composite and adhesive systems
  - Model to guide bonding based on characterization, surface prep. and material properties

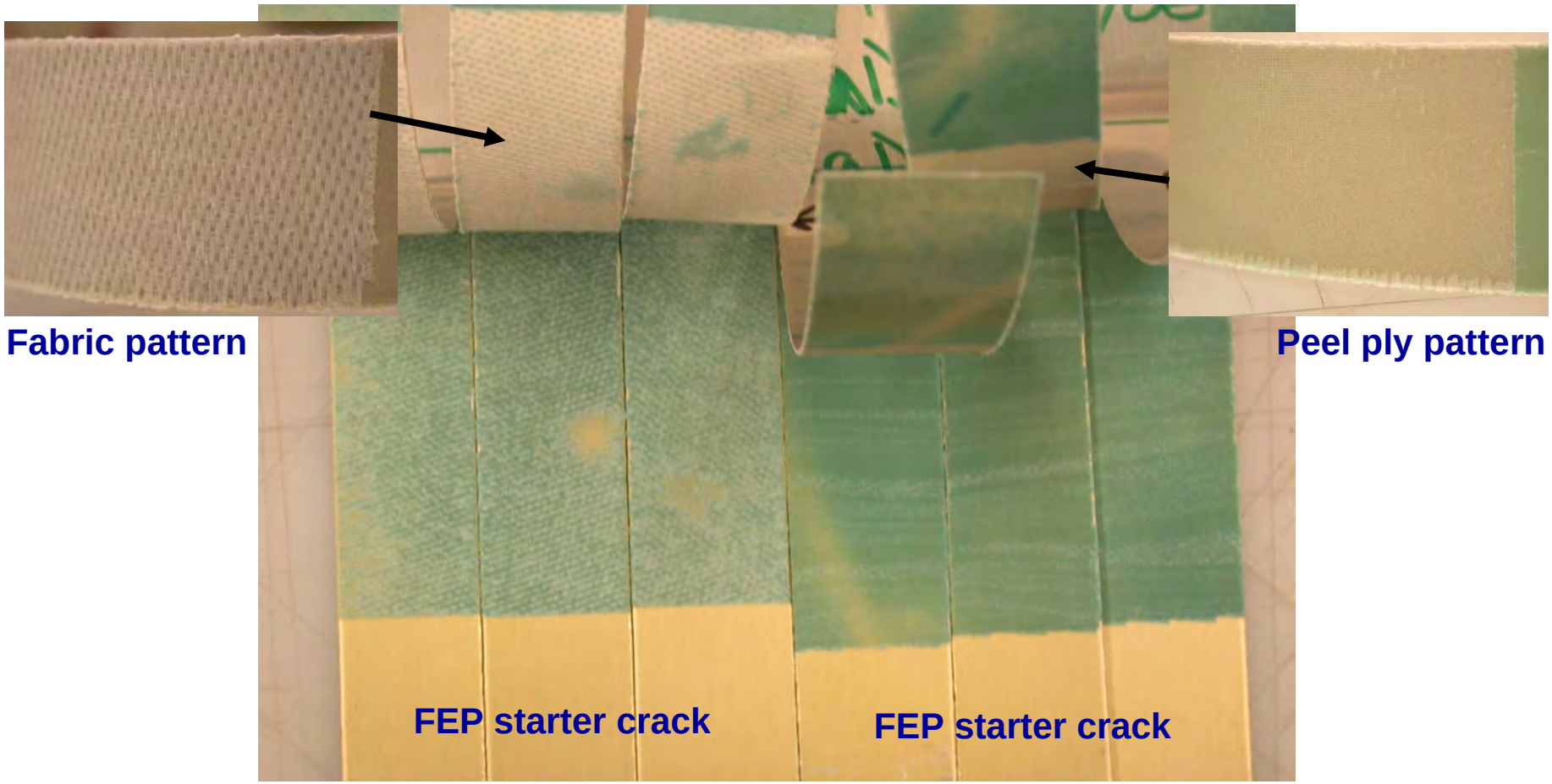
The Rapid Adhesion Test (RAT) Method

- A quick, low cost test which assesses the adhesion between metal-composite bonds.
- A modification of metal-to-metal peel test developed by Boeing.
- The backing adherend clamped to while the peeling adherend is removed
- Failure mode representative of bond
  - Adhesion Failure-Poor Bond
  - Cohesive Failure-Strong Bond
- Failure modes correlate with DCB test with ~90% less cost and flow time





RAT Method Assessment



Cohesive failure (left) vs. Adhesion failure (right)