Improving Adhesive Bonding of Composites Through Surface Characterization

(of Peel Ply Prepared Surfaces)

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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:
    - Task 1: Does contact angle (wettability) correlate with bonding?
    - Task 2: Effect of peel ply texture on surface and bonding?
    - Task 3: Effect of moisture in peel ply before cure?
    - Task 4: Does the source of peel ply influence bond quality?
    - Task 5: Does the degree of cure of laminates affect bond behavior?
    - Task 6: Are pre-impregnated peel plies more robust than dry peel ply?
- 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
  - Investigate the effect of peel ply material, texture and moisture content on the surface structure and bond performance of BMS8-276 form 3 (Toray) laminates using two different adhesives.
  - Peel/Release Plies
    - Materials: polyester, nylon and SRB release (siloxane finish)
    - Texture: Fine, medium and coarse weaves
    - Moisture Content: dry to saturated
    - Supplier
  - Adhesive Types
    - Cytec MB1515-3 and 3M AF555
  - Characterization
    - Surface chemistry, mechanical testing and fractography

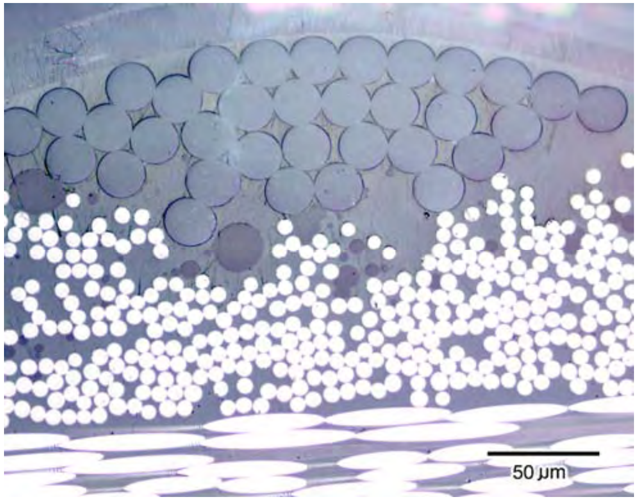
FAA Sponsored Project Information

- 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
- Other FAA Personnel Involved
  - Curt Davies, 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

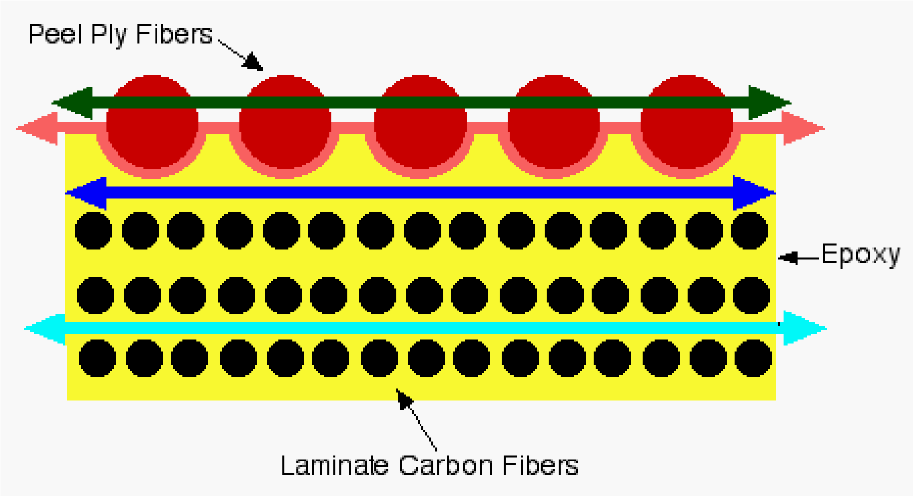
Background

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

Peel Ply Surface Preparation



Fracture Possibilities Upon Peel Ply Removal

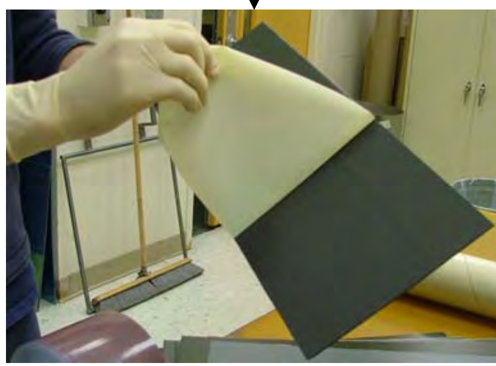


- Fracture of the epoxy between peel ply and carbon fibers
  - Fresh, chemically active, epoxy surface is created
- Interfacial fracture between the peel ply fabric fibers and the epoxy matrix
- Peel ply fiber fracture
- Interlaminar failure

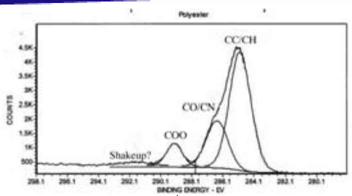
Samples were produced with standard composite processes and characterized

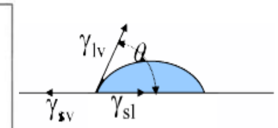
Unidirectional 10 Ply Toray Carbon Fiber Prepreg Laminates (BMS 8-276)

Autoclave Cure

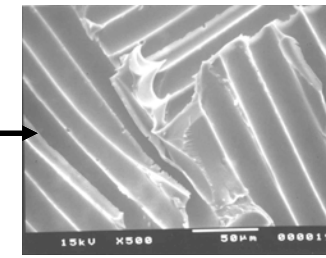


Peel ply removed before bonding



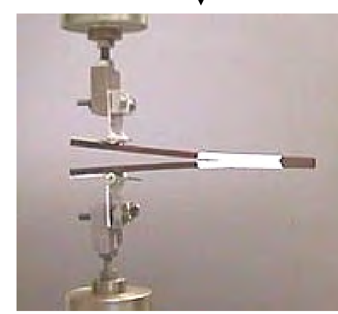


Characterization Via XPS,SEM, Contact Angle



Bonded with film adhesive AF555 or MB1515-3

Autoclave Cure

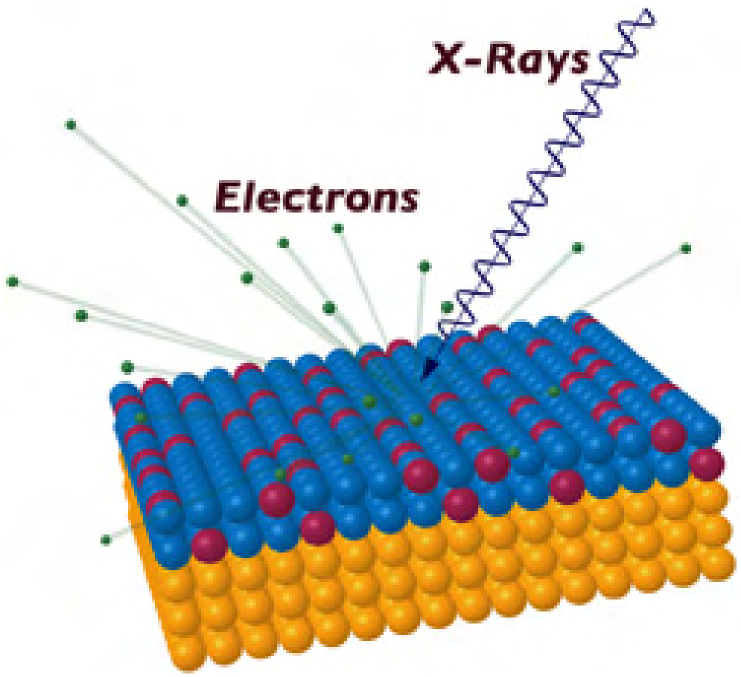


G_{IC} testing ASTM D-5528

Characterization and Testing

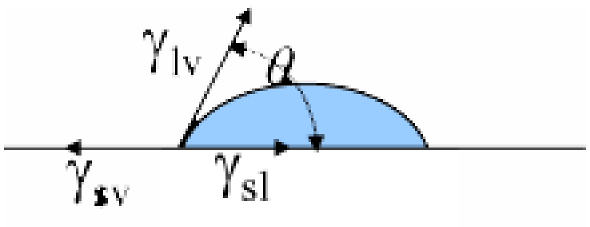
ESCA/XPS: X-Ray Photoelectron Spectroscopy

- 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

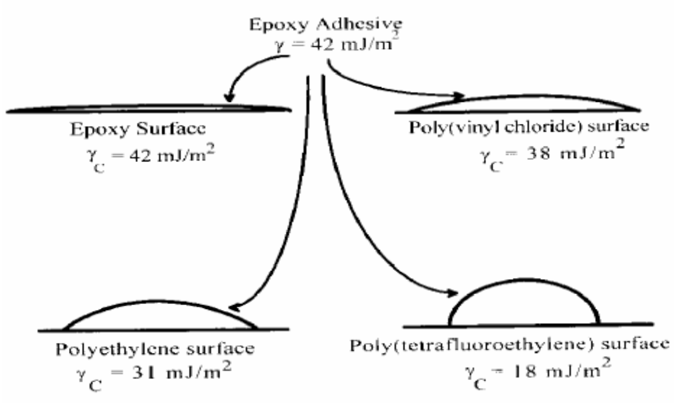


Characterization and Testing

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).

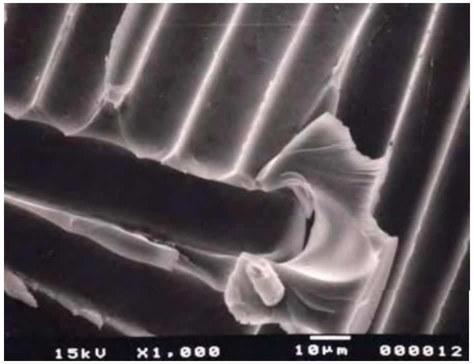


Task 1: Peel Ply Material Type

- Laminates produced with 3 peel/release plies
  - Polyester BMS 8-308 (Precision Fabrics 60001)
    - Currently used for primary structural bond prep.
  - Nylon scoured and heat set (Precision Fabrics 52006)
  - Super Release Blue (60001 with siloxane coating)
- Samples removed for surface characterization
  - SEM, XPS, Contact Angle (wettability), SIMS
- Laminates bonded and machined in to DCB specimens (ASTM 5573 & BSS-7273)

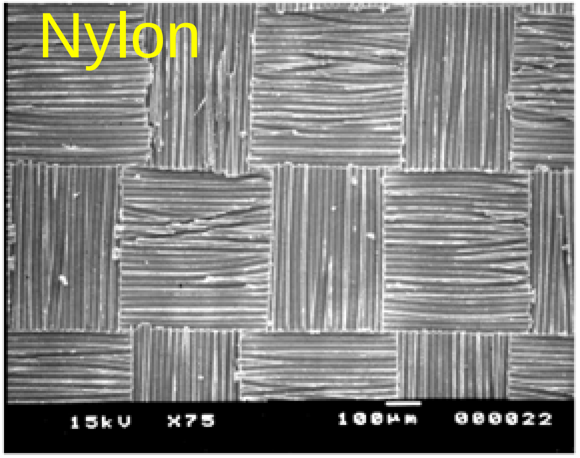
Peel Ply Surface Prep. - SEM Results

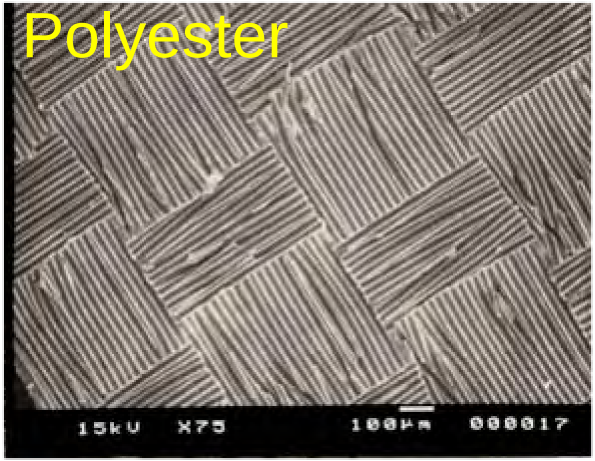
- All samples show acceptable surface on macro scale

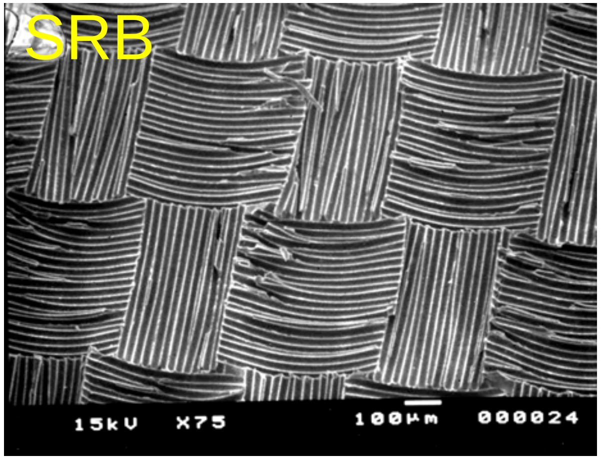


  - Interfacial fracture between the peel ply fabric fibers and the epoxy matrix
  - Limited epoxy fracture between peel ply fibers

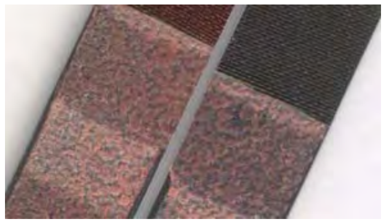
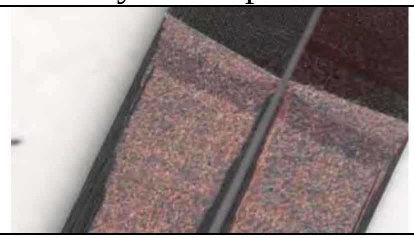
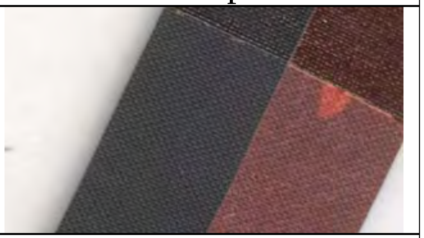
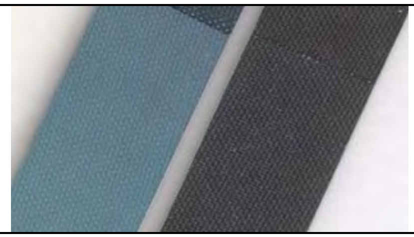
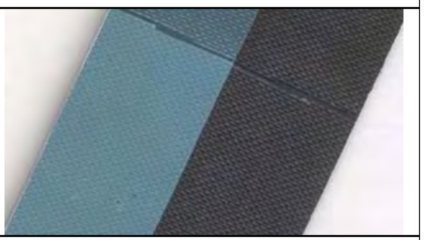
Composite surface after removal of:





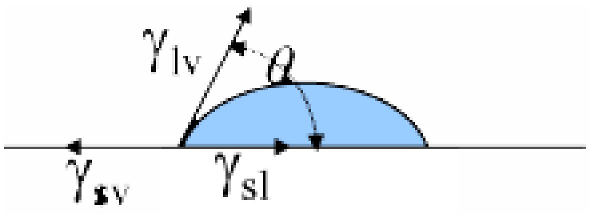


Task 1: Peel Ply Material Type

	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

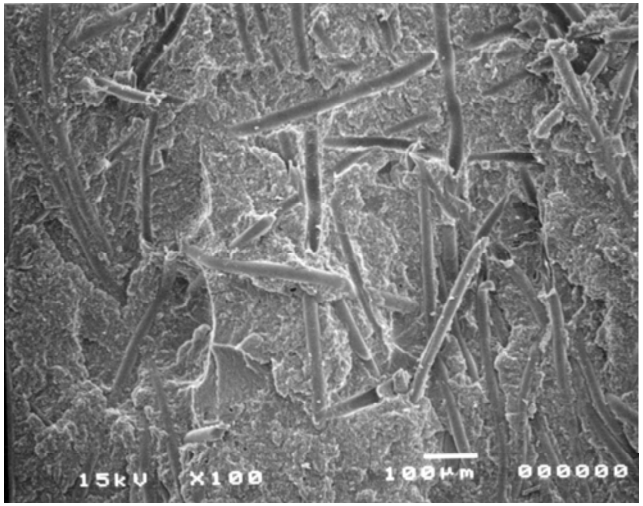
G_{IC} and H_2O Contact Angle do not always correlate

- G_{IC}: Polyester >>Nylon> SRB
- Contact Angle: Nylon < Polyester<< SRB

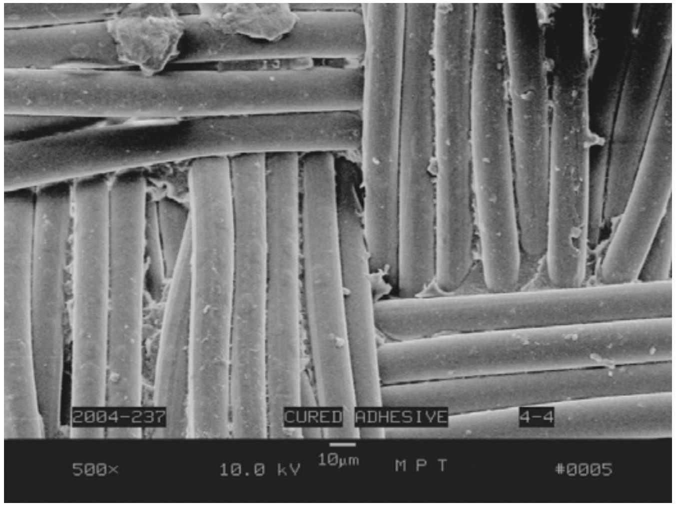


Fractography

- Cohesive failure - in adhesive layer
- Adhesion failure - at adhesive/adherend bondline
- SRB and Nylon/MB1515-3 clearly adhesion failure



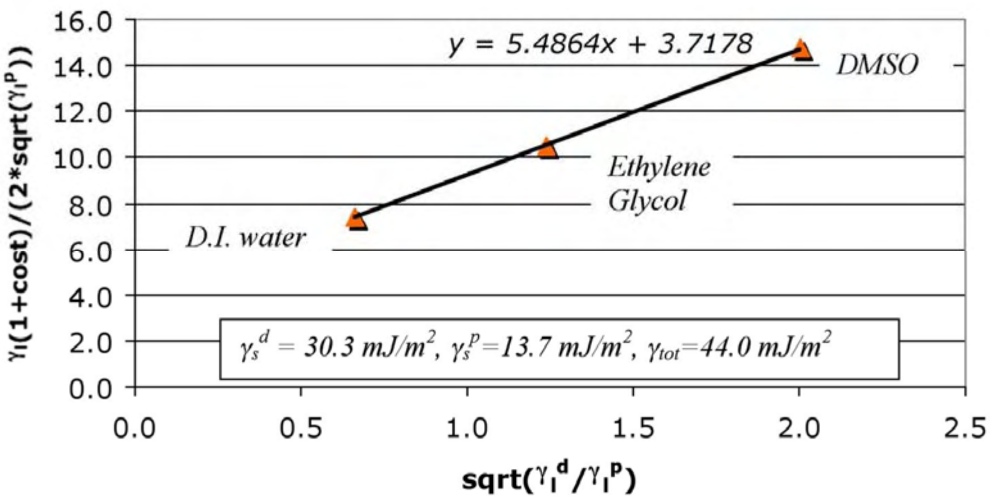
Cohesive Failure



Adhesion Failure

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: $\sqrt{\gamma_s^p}$



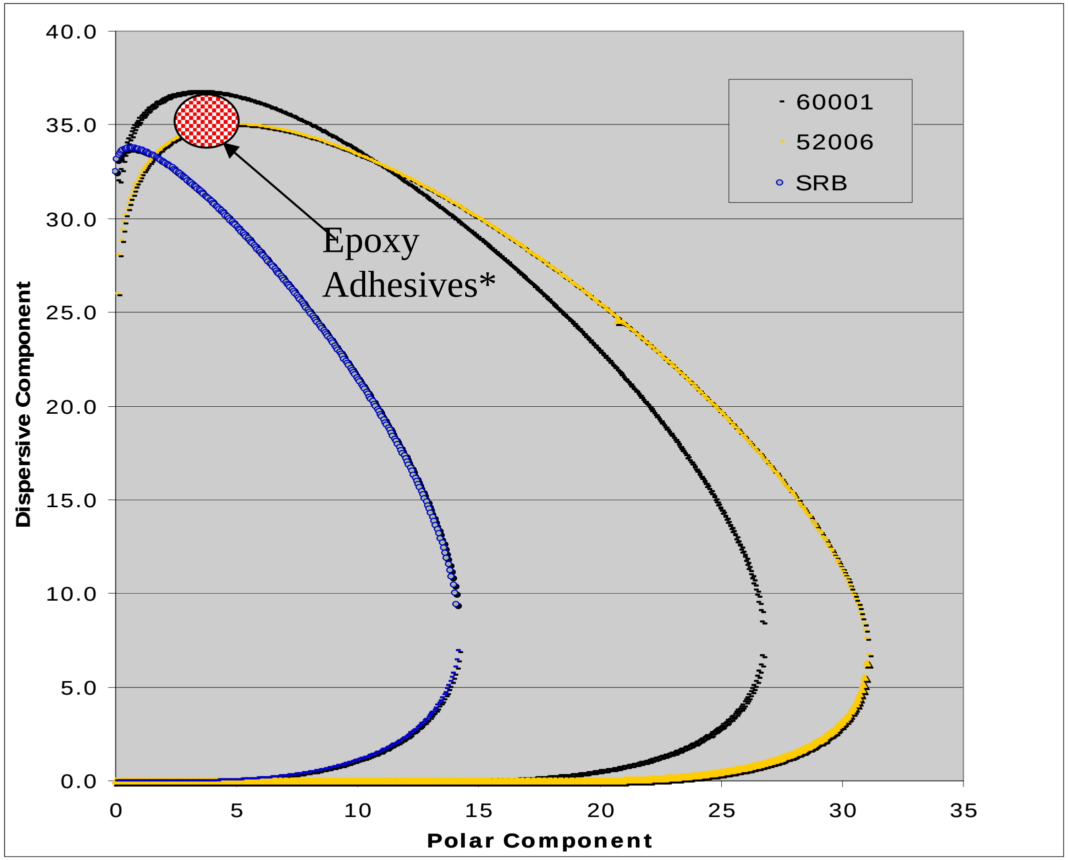
Peel Ply	γ_s^d	γ_s^p	γ_s^{total}
52006	25.0	20.3	45.3
60001	30.3	13.7	44.0

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

- 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

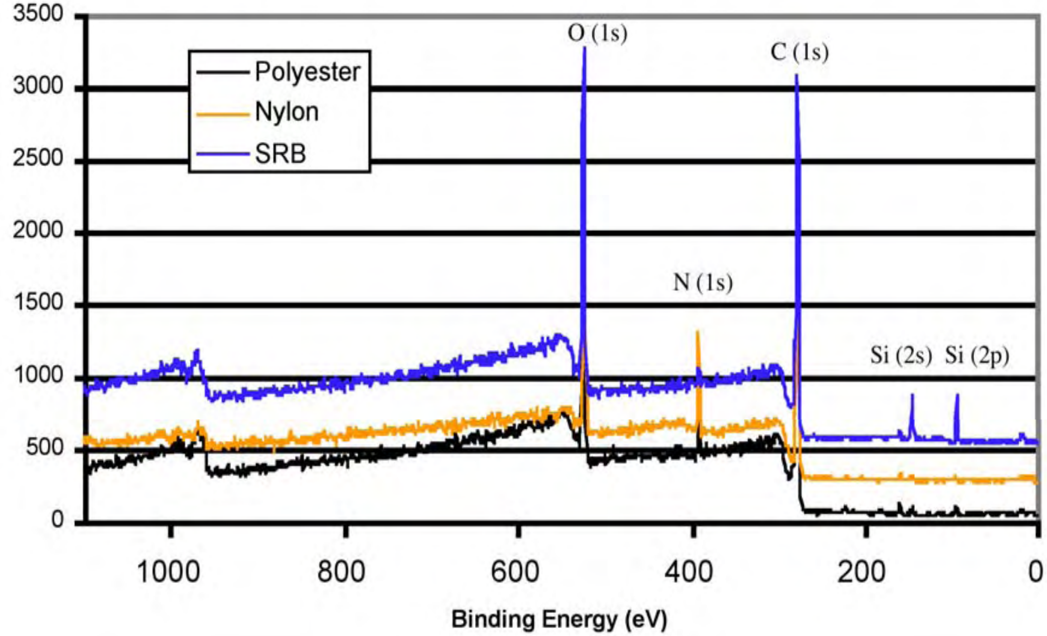


*** Literature values for aerospace epoxies**

- Curves generated using WET program (M. Tuttle)

XPS Survey Scan Results

Laminate surfaces before bonding, after peel ply removal



Laminate Surface Composition

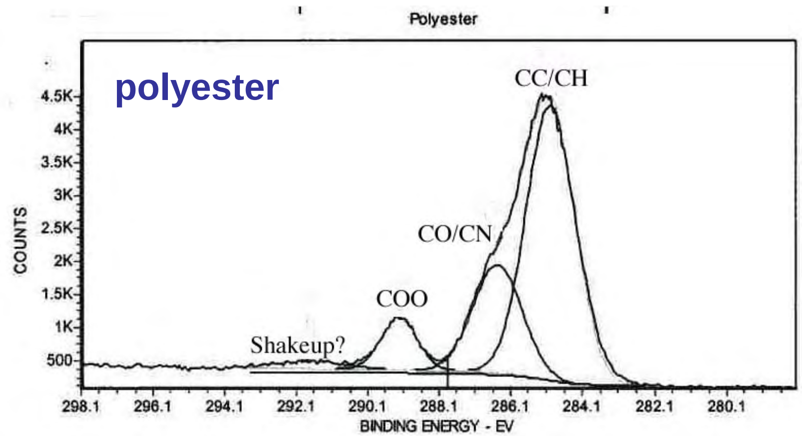
Peel Ply	%C	%O	%N	%Si
Nylon	77.5	12.6	9.8	Tr.
Polyester	75.5	21.6	1.9	Tr.
SRB	68	24.2	0.9	6.9

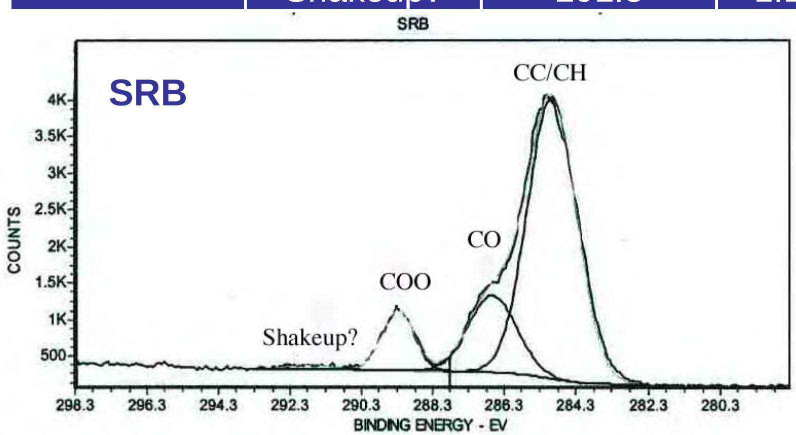
- Si explains SRB low bond quality….Siloxane coating transfers
- Amount of N on nylon peel ply prepared sample surprising

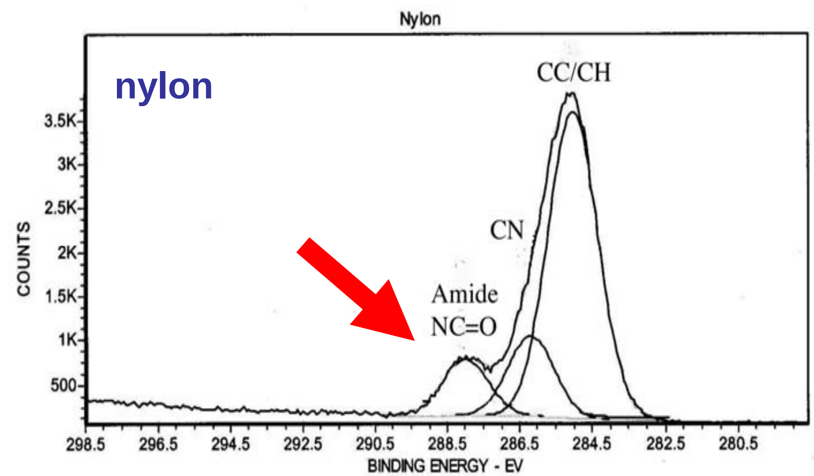
JAMS

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)



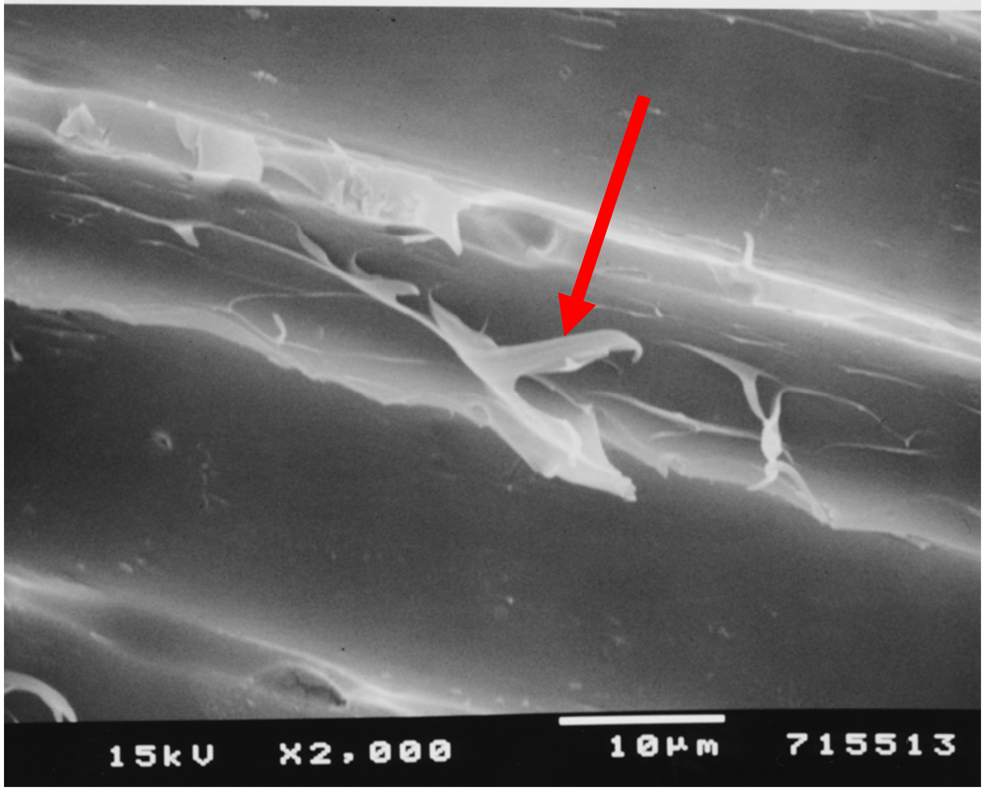




Amide detected on nylon prepared surface- nylon transfer to surface?

A Closer Look at the Laminate Surface

Laminate surface after removal of nylon peel ply



Nylon from peel ply on surface before bonding?

Task 1: Conclusions-Phase I

Peel Ply Material

- Polyester: high toughness bonds, cohesive failure
- SRB: very low toughness, adhesion failure
  - Due to silicon on surface
  - Siloxane coating does transfer
- Nylon: low toughness, adhesion failure–MB1515-3
  - Significant nitrogen, amide groups, detected
    - May have contributed to the poor bond quality
    - Further investigation needed
      - » Chemical or mechanical transfer?
- $H_2$0 Contact angle did not correlate well with G_{IC}
- Wettability envelopes more accurate

Task 1: Peel Ply Material

- Work in Progress
  - Secondary Ion Mass Spectrometry on Nylon
    - Provide spatial and molecular information
    - Mechanical or chemical transfer from nylon
  - More contact angle measurements
    - High temperature contact angle measurement
    - Surface energy of adhesives
  - Apply to different composite systems
    - (Phase II)

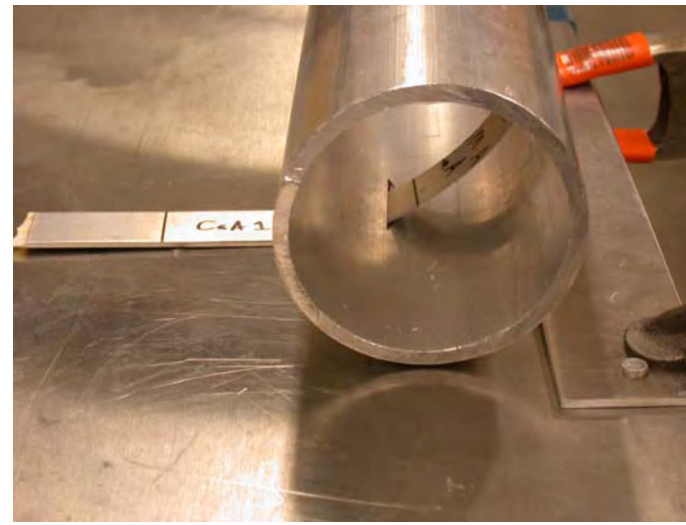
Task 1: Peel Ply Material Different Composite Systems

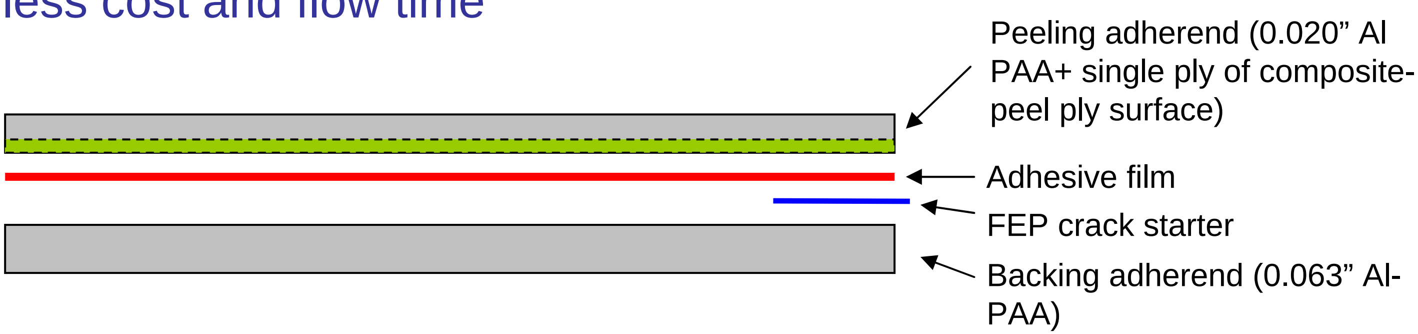
Phase II

- 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
  - Rapid Adhesion Test (RAT) method

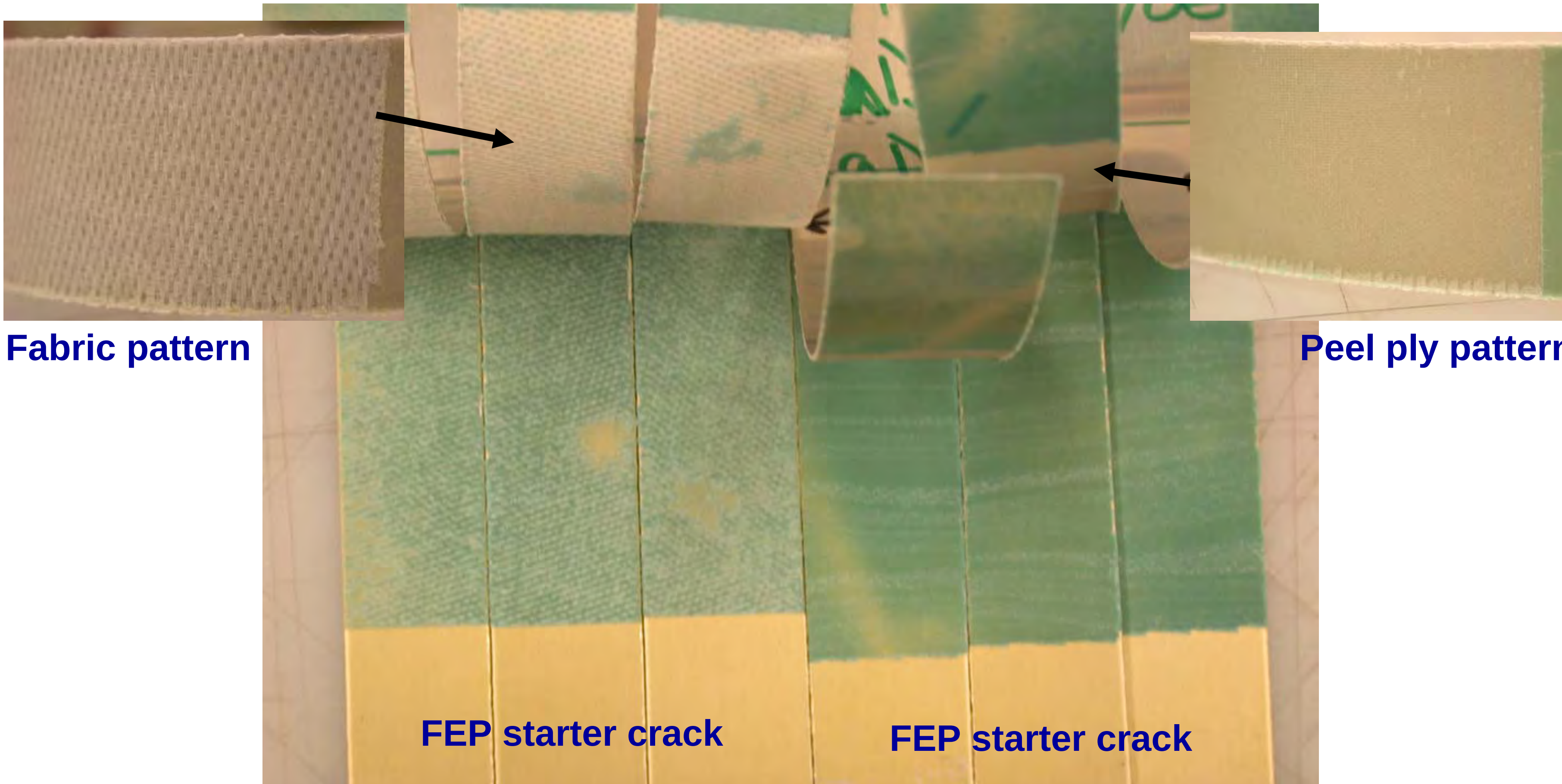
The Rapid Adhesion Test (RAT) Method

- 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)

Task 1: Peel Ply Material

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

Conclusions

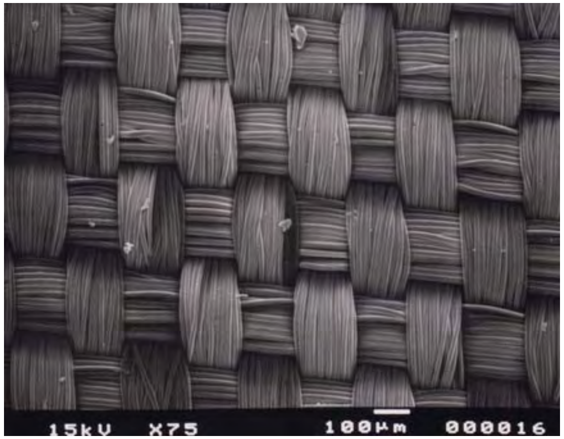
- Task 1: Peel Ply Material-Phase II
  - Polyester: Adhesion Failure
    - Except Cytec FMx209
  - Nylon: Cohesive Failure
  - Opposite results from Phase I: BMS8-279
  - Wettability envelopes may provide explanation

Task 2: Peel Ply Texture

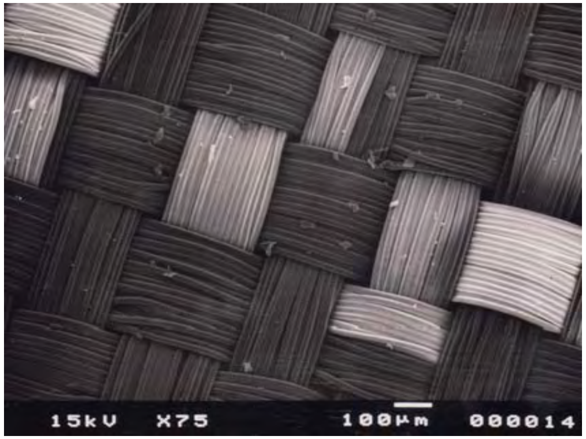
- Laminates produced with 9 different peel plies
  - 4 polyester and 5 nylon peel plies
  - Surface characterization: SEM, profilometry, contact angle
  - Bond quality: Measure with G_{IC}

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	

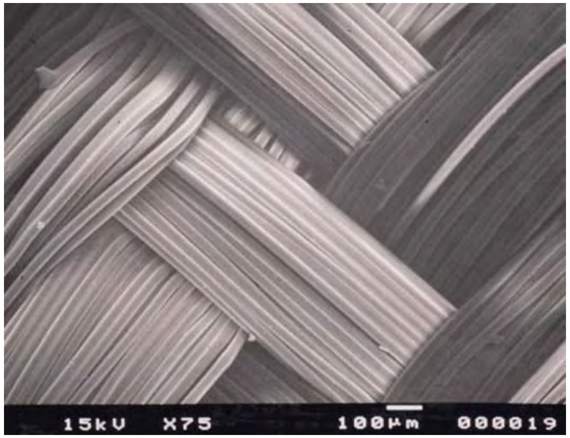
SEM's of As-Received Peel Plies



Fine 160 x103
(PF 52006)



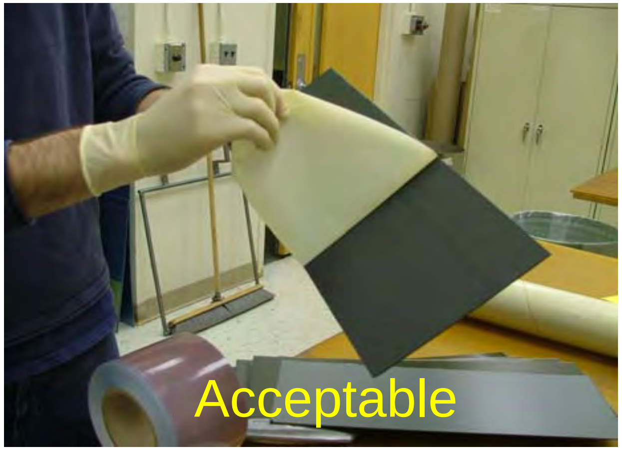
Medium 101 x 82
(PF 52008)

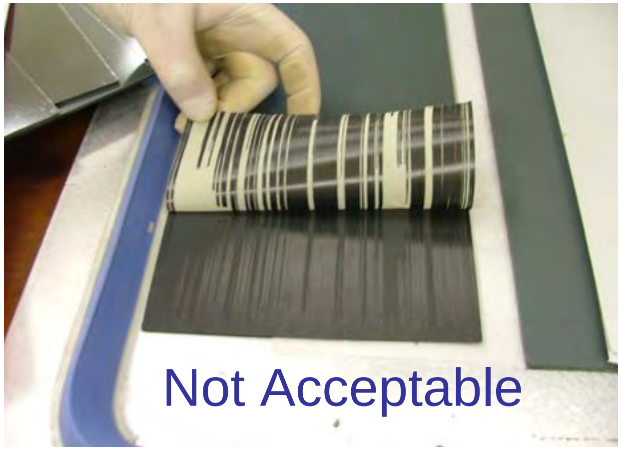


Coarse 60 x 50
(PF 52000)

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

Peel Ply Removal (?)



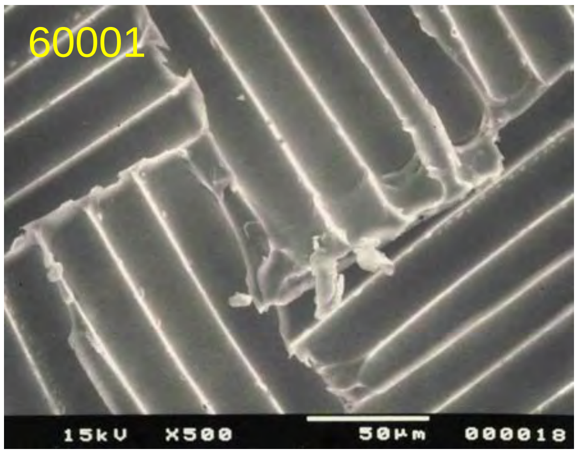


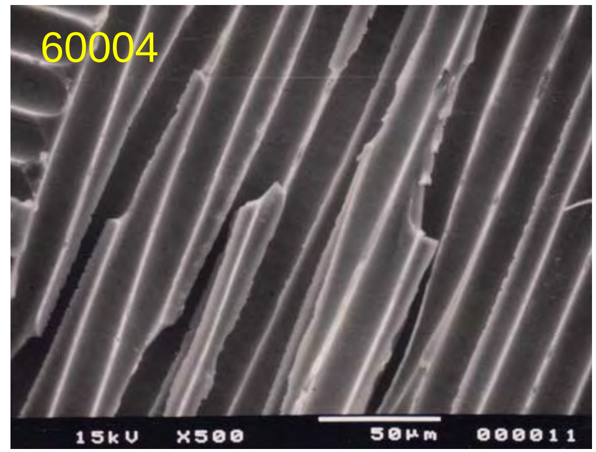
Task 2: Peel Ply Texture

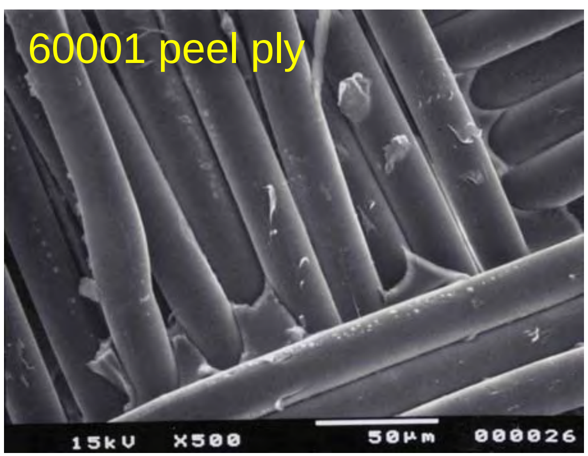
- All polyester peel plies successfully removed
- Nylon peel plies were more difficult to remove
  - Fine weaves were removed without damage
  - Coarse weaves have not been removed without damage to laminate (3 attempts, different technicians)

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

Task 2: Peel Ply Texture

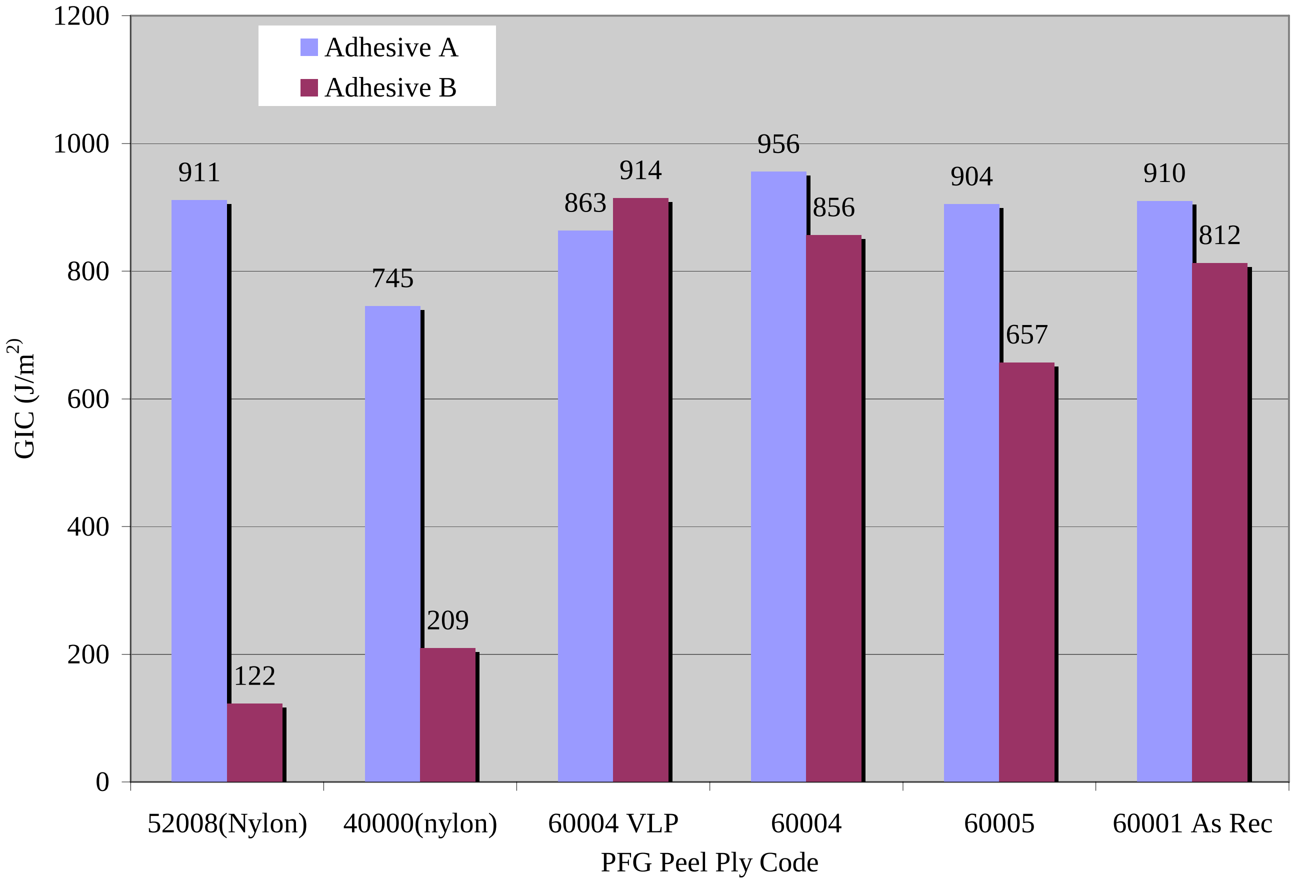






- Comparison of surfaces and polyester peel plies

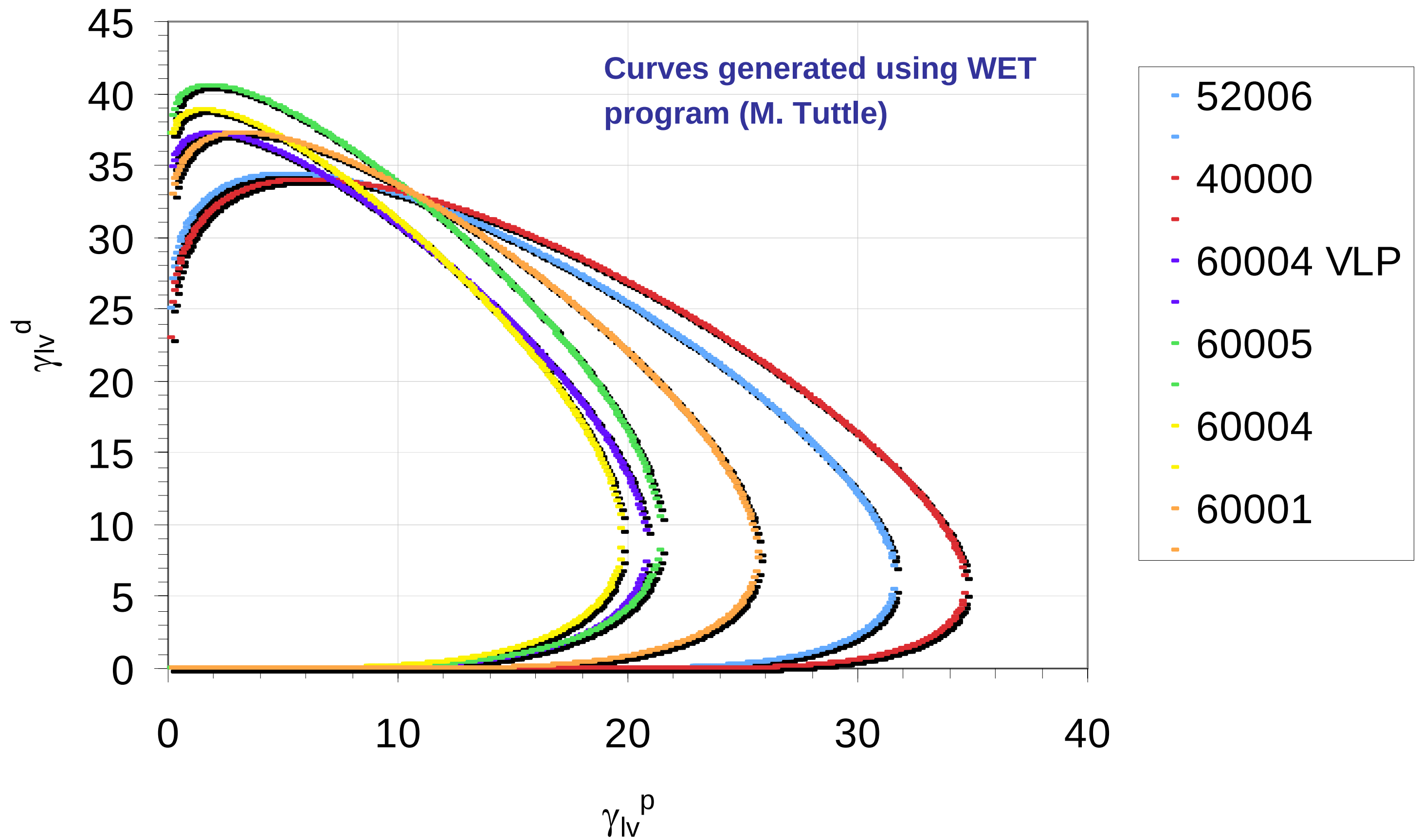
Task 2: Peel Ply Texture



- Peel ply texture does not seem to affect bond quality

Task 2: Peel Ply Texture

- Wettability Envelopes



Task 2: Conclusions

Peel Ply Material and Texture

- Polyester peel plies easy to remove
- 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}

Task 3: Peel Ply Moisture

Is bonding surface effected by “wet” peel ply?

(monsoon season in Japan)

No specifications on moisture content of peel ply

- Characterize moisture uptake of peel plies
- Prepare coupons using 60001 peel ply with various conditioning (moisture content)
- Characterize peel ply and composite surfaces
- Measure bond performance
- Fractography

Task 3: Peel Ply Moisture

- Saturation of polyester peel ply 60001
  - Dried peel ply
  - Soaked at 80°F/90% RH and 140°F/95% RH
  - Measured mass change at 0.5,1, 2, 4,and 18 hours
- No measurable weight change at 80º F/90% RH
- 25% weight gain at 140º F/95% RH after 0.5 hours, no change at longer times
- Laminates produced with dry and saturated peel plies, bonded with AF555

Task 3: Conclusions

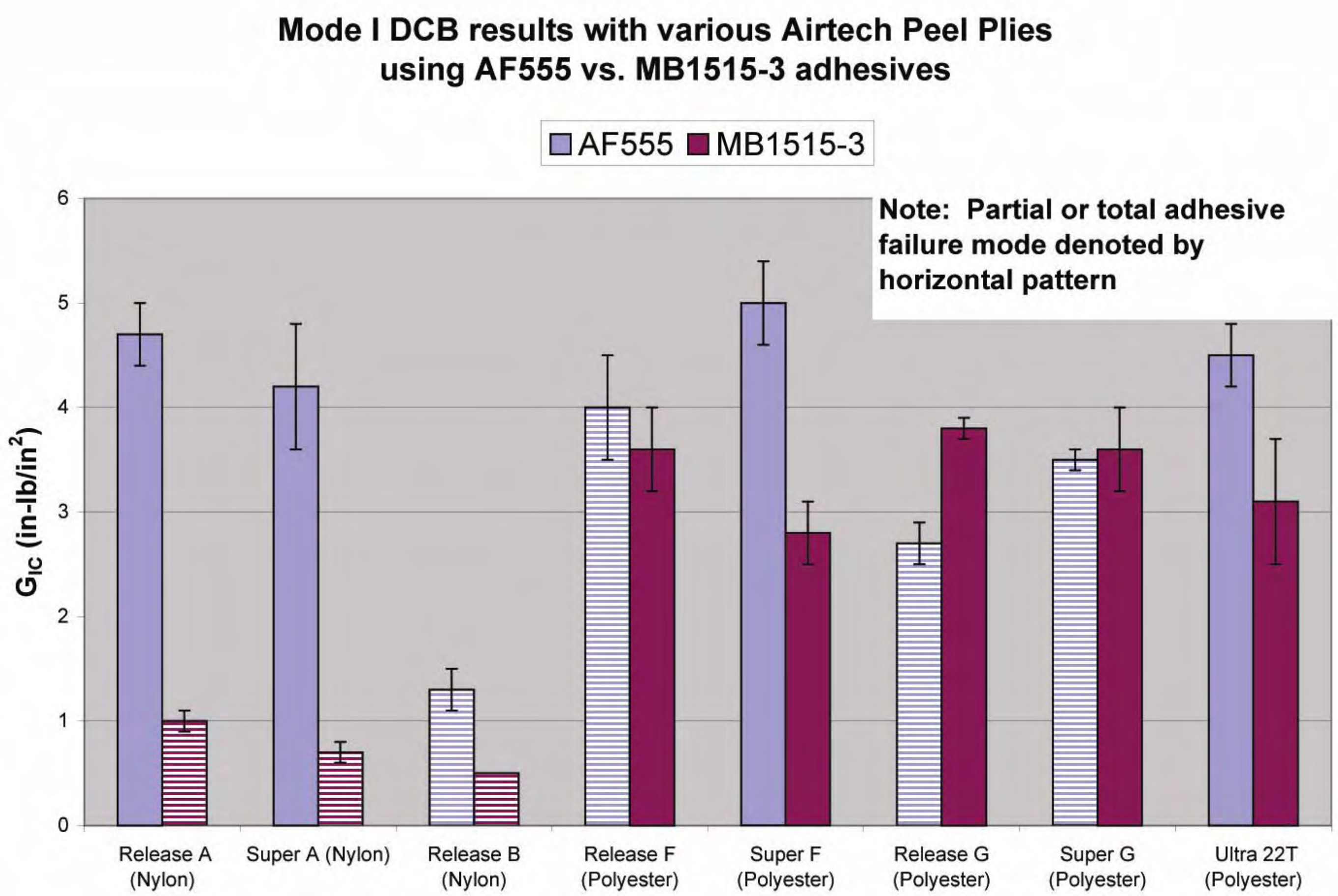
Peel Ply Moisture

- 60001 peel ply
  - No weight gain at 80º F
  - 25% weight gain at 140º F
- No detectable effect on surface chemistry
- Similar G_{IC} values with AF555 adhesive
- Cohesive failure in all samples

Task 4: 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

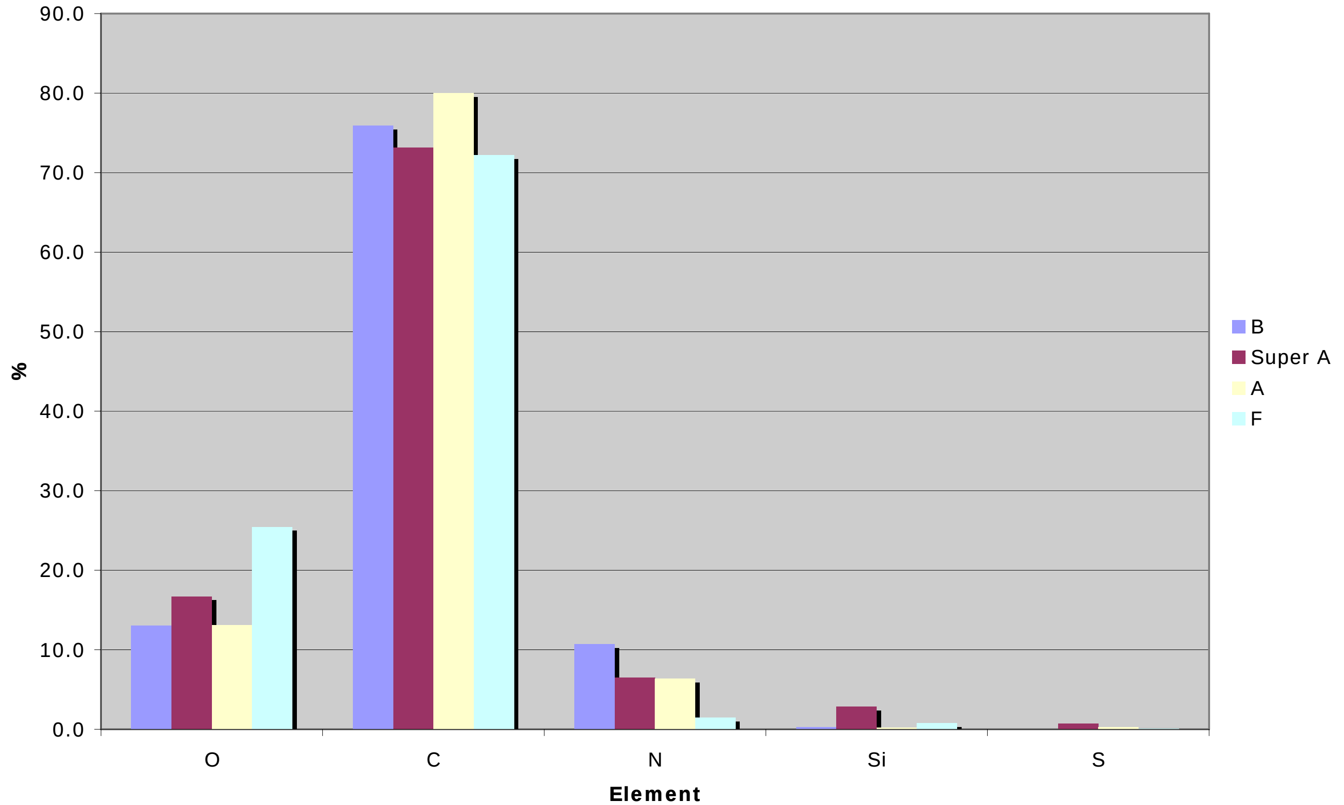
Peel Ply Material Source



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

Peel Ply Material Source

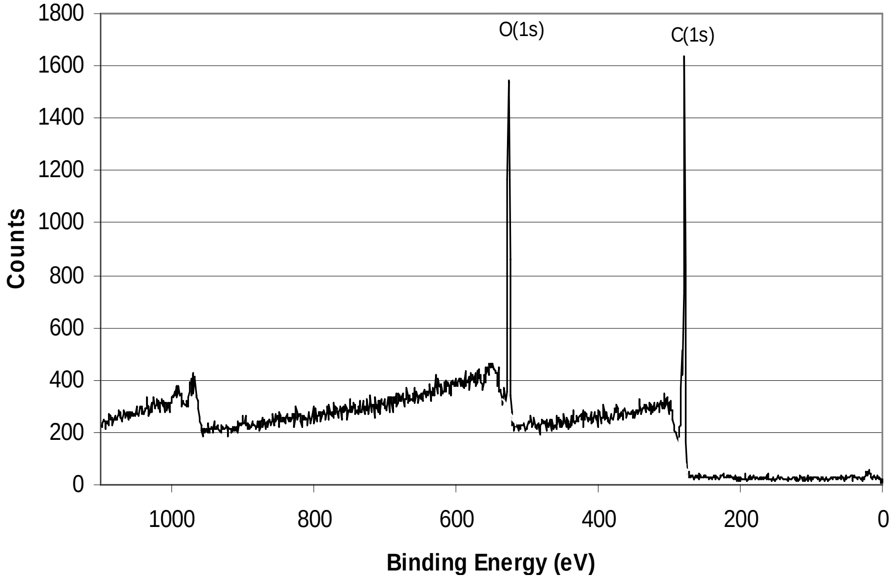
- XPS on Laminates Cured with Different Airtech peel plies



- **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

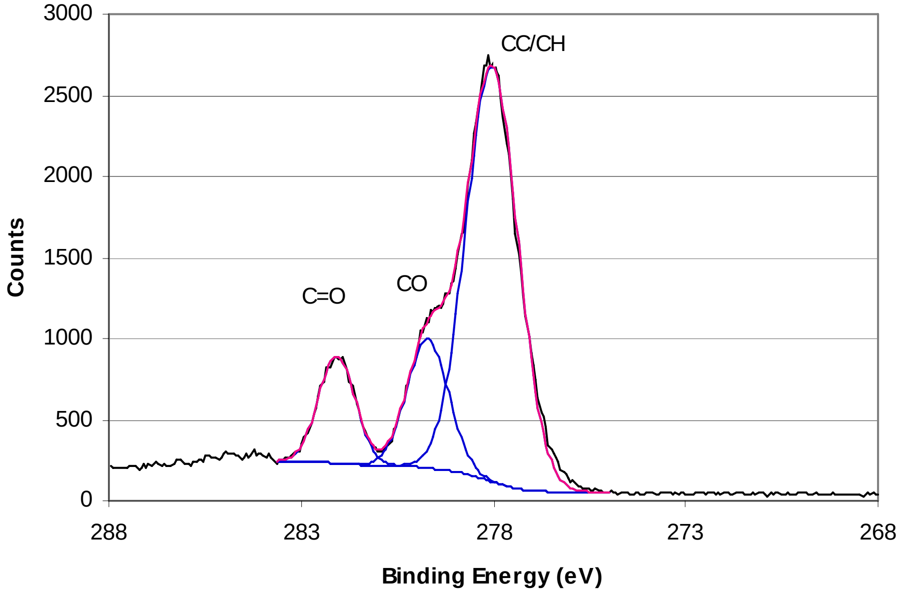
Peel Ply	Ply		C	O	N	
	60001	Mean	73.5	26.5	0.0	
		Stand Dev	0.9	1.0	0.0	
	Ply F	Mean	73.4	26.3	0.3	
		Stand Dev	0.6	0.4	0.1	
Laminate			C	O	N	S
	60001	Mean	74.8	22.5	1.8	
		Stand Dev	0.8	1.0	0.1	
	Ply F	Mean	73.2	24.1	1.5	1.1
		Stand Dev	1.3	0.9	0.2	0.6

Summary of composition scans

Peel Ply “F” close match to Precision 60001

Peel Ply Material Source

XPS on Laminates Cured with Airtech and PFG polyester peel plies



Typical High resolution scan on C(1s)

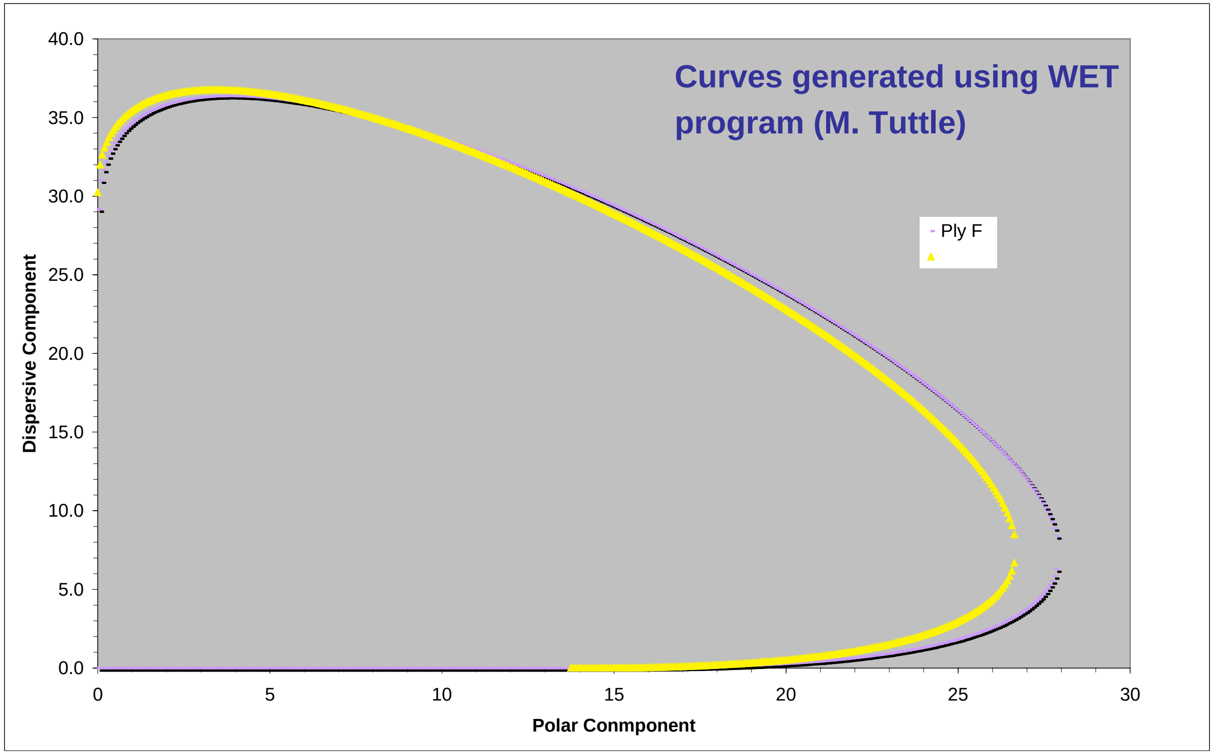
Unused Peel Ply	Ply	Species	BE	%
	Ply F	CC/CH	285	67.1
		CO	286.7	15.7
		C=O	288.9	15.9
	60001	CC/CH	285	61.4
		CO	286.5	20.7
		C=O	288.9	16.5
Laminate	Ply F	CC/CH	285	72.4
		CO	286.6	17.9
		C=O	289.1	9.6
	60001	CC/CO	285	74.5
		CO	286.7	15.7
		C=O	289	9.9

Summary of High resolution scan on C(1s)

- **Peel Ply “F” closest 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**

Task 4: Conclusions

Peel Ply Source

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

Work In Progress

– Task #5: Does the degree of cure of laminates affect bond behavior?
  - Analyzing cure model to guide curing conditions
  - Materials received, samples being processed

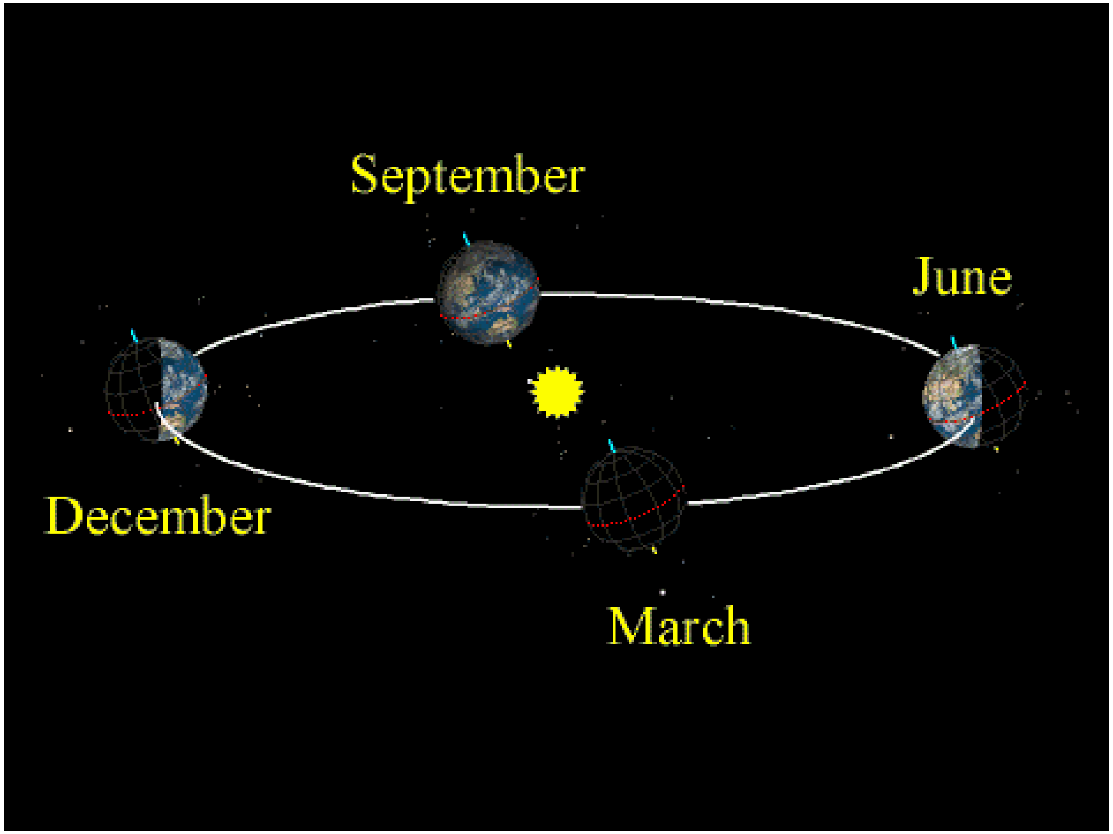
– Task #6: Does bonding of laminate surfaces prepared with dry peel plies vs. pre-impregnated peel plies differ?
  - Materials received, samples being processed

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
  - Mechanism of transfer from nylon peel ply
  - Peel ply-resin interactions
  - Applicability to other composite systems
  - Applicability to other adhesives

Task 7: Welcome Summer



SUMMER SOLSTICE!

Seattle: Sunrise 5:11AM Sunset 9:11 PM