Improving Adhesive Bonding of Composites Through Surface Characterization

(of Peel Ply Prepared Surfaces)

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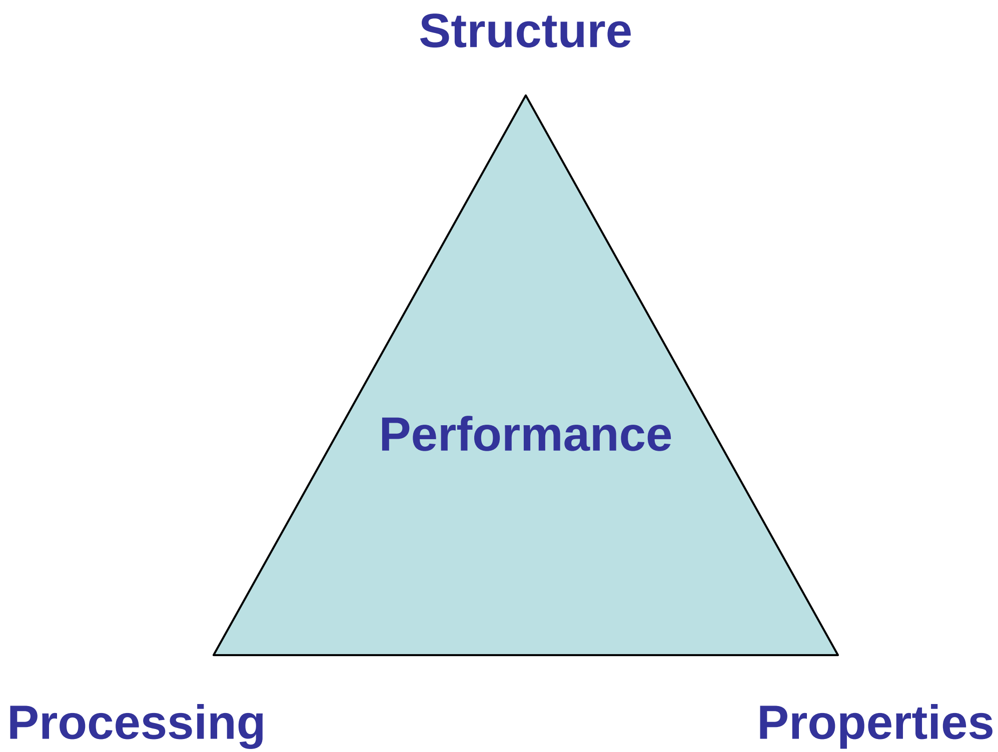
The Joint Advanced Materials and Structures Center of Excellence



The Materials Tetrahedron

Improving Adhesive Bonding of Composites Through Surface Characterization

- Motivation and Key Issues
  - Peel ply surface preparation is being used for bonding primary structure in 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 requirements for peel ply surface preparation to produce strong primary structural composite bonds with different substrates and adhesives

- Approach
  - Investigate the effect of various peel-ply and prepreg material systems on the adherend surface chemistry/structure and subsequent bond performance
  - Prepreg Materials:
    - Glass Fiber Epoxy 127º C (260 º F)
    - Carbon Fiber Epoxy 176º C (350 º F)
    - Peel Plies: Dry and Preimpregnated Nylon and Polyester
    - Adhesives 127º C (260º F) and 176º C (350º F)
  - Characterization
    - Surface chemistry, SEM, 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.)
  - Jeff Satterwhite (Masters student, U of Wa.)
- FAA Technical Monitor
  - Curt Davies (Peter Shyprykevich, Retired)
- Other FAA Personnel Involved
  - Larry Ilcewicz
- Industry Participation
  - Boeing: Peter Van Voast, William Grace, Paul Shelly
  - Precision Fabrics Group, Cytec, Toray, 3M, Henkel, Yokahama
- JAMS Participation
  - Mark Tuttle: Technical Discussions, 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

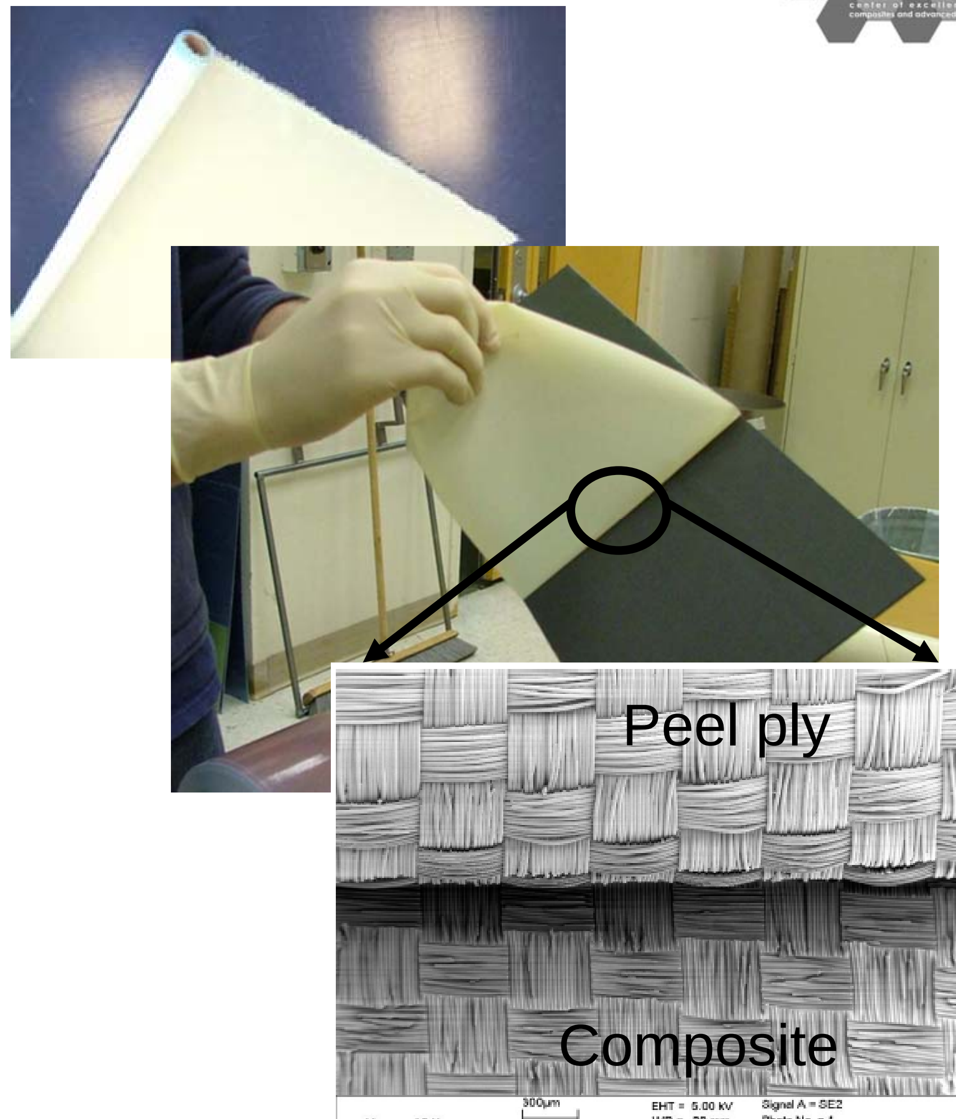
Surface preparation is a key ingredient
to most successful adhesive bonding applications

Background

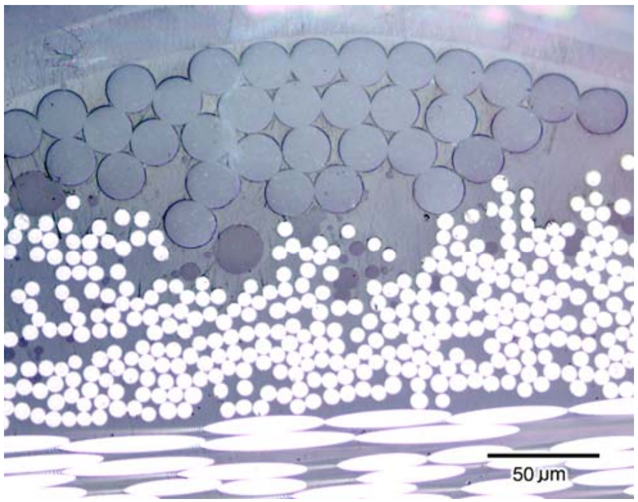
- John Hart-Smith- *Curse of the Nylon Peel Ply*
- Bardis and Kedward showed peel ply was not an effective method for some resin systems-adhesion failure, low fracture energy.
- Previous research on carbon fiber reinforced epoxy prepreg, BMS8-276 (177° C; 350° F) cure showed
  - Polyester peel-ply prepared surfaces produced good bonds
  - Nylon peel-ply prepared surfaces did not bond well
  - Remnants of nylon peel-ply found on surface (SEM, XPS)
- This research:
  - Glass fiber epoxy prepregs: BMS8-79 (127° C; 260° F) cure
  - Carbon Fiber epoxy prepregs: BMS8-256 and Toray 3631 (177º C)
  - Nylon and polyester peel plies (dry and preimpregnated)
  - Various film adhesives

Peel Ply Surface Preparation

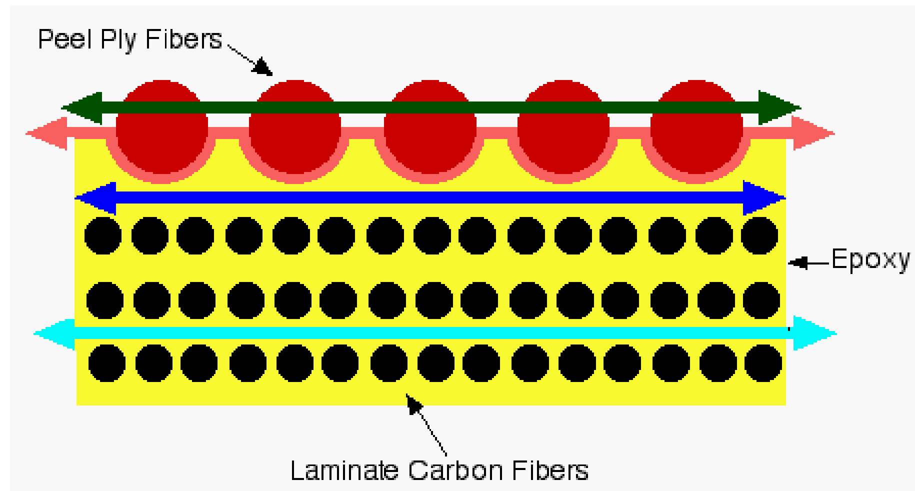
- Peel Ply-Woven fabric
  - Typically thermoplastic polymer
  - Placed on surface during layup
- Cured with the part – matrix resin infiltrates peel ply weave
- Removed just before bonding
- Ideally Leaves rough, clean, chemically active surface
- Benefits:
  - straightforward
  - consistent
- If only they always worked!



Peel Ply Surface Preparation



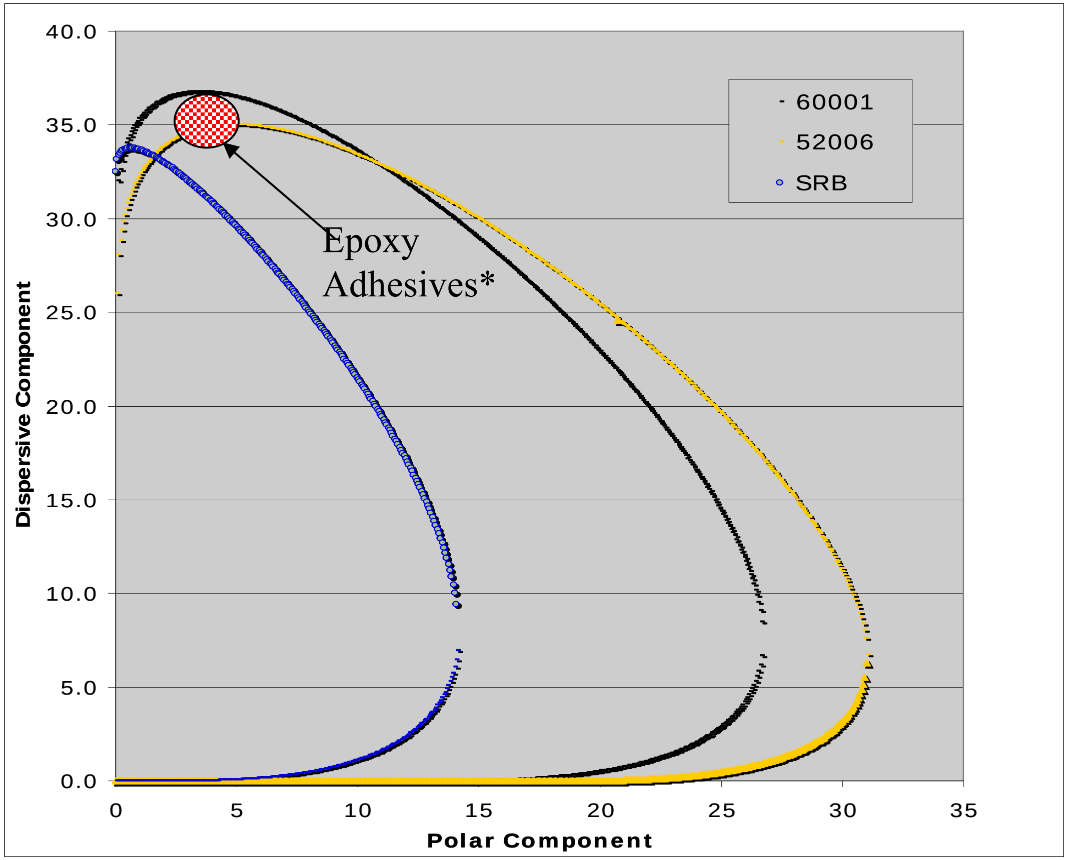
Fracture Possibilities Upon Peel Ply Removal



- 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

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



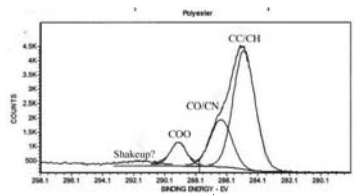
*** Literature values for aerospace epoxies**

- Curves generated using WET program (M. Tuttle)

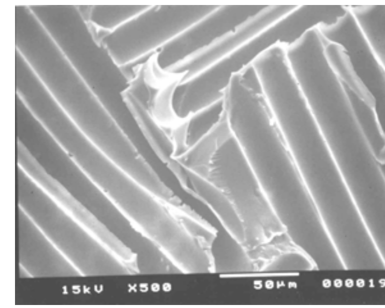
Samples were produced with standard composite processes and characterized

Autoclave Cure

Peel ply removed before bonding

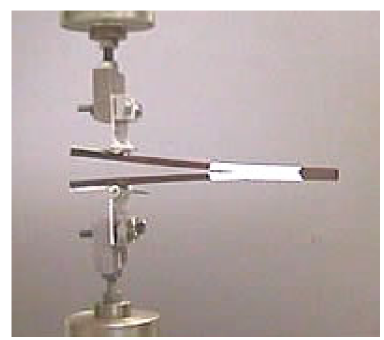


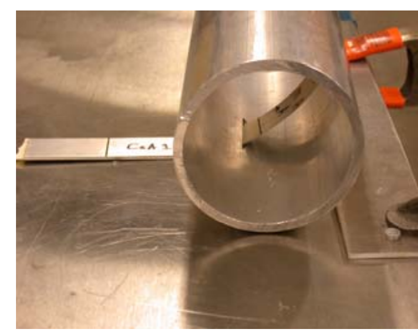
Characterization Via XPS,SEM,Contact Angle



Bonded with film adhesive

Autoclave Cure

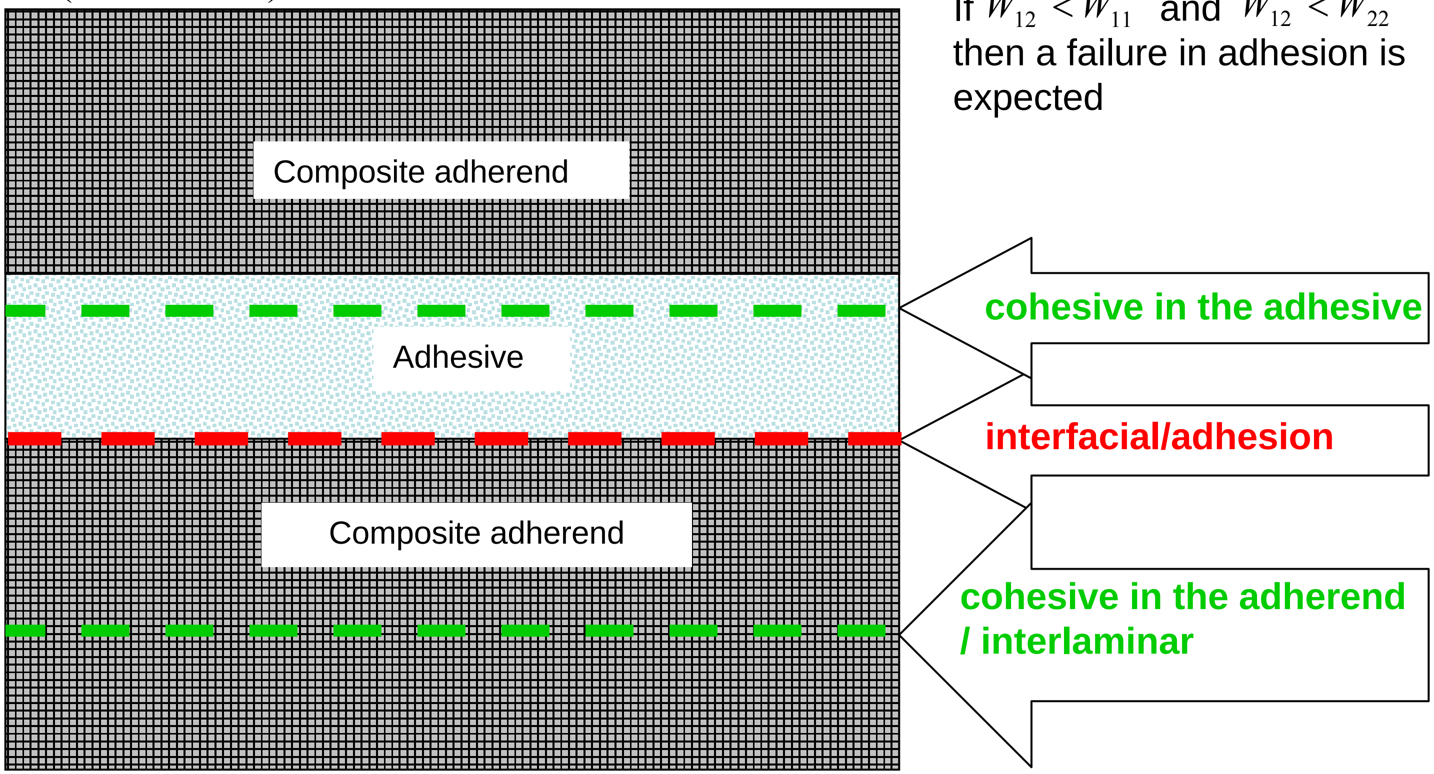




Mode I testing

Adhesive Bond Failure Modes

(not to scale)

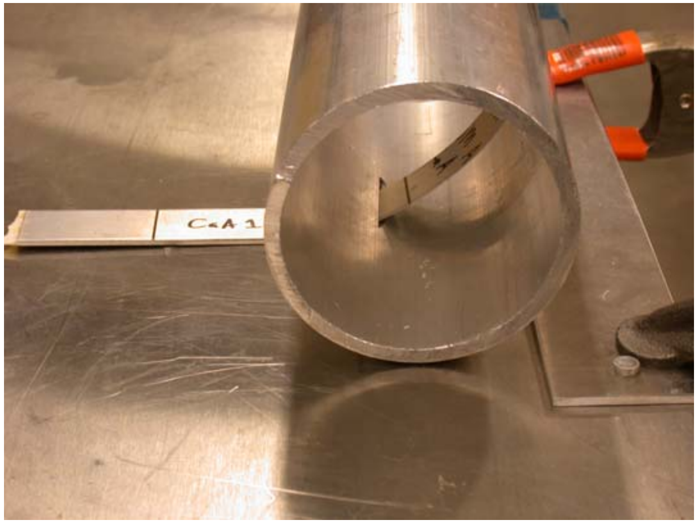


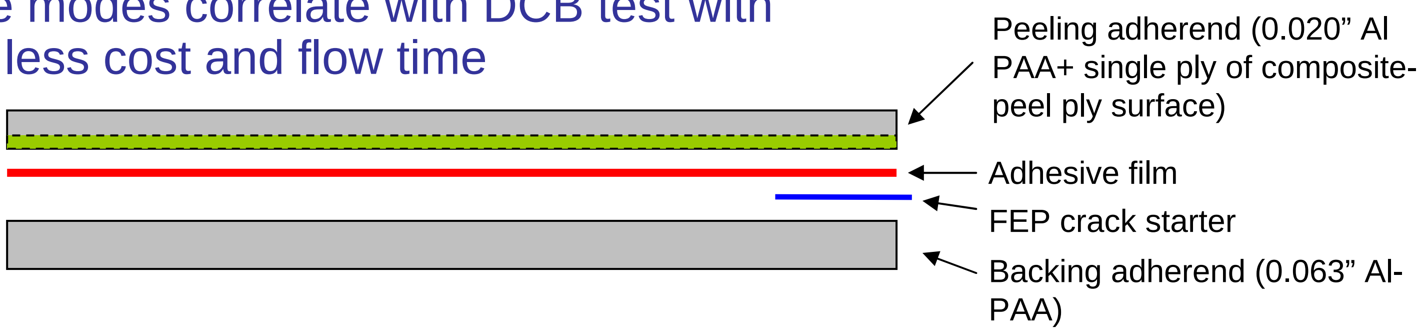
If $W_{12}^{A} < W_{11}^{C}$ and $W_{12}^{A} < W_{22}^{C}$ then a failure in adhesion is expected

Failure modes for adhesive bonds: cohesive/interlaminar or adhesion

The Rapid Adhesion Test (RAT) Method

- A quick, low cost test which assesses the adhesion between metal-composite bonds.
- Failure typically in composite-adhesive not metal-adhesive, therefore evaluates composite bond quality
- 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

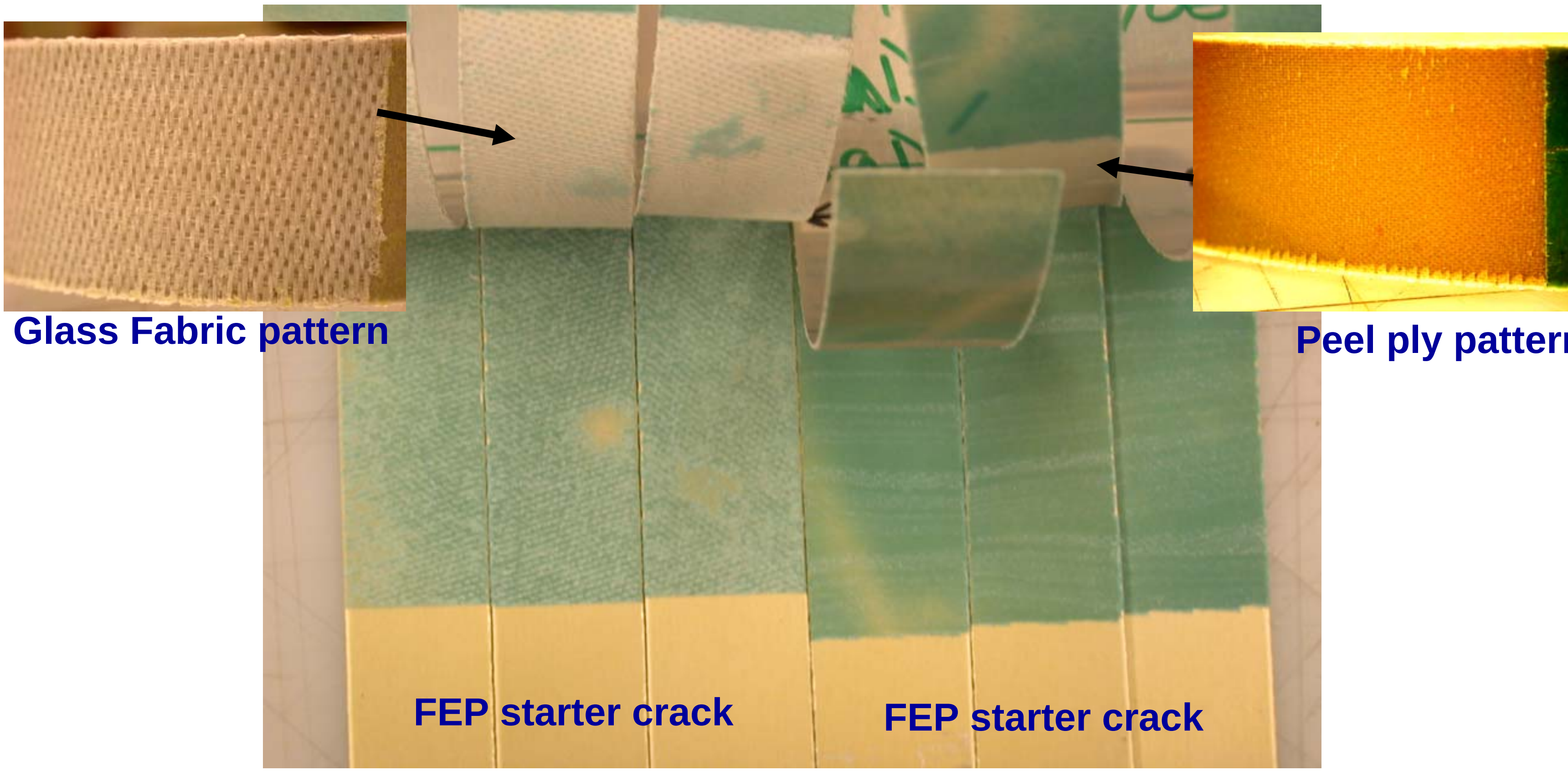




Rapid Adhesion Test (RAT)

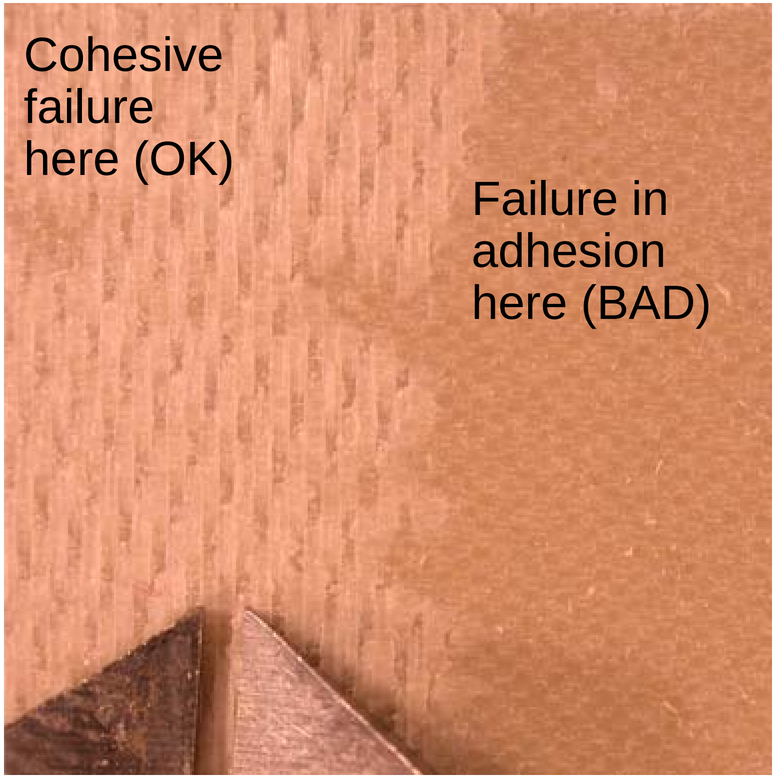
- RAT was created at Boeing as an easy, fast qualitative measure of bonding
- Mode I test
- Intended for screening out poor adherend-adhesive-surface prep combinations
- Found to have a qualitative agreement with DCB testing in terms of mode of failure
  - Cohesive / interlaminar failure: acceptable
  - Adhesion failure (failure at the adherend-adhesive interface): BAD!
- A tenth of the cost & time for DCB testing

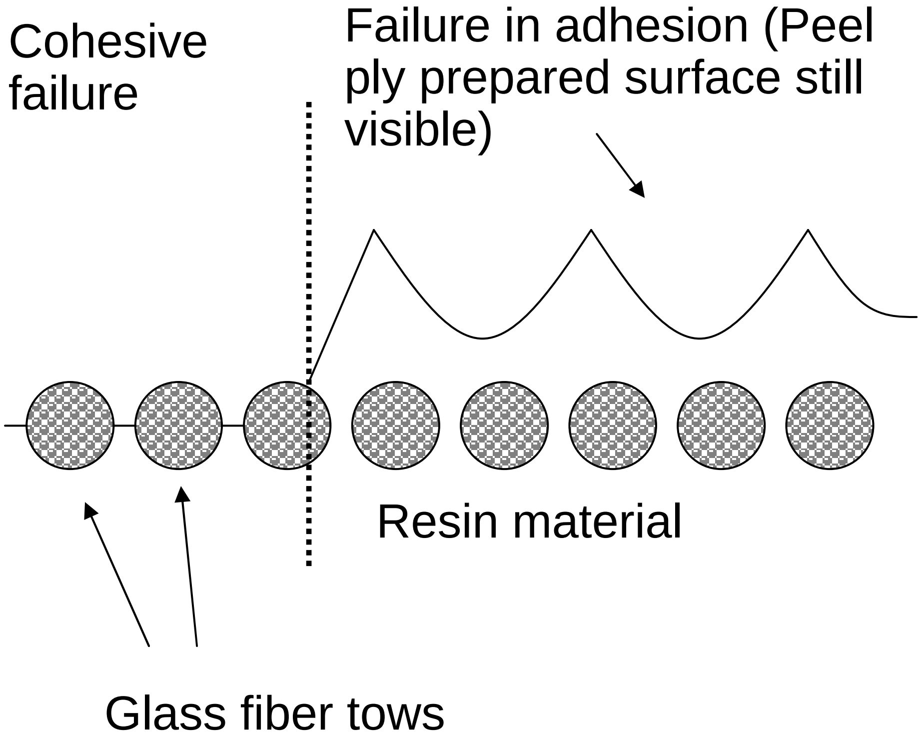
RAT Method Assessment



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

Rapid Adhesion Test (RAT)





Mixed failure mode of RAT specimen (looking at substrate surface after peeling off adhesive); Cytec Cycom MXB 7701/7781 – P 60001 – Cytec FMx209

Task 1 Objectives

Glass Fiber-Epoxy 126º C (260º F)

- The purpose of this task was to evaluate the effectiveness of peel ply surface preparation for adhesive bonding of GFRP
- Compatibility of different commercial prepregs, peel plies and adhesives
- Further fundamental understanding of peel ply surface preparation for adhesive bonding

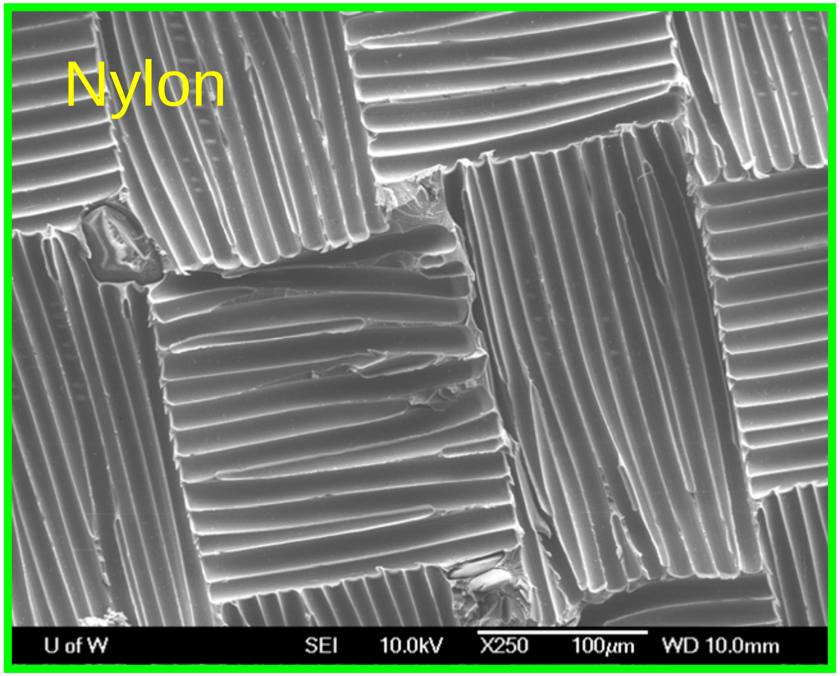
127^{o} C (260^{o} F) Cure Systems

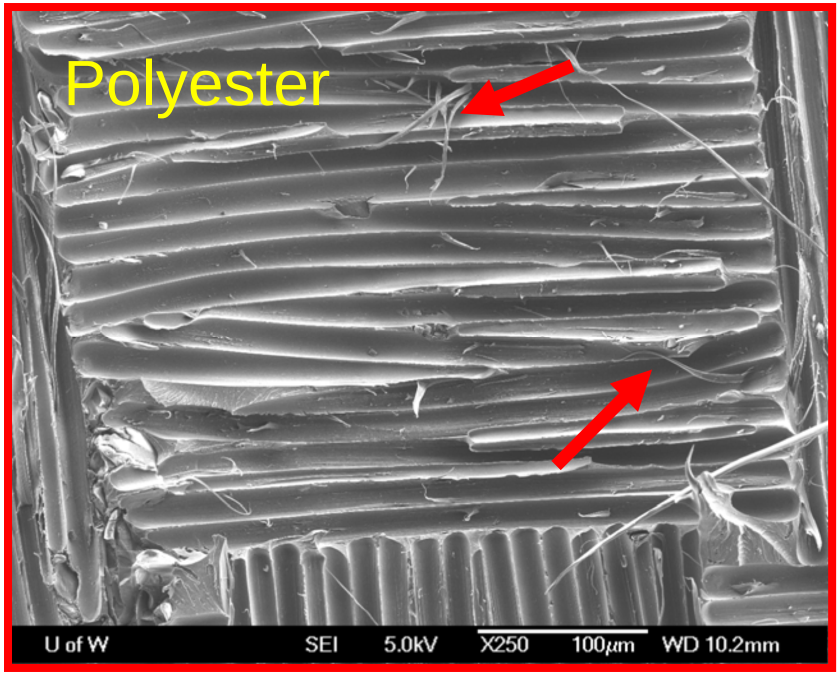
36 combinations (2x3x6)

- 2 Peel Plies: Polyester 60001 and Nylon 52006
- 3 prepregs-260º F cure
  - HexPly® F155
  - Yokohama G7781
  - Cytec MXB7701
- 6 adhesives-260º F 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 Surface Prep. - SEM Results

Composite surfaces after removal of peel ply:





Clean surface

Remnants of polyester peel ply fibers left on surface

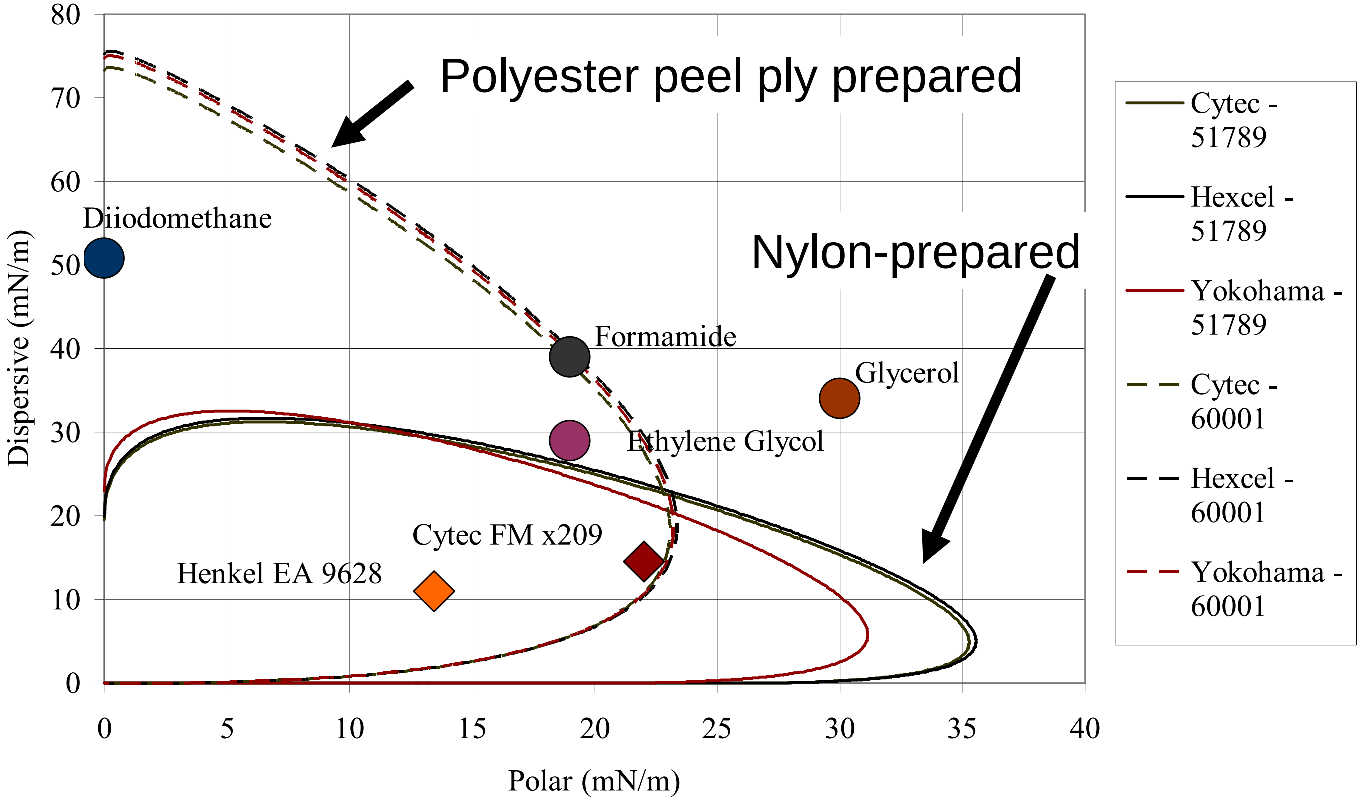
Surface Energy Measurement

Table of surface energies from contact angle data

Substrate with Peel Ply	Surface Energy (mN/m)		
	polar component, γ^d	dispersive component, γ^p	total surface energy, γ
Hexcel 1581-F155 with Nylon 51789	26.7	20.7	47.4
Hexcel 1581-F155 with Polyester 60001	0.7	66.4	67.0
Yokohama F6986 with Nylon 51789	20.2	23.9	44.1
Yokohama F6986 with Polyester 60001	0.5	66.8	67.4
Cytec Cycom MXB 7701/7781 with Nylon 51789	25.1	21.6	46.7
Cytec Cycom MXB 7701/7781 with Polyester 60001	1.3	60.3	61.6
Epoxy (ave. literature value)	34.1	2.6	36.7
Polyester (PET)-(ave. literature value)	4.5	37.9	42.4
Nylon-6,6-(ave. literature value)	33.6	7.8	41.4

- Peel ply type influenced surface energy of composite

Wettability envelopes for peel-ply prepared surfaces



- Fluids inside the envelope will wet spontaneously
  - Critical condition for bonding?
- Epoxy adhesives* on boundary for polyester prepared surfaces

Rapid Adhesion Test Results

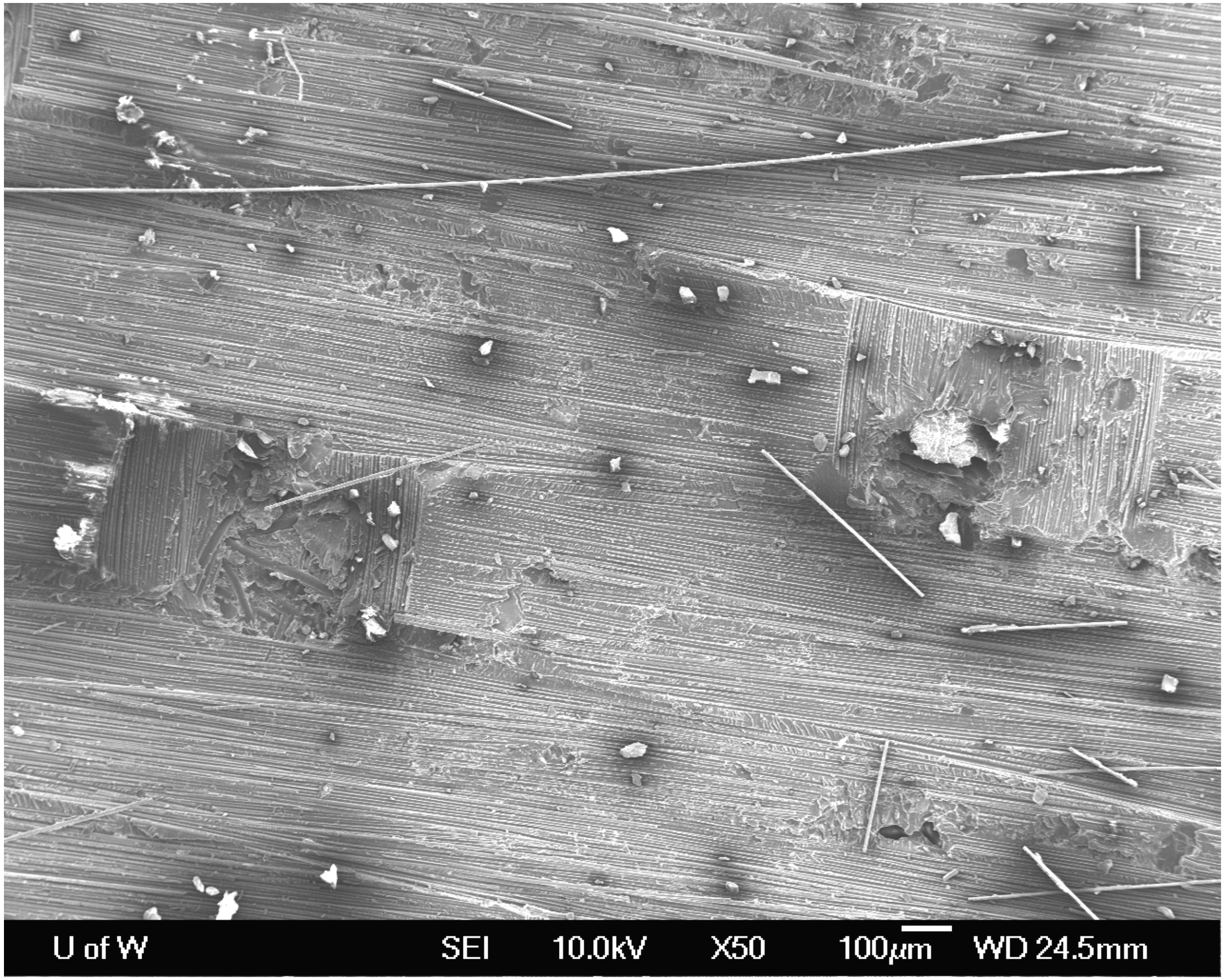
Nylon peel ply (Precision code 51789-52006)

Adhesive	Hexcel 1581-F155	Yokohama F6986	Cytec Cycom MXB 7701/7781
3M AF500	COHESIVE	COHESIVE	COHESIVE
3M AF 163-2M	COHESIVE	COHESIVE	COHESIVE
Cytec FM 94	COHESIVE	COHESIVE	COHESIVE
Henkel Hysol EA 9696	COHESIVE	COHESIVE	COHESIVE
Cytec FM x209	COHESIVE	COHESIVE	COHESIVE
Henkel Hysol EA 9628	COHESIVE	COHESIVE	COHESIVE

Polyester peel ply (Precision 60001)

3M AF500	ADHESION	ADHESION	ADHESION
3M AF 163-2M	ADHESION	ADHESION	ADHESION
Cytec FM 94	ADHESION	ADHESION	ADHESION
Henkel Hysol EA 9696	ADHESION	ADHESION	ADHESION
Cytec FM x209	MIXED	MIXED	MIXED
Henkel Hysol EA 9628	ADHESION	ADHESION	ADHESION

SEM – RAT bond fracture



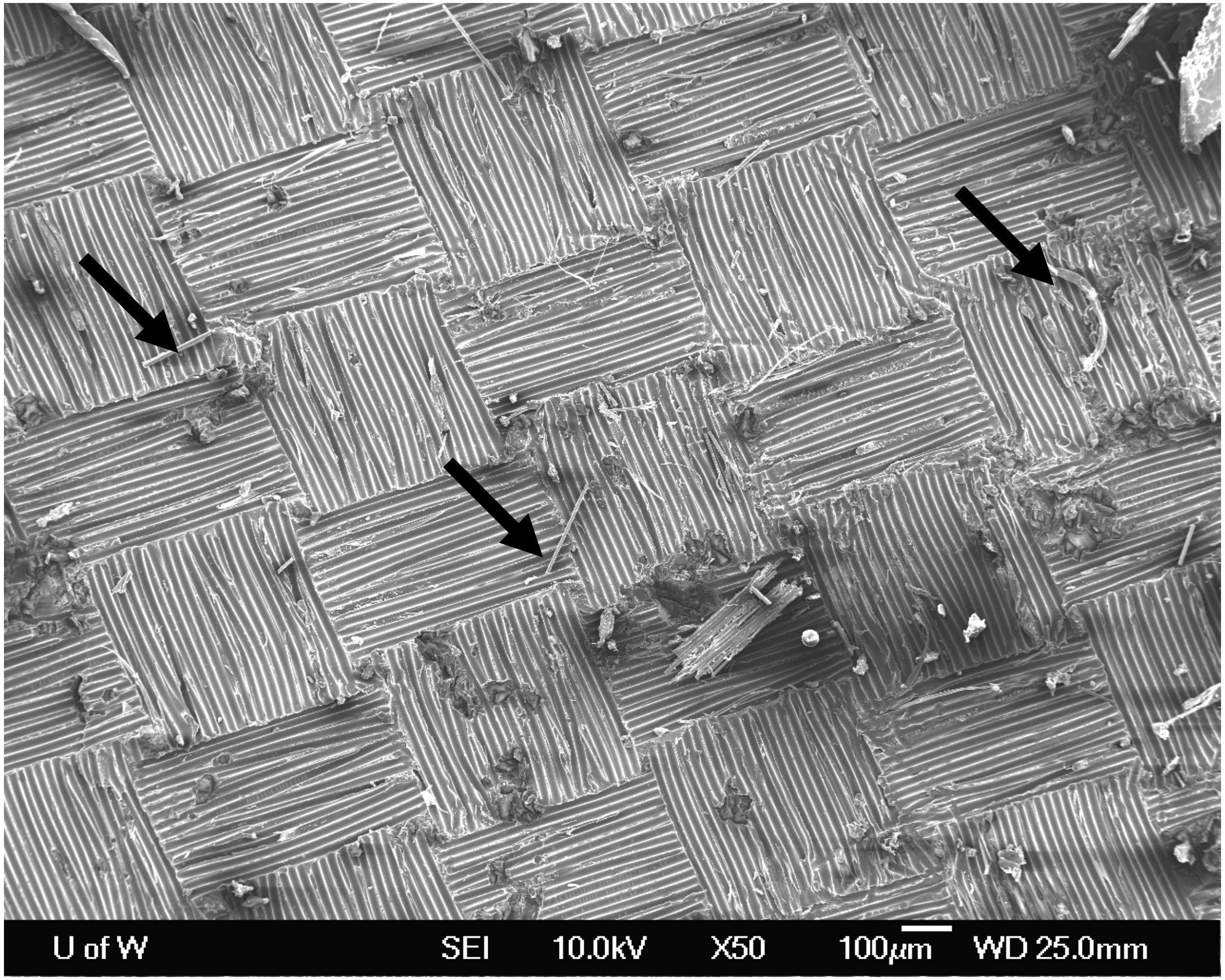
Nylon-prepared surface *after* performing RAT (Cytec 7701/7781, Henkel EA 9628)

=> Good bond

Glass fibers are clearly visible, post-fracture

❖ **Cohesive Fracture in GFRP substrate**

SEM – RAT bond fracture



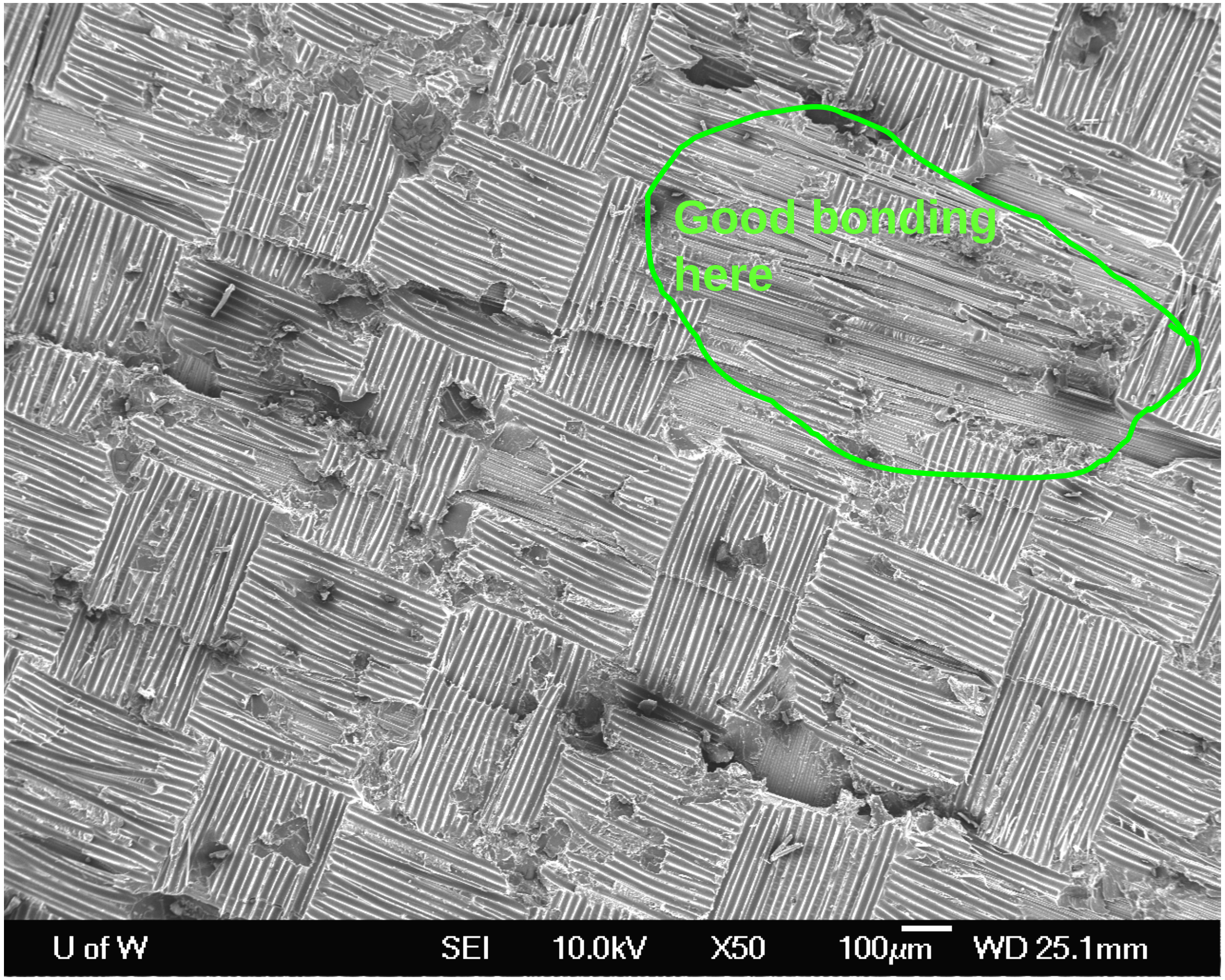
Polyester-prepared surface *after* performing RAT (Cytec 7701/7781, Henkel EA 9628)

=> BAD BOND

Tendrils of peel ply originally left behind seem to be still present

❖ **Adhesion Failure at Bond Line**

SEM – RAT bond fracture



Polyester-prepared surface *after* performing RAT (Cytec 7701/7781, Cytec FMx209)

=> Mixed result

- **Mixed Adhesion(~80%) and Cohesive (~20%)**

Task 1 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 to all surfaces
- Opposite Trend than BMS8-276 (350 F) system
  - Nylon bad, Polyester good
- The wetting envelopes generated for the various prepared surfaces gave no real insight into why polyester was inadequate.
  - Surface energy of polyester surfaces>nylon surfaces
- The SEM surface examination revealed a potential cause of the problem – the polyester peel ply is interacting with the matrix to leave tendrils of material, indicates contamination

Future Work-Task 1

- Investigate fiberglass prepregs with higher temperature cure cycles with nylon and polyester peel plies
- Conduct similar tests using different weaves of peel plies of the same materials
- Determine role (if any) of curing and toughening agents in epoxies
- Examine other surface characterization techniques that may predict poor bonding behavior of the polyester peel ply surfaces

Task 2 Objectives

- Expand study to 2 additional 176º C carbon fiber prepreg systems
- Expand to other peel-plies, including epoxy preimpregnated polyester and nylon (“wet”)
- 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

Task 2-Materials Evaluated

Aerospace carbon fiber-epoxy prepregs

- UD Toray 3631 toughened hot melt epoxy with T-800 fiber
- Cytec-Cycom 970 toughened epoxy and plain weave 3K-70

Aerospace grade film adhesives

- Cytec Metal Bond 1515-3
- 3M AF 555

Peel plies

- Dry polyester – Precision Fabrics 60001 Nat
- Dry nylon – Precision Fabrics 52006/51789 Nat
- Epoxy-preimpregnated polyester – Henkel EA-9895
- Epoxy-preimpregnated nylon – Cytec MXM 7934/52006

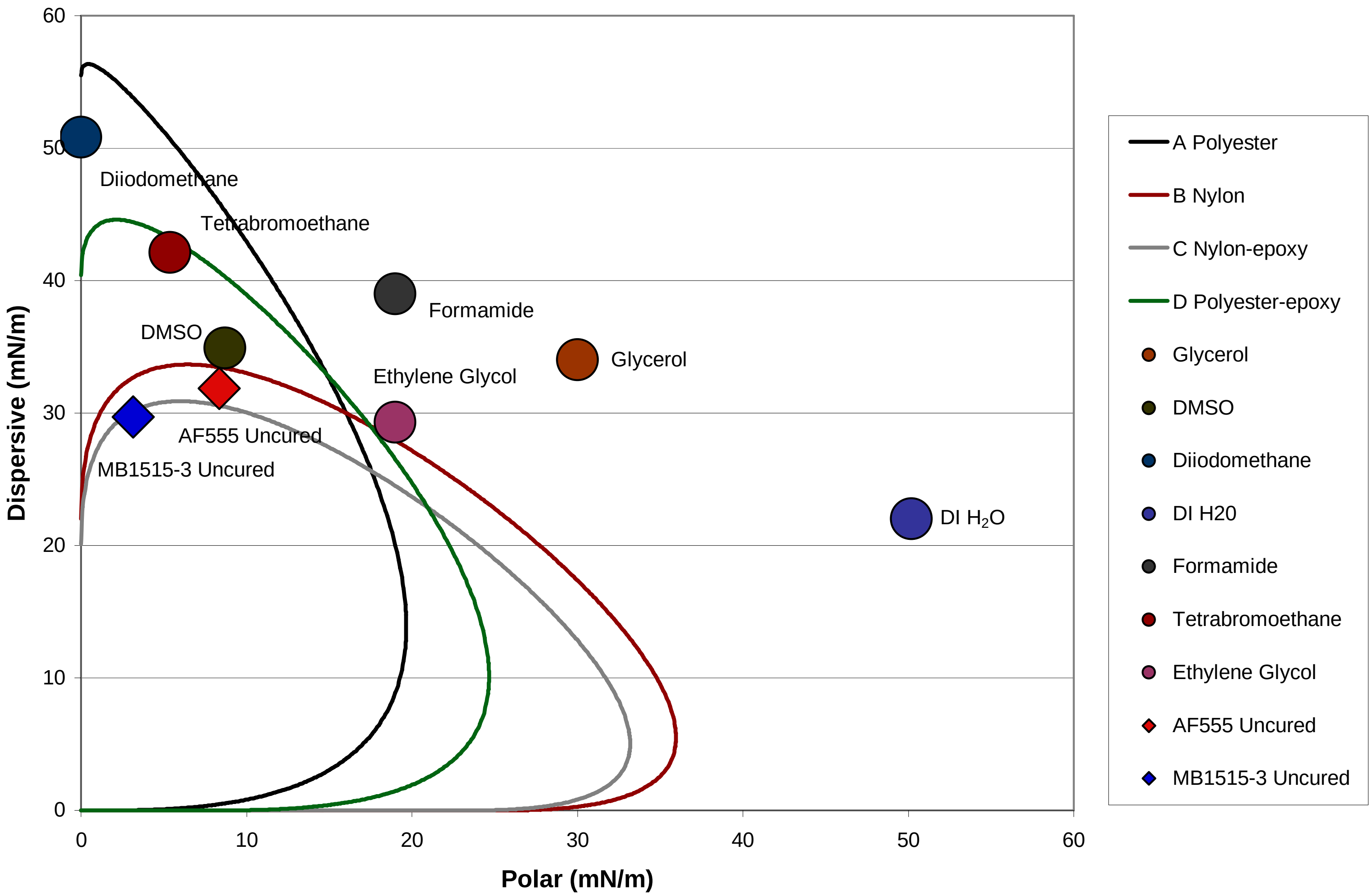
Contact angle results

- Using the contact angles for four fluids—ethylene glycol, deionized water, glycerol and formamide—Kaelble plots were generated and the polar and dispersive surface energies evaluated for each prepreg-peel ply combination
- Notably, nylon-prepared surfaces exhibit a greater polar surface energy component and polyester-prepared surfaces exhibit a greater dispersive surface energy component

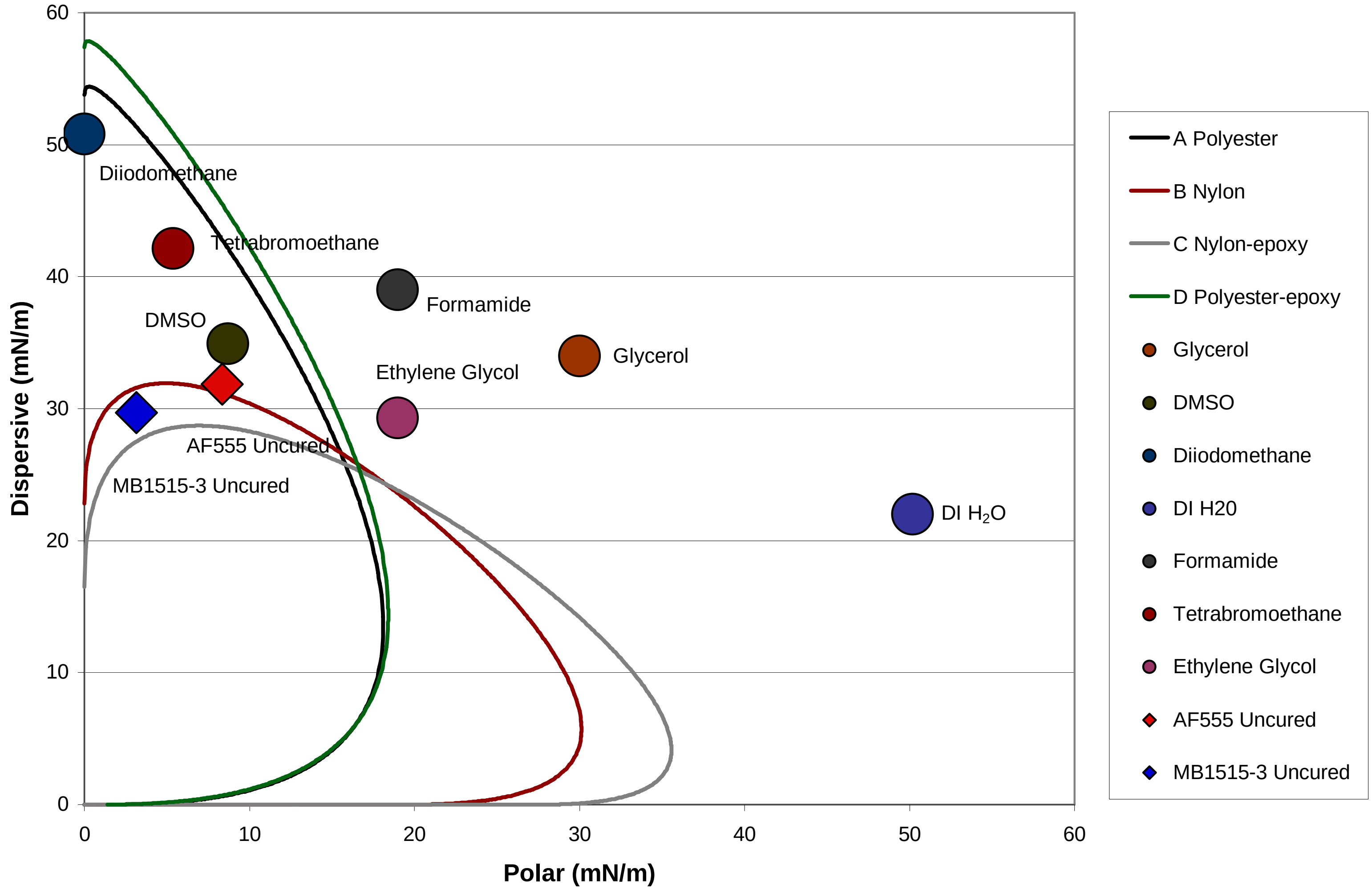
Substrate - Peel ply *	γ_d	γ_p	γ_{tot}
Cytec970 – 60001 polyester	55.5	1.7	57.2
Cytec970 – 51789 nylon	22.0	25.8	47.8
Cytec970 – EA9895 polyester/epoxy	40.4	8.6	49.0
Cytec970 – nylon/epoxy	20.1	23.9	44.0
Toray 3631 – 60001 polyester	53.8	1.2	55.0
Toray 3631 – 51789 nylon	22.8	19.8	42.6
Toray 3631 – EA9895 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*

* Units in mN/m

Wetting envelopes: Cytec 970



Wetting envelopes: Toray 3631



X-Ray Photospectroscopy results

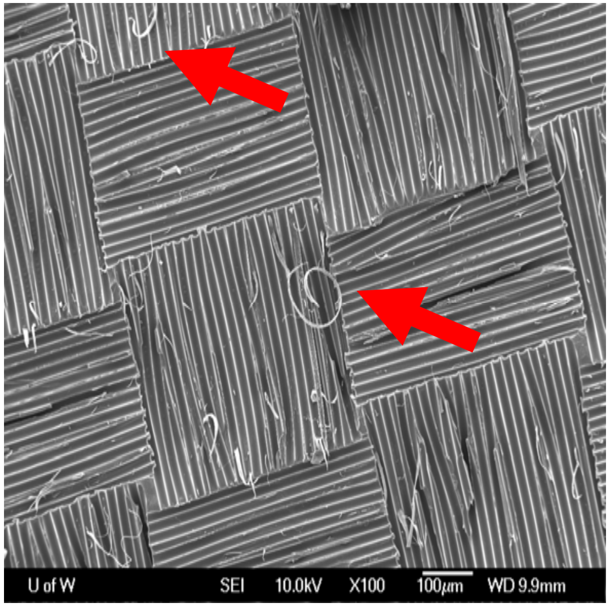
- XPS was carried out on all of the peel ply-prepared surfaces to determine composition
- The polyester-prepared surfaces demonstrated high oxygen content due to the C=O bonds within polyester fiber; the nylon-prepared surfaces demonstrated high nitrogen content due to the presence of amide C=N bonds in the nylon

Substrate - Peel ply	**C (At.%)**	**O (At.%)**	**N (At.%)**	**Si (At.%)**	**Br (At.%)**	**S (At.%)**
Cytec 970 - PF60001	73.8	25.2	1.0	**	**	**
Cytec 970 - PF51789	76.1	12.4	11.5	**	**	**
Cytec 970 - Epoxy/nylon	77.5	12.9	9.6	**	**	**
Cytec 970 - EA9895	76.8	19.6	3.1	**	0.5	**
Toray 3631 - PF60001	70.5	25.9	1.6	1.3	**	0.6
Toray 3631 - PF51789	77.1	13.3	9.0	**	**	0.7
Toray 3631 - Epoxy/nylon	76.2	12.1	10.7	**	**	1.0
Toray 3631 - EA9895	79.0	18.3	1.2	**	1.5	**

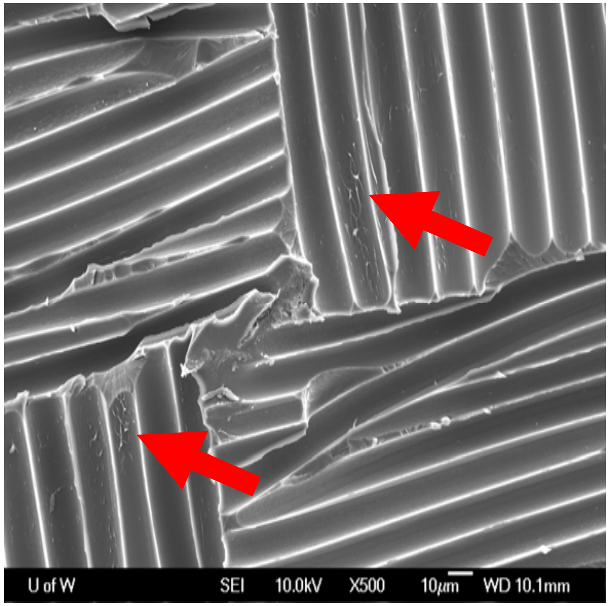
SEM Results: peel ply removed

- SEM imaging was carried out on the prepreg surfaces both immediately subsequent to peel ply removal as well as after Mode I fracture by the rapid adhesion test
- The images below are those taken after peel ply removal; only the Cytec 970 resin system is imaged because the peel ply texture is the same for both the Cytec 970 and Toray 3631

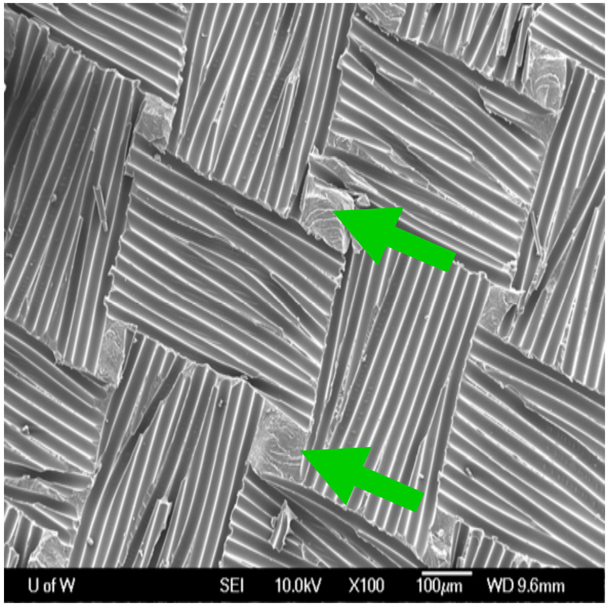
Cytec 970-dry polyester



Cytec 970-dry nylon

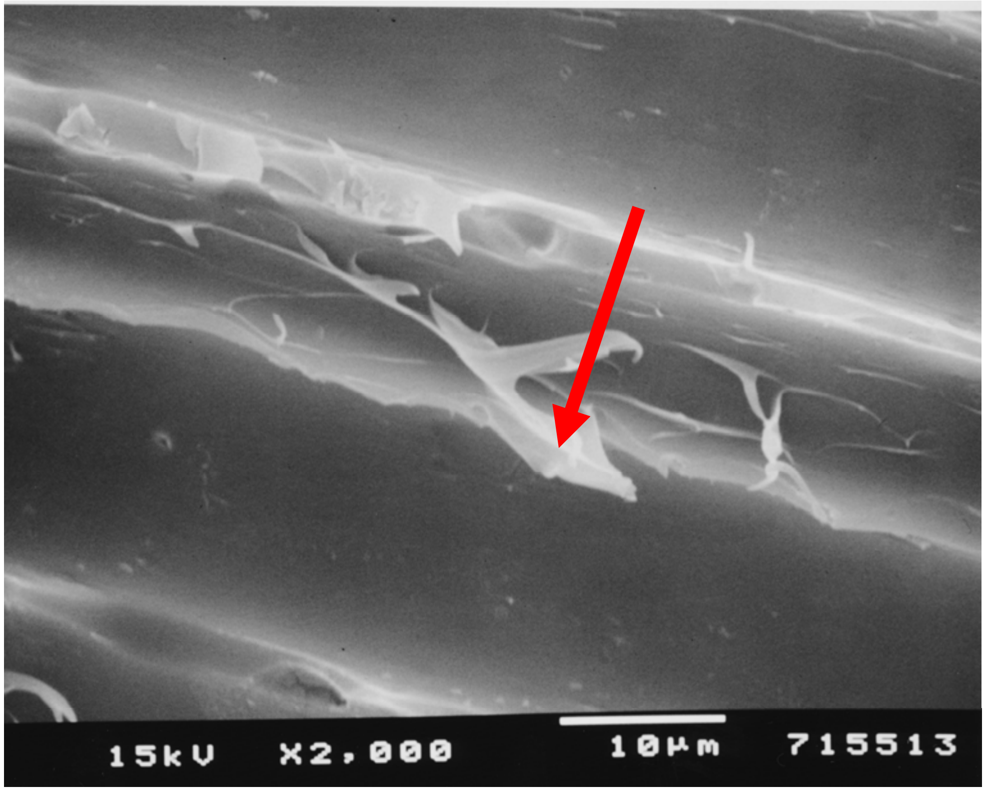


Cytec 970-wet polyester



A Closer Look at the Laminate Surface

Laminate surface after removal of nylon peel ply



Nylon from peel ply on surface before bonding?

Rapid Adhesion Test results

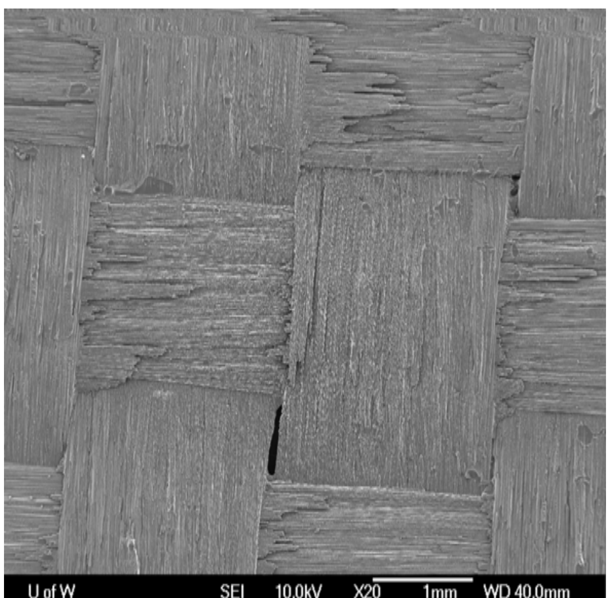
- Samples which exhibited cohesive failure (interlaminar in the composite, or cohesively within the epoxy/adhesive zone) were classified as **good bonds**; those which exhibited adhesion failure (along the adhesive-matrix bondline) were classified as **poor bonds**
- Bonds with a significant fraction of both are labeled mixed

	Peel ply			
Substrate - Adhesive	PF60001 (dry polyester)	PF51789 (dry nylon)	EA9895 (polyester-epoxy)	Nylon-Epoxy
Cytec 970 - MB1515-3	Mixed	Adhesion	Cohesive	Adhesion
Cytec 970 - AF555	Mixed	Mixed	Cohesive	Cohesive
Toray 3631 - MB1515-3	Adhesion	Adhesion	Cohesive	Adhesion
Toray 3631 - AF555	Adhesion	Adhesion	Cohesive	Adhesion

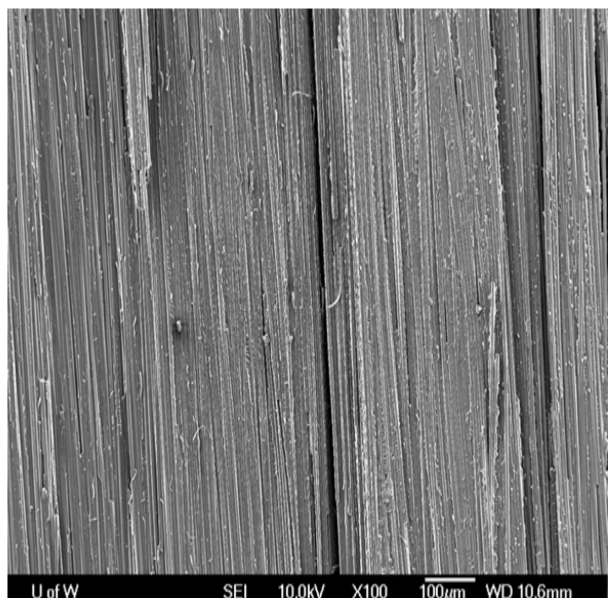
SEM: post-RAT fracture

- The images below are taken after the adhesively bonded samples are failed by the Mode I fracture Rapid Adhesion Test
- Prepregs which had been prepared with the Henkel EA-9895 epoxy-preimpregnated polyester peel ply all demonstrated the highly desirable 100% cohesive character in their failure mode

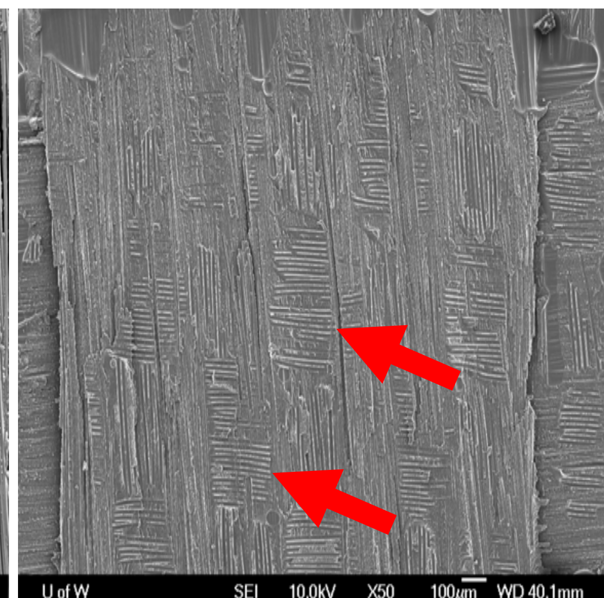
Cytec 970-wet polyester



Toray 3631-wet polyester



Cytec 970-dry polyester



Task 2 Discussion

- The Henkel EA-9895 peel ply-prepared surfaces performed well in actual adhesive bond quality and also contained the adhesive compounds within the wetting envelopes; surfaces after peel ply removal exhibited fractured epoxy regions and no visible fiber remnants
- Although surfaces prepared with the dry polyester peel ply contained the adhesives well within their wetting envelopes, they did not show substantial cohesive character in failure
- Cytec 970 prepared with the wet nylon peel ply and 3M AF 555 adhesive showed cohesive failure even though the adhesive was outside the boundaries of the wetting envelope
- Surfaces which had visible peel ply contamination when observed by SEM did not produce strong bonds

Task 2 Conclusions

- A given peel ply surface preparation that works with one prepreg-adhesive system will not necessarily work with any other prepreg-adhesive system; **each combination yields its own unique characteristics**

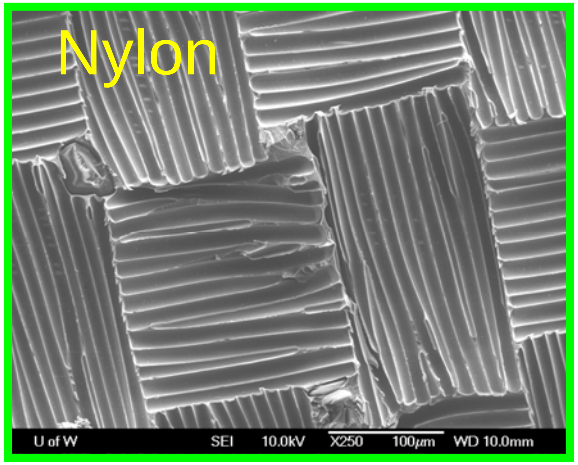
- Henkel EA9895 epoxy-preimpregnated polyester peel ply produced high quality bonds in all of the systems investigated

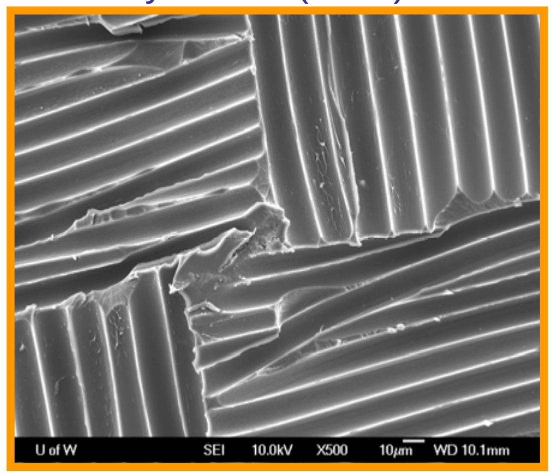
- Surface wetting is a **necessary but insufficient condition** for the formation of strong adhesive bonds in the composites tested
- High O/C or N/C ratio’s did not correlate to bond quality.

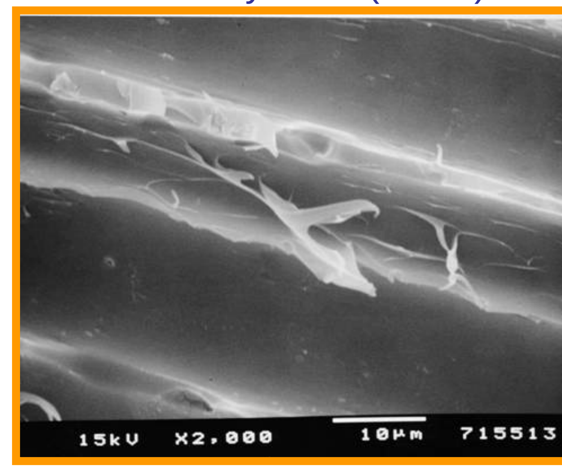
Peel Ply Surface Prep. - SEM Results Summary

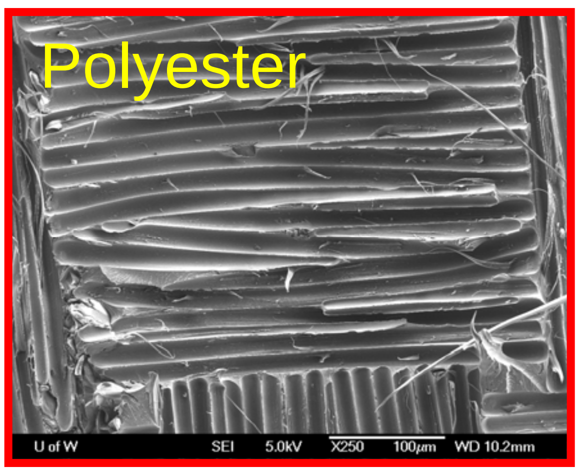
Composite surface after removal of dry peel plies:

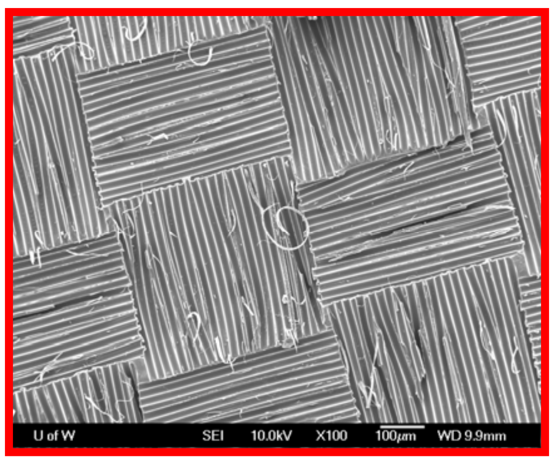
260 F cure GFRP | Cytec 970 (360F) | Toray 3900 (360 F)

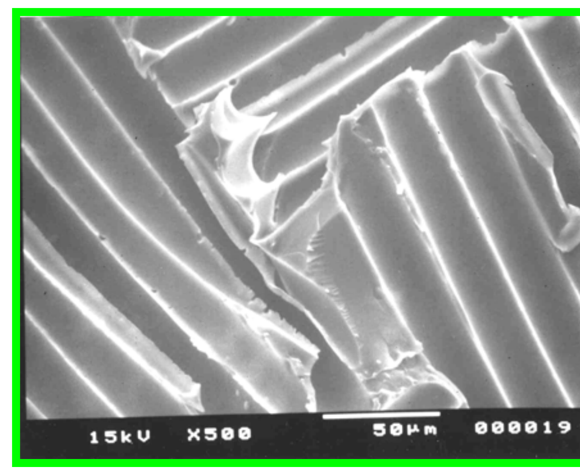












Summary

- Bonding Depends on
  - Prepreg system (Resin and Fiber(?))
  - Peel Ply Material and Source
  - Adhesive
- Characterization Techniques (XPS, SEM and Surface Energy) provide useful information to help understand bonding requirements

Expected Outcomes

- Further dissemination and acceptance of quick, inexpensive bond quality test- RAT method
- Initial stages of prepreg-peel ply-adhesive compatibility data base
- Contribute to fundamental understanding necessary to develop inspection techniques to determine the suitability of peel ply surfaces for bonding

The Future

- Continued exploration of the correlations between surface characterization and the actual bond quality as determined experimentally is needed
- Each characterization method may provide criteria which are exclusive to the formation of good bonds though no single technique can currently explain whether or not a good bond will result
- Determining the quality of a bond using theoretical means with close correlation to experimental results is desired
- Even more tantalizing is the possibility of realizing new material combinations which could produce stronger bonds

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
  - Does fiber type (glass, pitch, PAN) effect bonding?
  - Peel ply-resin interactions
  - Applicability to other composite and adhesive (paste) systems
  - Model to guide bonding based on characterization, surface prep. and material properties

Acknowledgements

- Funding FAA JAMS-AMTAS
- Peter Van Voast & Will Grace at The Boeing Company
- Mark Tuttle for his technical input and “WET” software utility
- Material donations from Cytec-Cycom, Toray Composites America, Airtech International, Henkel, Richmond Aerospace, Yokahama and Precision Fabrics
- UW- MSE Undergraduates: Rockey Aye, Eric Brutke, Neil Golke, Dinda Padmasana

Surface Wetting

Can surface energy guide bonding?

- Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta$$

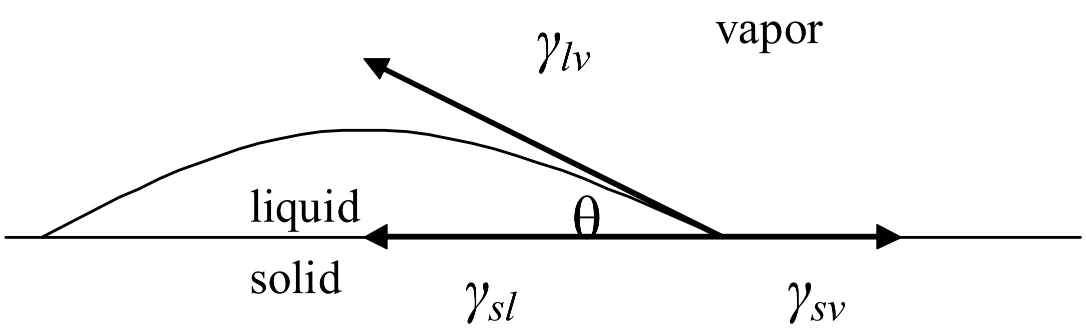
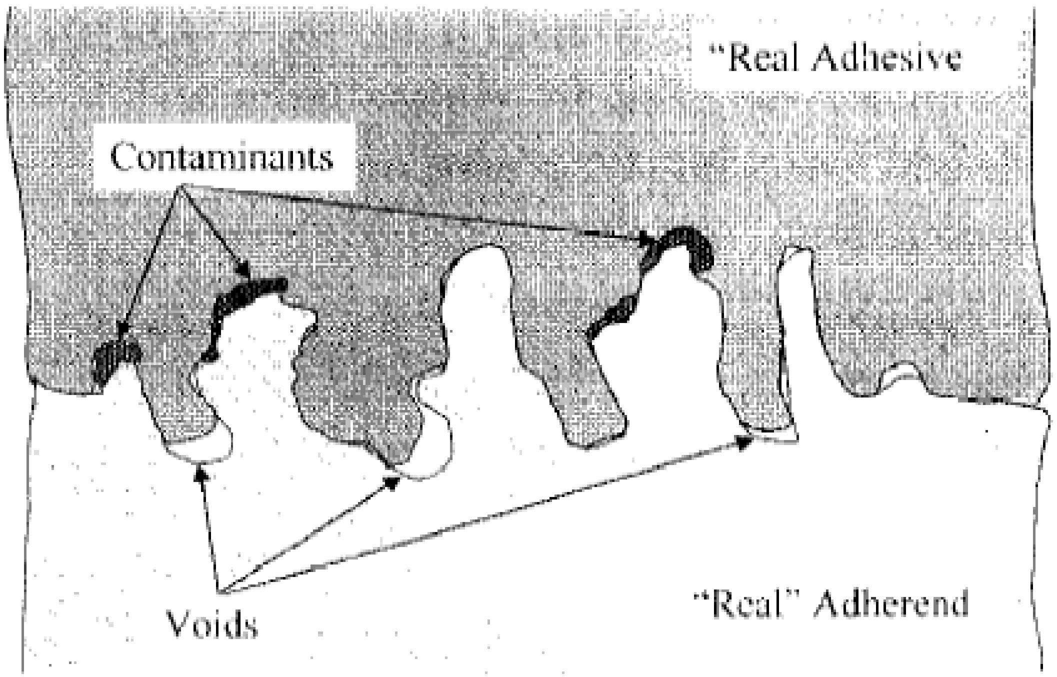


Illustration of Young's equation – drop of liquid on a solid surface

- Surface preparations try to increase the solid's surface energy and clean off contaminants
- Contaminants lower the solid's surface energy
- Complete wetting means θ approaches zero

Surface Wetting

Weak boundary layer due to voids and contaminants



- Wetting required for good bond

Figure from Pocius, A., *Adhesion and Adhesives Technology: An Introduction*, 2nd ed., 2002, Hanser Gardner, New York.

Contact Angle Measurement

- Is there a relation between surface energy and bond quality?
- Measuring the contact angles of multiple test liquids on the prepared surfaces allowed calculation of the substrates' surface energy
- The two-parameter Owens and Wendt model of surface energy was used, with a polar and dispersive component

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

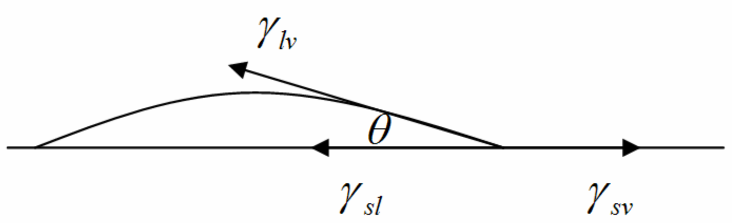
$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sv}^{d}\gamma_{lv}^{d}} - 2\sqrt{\gamma_{sv}^{p}\gamma_{lv}^{p}}$$

- Peel-ply prepared surfaces were measured (before adhesives were added)

Examination by contact angle

Contact angle analysis by goniometer

- Various fluids are used in a Ramé-Hart Tilting Contact Angle Goniometer, model 100-00 115, to form small droplets on the peel ply-prepared surfaces
- The contact angle these fluids form with the surface is recorded and applied to Owen and Wendt’s surface energy model to generate a Kaelble plot
- The Kaelble plot allows determination of the polar and dispersive surface energy components of the solid by linear regression; a wettability envelope may then be generated



$$\frac{\sigma_l(\cos\theta+1)}{2\sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p}\left(\sqrt{\frac{\sigma_l^p}{\sigma_l^d}}\right)+\sqrt{\sigma_s^d}$$

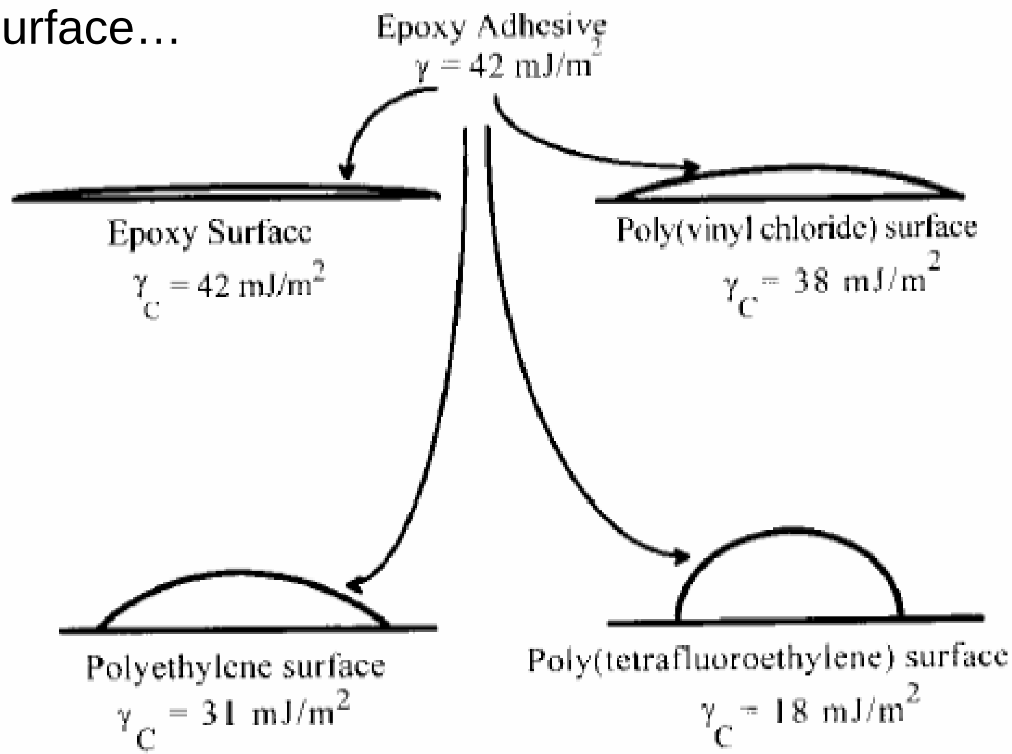
Contact angle results, cont

- Subsequent to the development of the Kaelble plots, wettability envelopes were generated with BKCWet 1.1, a program initially devised by Mark Tuttle and modified by Brian Clark, both of the University of Washington
- It is supposed that any fluid whose dispersive and polar surface energies plot its point within the wetting envelope of a solid will wet out on the surface
- Points excluded from a wetting envelope are assumed not to spontaneously wet out on the surface
- The reality is that the break-even point of energetic favorability represented by the wetting envelope is not always a guaranteed predictor of bond quality

Surface Wetting

A liquid epoxy adhesive is on each surface.

Highest energy surface… …lower…



…even lower… …lowest.

Figure from Pocius, A., *Adhesion and Adhesives Technology: An Introduction*, 2nd ed., 2002, Hanser Gardner, New York.