Improving Adhesive Bonding of Composites Through Surface Characterization

(of Peel Ply Prepared Surfaces)

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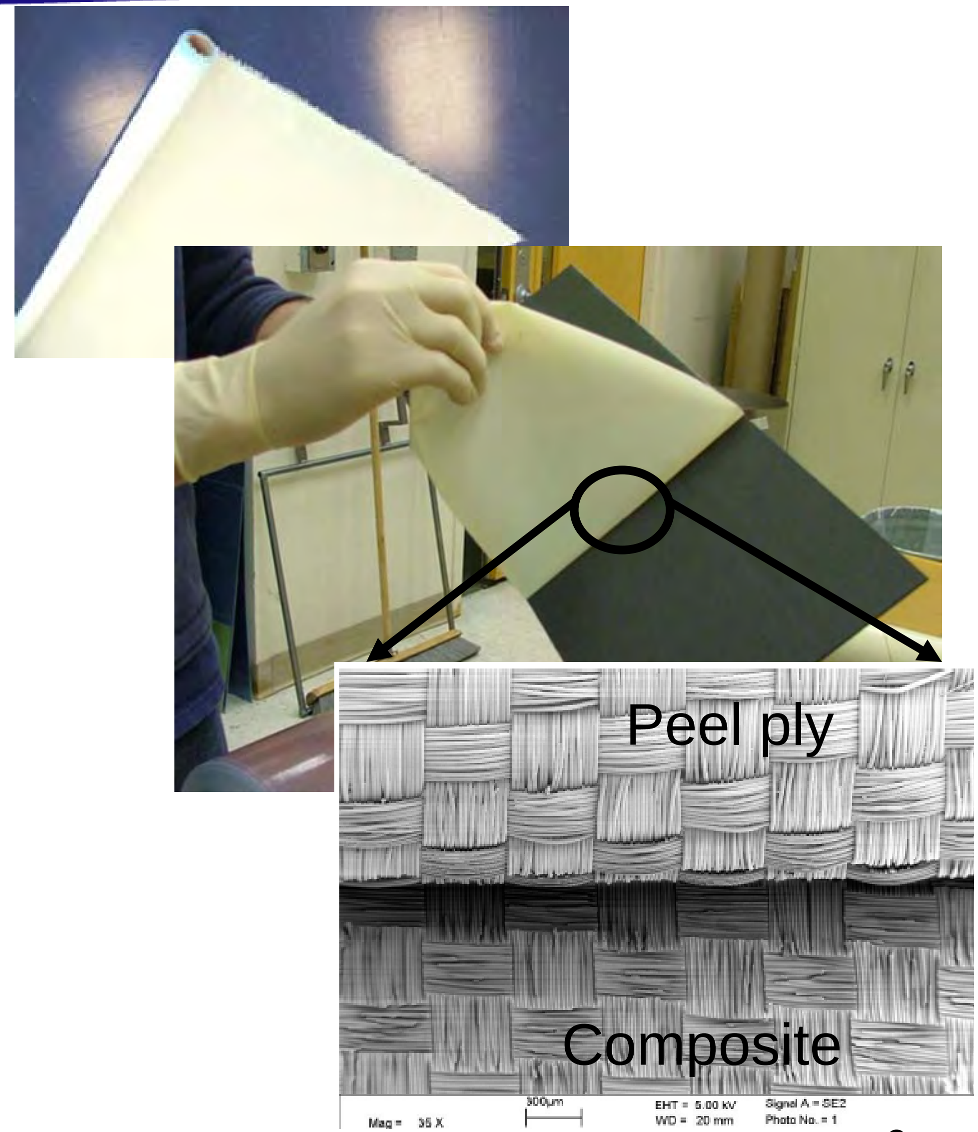
The Joint Advanced Materials and Structures Center of Excellence

Our work studies bonding by examination of peel ply prepared composite surfaces.

- 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!



Historically peel plies are a prime example of system specificity of composites.

- 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; 250° F) cure
  - Carbon Fiber epoxy prepregs: BMS8-256 and Toray 3631 (177º C)
  - Nylon and polyester peel plies (dry and preimpregnated)
  - Various film adhesives

Needs Identified in Spring Breakout Sessions

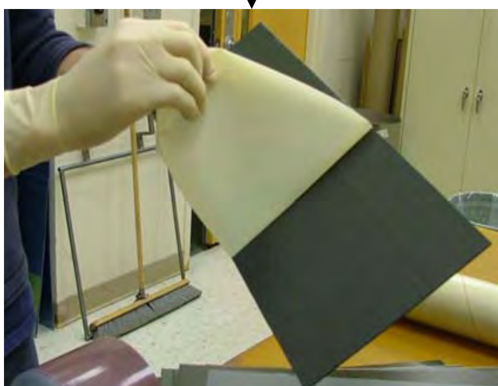
- Adhesive bond long term performance
  - Correlation of accelerated aging method to actual service
- Quantify service environment
  - Load, temperature, moisture, solvents
- Make wettability work more quantitative/predictive
  - Understand temperature effects
- Fundamental understanding of surfaces created and why

➔Improved fundamental and empirical understanding

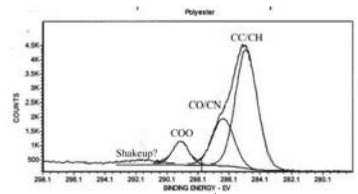
➔Quantifiable prebond litmus test

Samples are produced by standard processes, then the bonds and surfaces are characterized.

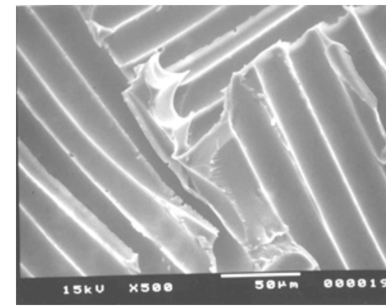
Autoclave Cure



Peel ply removed before bonding

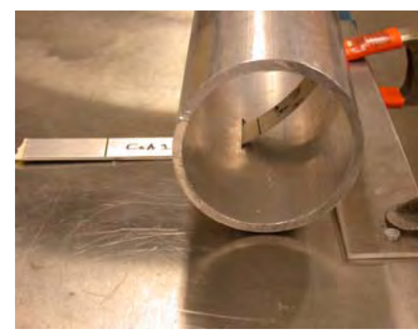


Characterization Via XPS,SEM,Contact Angle



Bonded with film adhesive

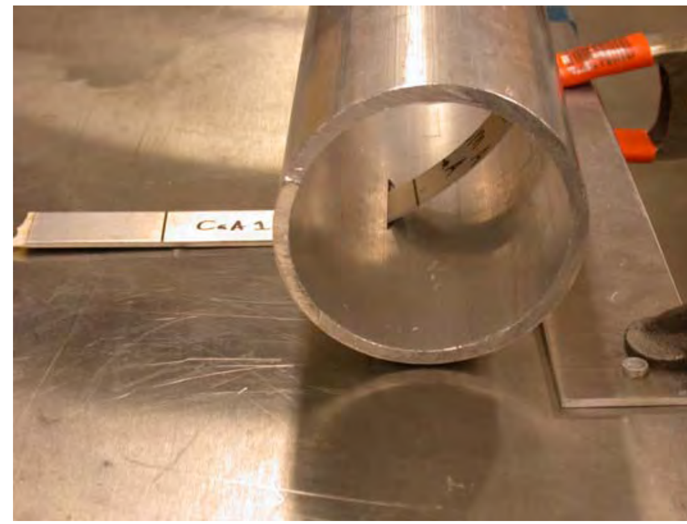
Autoclave Cure

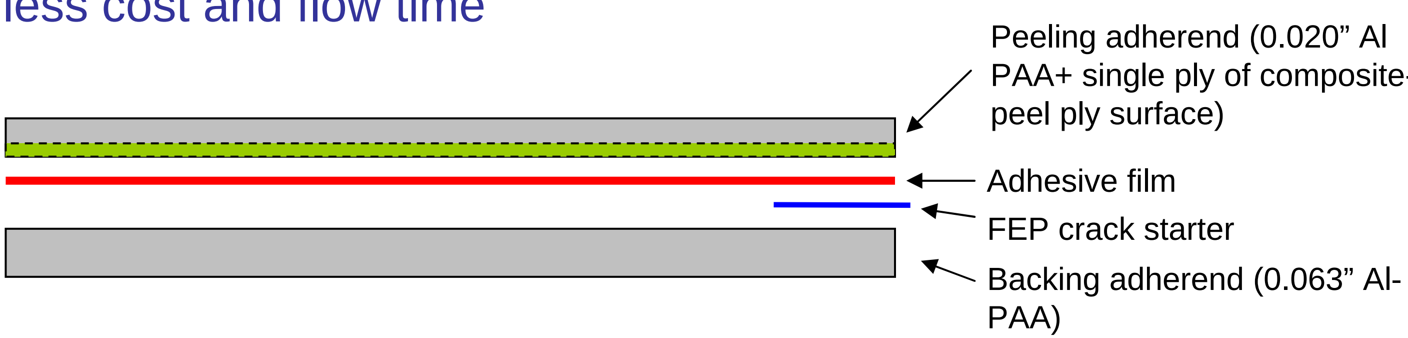


Mode I testing

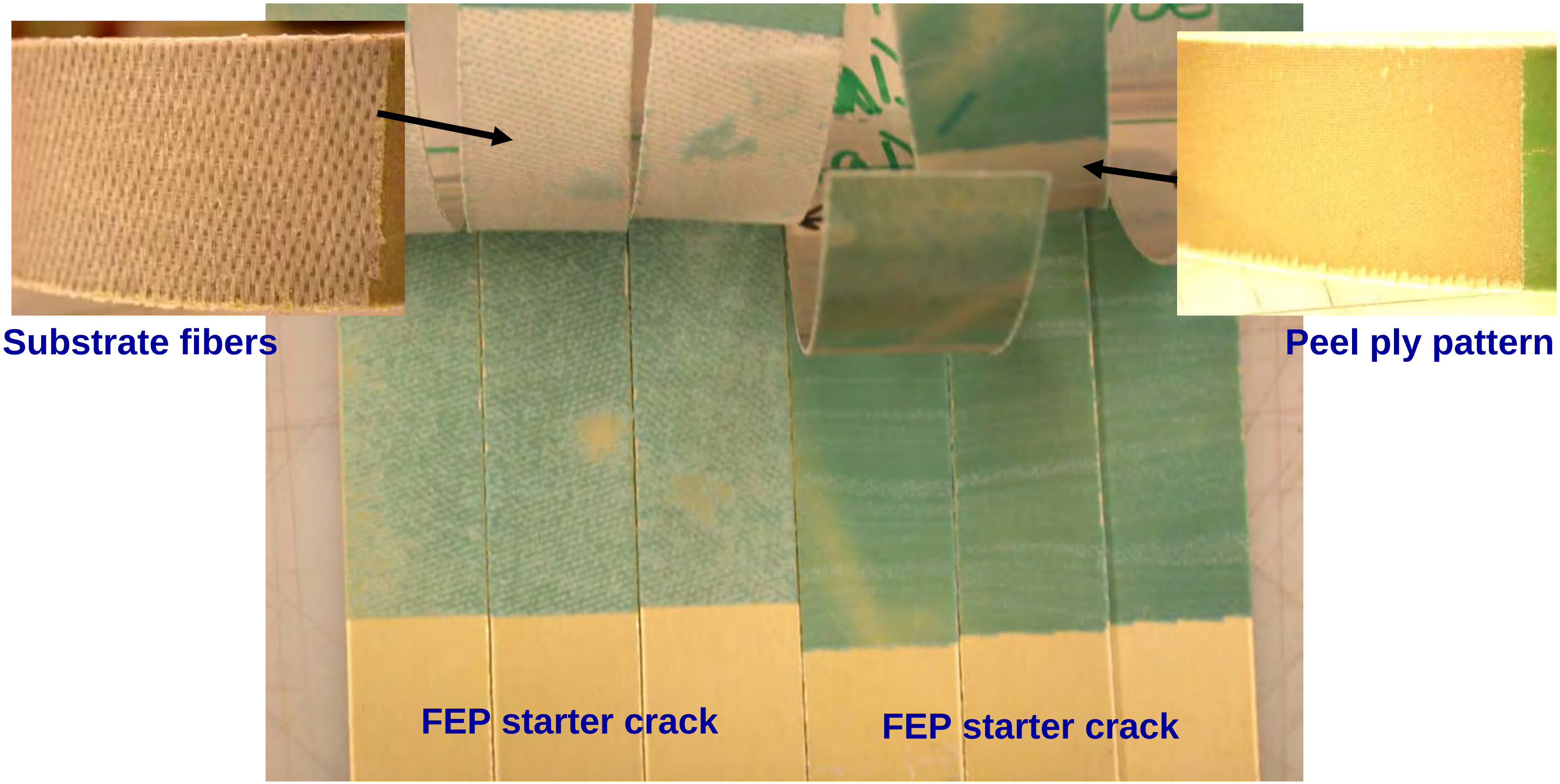
The Rapid Adhesion Test (RAT) is a quick, cheap test to assess composite bond adhesion.

- A modification of metal-to-metal peel test developed by Boeing.
- The backing adherend clamped to while the peeling adherend is removed
- Qualitative Mode I test for bond quality
  - Adhesion Failure-Poor Bond
  - Cohesive Failure-Strong Bond
- Intended for screening out poor adherend-adhesive-surface prep combinations
- Failure modes correlate with DCB test with ~90% less cost and flow time





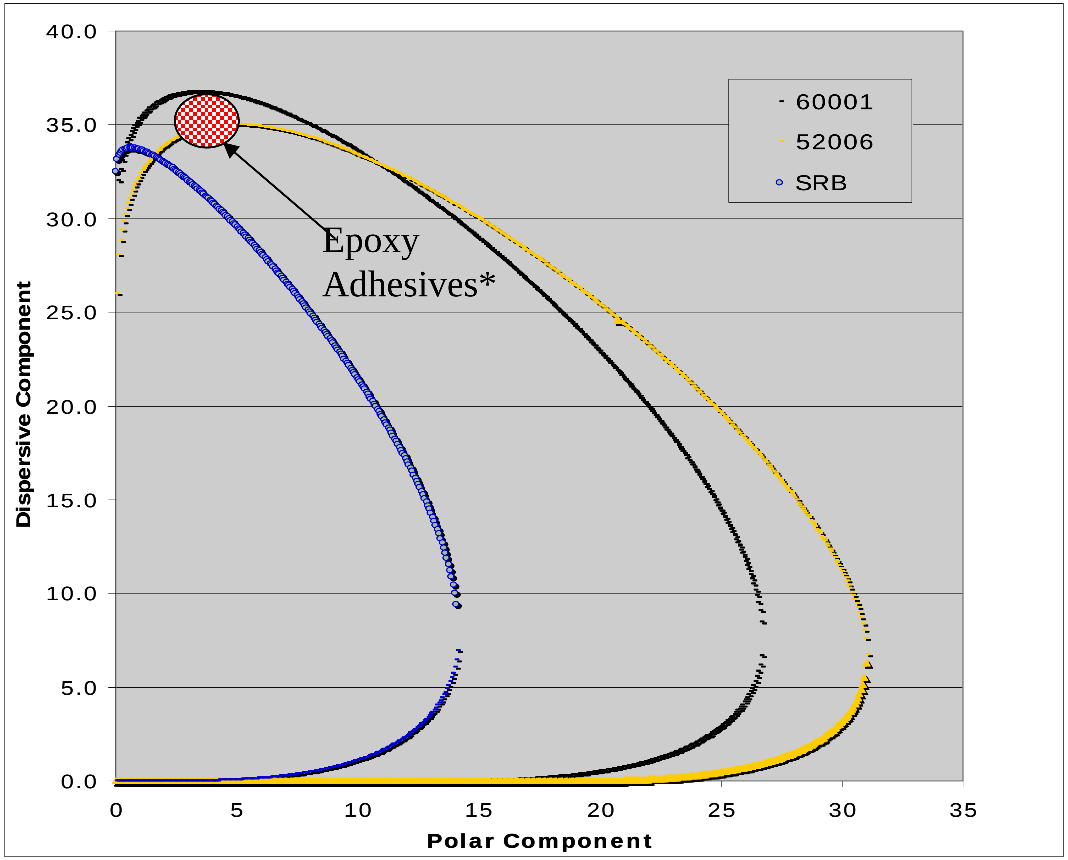
RAT Method Assessment



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

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)

250F Cure Systems

- 2 Peel Plies: Polyester 60001 and Nylon 52006
- 3 prepregs-250 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 (RAT)
  - Adhesion (poor) vs. Cohesive (good)

350F Cure Systems

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

250F 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

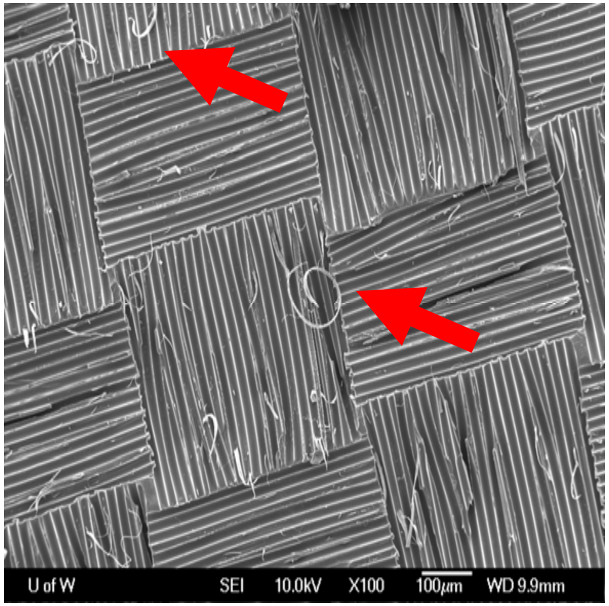
Peel Ply Material-350F Cure CFRP

	PEEL PLY USED FOR SURFACE TREATMENT				
Substrate Adhesive	PF60001 Polyester	PF51789 Nylon	Fiberglass-Epoxy	EA9895 PE-Epoxy	Nylon-Epoxy
Cytec 970 MB1515-3	MIXED	ADHESION	COHESIVE	COHESIVE	ADHESION
Cytec 970 AF555	MIXED	MIXED	COHESIVE	COHESIVE	COHESIVE
Toray 3631 MB1515-3	ADHESION	ADHESION	NA	COHESIVE	ADHESION
Toray 3631 AF555	ADHESION	ADHESION	NA	COHESIVE	ADHESION
Toray 3900 MB1515-3	COHESIVE	ADHESION	NA	NA	NA
Toray 3900 AF555	COHESIVE	COHESIVE	NA	NA	NA

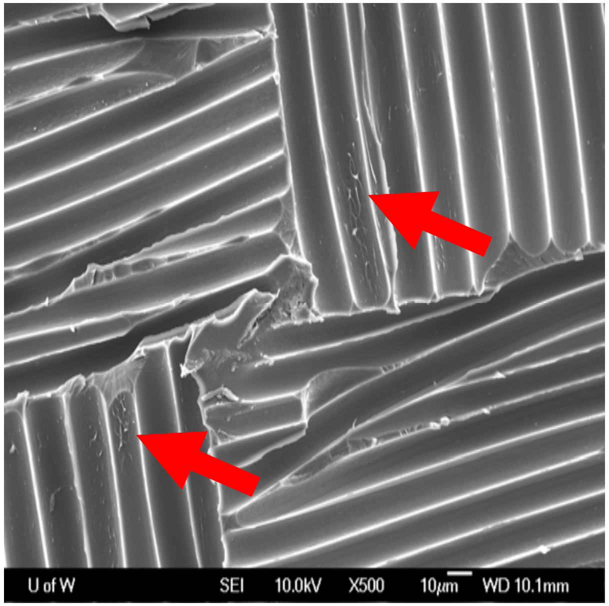
SEM Results: peel ply removed

- 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

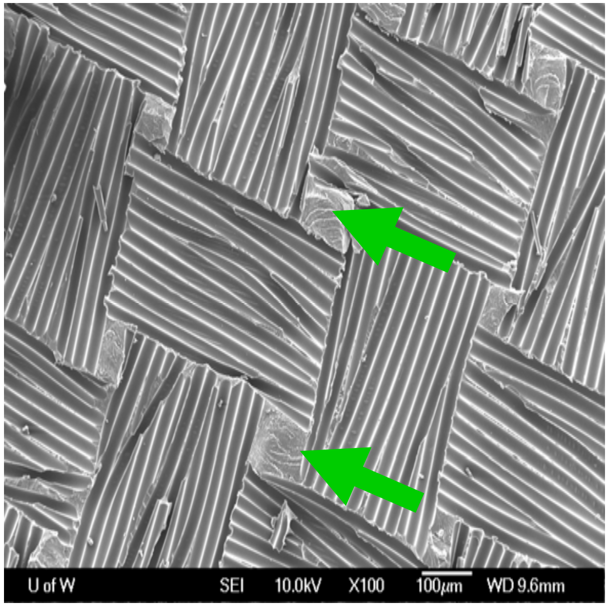
dry polyester



dry nylon (wet similar)

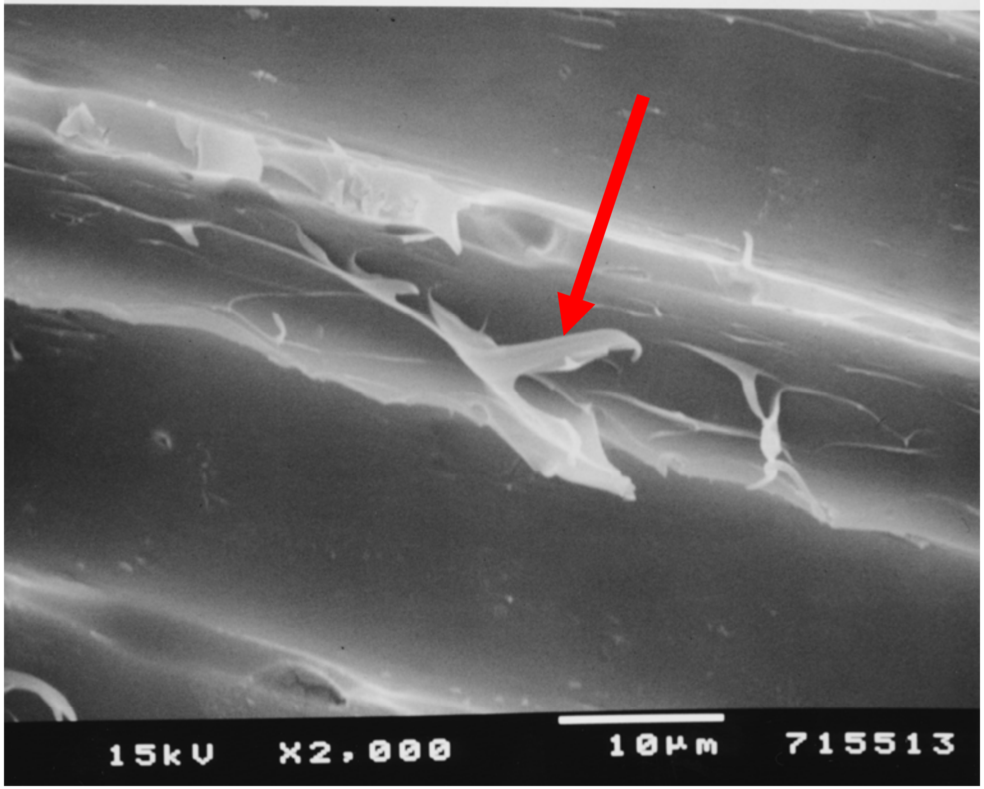


wet polyester (EA9895)



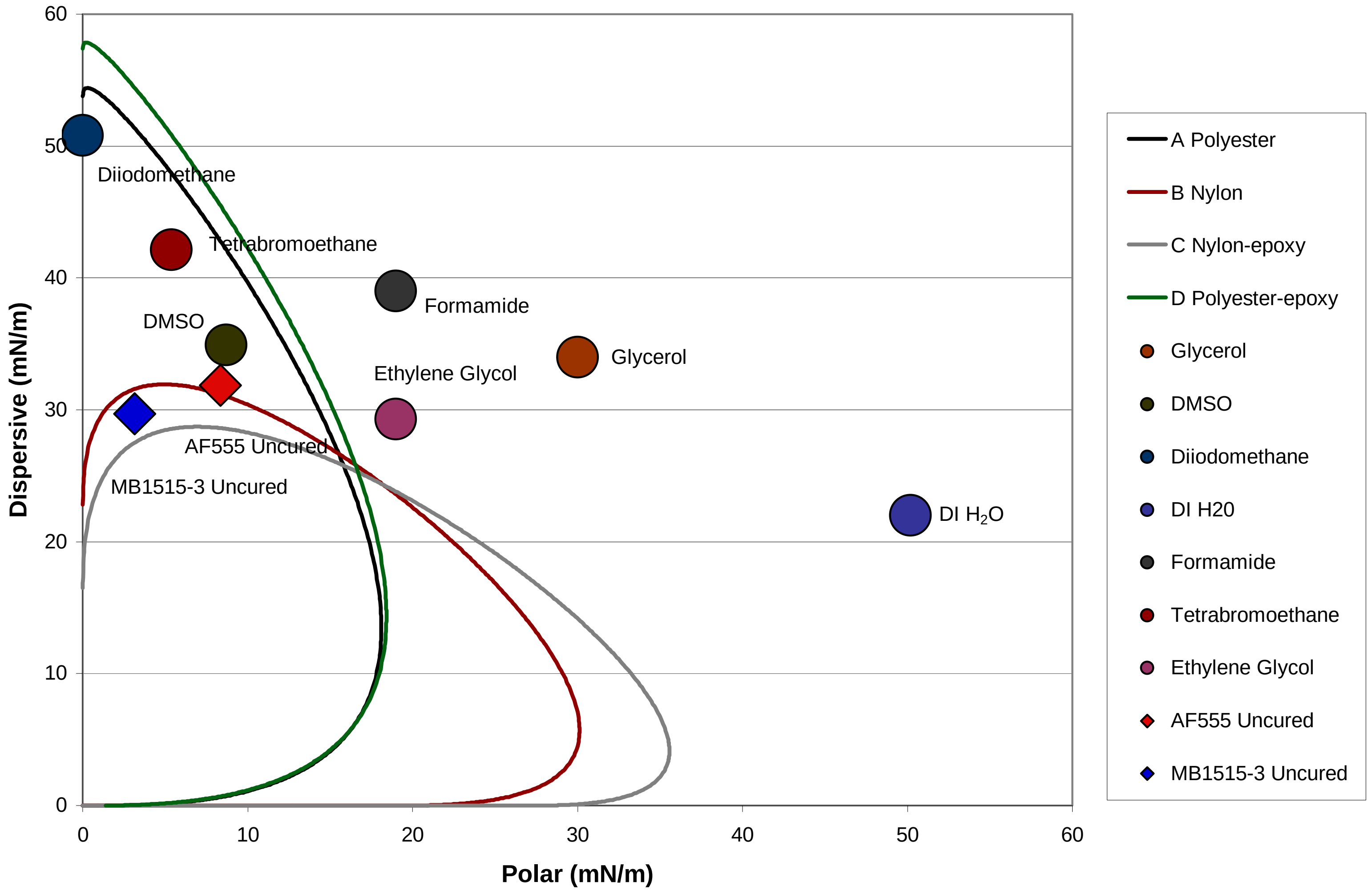
A Closer Look at the Laminate Surface

Laminate surface after removal of nylon peel ply



Nylon from peel ply on surface before bonding?

Wetting envelopes: Toray 3631



X-Ray Photospectroscopy results

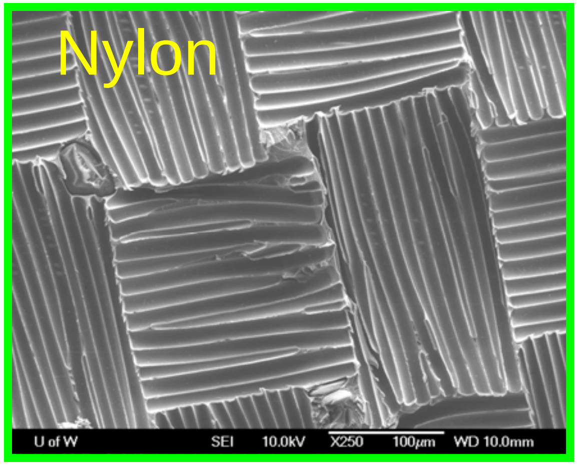
- XPS was carried out on all of the peel ply-prepared surfaces to determine composition
- The polyester-prepared surfaces demonstrated high oxygen content due to the C=O bonds within polyester fiber; the nylon-prepared surfaces demonstrated high nitrogen content due to the presence of amide C=N bonds in the nylon
- Br detected in EA9895 resin- compatibility issues with substrate?

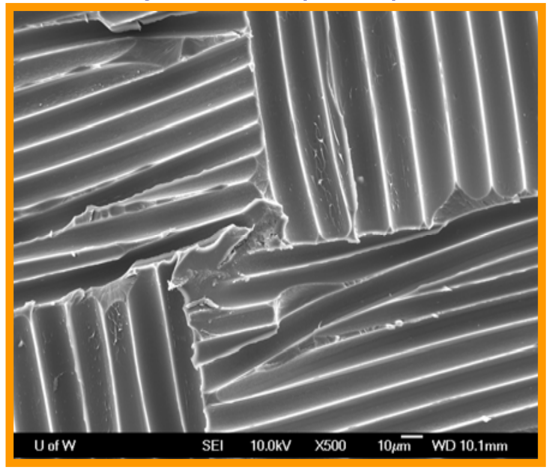
Substrate - Peel ply	C (At.%)	O (At.%)	N (At.%)	Si (At.%)	Br (At.%)	S (At.%)
Cytec 970 - PF60001	73.8	25.2	1.0	**	**	**
Cytec 970 - PF51789	76.1	12.4	11.5	**	**	**
Cytec 970 - Epoxy/nylon	77.5	12.9	9.6	**	**	**
Cytec 970 - EA9895	76.8	19.6	3.1	**	0.5	**
Toray 3631 - PF60001	70.5	25.9	1.6	1.3	**	0.6
Toray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

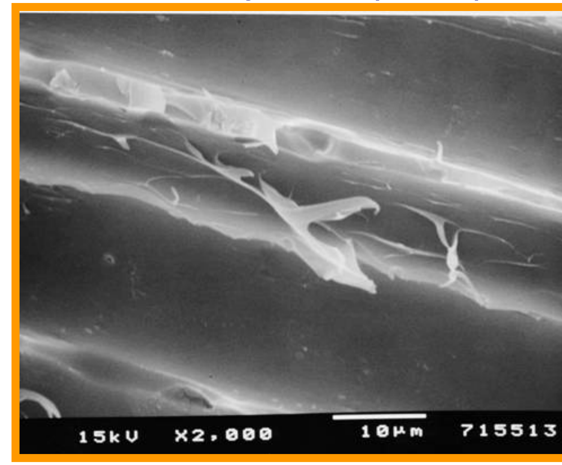
Peel Ply Surface Prep. - SEM Results

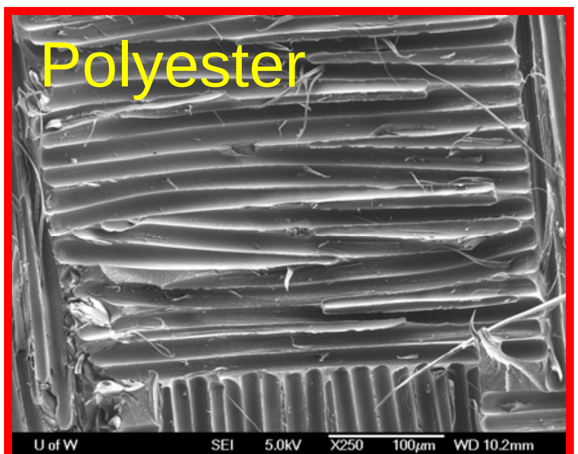
Composite surface after removal of:

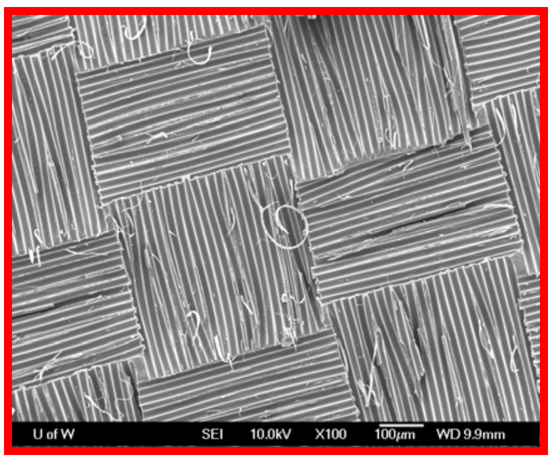
260 F cure GFRP	Cytec 970 (360F)	Toray 3900 (360 F)

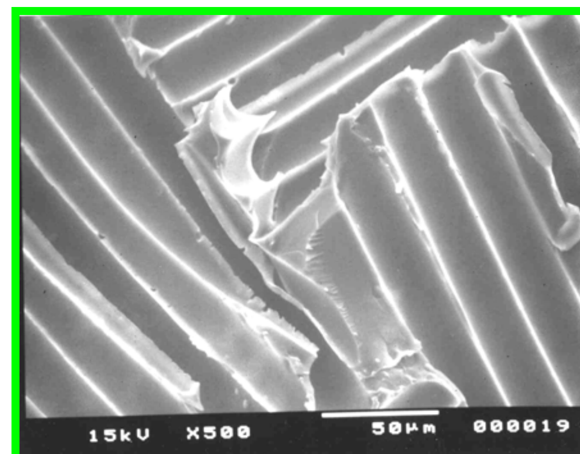












250F Summary

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

350F Summary

- The Henkel EA-9895 peel ply-prepared surfaces performed well
  - Contained the adhesive compounds within the wetting envelopes;
  - Surfaces after peel ply removal exhibited fractured epoxy regions
  - No visible fiber remnants
- Surfaces from dry polyester peel ply contained the adhesives well within their wetting envelopes
  - Did fail in cohesive
- Cytec 970 / wet nylon peel ply / 3M AF 555 had cohesive failure
  - 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

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.

The Future
1) Degree of Cure before bonding

- Effect of Over Cured Substrate on surface energy and bonding characteristics
  - Local exotherms
  - Rework
- Effect of partial cure of prepregs on surface energy and bonding characteristics
  - If prepreg is not fully cured how does this effect:
    - Peel ply- resin interactions
    - Easy of peel ply removal
    - Surface to be bonded- are there uncrosslinked sites that can bond to adhesive
- Prepreg gets full cure during adhesive cure

The Future
2) Additional Systems

- New systems (General aviation prepregs/peelplys/adhesives)
  – Toray 2500 series (interest from Toray –L. Cooke)
  – Paste Adhesives
  – Surface Preparation Parameters

The Future
3) 250 vs. 350 Cure systems

- Further investigation of differences in 250 vs. 350 cure prepreg/peel ply interactions (related to 1 and 2)
  - So far Nylon Peel ply works at 250, Polyester at 350
  - Why?
  - Will a 350 Polyester peel ply prepared surface bond with a 250 adhesive?

The Future
4) Temperature and Pressure

- To date surface characterization performed at ambient conditions. Does surface change substantially at High T &P?
- Temperature and Pressure effects on surface energy, prepreg/peel ply interactions and adhesive/substrate interactions

The Future
5) Standard Methods

- Development of standard surface energy measurements for composite surfaces (peel ply, sanded, Grit blasted, Scarfed)
- Contact angle varies with
  - Peel ply texture
  - Fiber geometry
  - Roughness
- Other methods for surface energy
  - Inverse GC
  - Tenisometry
  - Other?

The Future
6) Prepared Surface "Out time"

- Effect of time/environment (UV, etc.) on composite surfaces after surface preparation (peel ply, sanding)-i.e. how long can you wait to bond a surface after preparation
- Surface energy
- Composition- adsorbed species using XPS
- Bond Quality

Future Possibilities

- The main areas of interest for future work are:
- Effect of partial cure of prepregs on surface energy and bonding characteristics
- New systems (General aviation prepregs/peelplys/adhesives)-Toray
- Further investigation of differences in 250 vs. 350 cure prepreg/peel ply interactions (related to 1 and 2)
- Temperature and Pressure effects on surface energy, prepreg/peel ply interactions and adhesive/substrate interactions
- Development of standard surface energy measurements for composite surfaces (peel ply, sanded, Grit blasted, Scarfed)
- Effect of time/environment (UV) on composite surfaces after surface preparation (peel ply, sanding)-i.e. how long can you wait to bond a surface after preparation
- NEED TO PRIORITIZE- Your input is important

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

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