Modified Epoxy Matrix Resins for Reduced Dependence on Redundant Fasteners in Secondary-Bonded Composite Structures

Frank Palmieri[1], Tyler Hudson[1], Austin Smith[1], Yi Lin[2], Jin Ho Kang[2], Isaac Barnett[3], Bryson Clifford[3], Roberto Cano[1] & John Connell[1]

1. NASA Langley Research Center, Hampton VA
2. National Institute of Aerospace, Hampton, VA
3. NASA Internships Fellowships and Scholarships, Hampton, VA

ACS Spring 2020 National Meeting & Expo

Philadelphia, PA

March 23rd, 2020

The Challenge

Global Growth in Aviation

2017

4 BILLION

PASSENGER TRIPS

2036

7.8 BILLION

PASSENGER TRIPS

Airbus / Europe

Bombardier / Canada

Irkut / Russia

Comac / China

Embraer / Brazil

41,030
New Aircraft Deliveries

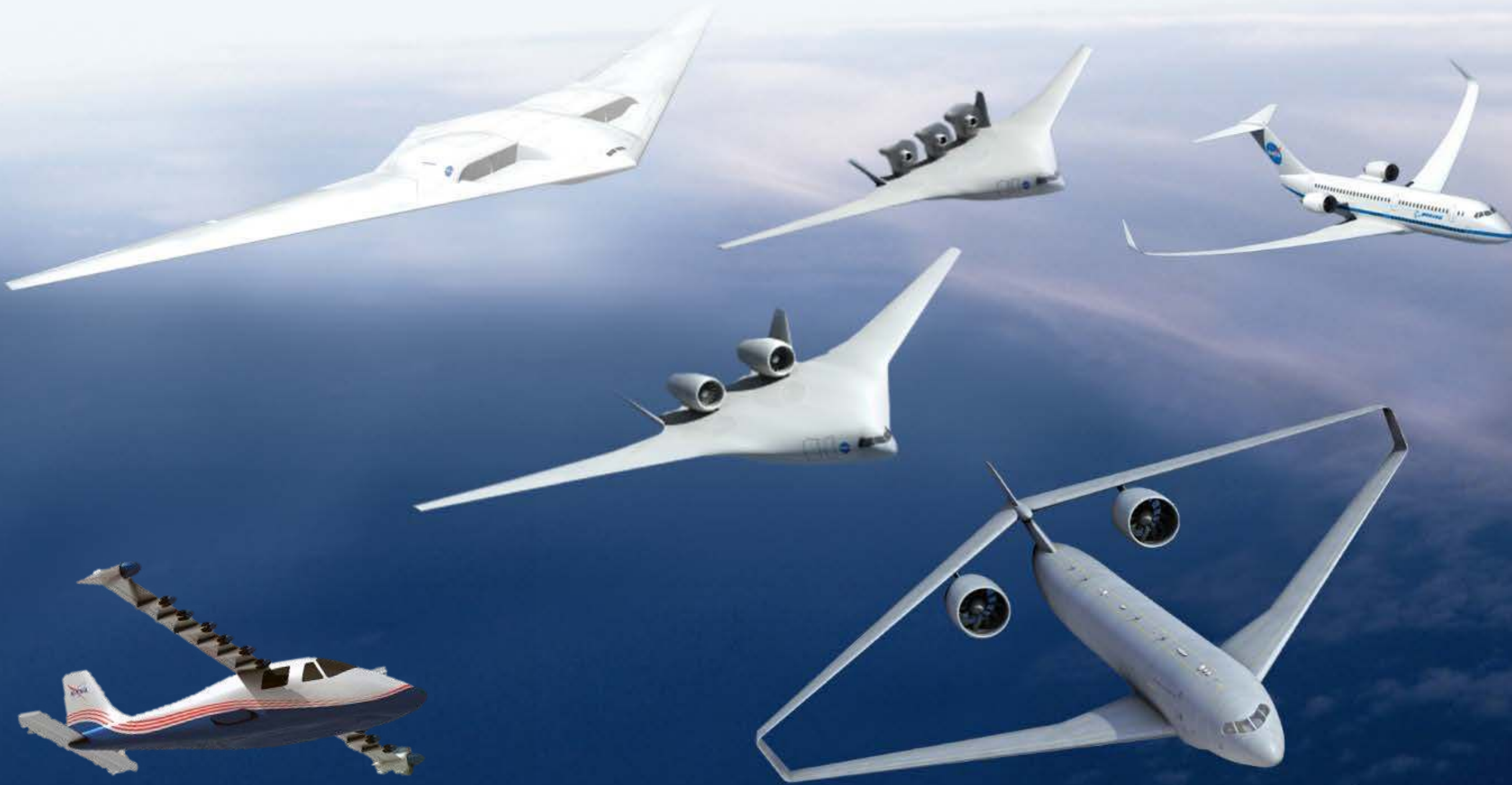
$6.1 Trillion
Market Value

78%
of New Aircraft Deliveries are Single Aisle Class (including Regional Jets)

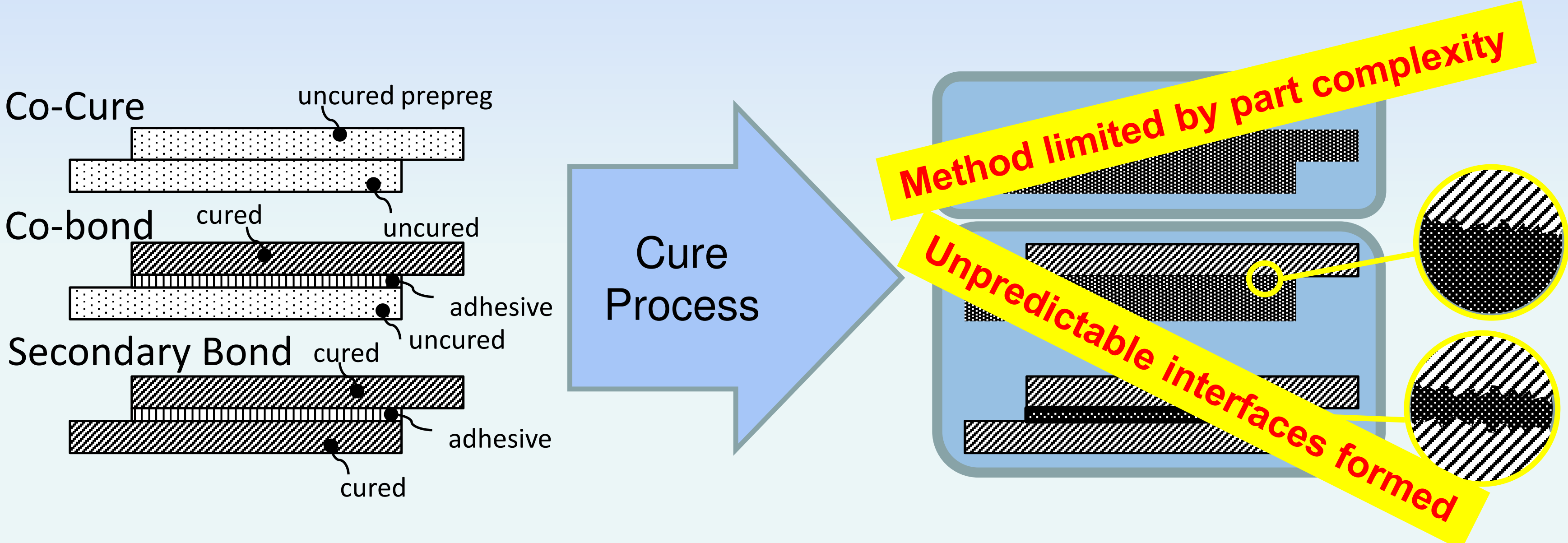
Asia-Pacific Market is Nearly
40%
of New Aircraft Deliveries

Global Competitors

Efficient Composite Airframes



Assembly of Composites



- Co-cure produces predictable components and joints but is limited by complexity
- Bonded/Co-bonded joints are susceptible to weak bonds
- Unpredictable bonds are a concern in primary structure
- A **redundant load path is required** to ensure structural integrity

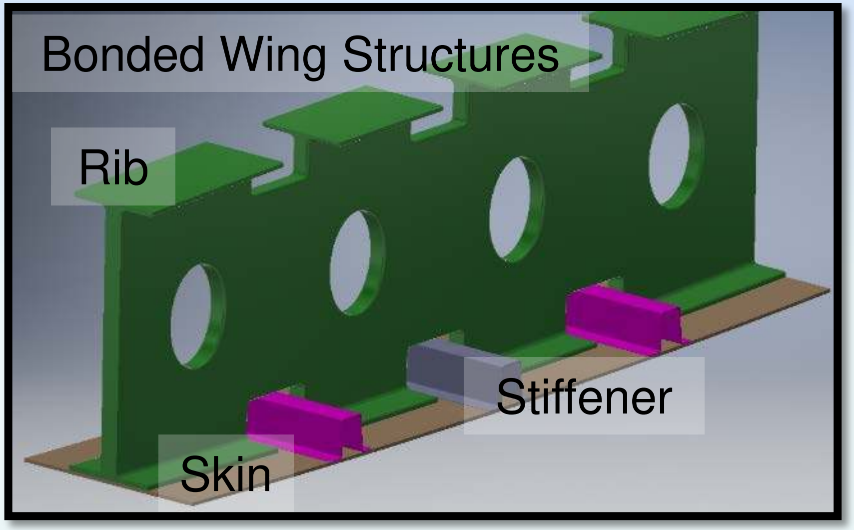
Manufacturing Bottleneck

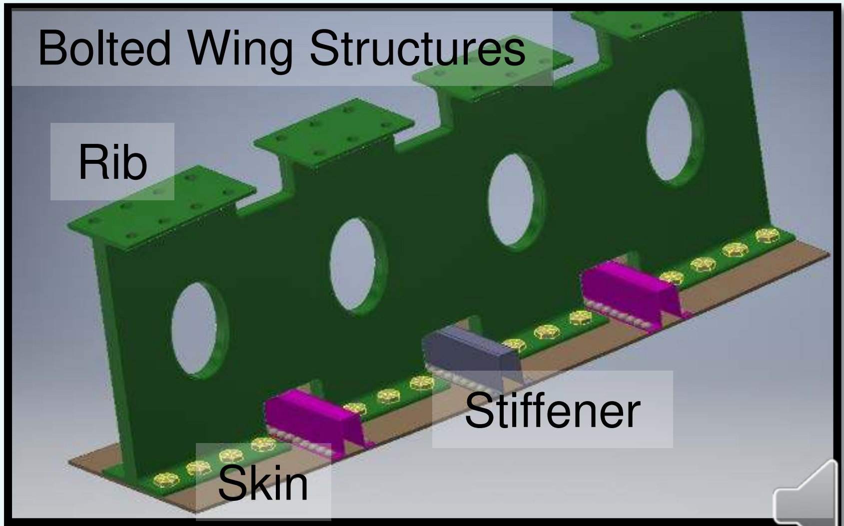
Airframes are assemblies of many parts

- Composites can be assembled rapidly with adhesives
- Redundant load path (bolts) is required for certification
- **<u>Thousands of drilling and installation steps</u>**

Composites should be replacing metals in aircraft but…

- Fastener installation is **<u>too slow</u>** causing a bottleneck
- Production rates can't meet demand

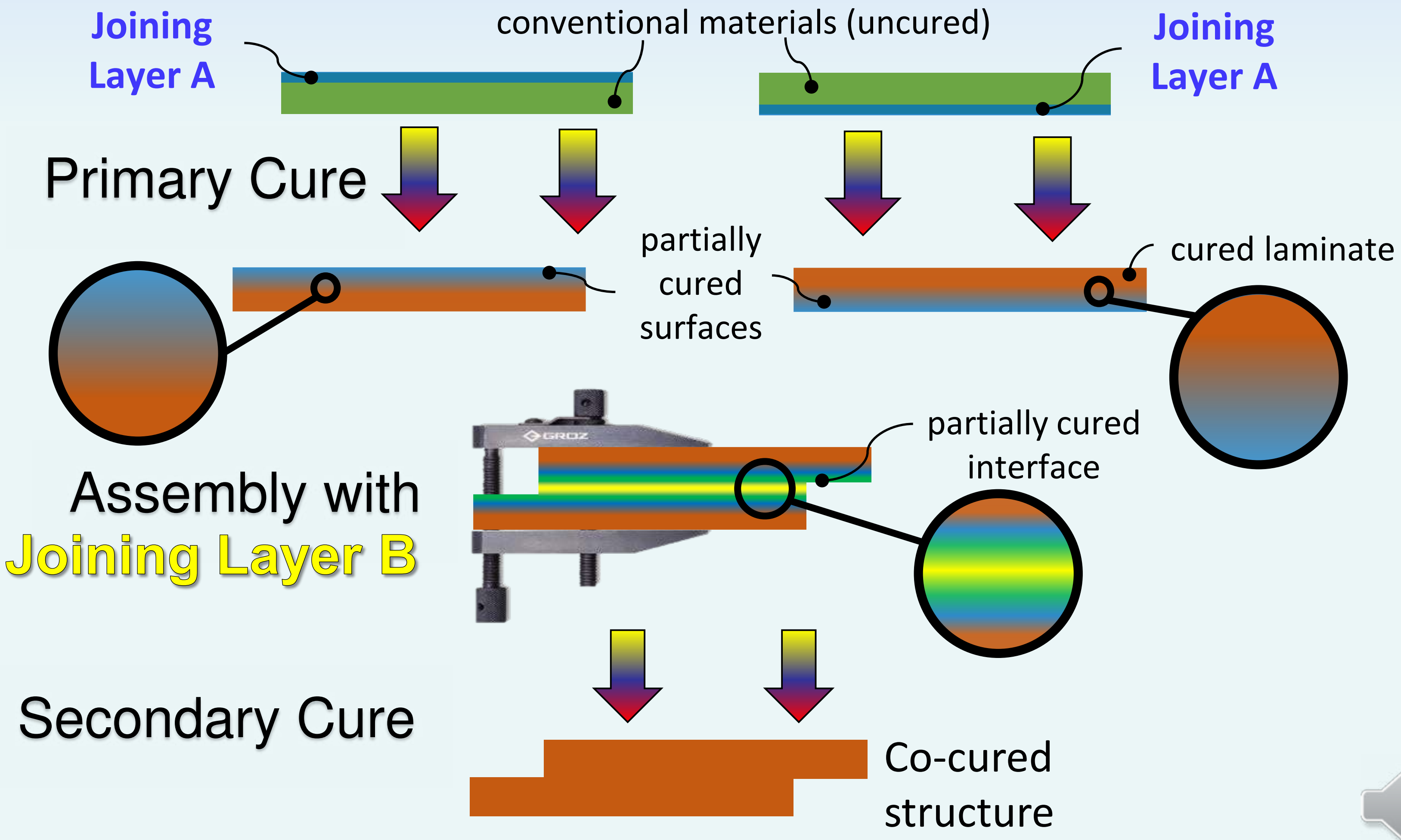




Fasteners in a Single-Aisle Composite Airframe

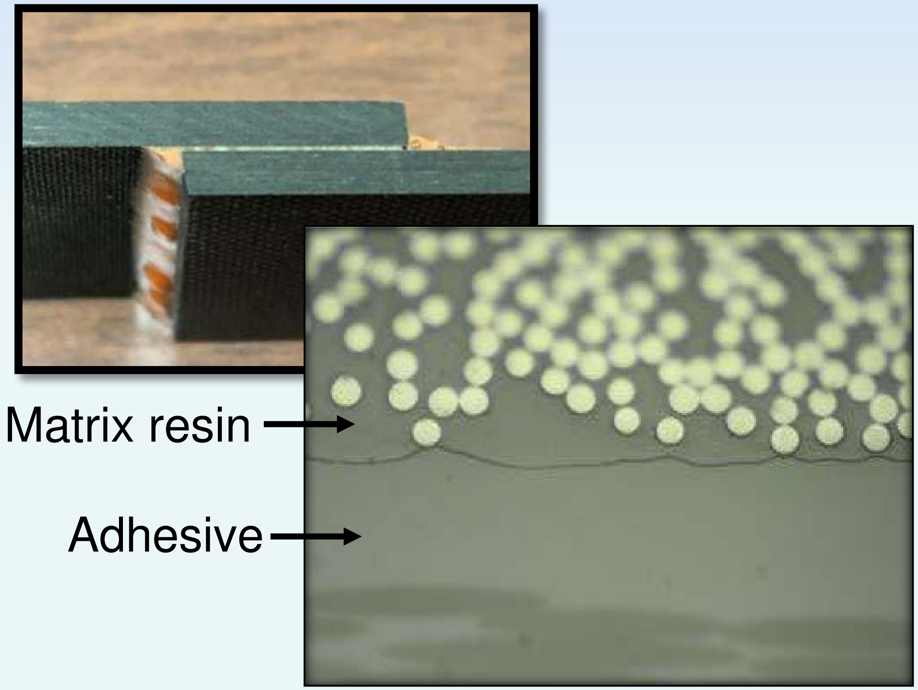
The AERoBOND Method

*The **reliability** of **co-cure** in a **"bonded" assembly***



Adhesive Bondline vs. AERoBOND

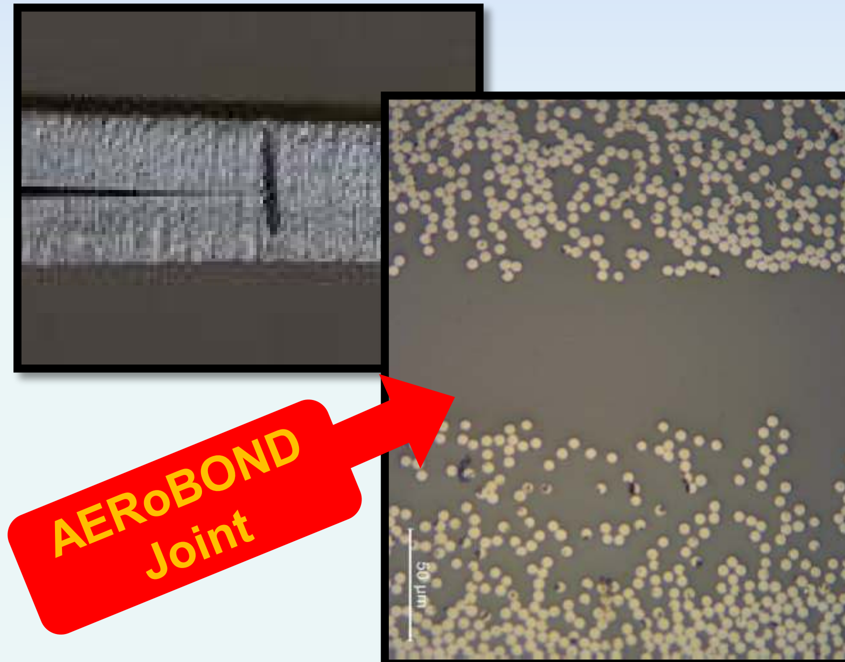
Adhesive Bondline



- Cured matrix resin cannot mix with adhesive

Potential for weak bonds

AERoBOND Joint

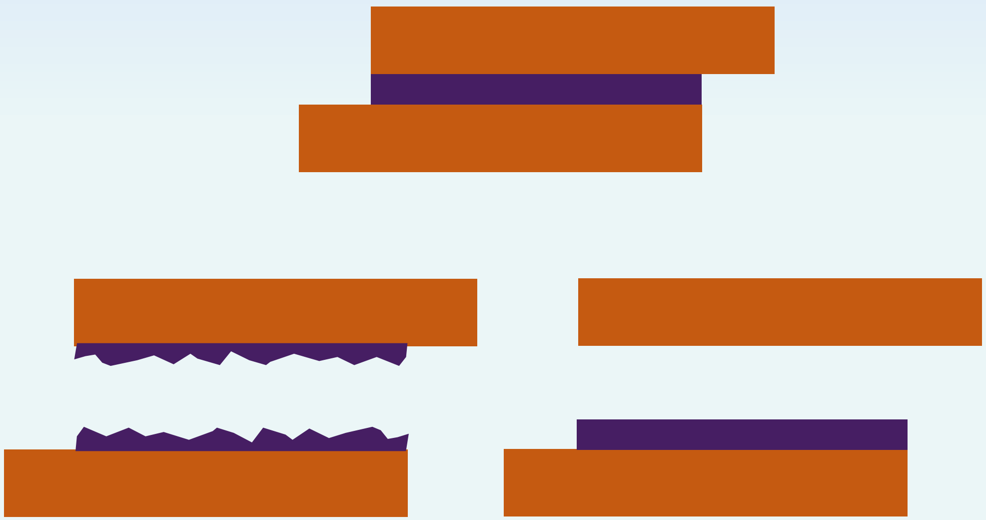


- The AERoBOND joint is *indistinguishable* from the matrix resin of adherends

Quantifiable, certifiable resin properties

Failure Mode and Certification

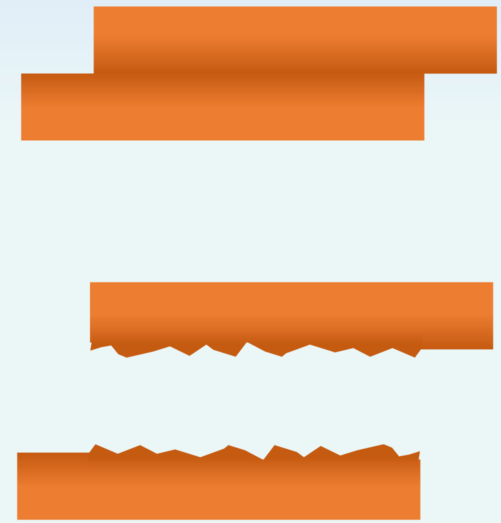
Bond Failure



Cohesive Failure

Adhesive Failure

AERoBOND Failure

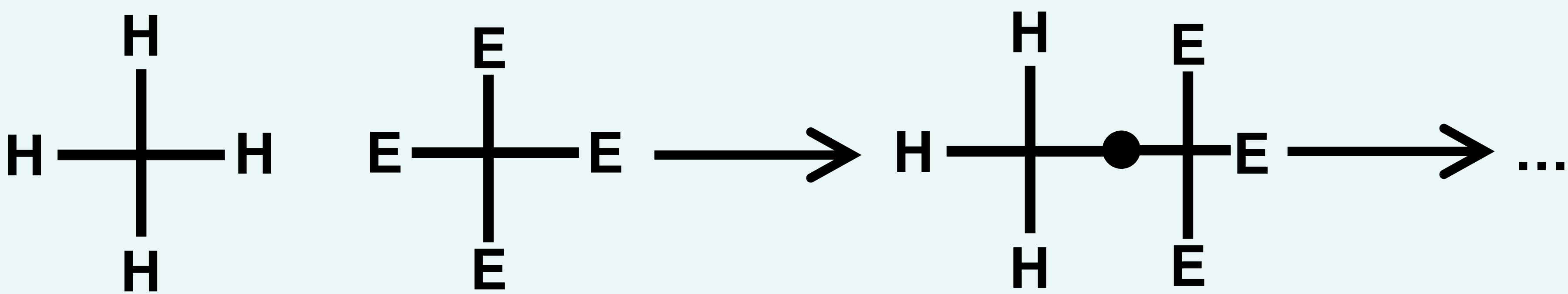


Cohesive Failure

- AERoBOND **eliminates** the potential for **weak bond failure** mode
- **Goal:** AERoBOND mechanical properties **similar to** conventional co-cured laminates.

Thermoset Epoxy Basics

- Hardener groups (H) react with epoxy groups (E) to form polymer.

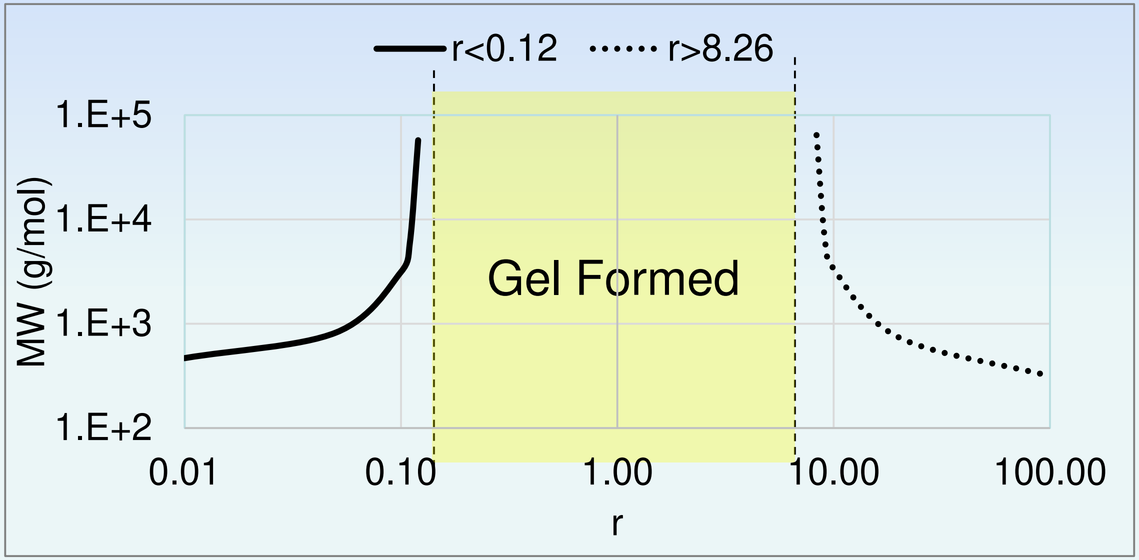


- Molecular weight is limited by applying an offset to the stoichiometry

$$\frac{hardener}{epoxy} = r = \frac{moles\ H}{moles\ E}$$

$r = 1$: Equivalent Mixture
$r > 1$: Hardener Rich (HR)
$r < 1$: Epoxy Rich (ER)

Offset, Molecular Weight, and Gelation



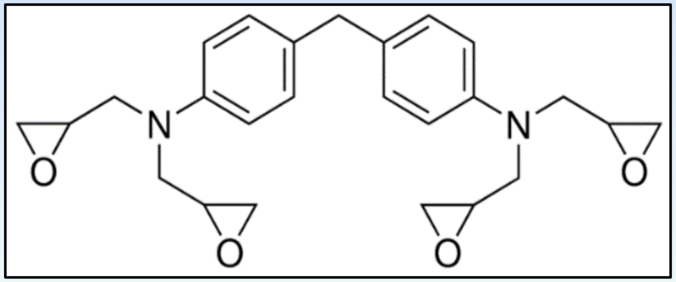
$$r_{gel}P_{gel}^2 = \frac{1}{(f_e - 1)(g_e - 1)}$$

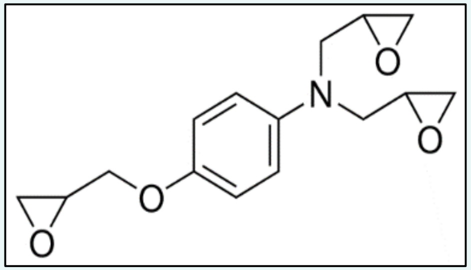
- Monomer functionalities, $f_e = 4$ and $g_e = 3.75$, for tetrafunctional hardener and a mixture of tetra- and tri-functional epoxies
- For 100% conversion of the limiting monomer, gelation occurs for: $0.12 < r < 8.25$

Macosko, Miller. Molecular Weights of Nonlinear Polymers. 9(2) 1976.

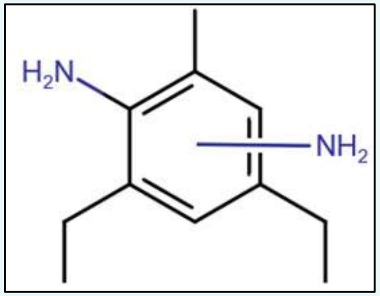
Resin Chemistry

- Kaneka API-60 Part A
  - ~65% tetrafunctional epoxy
  - ~20% trifunctional epoxy
  - ~15% proprietary toughener
  - Epoxy equivalent weight known! EEW = 131 g/mol



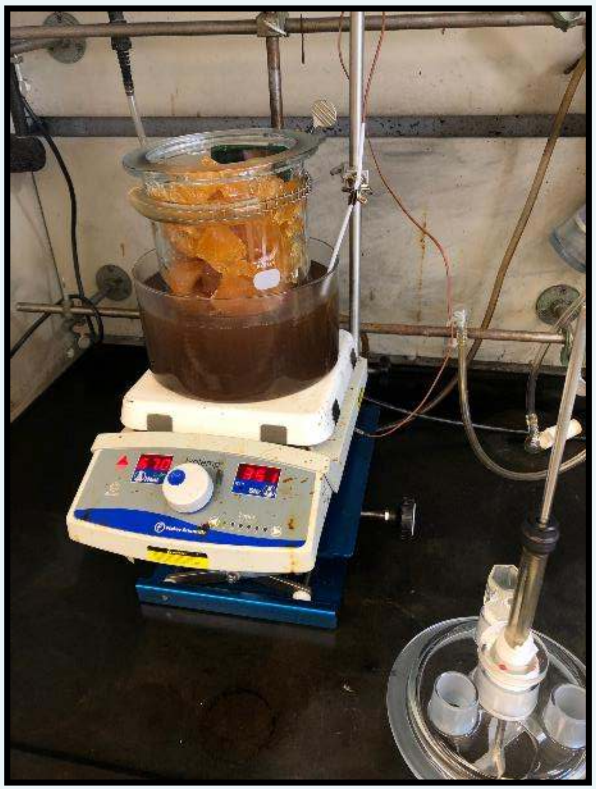


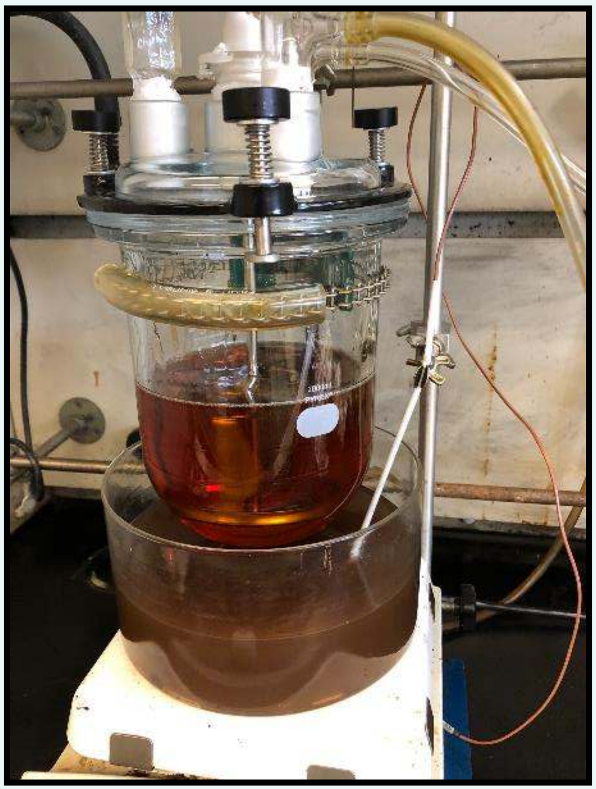
- Diethyltoluenediamine (DETDA)
  - Ethacure® 100 from Albemarle® Corp.
  - Mixture of isomers
  - Liquid at RT
  - Equivalent weight, EW = 44.6 g/mol

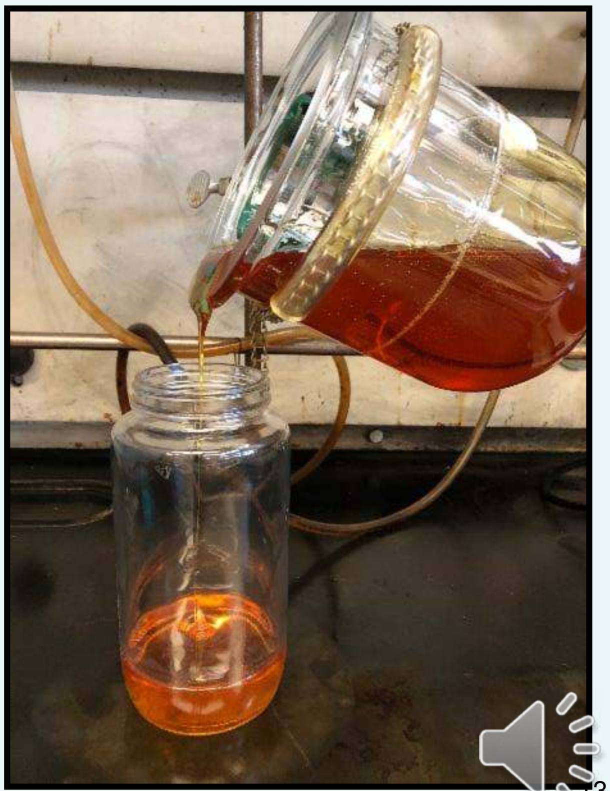


Resin Preparation

- API-60 Part A and DETDA stirred 1 - 2.5 h at 100 -110 °C
- Prepolymer diluted with 15 wt.% methyl ethyl ketone (MEK) prior to producing prepreg







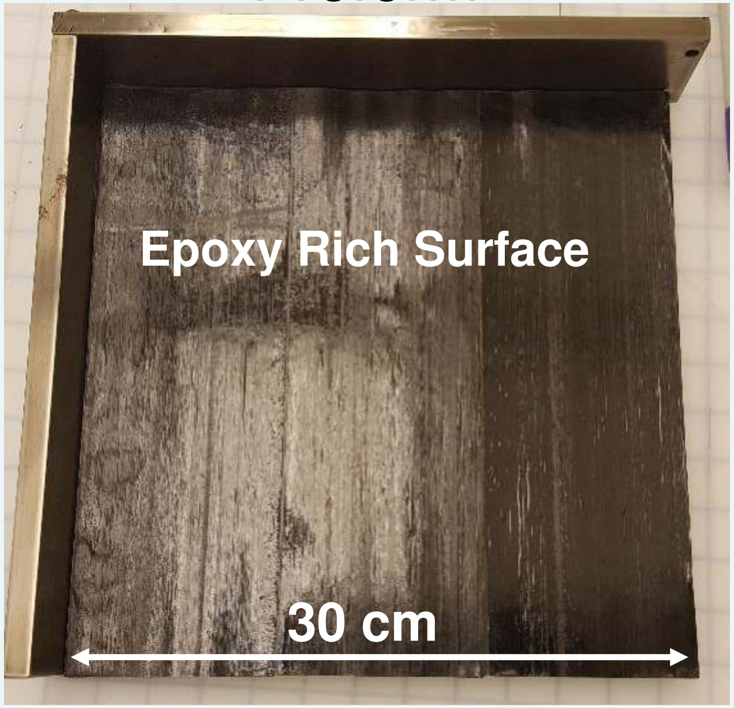
Prepreg Tape Production

- Prepared prepreg tape using a custom tape machine at NASA Langley Research Center
  - Fiber: IM7G 12k, 14 to 16 tows, 75-100 mm wide tape
  - Better uniformity and larger batches compared to hand painted film
  - Process development is complex/challenging

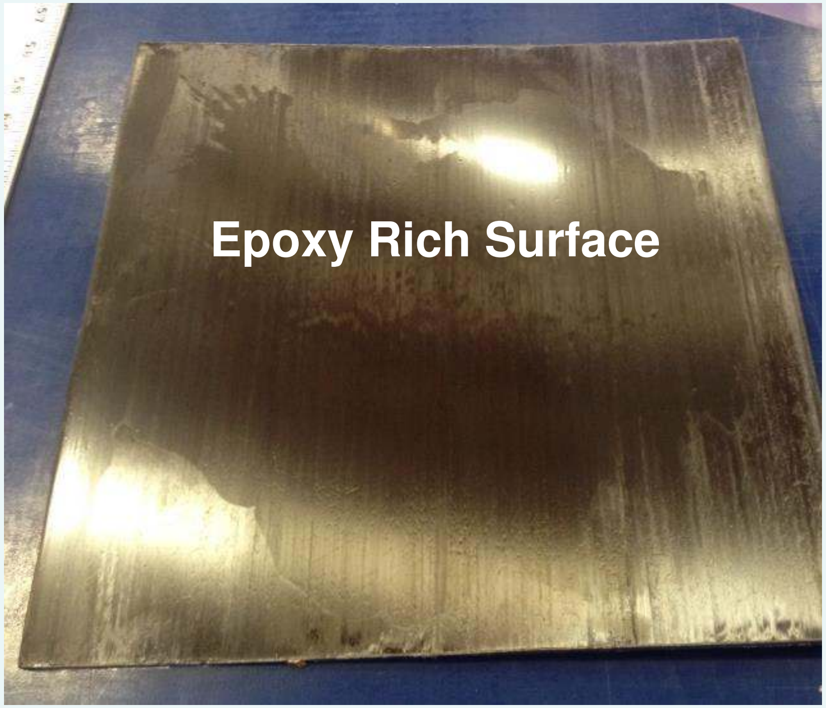
Manufacturing Panels

- Offset prepreg on conventional prepreg
- Panels cured in autoclave

Preform



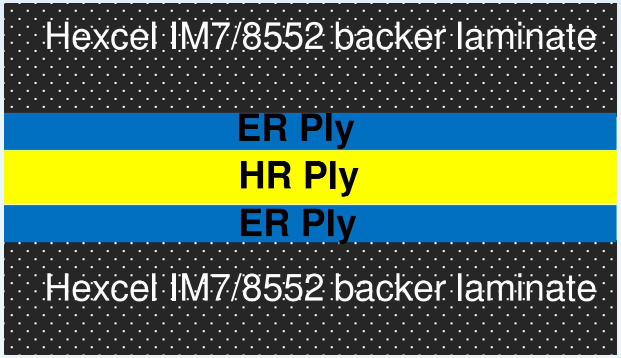
Cured Half-Panel



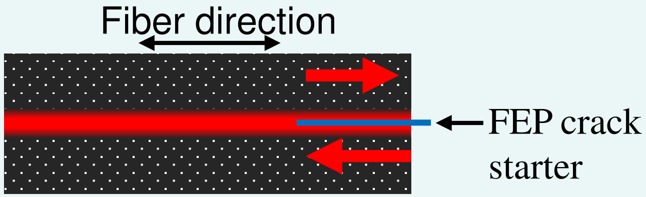
Preliminary Development and Testing

- Two-step fabrication process
  - 1. Fabricate “half-panels” with ER surfaces
  - 2. Join ER panels with HR “adhesive” ply
- Conventional material used in backer laminate
  - Hexcel® IM7/8552 prepreg
  - 190 g/m^2 fiber areal weight (FAW), 35% resin content
- Test Parameters
  - Resin formulation (*r*-value, degree of cure)
  - Ply thickness & resin content
  - Cure process (time and temperature)
  - Bagging scheme
- Rapid Screening with End-Notched Flexure (ENF) test
  - Mode II (Shear) Fracture Toughness
  - Simple specimen fabrication and testing

Laminate Configuration



End-Notched Flexure (ENF) Test



- Layup: $[0]_{24}$
- Non-Precracked (NPC) vs Precracked (PC)

Process Development

Test	Date	Half Panel 1	Half Panel 2	ER	Outcome
1	april, 2019	IM7/8552(11-ply)+r=0.15(1-ply)	IM7/8552(11-ply)+r=6.7(1-ply)	[illegible]	more than 50% bonded, disbonded during machining
2	april, 2019	IM7/8552(11-ply)+r=0.15(1-ply)	IM7/8552(11-ply)+r=0.15 (1-ply)	[illegible]	About 40% bonded, disbonded during machining
3	april, 2019	IM7/8552(11-ply)+r=0.15(1-ply)	IM7/8552(11-ply)+r=6.7(1-ply)	[illegible]	No Bond
					90% bonded, partial disbond on water jet,
29	2/6/2020	6"x12", fiber in 12" dimension, SGP196P/8552 PW(2-ply) + IM7/8552(7-ply) + r=0.15(2-ply) TM390	6"x12", fiber in 12" dimension, SGP196P/8552 PW(2-ply) + IM7/8552(8-ply) + r=0.15(2-ply) TM390	[illegible]	
30	10/17/2019	6"x12", fiber in 12" dimension, IM7/8552(9-ply)+r=0.15(2-ply) TM388	6"x12", fiber in 12" dimension, IM7/8552(10-ply)+r=0.15(2-ply) TM388	[illegible]	Repeat 23 for DCB

- Completed testing on 30+ AERoBOND configurations using 18+ material systems
  - End-notched flexure
  - Failure locus, hardness
  - Chemical analysis
- Each configuration spans 3+ weeks of effort

Run Number	r-value	Hardener	Epoxy	Formulation Temperature	Formulation Time	Fiber	FAW (g/m^2)	Solvent Content (wt%)	Resin Content (wt%)
TM376	0.8	DDS	API-60			IM7G UD 14 tows	74-131	4.7%	45 to 50%
TM377	0.15	DDS	API-60 Part A			IM7G UD 14 tows	81	5%	52%
TM378	6.7	DDS	API-60 Part A			IM7G UD 14 tows	155	7%	45-60%
TM379A	0.8	DDS	API-60			IM7G UD 14 tows	37-54	5 to 6%	45 to 60%
TM379B	6.7	DETDA	API-60 Part A			IM7G UD 14 tows	56	12%	20-24%
TM380	0.15	DETDA	API-60 Part A			IM7G UD 14 tows	58-62	5-6%	60-65%
TM381	6.7	DETDA	API-60 Part A			IM7G UD 14 tows	70-90	10%	16-38%
TM382	6.7	DDS/DETDA (50/50)	API-60 Part A			IM7G UD 14 tows	70	13%	56%
TM383	0.15	DETDA	API-60 Part A	100 °C	1 h	IM7G UD 14 tows	72	3-4%	36
TM384A	0.15	DETDA	API-60 Part A	100 °C	1 h	IM7G UD 14 tows	66-74	5.7-6.6%	55-61%
TM384B	0.15	DETDA	API-60 Part A	100 °C	1 h	IM7G UD 14 tows	74-63	7.6-6.7%	62%
TM385	2.5	DETDA	API-60 Part A	100 °C	1 h	IM7G UD 14 tows	73-78	9%	43-60
TM386	0.15	DETDA	API-60 Part A	100 °C	90 min	IM7G UD 14 tows	70-78	5.6-6.8 %	57-62%
TM387	2.5	DETDA	API-60 Part A	100 °C	90 min	Carbon fabric	195	14.7-15.3%	46-48%
TM388	0.15	DETDA	API-60 Part A	100 °C	90 min	IM7G UD 16 tows	76-78	5-6.5%	62-69%
TM389	2.5	DETDA	API-60 Part A	100 °C	105 min	IM7G UD 16 tows	75-80	7.4-[illegible]%	68-76%
TM390	0.15	DETDA	API-60 Part A	100 °C	135 min	Carbon Fabric	195	8%	43-53%

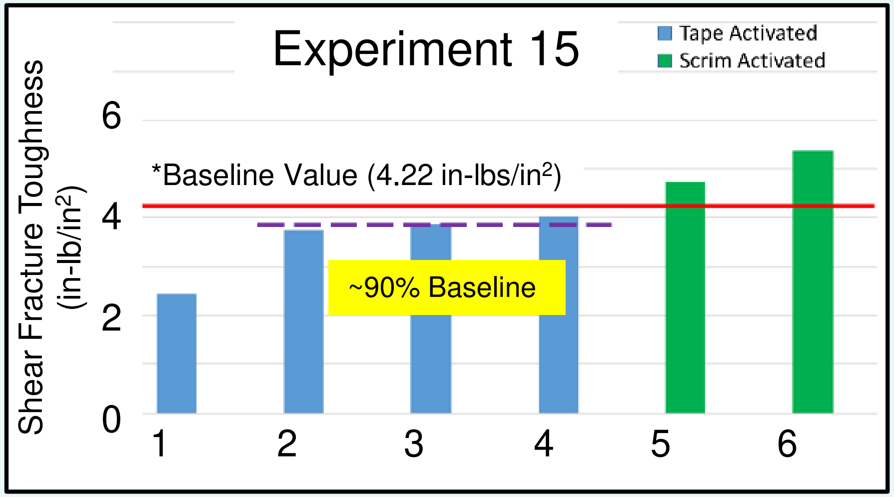
Some Vague Details

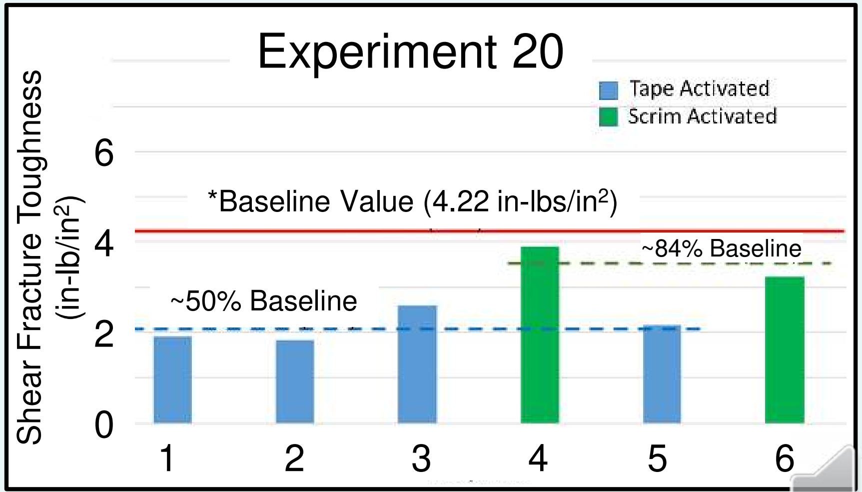
Material	*r*-value	FAW (g/m^2)	RAW (g/m^2)	Number of Plies	Primary Cure Cycle
ER Ply Ranges	0.15	37-90	60-125	1-2	1-3 h @ 177 °C
HR Ply Ranges	2.5-6.7	56-155	20-90	1-2	1-4 h @ 177 °C
Round 1 ER	0.15	77	150	2	1 h @ 177 °C
Round 1 HR	2.5[A]	70	225[B]	1	4 h @ 177 °C

A. Stoichiometric offset to r = 2.5 does not prevent gelation, HR ply only sees 2nd cure cycle
B. Hand painted resin onto carrier scrim cloth to achieve higher resin loading

Key Preliminary Results

- Experiment 15 exceeded expectations (90% of baseline)
  - But successful results were difficult to repeat
  - Used hand painted resin film for HR ply
- Experiment 20 was also interesting (50% of baseline)
  - Also prepared from a *large batch* of hand painted film
- Used configuration from experiment 20 for *Round 1* samples





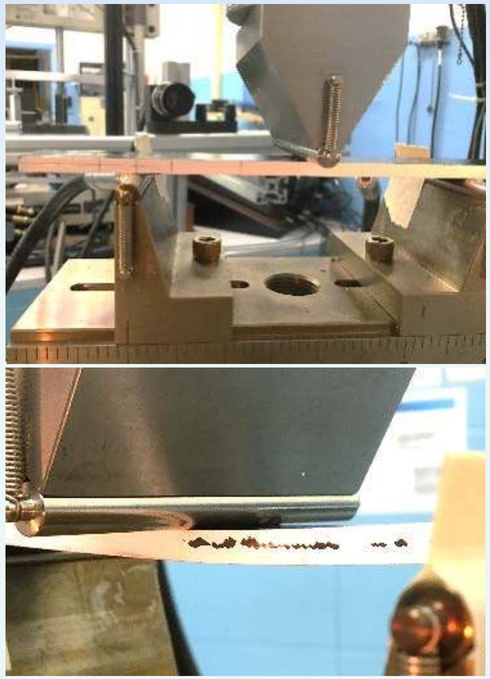
IM7/8552 material property (not part of baseline dataset) *Units conversion: 1 in-lb/in² = 175 J/m²*

Baseline Properties

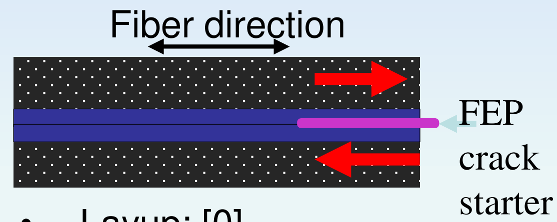
- Measured properties for a series of laminates fabricated using:
  - AERoBOND materials (epoxy and hardener)
  - $r = 0.8$ (conventional ratio)
  - Co-cure process
- Baseline properties used to set AERoBOND performance goals

End-Notched Flexure (ENF) Test

Test setup



Mode-II Interlaminar Fracture Toughness



- Layup: $[0]_{24}$

Large amount of data scatter due to multiple failure mechanisms but close to 50% goal.

G_{IIc} (J/m^2)	Round 1 (50%)	Round 2 (80%)
Goals*	370	591
Measured	347±97 (47%)	--

*Based on precracked value measured on IM7/8552

<u>Baseline Properties</u>

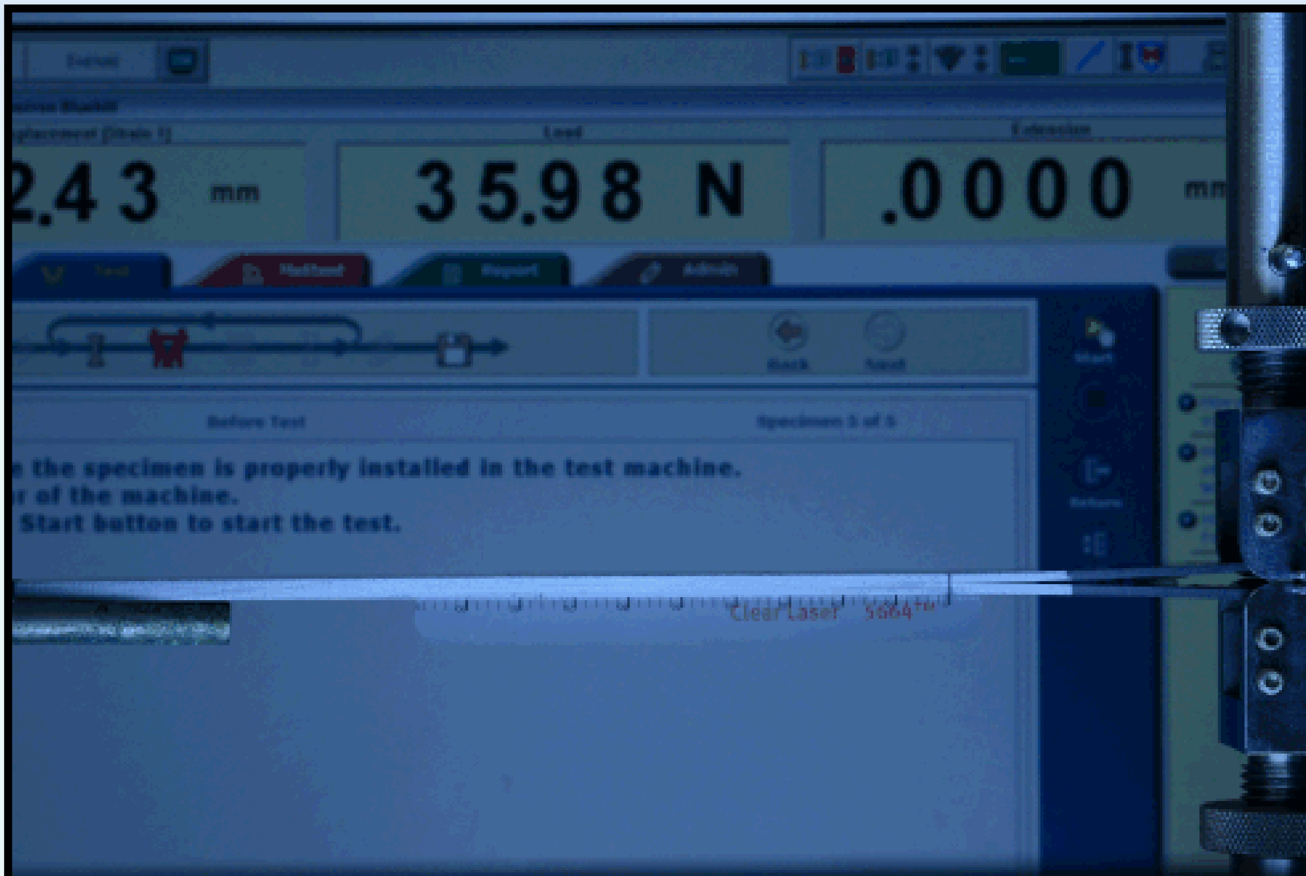
*Ave G_{IIc-PC}: **740** J/m^2

*Std Dev: 50.4 J/m^2

*Cof Var: 6.8 %

Double Cantilever Beam (DCB) Test

Mode I Fracture Toughness



Summary of Joint Properties

Strength	ILT^{CB} (MPa)	ILT^{FWT} (MPa)	ILS^{SLS} (MPa)	ILS^{DLS} (MPa)
Baseline	61.5	41.8	31.4	41.6
Round 1	23.5±2.2	37.5	25.7±2.2	9.85±1.5
% of Baseline	41%	59%	82%	24%

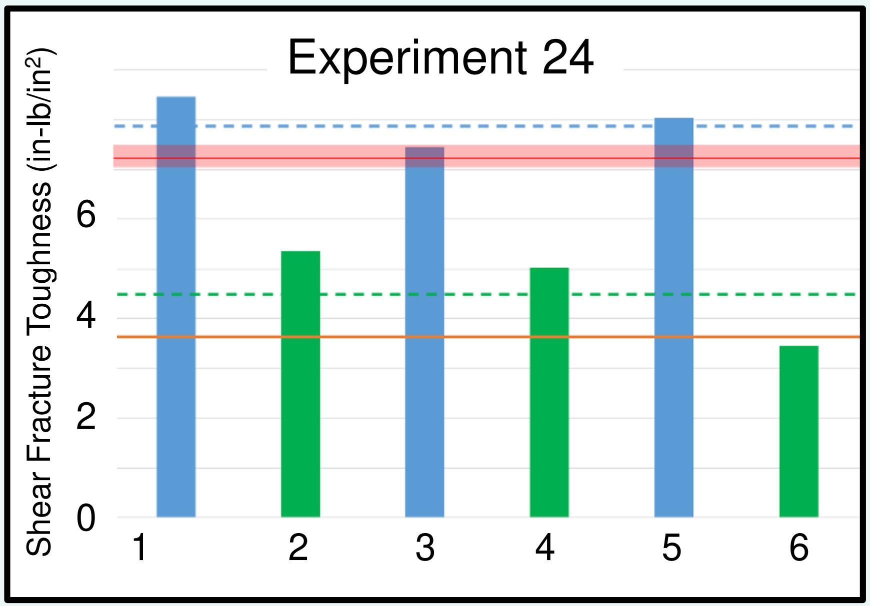
Interlaminar Tensile (ILT), Curved Beam (CB), Flatwise Tension (FWT), Single-Lap Shear (SLS), Double-Lap Shear (DLS)

Fracture Toughness	G_{Ic_init} (J/m^2)	G_{Ic_ss} (J/m^2)	G_{IIc_NPC} (J/m^2)	G_{IIc_PC} (J/m^2)
Test method	DCB	DCB	ENF	ENF
Baseline	180	203	1255	740*
Round 1	16±3.6	36±16	372±99	347±97
% of Baseline	9%	19%	27%	47%

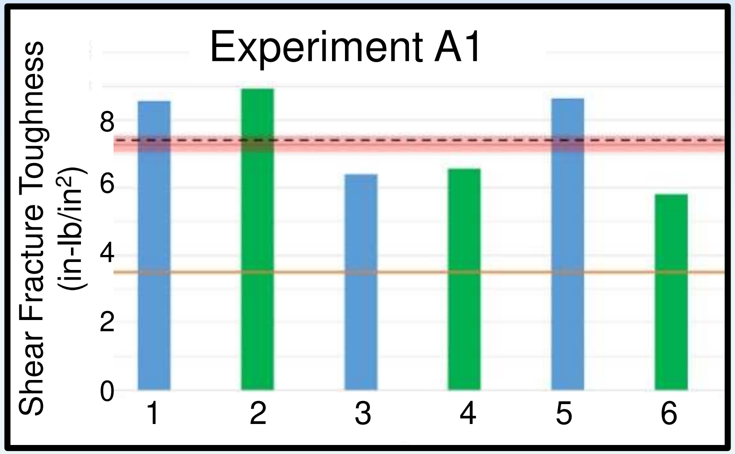
Double Cantilever Beam (DCB), End-Notched Flexure (ENF), Critical strain energy release rate for mode-I (G_{Ic}) initiation (init) and steady-state (ss), and mode-II (G_{IIc}) non-precracked (NPC),and precracked (PC)
**IM7/8552 material property (not part of baseline dataset)*

Progress Since Round 1 (G_{IIc_NPC})

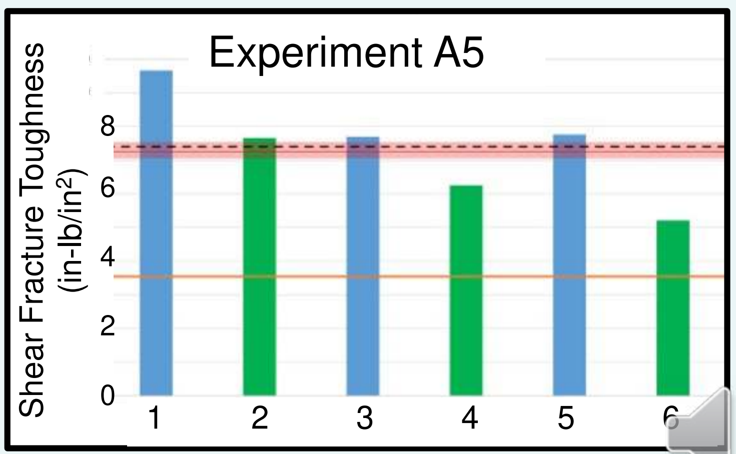
- Recent tests improved over Round 1 (27%) and even **exceeded baseline toughness**
  - Baseline ±σ indicated with red bar
  - 50% baseline indicated with orange line
- ER activated (**blue bars) 111% of baseline**
- HR activated (green bars) 64% of baseline



Ave: 7.496 in-lbf/in² %Baseline: **105%**



Ave: 7.379 in-lbf/in² %Baseline: **103%**



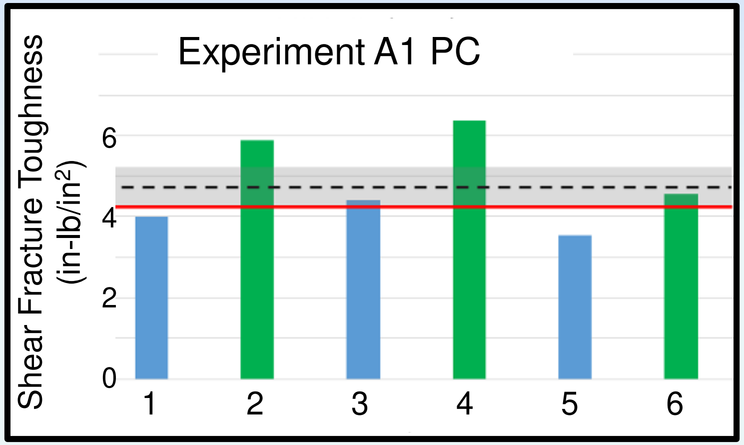
Units conversion: 1 in-lb/in² = 175 J/m²

Progress Since Round 1 (G_{IIc_PC})

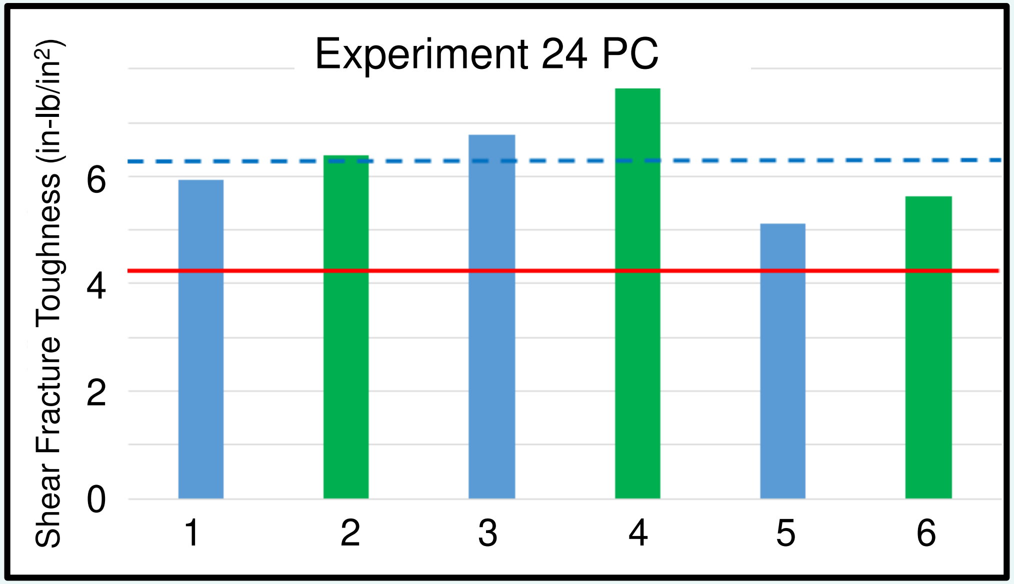
- Recent tests improved over Round 1 (47%) and even **exceeded baseline toughness**
  - Baseline indicated with red line
  - 50% baseline indicated with orange line

<u>Greatly improved shear fracture toughness</u>

Ave: 4.79 in-lbf/in^2 %Baseline*: **113%**

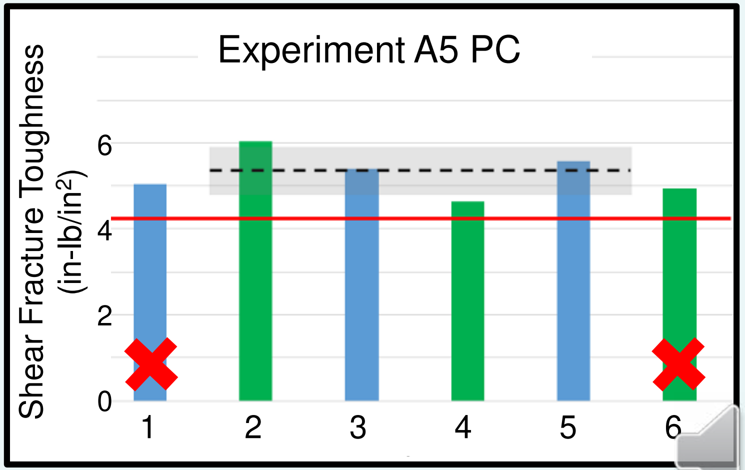


Ave: 6.26 in-lbf/in^2 %Baseline*: 148%



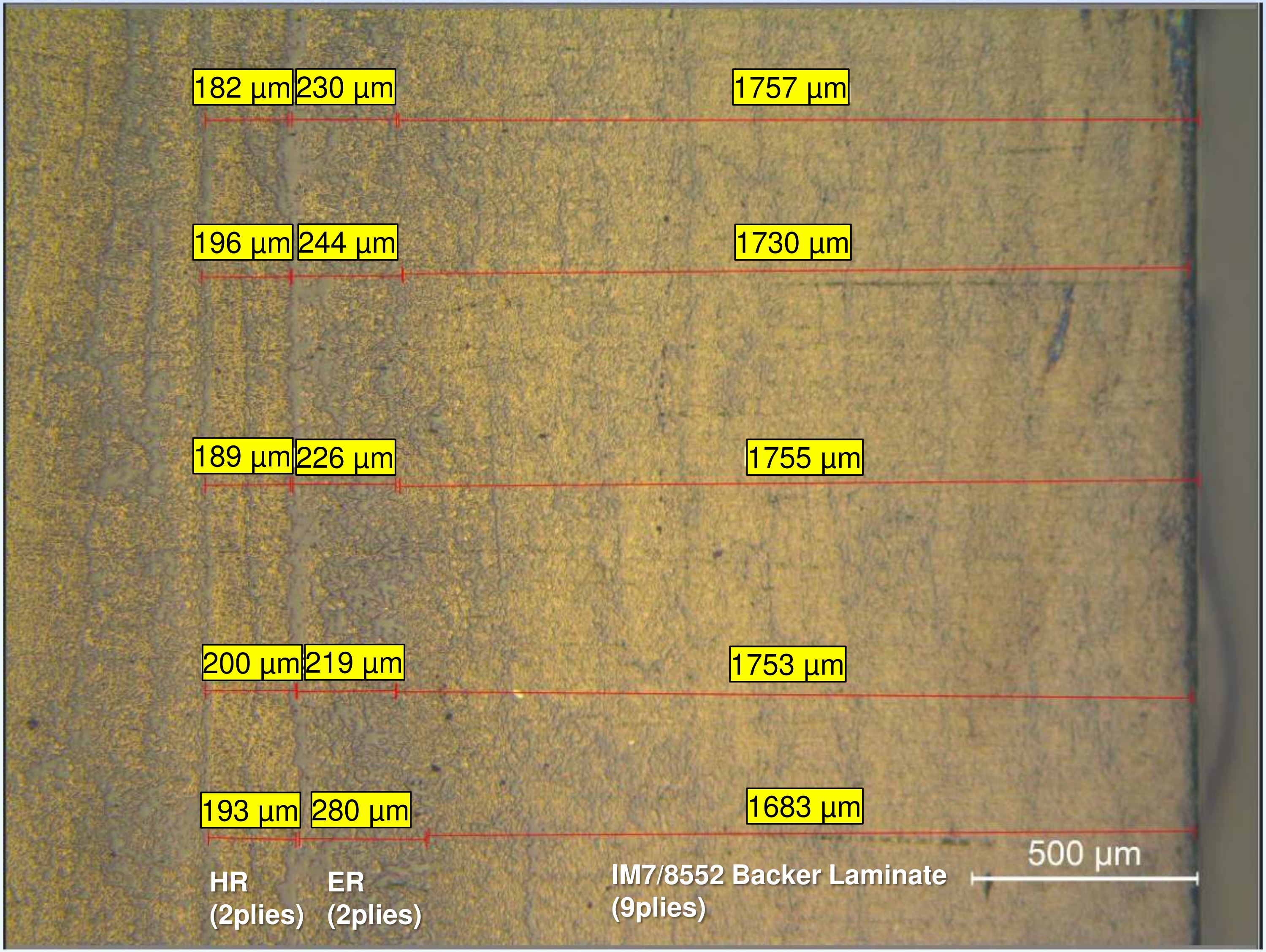
**IM7/8552 material property (not part of baseline dataset)*

Ave: 5.410 in-lbf/in^2 %Baseline* : 128%

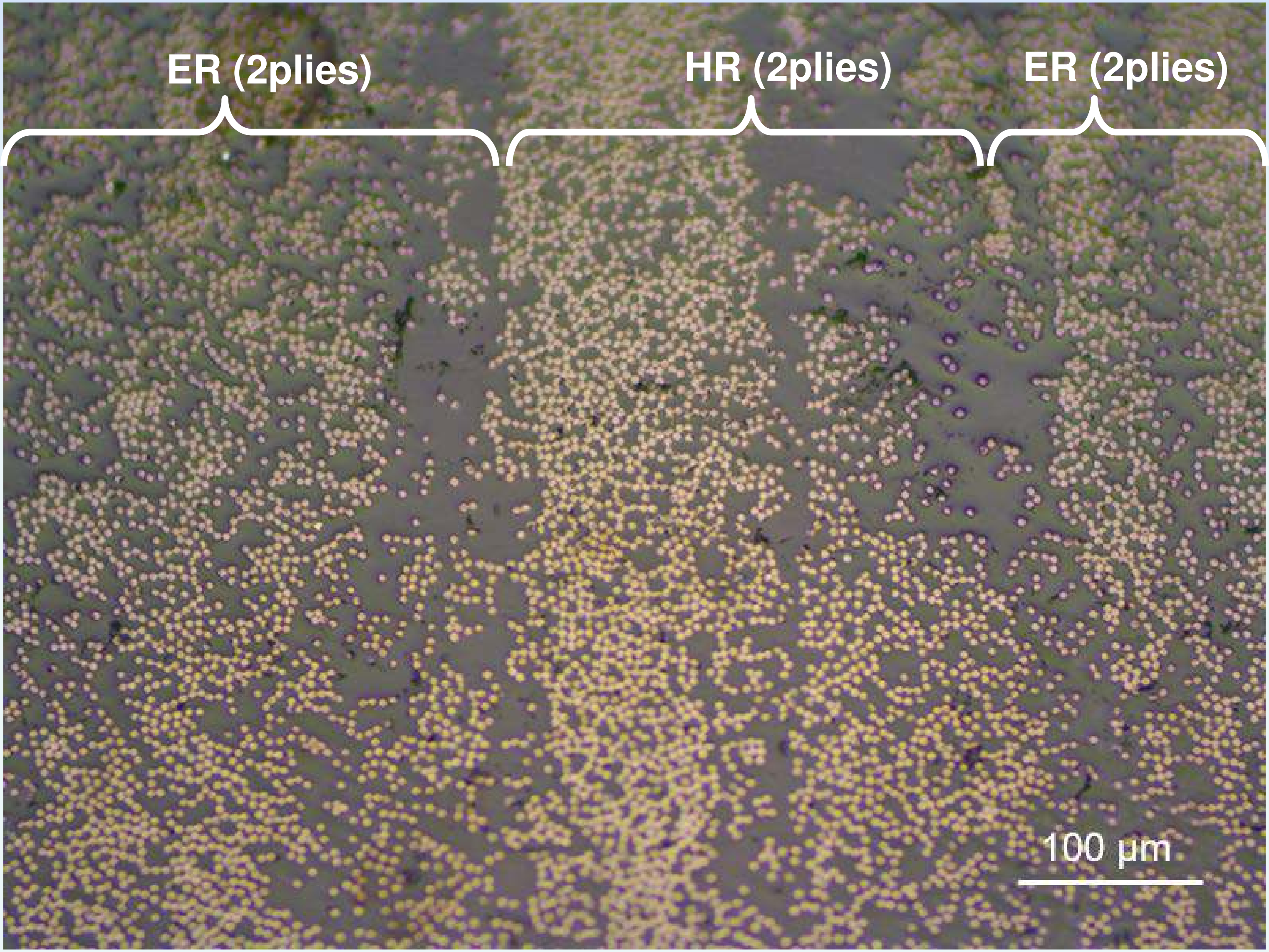


Unit conversion: 1 in-lb/in^2 = 175 J/m^2

Optical Inspection of Interface



No Visible Discontinuity



Conclusions

- AERoBOND approach:
  - Achieve predictability of co-cured joints with the manufacturing simplicity of secondary bonding
  - AERoBOND joint should be indistinguishable from interlaminar joint and similar in properties
- Microscopic inspection indicates good mixing at AERoBOND interface
- Several tests indicate we have reached our preliminary goal of 50% baseline properties
  - Interlaminar shear (SLS) and tensile (FWT, CB) strengths
  - Shear fracture toughness (ENF) is close to goal
- Recent results (ENF) indicate AERoBOND process can match co-cure properties

Acknowledgements

- Glenn Research Center:
  - Mechanical testing: Jon Salem & Mike Pereira
- Langley Research Center:
  - Engineering: James Ratcliffe
  - Laminate fabrication: Sean Britton, Hoa Luong, & Kelvin Boston
  - Machining: Mike Oliver & Thomas Hall

Thank You!

(frank.l.palmieri@nasa.gov)

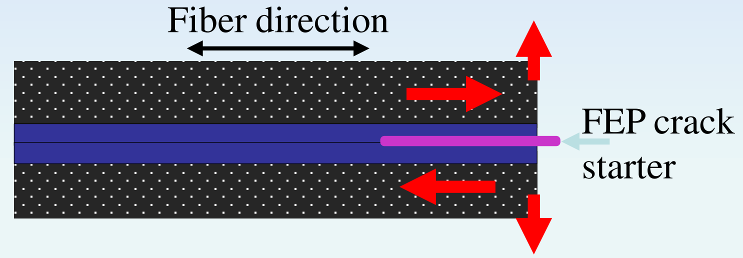
Start Extra Material

Mechanical Test Methods 1

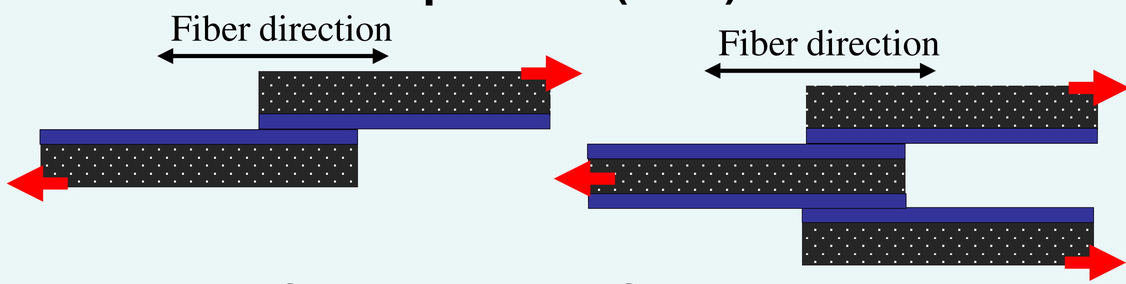
Quasi-static testing

- ASTM D5528 (DCB) & D7905 (ENF) for mode I & mode II interlaminar fracture toughness
- ASTM D3165 (SLS) & D3528(DLS): Apparent shear strength
- ASTM D6415 (CB): Interlaminar tensile strength

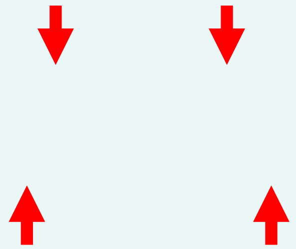
Double Cantilever Beam (DCB) & End-Notched Flexure (ENF)



Single-Lap Shear (SLS) & Double-Lap Shear (DLS)



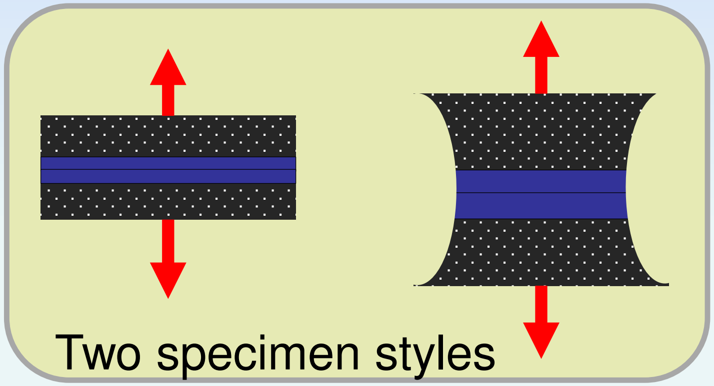
Curved Beam (CB)



Mechanical Test Methods 2

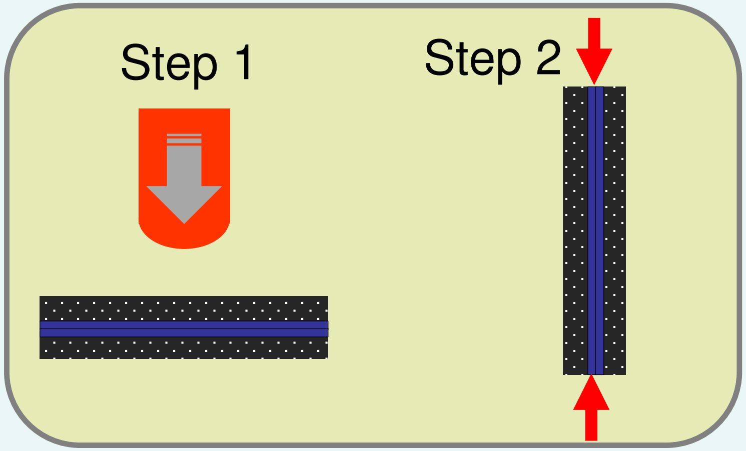
- ASTM D7291:Interlaminar Tensile Strength

Flatwise Tension (FWT)

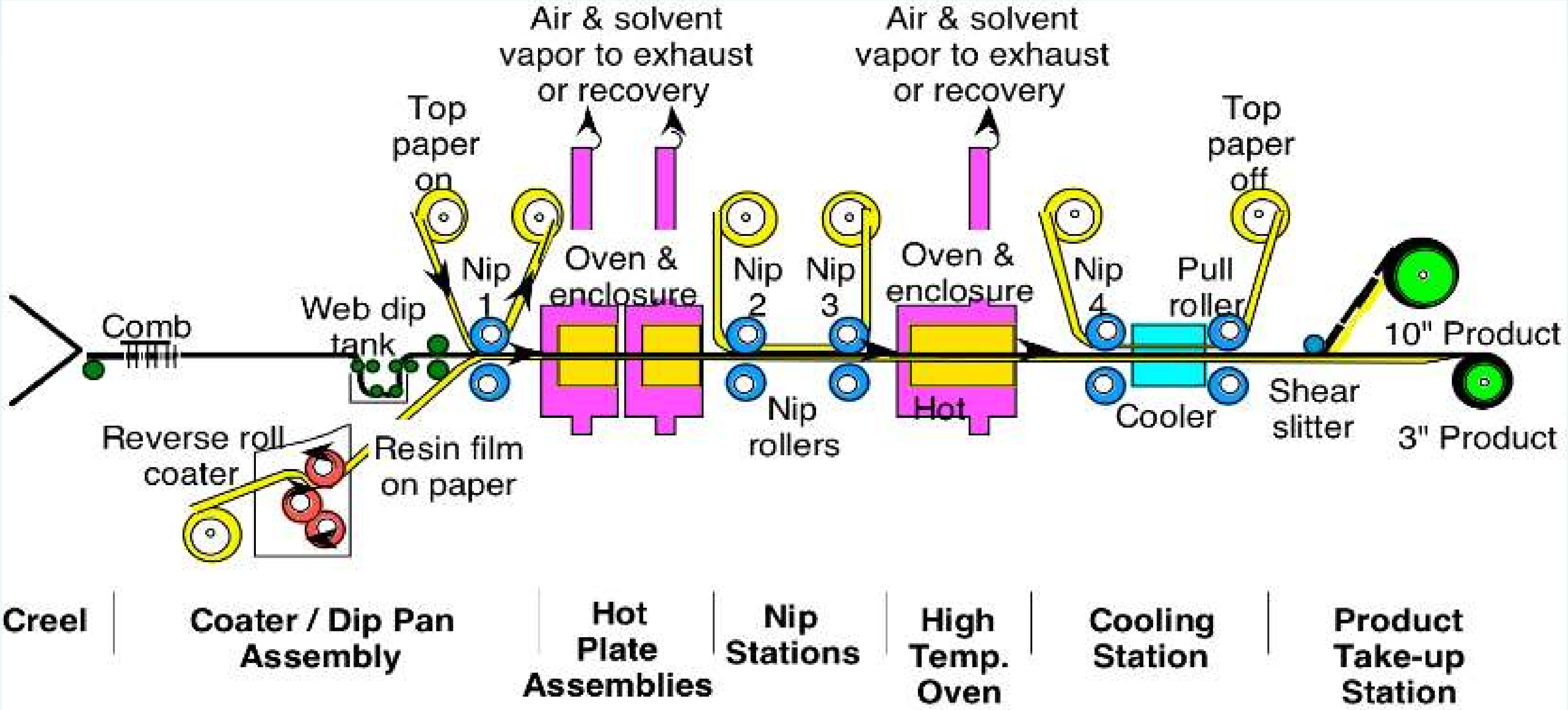


- ASTM D7136 (BVID) and ASTM D7137 (CAI): Damage tolerance

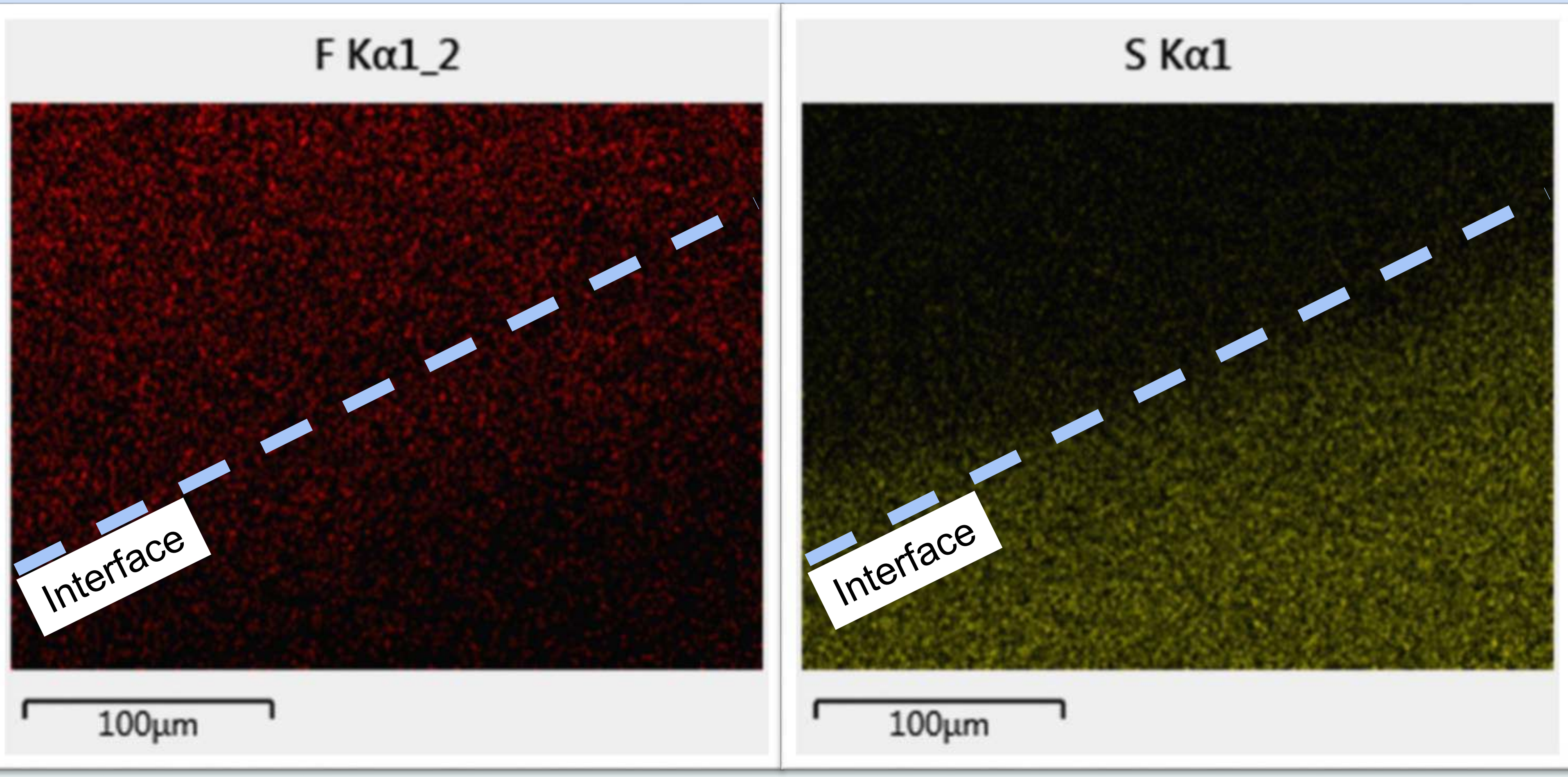
Barely Visible Impact Damage (BVID) & Compression After Impact (CAI)



Prepreger Details



2) EDS Map of Interface



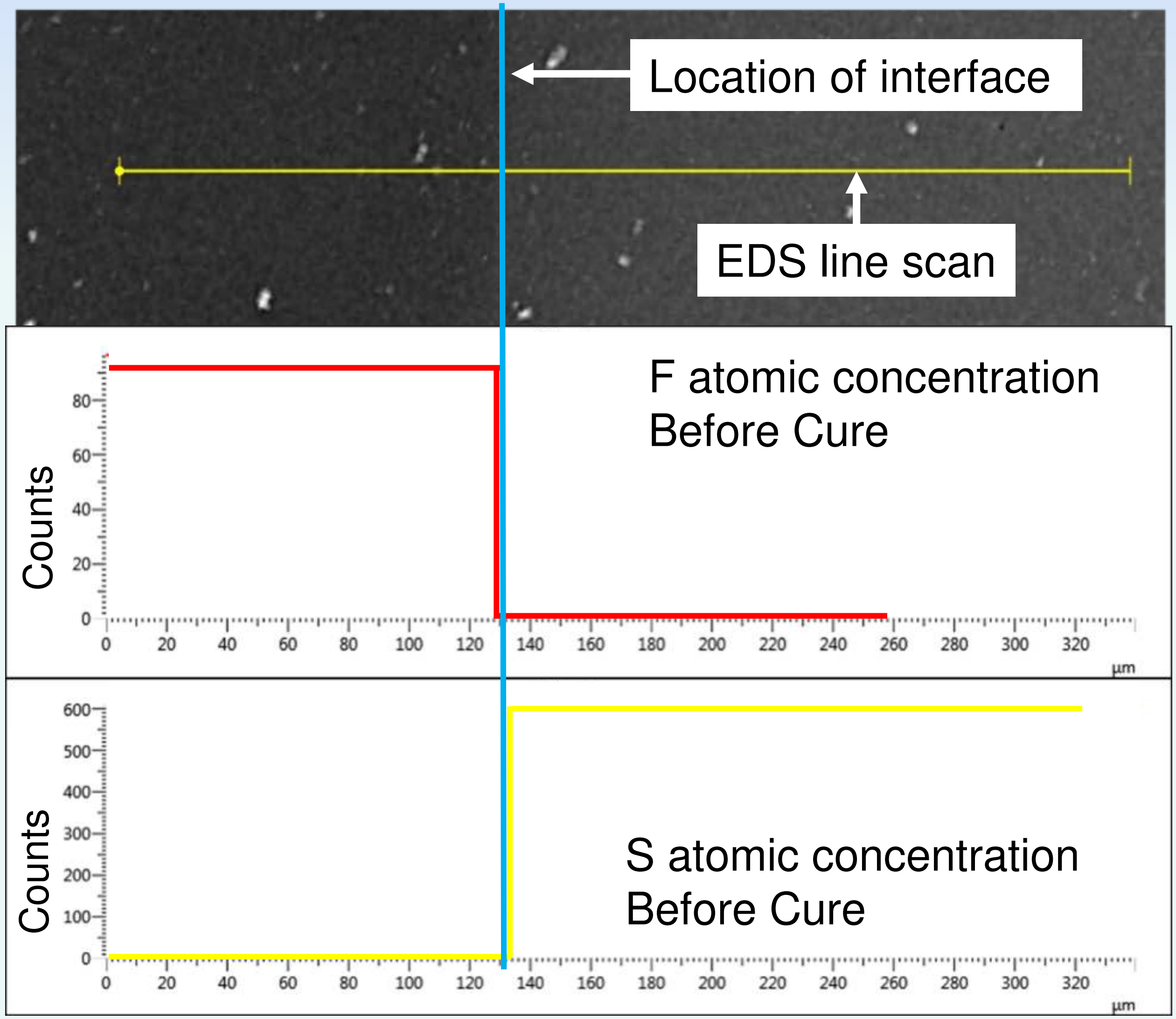
- F and S atoms diffuse across interface

2) Interdiffusion at Interface

Electron Micrograph

After Cure

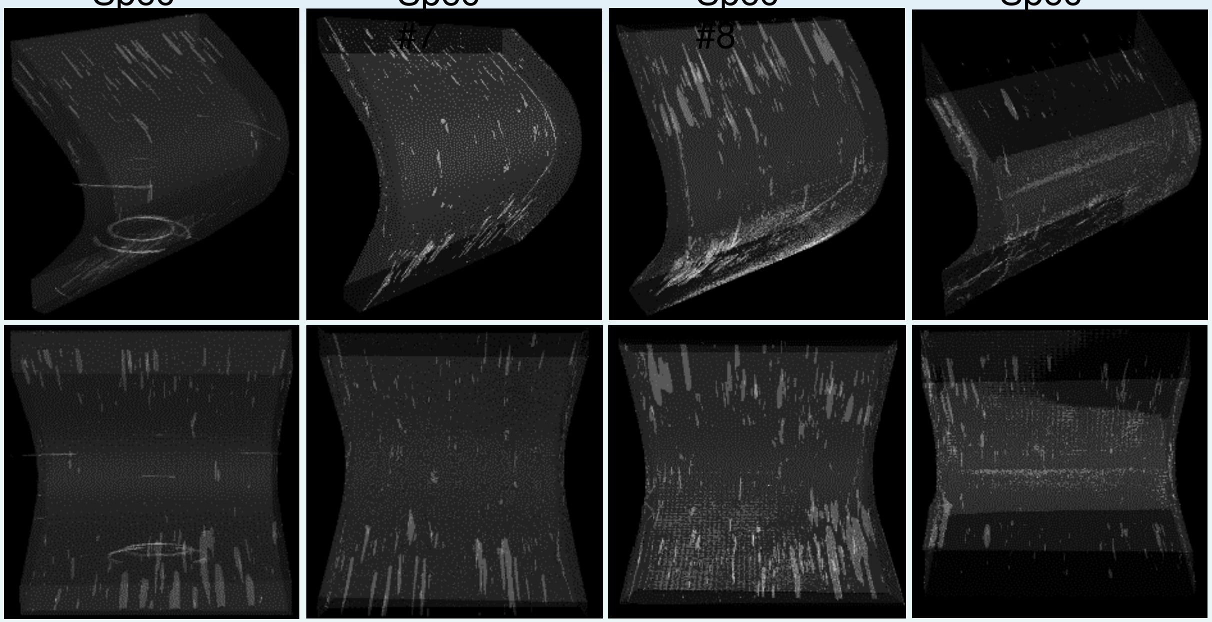
EDS Line Scan Data



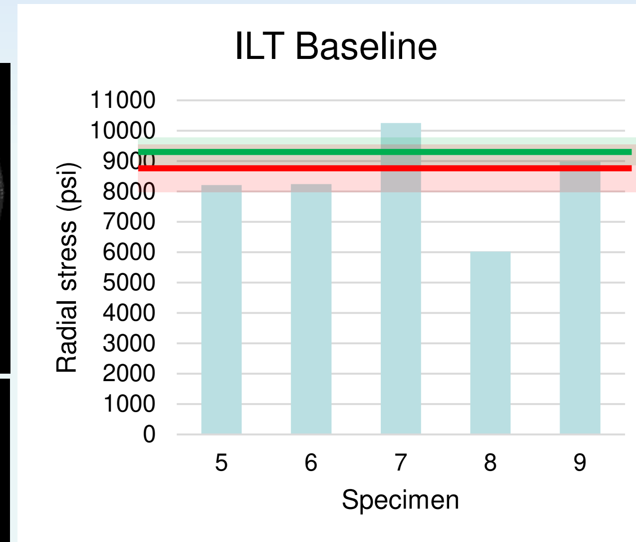
Variation in Curved Beam Test Data

- X-Ray Computed Tomography Inspection

Spec | Spec #7 | Spec #8 | Spec



Low porosity | Low porosity | **High porosity** | Low porosity



Ave Str: 8341 psi (w/out 8): **8921 psi**

Std Dev: 1377 psi (w/out 8): **830 psi**

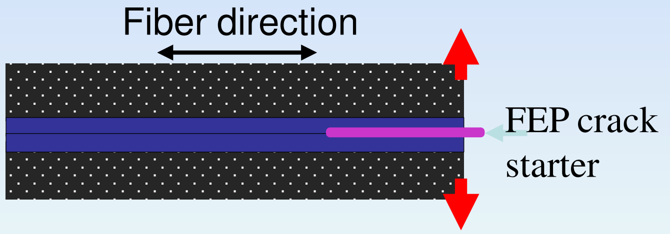
Cof Var: 17 % (w/out 8): **9 %**

	Goals for:	DOE 1 (50%)	DOE 2 (80%)
(w/ 8)	ILS (psi)	4171	6673
(w/out 8)	ILS (psi)	4461	7137

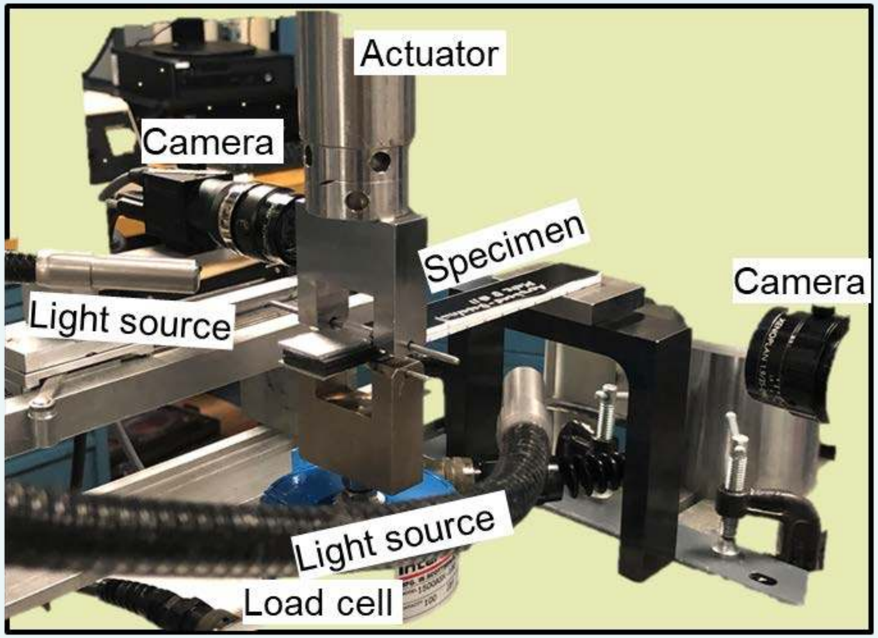
4

Double Cantilever Beam (DCB) Test

Mode-I Interlaminar Fracture Toughness



Test setup



Short of goal. AERoBOND resins are not toughened like commercial systems

G_{Ic} (J/m^2)	Round 1 (50%)	Round 2 (80%)
Goals	102	161
Measured	39±16 (19%)	--

Baseline Properties

Ave $G_{Ic\text{-}ss}$: 203 J/m^2
Std Dev: 8.94 J/m^2
Cof Var: 4.4 %

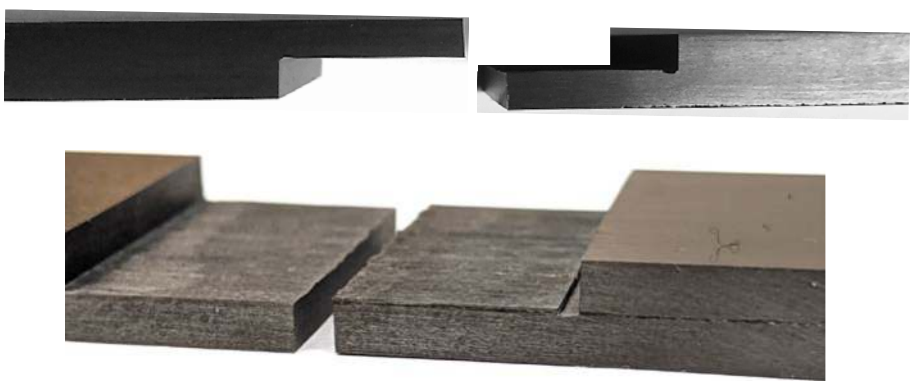
Statistics for Δa > 0.6 in. (steady state)

Single-Lap Shear (SLS) Test

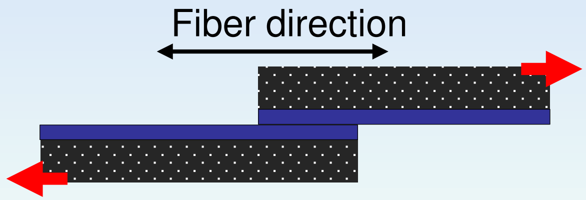
Test Specimen

Pre-test

Post-test



Interlaminar Shear Strength



- Layup: $[0]_{36}$

Specimens often failed away from AERoBOND interface due to stress concentrations at different depths in cross-section.

ILS (MPa)	Round 1 (50%)	Round 2 (80%)
Goals	15.7	25.1
Measured	25.7±2.2 (82%)	--

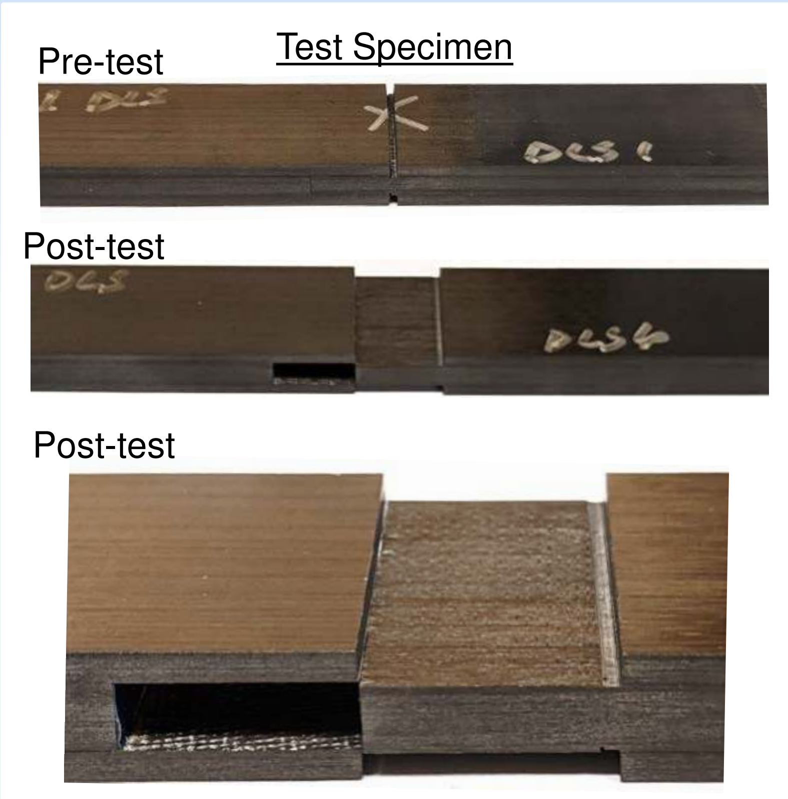
Baseline Properties

Ave ILS: **31.4** MPa

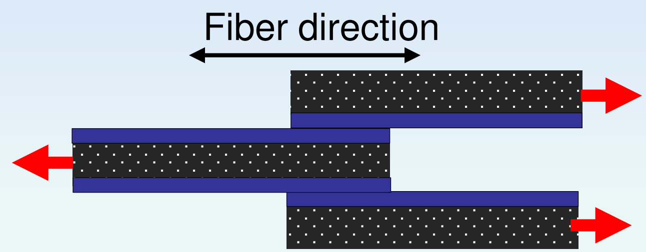
Std Dev: 1.6 MPa

Cof Var: 4.35 %

Double-Lap Shear (DLS) Test



Interlaminar Shear Strength



Lower than expected properties that may be related to complexity of fabrication.

ILS (MPa)	Round 1 (50%)	Round 2 (80%)
Goals	20.8	33.3
Measured	9.8±1.5 (24%)	--

Baseline Properties

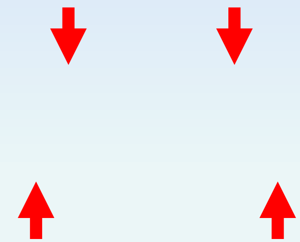
Ave ILS: **41.6** MPa

Std Dev: 2.2 MPa

Cof Var: 5.17 %

Curved Beam (CB) Test

Interlaminar Tensile Strength



Test setup

Properties are near 50% goal and surprisingly good based on complexity of build. No matched tooling was available to make matched "L" shaped parts.

ILT (MPa)	Round 1 (50%)	Round 2 (80%)
Goals	28.8	46.0
Measured	24.6±2.2 (43%)	--

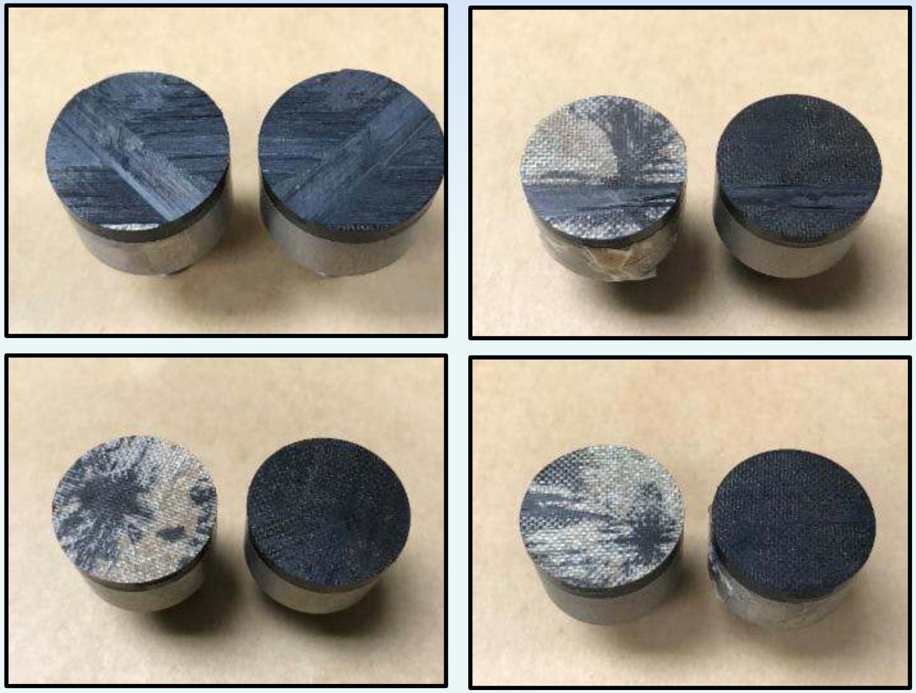
Baseline Properties

Ave ILT: **57.5 MPa**

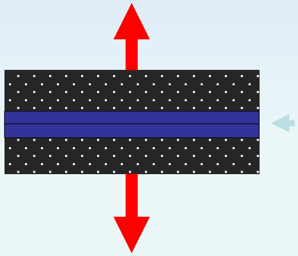
Std Dev: 9.5 MPa

Cof Var: 17 %

Flatwise Tension (FWT) Test



Interlaminar Tensile Strength



Panels failed at the AERoBOND joint near the ER-to-HR interface in most cases. Failure locus is away from machined surface indicating an accurate measurement.

ILT (MPa)	Round 1 (50%)	Round 2 (80%)
Goals	32.1	33.4
Measured	37.5 (59%)	--

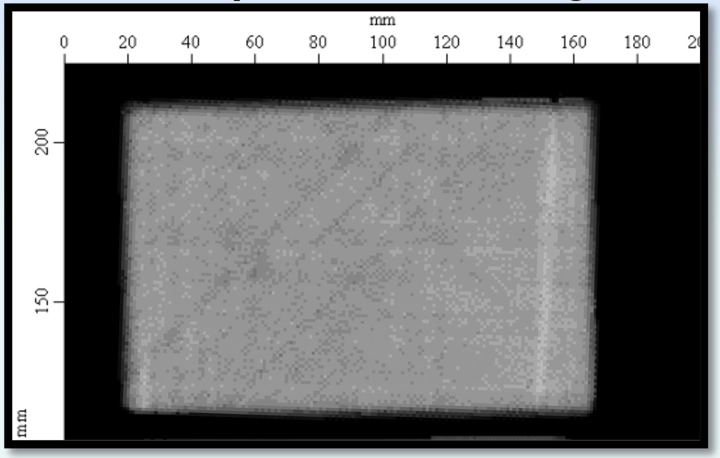
<u>Baseline Properties</u>

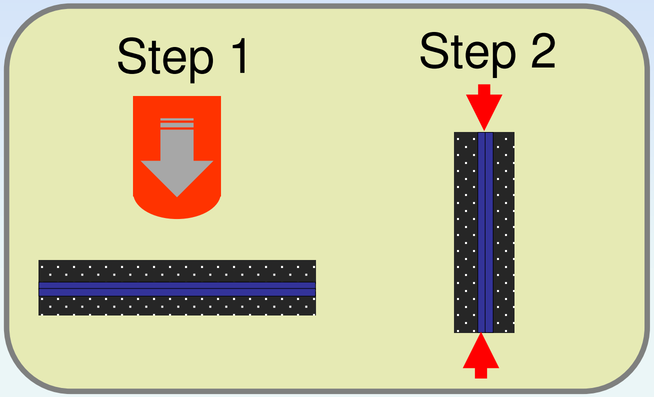
Ave ILT: 64.1 MPa

Std Dev: 6.4 MPa

Preliminary Impact Testing

Pre-Impact C-Scan Image





Post-Impact Inspection

(Impact energy: 5.5 J)

Damage too close to clamped region at edge of panel. Re-evaluating impact energy.