A Cooperative R&D Program on Interfacial Properties of Electron Beam Cured Composites

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Background

- **Many of the properties for the BEST EB cured composites are comparable to high-performance, autoclave cured composites (i.e. IM7/977-2, IM7/977-3)**

- **Deficiencies exist in the interfacial properties, particularly interlaminar shear strength (ILSS).**

Latest Results on Electron Beam Cured* vs. Autoclave Cured Unidirectional IM7/Epoxy Laminates

* The EB cured laminates were prepared using intermediate, room temperature vacuum debulks (14 psi) every 4 plies & a final vacuum debulk @ 160°F

vs.

the autoclave cured laminates cured @ 85 psi and 350°F

IM7 Laminate Properties (Data Norm. to 62% F.V.) Electron Beam Cured vs. Autoclave Cured

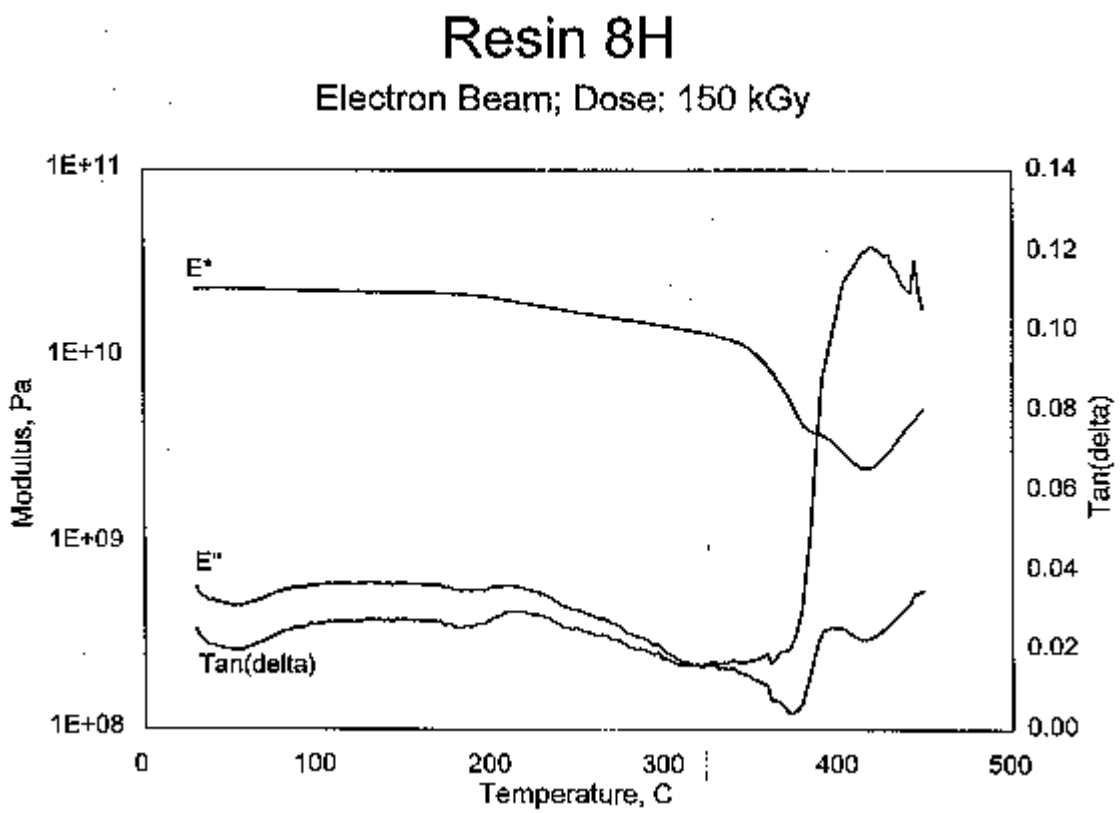
Resin Systems	Fiberite 977-2 (Fiberite Data)	Fiberite 977-3 (Fiberite Data)	Cytec 5250-4 BMI (Cytec Data)	*EB Resin 8H*	*EB Resin 10H*	*EB Resin 9H*	*EB Resin 3K*	*EB Resin 1K*	*EB Resin 1L*
Cure Conditions	Autoclave Cured (6 hrs. @ 350F @ 85 psi)	Autoclave Cured (3 hrs. @ 355F @ 85 psi)	Autoclave Cured (up to 20 hrs. @450F @ 85 psi)	*250 kGy (Sec.-Min. @ RT@ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*	*150 kGy (Sec.-Min. @ RT @ Vacuum Bag Press. Only)*
Void Volume, %	Not Reported	Not Reported	Not Reported	*1.77*	*0.72*	*1.24*	*0.64*	*1.18*	*1.7*
Tg, ^{o}C (Tan Delta)	200	190/240	300	*396*	*392*	*232*	*212*	*212*	*237/400*
O^{o} Tens. Str., MPa (ksi)	2537 (368)	2510 (364)	2423 (352)	*1869 (271)*			*2200 (319) Within 9%*		*2262 (328) Within 7%*
O^{o} Tens. Mod., GPa (msi)	166 (24.1)	162 (23.5)	150 (21.7)	*168 (24.3)*			*157 (22.8)*		*164 (23.8)*
180F Hot/Wet O^{o} Tens. Str., MPa (ksi)	2362*** (343)			*2282** (331)*			*2365** (343)*		*2386** (346)*
180F Hot/Wet O^{o} Tens. Mod., GPa (msi)	167*** (24.3)			*172** (24.9)*			*177** (25.7)*		*166** (24)*
O^{o} Flex. Str., MPa (ksi)	1641 (238)	1765 (256)	1594 (231)	*1986 (288)*	*2006 (291)*	*1793 (260)*	*1765 (256)*	*1710 (248)*	
O^{o} Flex. Mod., GPa (msi)	147 (21.3)	150 (21.7)	144 (21)	*196 (28.5)*	*163 (23.6)*	*163 (23.7)*	*154 (22.3)*	*150 (21.8)*	
O^{o} Comp. Str., MPa (ksi)	1580 (230)	1682 (244)	1499 (217)	*1683 (244)*			*1428 (207)*		*1524 (221)*
O^{o} Comp., Mod., GPa (msi)	152 (22)	154 (22.3)	146 (21.3)	*149 (21.6)*					
180F Hot/Wet O^{o} Comp. Str., MPa (ksi)	1240*** (180)			*1407** (204)*			*1324** (192)*		*1386** (201)*
O^{o} ILSS, MPa (ksi)	110 (16)	127 (18.5)	139 (20.2)	*77 (11.2) Within 30%*	*79 (11.5) Within 28%*	*79 (11.5) Within 28%*	*89 (12.9) Within 19%*	*77 (11.2) Within 30%*	
Hot/Wet O^{o} ILSS*, MPa (ksi)	72 (10.4)	89 (12.9)		*61 (8.8) Within 32%*					
H_2 Perm., Kp (Perm. Rate Constant, Uncycled @ RT & -320F) scc mm/atm sec cm^2				*9.22×10^{-9} & $<2.97 \times 10^{-9}$*			*3.43×10^{-8} & 1.62×10^{-8}*		*1.03×10^{-8} & $<4.90 \times 10^{-9}$*
* 1 wk. in H_2O @ 160F, 977-3 & EB 1 tested @ 220F (977-2 tested @180F)	** 4 days in H_2O @ 180F	*** 7 days in H_2O @165F	EB comps. prepared using conv. lay-up methods. Int. debulks @vacuum/4plies @ RT, 15 min. Final debulk @vacuum, 70C, 1 hr.						

Shaded Boxes Signify EB Material Properties Which Are Within 5% Or Greater Than Fiberite's Autoclave Cured 977-2, 977-3, And/Or Cytec's 5250-4 Properties

Patents* Covering Electron Beam Curable Cationic Epoxy Resins

- **No. 5,877,229 (March 2, 1999)**
  - Electron Beam Curing of Epoxy Resin Systems Incorporating Cationic Photoinitiators
- **No. 5,726,216 (March 10, 1998)**
  - Toughened Electron Beam Curable Cationic Epoxy Resin Systems and A Method Thereof
- **Other Patents Pending**

* Assignee: Lockheed Martin Energy Systems, Inc., Oak Ridge, Tennessee



The 8H EB cured epoxy resin has the highest Tg (approx. 400°C = 750°F) ever reported for ANY commercially available epoxy resin

Fiber-Resin Interface Research Is Needed

- **Interlaminar shear strength is 20-30% lower in EB cured, HAND LAID-UP composites**

- **Low interlaminar shear strength is a key barrier to the successful acceptance and implementation of EB cured composites in the aerospace industry**

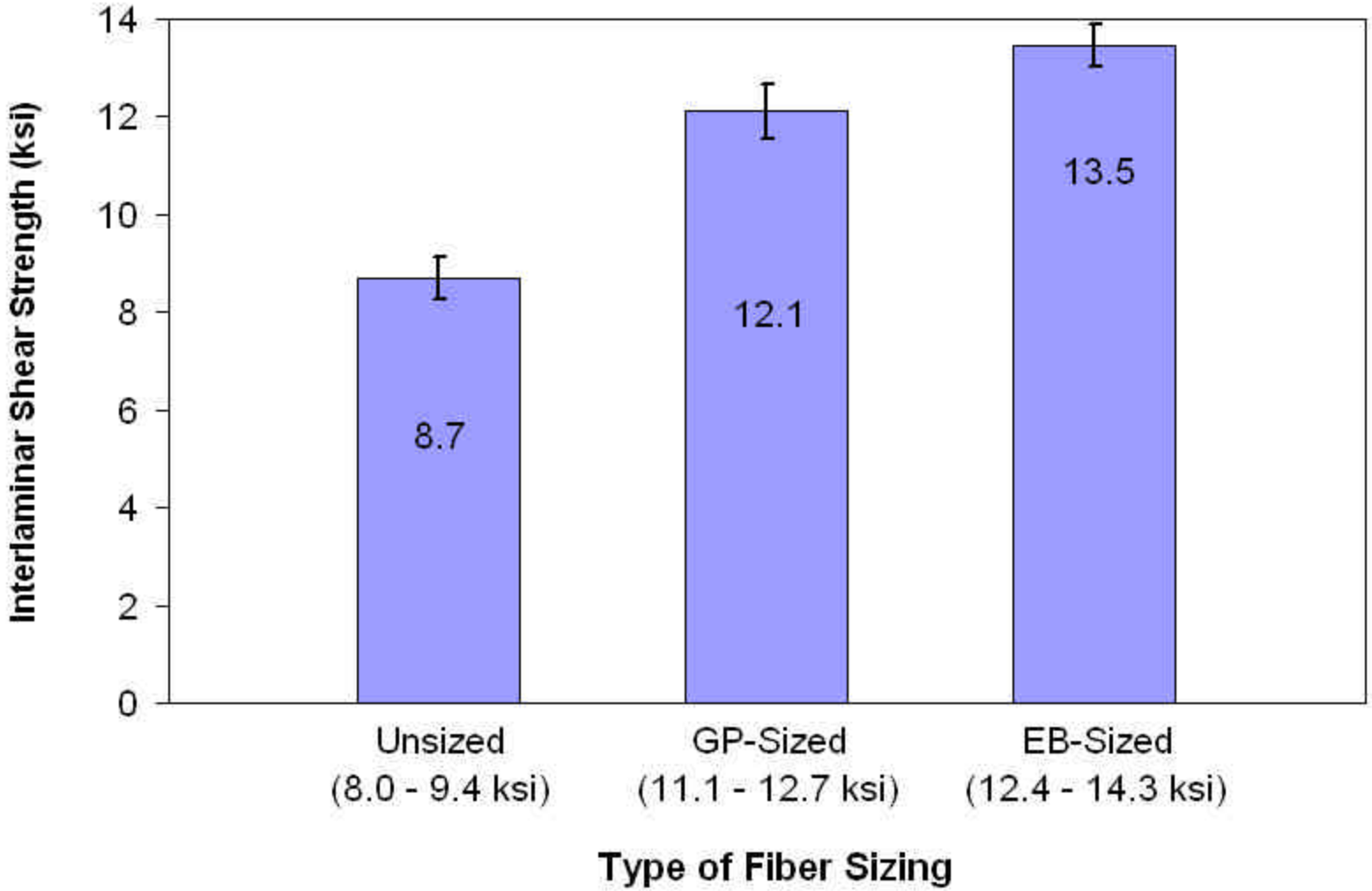
- **Preliminary research suggests that the fiber-resin interface is one of the major sources of deficient shear properties**

Promising Preliminary Work

- **Simple formulation and process changes are NOT sufficient to significantly improve interfacial properties**
  - **Preliminary work at ORNL and MSU**

- **EB curable fiber coatings (sizings) IMPROVE interfacial shear strength and ILSS**
  - **Microindentation testing**
  - **Filament Wound ILSS**

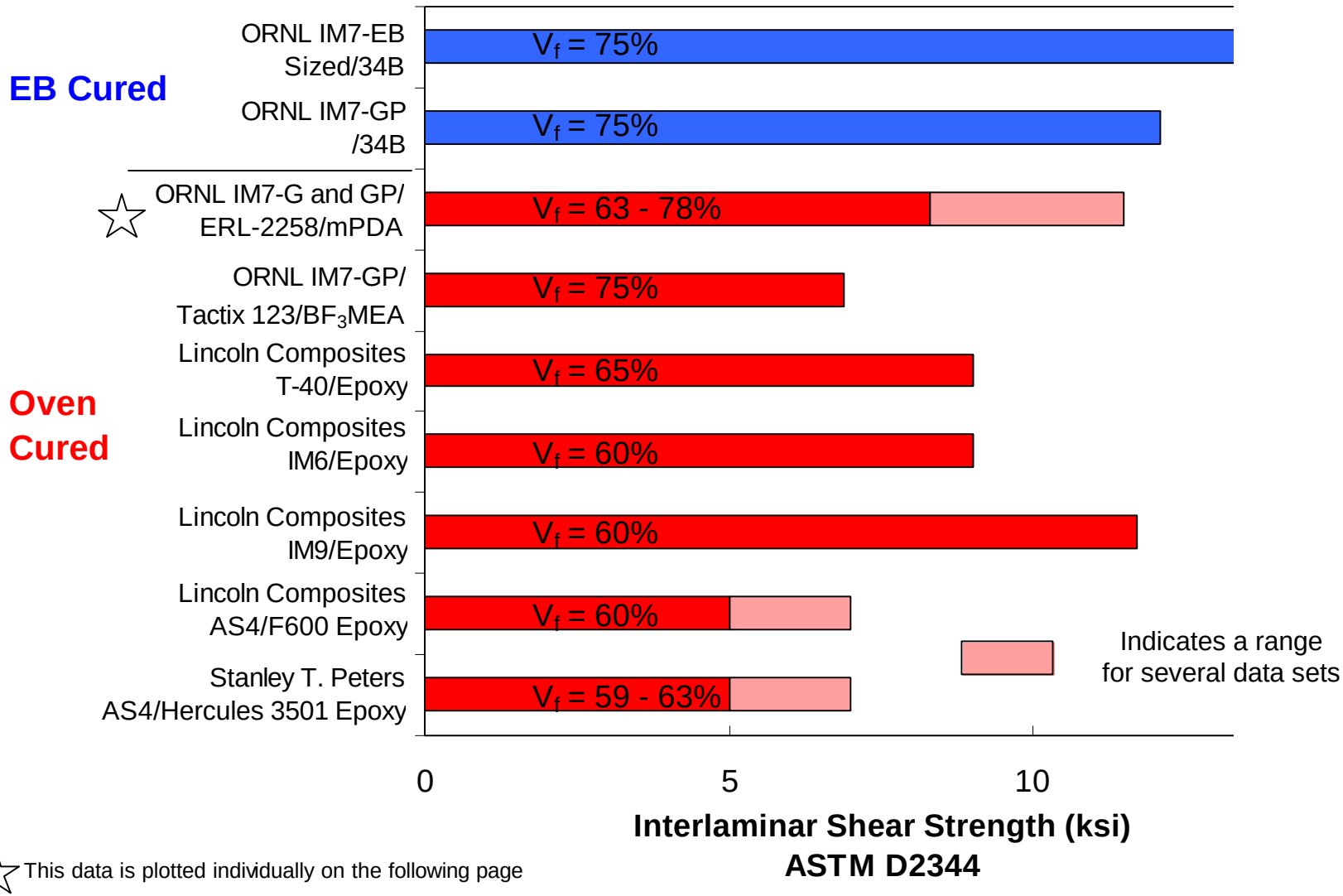
Effect of Fiber Sizing on the ILSS of EB Cured, IM7/Epoxy, Filament Wound Composites



Note: Each sample fabricated and cured with 34B resin under identical conditions.
6" dia x 0.125", cure dose: 150 kGy, 17 kGy/pass, n = 18
Tested per ASTM 2344, Error bars = ±1 standard deviation

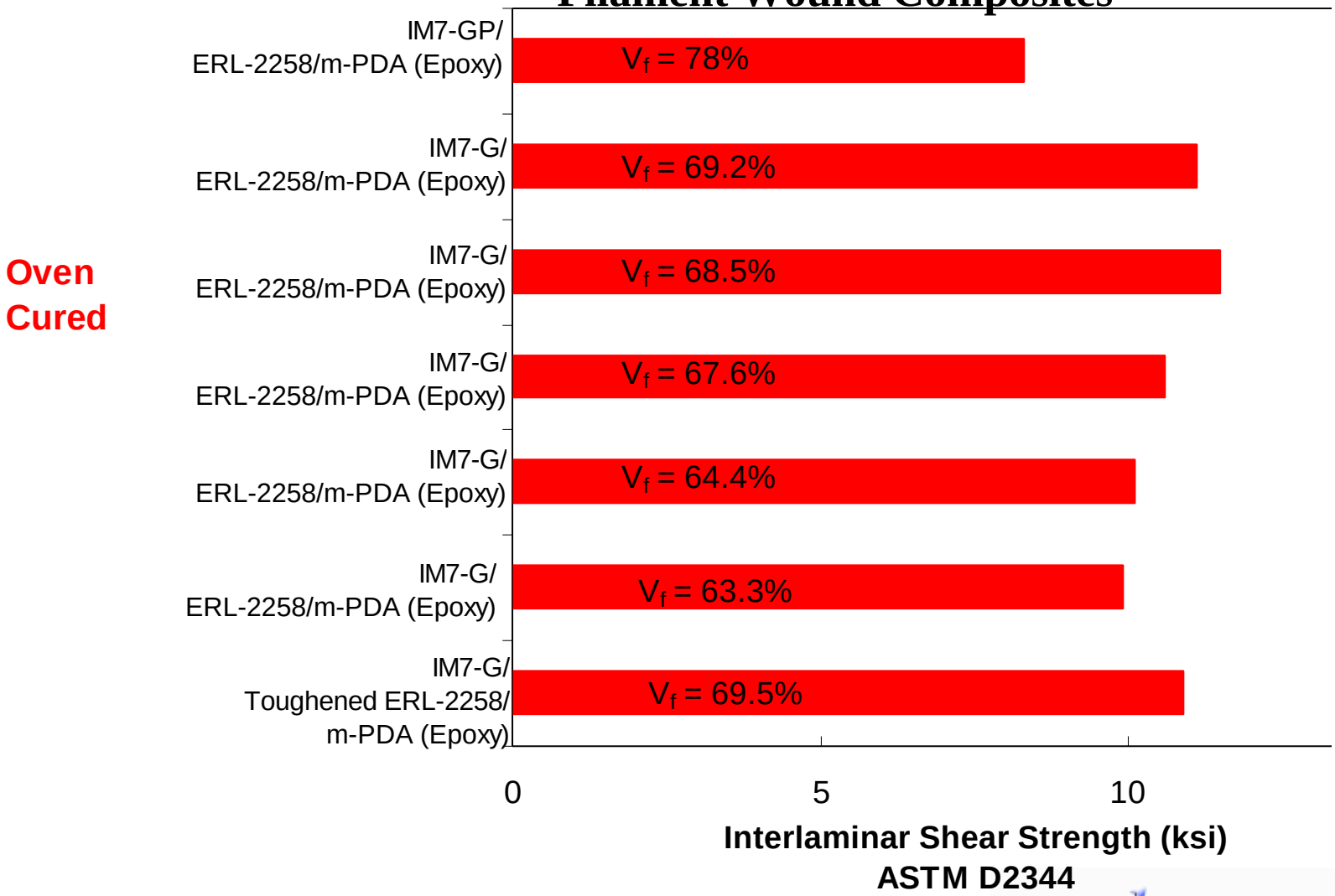
ILSS of EB Cured vs. Thermal Cured Filament Wound Composites

No Deficiency in Interlaminar Shear Strength
EB Cured Composites Have Highest Values



☆ This data is plotted individually on the following page

ILSS of ORNL Thermal Cured Filament Wound Composites



Latest Results on Electron Beam Cured vs. Oven Cured IM7/Epoxy Laminates (manufactured via wet filament winding)

Laminate Properties (From Low Viscosity Resins) Electron Beam Cured vs. Thermal Cured

Carbon Fiber: IM7-GP-12K; Cylinder Dimensions: Dia. = 15.24 cm (6 in.); t = 0.3175 cm (0.125 in.)			
Resin Systems	EB Cured Resin 34B*	Thermal Cured Resin 1 (Oven Cured)	Thermal Cured Resin 2 (Oven Cured)
Cure Conditions	150 kGy	3 hours @ 121°C, 3 hrs @ 150°C, then 4 hrs @ 177°C	3 hours @ 121°C, 3 hrs @ 150°C, then 4 hrs @ 177°C
Void Volume, %	< 1 %	< 1%	< 1%
Percent Fiber Content	75.8	77.8	74.6
Tg, ^{o}C (Tan Delta)	192	218	165
O^{o} Tensile Strength, MPa (ksi) - Norm. to 75% F.V.	2358 (342)	1986 (288)	1538 (223)
O^{o} Tensile Strength, Cycled*, MPa (ksi) - Norm. to 75% F.V.	2337 (339)	2379 (345)	1565 (227)
90° Flexure Strength, MPa (ksi) - Concave up	70.3 (10.2)	68.3 (9.9)	57.2 (8.3)
90° Flexure Strength, Cycled*, MPa (ksi) - Concave up	77.9 (11.3)	77.2 (11.2)	64.1 (9.3)
O^{o} Interlaminar Shear Str., MPa (ksi)	83.5 (12.1)	57.2 (8.3)	47.6 (6.9)
O^{o} Interlaminar Shear Str., Cycled*, MPa (ksi)	82.7 (12.0)	56.5 (8.2)	46.9 (6.8)
* Cycling Procedure: Specimens placed in liquid nitrogen (-194°C) for 30 min.; Allowed to warm to room temp. for 30 min.; Placed in oven @ 121°C for 30 min.; Allowed to warm to room temp. for 30 min.; Cycle repeated 3 times.			

***34B is a very low viscosity (about 100 cps) epoxy resin amenable to RTM, VARTM, and Wet Filament Winding. It possesses an excellent property profile including fiber and resin dominated properties and performs very well after thermal cycling.**

U. S. Department of Energy
Cooperative Research and Development Agreement (CRADA)

"Interfacial Properties of Electron Beam Cured Composites"

Sponsored By:

DOE - Laboratory Technology Research Program

of the Office of Science

U.S. Air Force Research Laboratory Materials Directorate

NASA - Langley

3 Year, $3.2 Million Project

DOE CRADA Team

CRADA Partners/Participants/Subcontractors	Responsibility
1. Acsion Industries, Inc.	EB Irradiator, Interface/Materials/Process Dev.
2. Adherent Technologies, Inc.	Interface/Materials/Process Dev.
3. Air Force Research Laboratory (Participant)	Interface/Materials/Process Dev.
4. BP Amoco Chemicals	C-Fiber Manufacturer, Interface/Materials Dev.
5. Applied Poleramic, Inc.	Interface/Materials/Process Dev.
6. Boeing Information, Space and Defense Systems	EB Irradiator, Interface/Materials/Process Dev.
7. E-BEAM Services, Inc.	EB Irradiator, Process Dev.
8. Hexcel Composites - Fibers Business Unit	C-Fiber Manufacturer, Interface/Materials Dev.
9. Lockheed Martin Tactical Aircraft Systems	Project Management, Interface/Process Dev.
10. Michigan State Univ. (Subcontractor)	Interface/Materials/Process Dev.
11. Oak Ridge National Laboratory	Project Mgt., Interface/Materials/Process Dev.
12. STERIS Isomedix Services	EB Irradiator, Process Dev.
13. UCB Chemicals Corp. - Radcure Business Unit	Interface/Materials/Process Dev.
14. YLA, Inc.	Interface/Materials/Process Dev.

Purpose of CRADA

Understand and Resolve the Fiber-Resin Interface Property Deficiencies in Electron Beam Cured Composites

Project Objectives

- Investigate the causes of the deficient shear properties;
- Determine the chemical, physical and/or mechanical mechanisms responsible for poor fiber-matrix adhesion;
- Develop and evaluate new EB compatible treatments and materials to increase the interfacial properties
  - Carbon fiber surface treatments
  - Carbon fiber sizings and/or coatings
  - Various chemical agents
  - Improved EB curable epoxy resins
- Develop, evaluate, and optimize fabrication and EB processing methods for increasing interfacial properties

Possible Mechanisms for Lower Interfacial Properties in EB Cured Composites

Interface

- **Poor fiber-matrix adhesion**
  - **EB incompatible fiber surface treatments and/or fiber sizings**
- **Contaminants on C-fiber surface**
  - **Moisture, oils, CO_2, CO, other**
- **Cure inhibition on C-fiber surface**
  - **Nitrogen containing species (or other) inhibiting cationic cure reaction**
- **Interphase region with lower shear modulus or fracture toughness than bulk resin**
- **Deleterious state of residual stress in interphase region**
  - **High matrix shrinkage**
  - **Absorption of energy and consequent increase in the temperature of the C-fiber**

Possible Mechanisms for Lower Interfacial Properties in EB Cured Composites

Resin

- Resin may be too brittle (high crosslink density)
  - Epoxide homopolymerization reactions
- Poor fiber wet-out
  - Resin viscosity or surface tension too high

Prepreg/Fabrication

- Prepreg and/or fabrication parameters may not be fully optimized
  - Fiber impregnation, compaction method, debulking parameters

EB Processing

- EB processing parameters may not be optimized
  - total dose, dose/pass, dose rate, initiator conc.

Technical Approach
Major Tasks

1. **Interface Characterization**

2. **Materials Development**

3. **Process Development**

Interface Characterization

- The fiber-resin interface will be chemically & mechanically characterized on incumbent & newly developed EB materials
  - Compare with database on thermally cured interfaces
  - Chemical characterization of EB processed interface
    - Determine type and quantity of chemical species remaining or chemisorbed on C-fiber surface subsequent to EB processing
      - Solvent extraction
      - X-ray photoelectron spectroscopy (XPS)

Interface Characterization (Continued)

- Mechanical characterization of EB cured interface
  - Microindentation, single-fiber fragmentation, cruciform, and wet filament wound ILSS testing
- Identify interfacial failure mechanisms on EB cured composites
  - Scanning and transmission electron microscopies (SEM, TEM)
- Model fiber-matrix interface
  - Determine physical and chemical changes occuring during EB curing

Materials Development

- **Develop EB compatible C-fiber surface treatments for improving fiber-matrix adhesion possibly including:**
  - **Post-oxidation treatments or other reactive treatments**
  - **Varying the composition or other process parameters during the fiber electrolytic surface treatment phase**
  - **Various Plasma treatments**

Materials Development (Continued)

- **Develop EB compatible chemical agents for improving the fiber-matrix adhesion including:**
  - **Difunctional coupling agents**
    - **Acts as fiber-matrix chemical bridge**
  - **Wetting agents**
    - **Improves fiber wet-out thus decreasing void formation at interface and improving F-M adhesion**
  - **Reactive finishes**
    - **Contains coupling and wetting agents**
  - **Fiber sizings or fiber coatings**
    - **Esp. those yielding a greater resin shear modulus at the interface (this coating approach has proved successful on thermal cured composites; Drzal, et. al.)**

Materials Development (Continued)

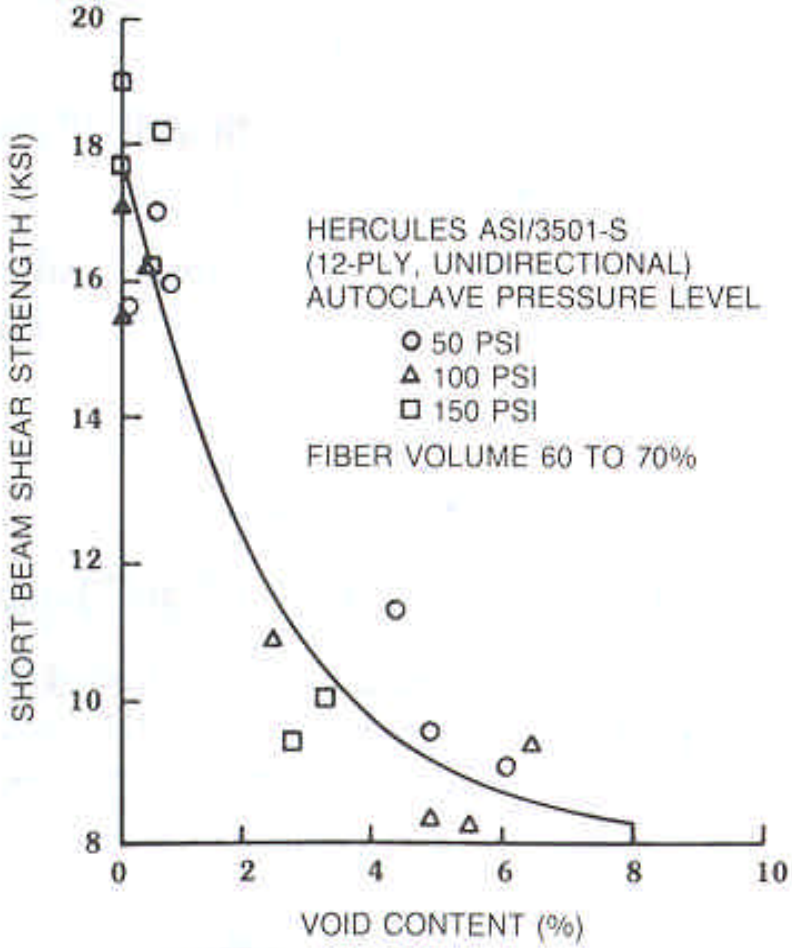
- **Develop TOUGHER and BETTER EB curable epoxy resins (without sacrificing modulus and hot/wet properties)**
  - **Epoxy resin modifications**
    - **Combine resin with reactive or nonreactive tougheners**
    - **Modify resin backbone**
      - **Chain extension agents, coreactants**
    - **Vary base resin functionalities**
    - **Optimize resin rheology**
      - **Viscosity, surface tension, tack**
  - **Resin testing**
    - **IR spectroscopy, viscosity profiling, dynamic mechanical analysis, cured neat resin mech. and phys. properties**

EB Processing Development

(To be conducted in parallel with Materials Development Tasks)

- **Develop OPTIMIZED material processing parameters**
  - **Prepregging**
    - **Fiber impregnation**
  - **Handling**
    - **Fiber storage**
    - **Possible pre-processing of fiber**
      - **Drying to remove moisture or other volatile contaminants**
    - **Shipping laminates to EB processor**

Effect of Void Content on ILSS



EB Processing Development (Continued)

(To be conducted in parallel with Materials Development Tasks)

- **Develop OPTIMIZED fabrication parameters**
  - **Laminate lay-up (Must minimize void content)**
    - Compaction pressure
      - Method?, quantity?
    - Vacuum debulking conditions
      - Frequency?, time?, temperature?

EB Processing Development (Continued)

(To be conducted in parallel with Materials Development Tasks)

- **Develop OPTIMIZED EB curing parameters**
  - Total dose
  - Dose/pass
  - Instantaneous and/or average dose rate
  - Temperature profile during cure

Materials Development (Continued)

- **Develop OPTIMIZED EB Cured Composite**
  - **Composite system optimization**
    - **Integrate BEST fiber treatments, materials and optimized fabrication and EB processing parameters into composite**
  - **Composite testing**
    - **Mechanical and Thermal Properties**
      - **Microindentation, Single-Fiber Fragmentation, Cruciform**
      - **ILSS, Transverse Properties**
      - **Compression/Flexural/Tensile Strength and Modulus**
      - **Fracture Toughness, CAI**
      - **DMA**
    - **Analysis of failed specimens (i.e. voltage contrast XPS, Atomic force microscopy, SEM, TEM)**