Fiber-Matrix Interface Studies on Electron Beam Cured Composites

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Outline

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- Background
  - Electron beam (EB) cured laminate properties
  - Possible mechanisms for deficient interlaminar shear strength (ILSS)
  - Promising preliminary work
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  - Fiber coating formulations
  - Specimen preparation and ILSS testing
- Results
- New CRADA Start
- ILSS contradictions of hand laid up vs. filament wound, EB cured composites
- Conclusions

Problem

- Interlaminar shear strength is lower in hand laid-up, EB cured composites vs. high performance, autoclave cured composites

Background

- Many of the properties for the BEST EB cured, hand laid-up composites are comparable to high-performance, autoclave cured composites (i.e. IM7/977-2, IM7/977-3)
- Deficiencies exist in the interfacial properties, particularly ILSS.

Latest Results on EB 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^{o}F

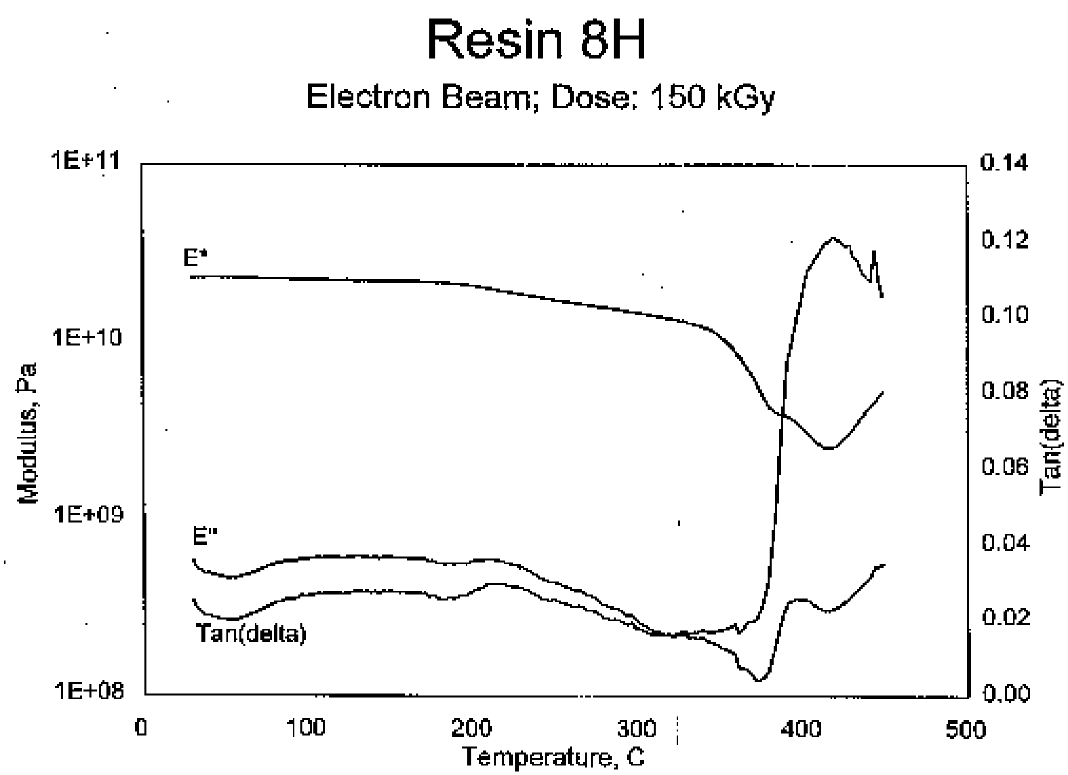
vs.

the autoclave cured laminates cured @ 85 psi and 350^{o}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



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 electron beam 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

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

<u>Resin</u>

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

<u>Prepreg/Fabrication</u>

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

<u>EB Processing</u>

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

Promising Preliminary Work

- Preliminary work has shown that EB curable fiber coatings (sizings) IMPROVE interfacial shear strength and ILSS
  - Microindentation testing (MSU)
  - Filament Wound ILSS (ORNL)

Fibre Coatings

- 22 *Different* coatings were evaluated on surface treated, unsized IM7-12K fiber
  - Coatings varied by:
    - Epoxy resin type
    - Initiator concentration
    - Coating thickness
- 2 Controls were also evaluated
  - Unsized fiber
  - Conventional GP-sized fiber

Fiber Coating Constituents

- Epoxy resins:
  - Epon 1007F (Solid bisphenol A epoxy)
    - High visc. (m.p. 125°C), high MW, low % epoxide (2.2%), EEW = 2000
  - Epon 1001F (Solid bisphenol A epoxy)
    - High visc. (m.p. 79°C), high MW, low % epoxide (8%), EEW = 540
  - DEN 439 (Solid epoxy novolac)
    - High visc. (m.p. 53°C), high % epoxide (21.5%), EEW = 200
  - Epon 826 (Liquid bisphenol A epoxy)
    - Low visc. (7800 cps at RT), high % epoxide (23.7%), EEW = 182
- Cationic initiator conc. varied from 0 - 3 phr

Fiber Coating Characteristics

- Coating thicknesses ranged from approximately 3.5 nm - 165 nm
  - translates into fiber sizing contents ranging from 0.2 - 9% by weight
    - conventional fiber sizing contents typically range from 0.2 - 1% by weight

Fiber Coating Compositions

Epoxy Coating System	Soln. Conc. (Phr Epoxy)
Epon 1001F	1, 2.25, 3.5, 6, 10
Epon 1001F w/1 phr SR1012	1, 6
Epon 1001F w/3 phr SR1012	1, 6
Epon 1007F	1, 6
Epon 1007F w/1 phr SR1012	1, 6
Epon 1007F w/3 phr SR1012	6
DEN 439	1, 6
DEN 439 w/ 3 phr SR1012	6
Epon 826	1, 6
Epon 826 w/ 1 phr SR1012	1
Epon 826 w/ 3 phr SR1012	1, 6

Preparation and Testing of Electron Beam Cured, IM7-12K Fiber Coated Composite Samples

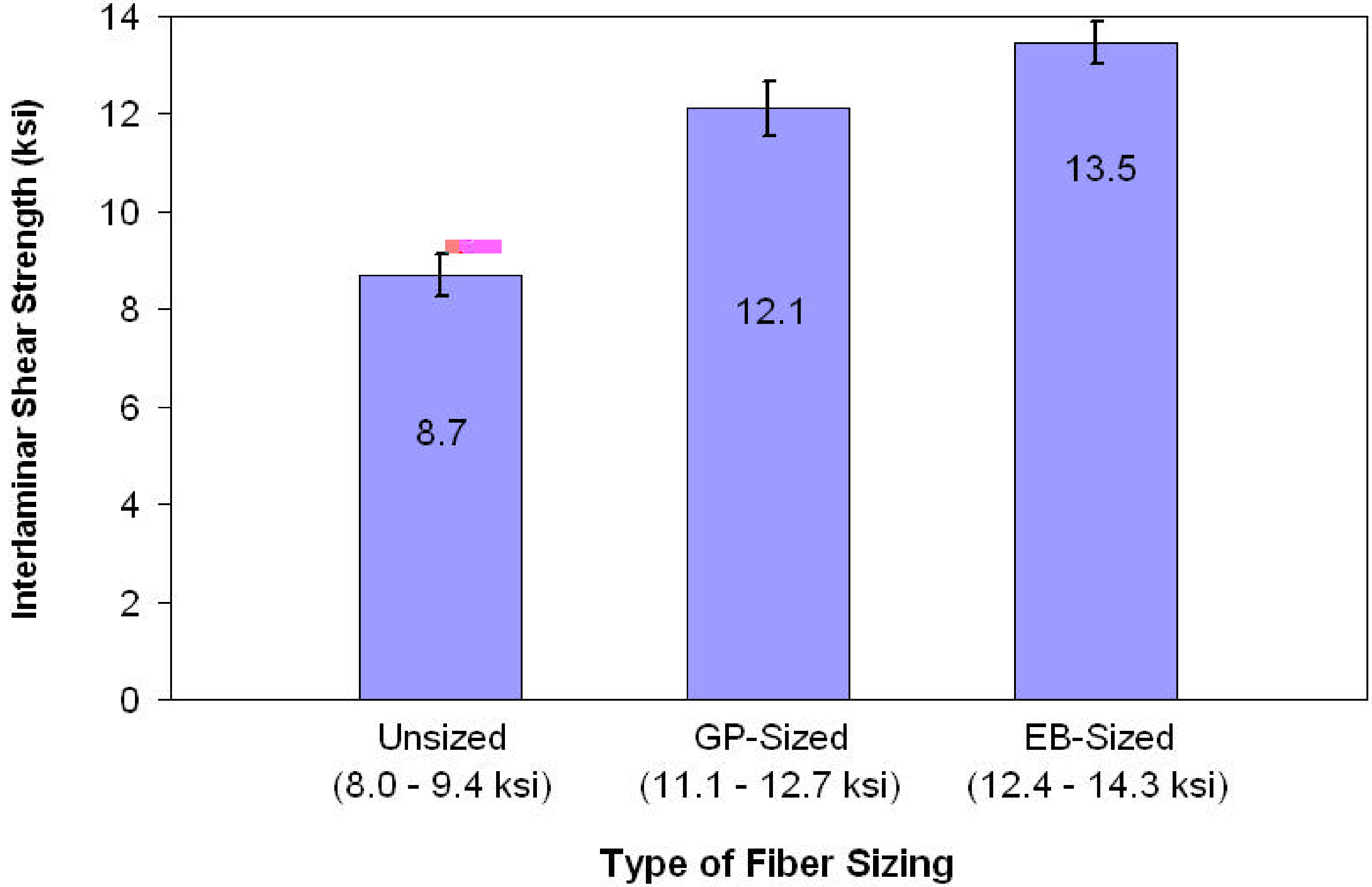
- Surface treated, unsized fibers were coated with an epoxy resin solution
- Solvent was evaporated leaving a thin, uncured coating on fibers
- Coated fibers and EB curable epoxy resin were used to wet filament wind, hoop wound cylinders
- Composite cylinders electron beam cured at 150 kGy
- Interlaminar shear strength samples machined and tested in accordance with ASTM D 2344
- Also fabricated, EB cured, and tested Control cylinders (1st control - surface treated, unsized IM7 fibers; 2nd control - surface treated, GP-sized IM7 fibers)

Results

- Ø EB compatible fiber coatings improved composite ILSS by up to 55% vs. surface treated, unsized fibers

- Ø One EB curable fiber coating improved ILSS by over 11% relative to surface treated, GP-sized fibers

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

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

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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.

Purpose of CRADA

- Understand and Resolve the Fiber-Resin Interface Property Deficiencies in hand laid-up, EB Cured Composites

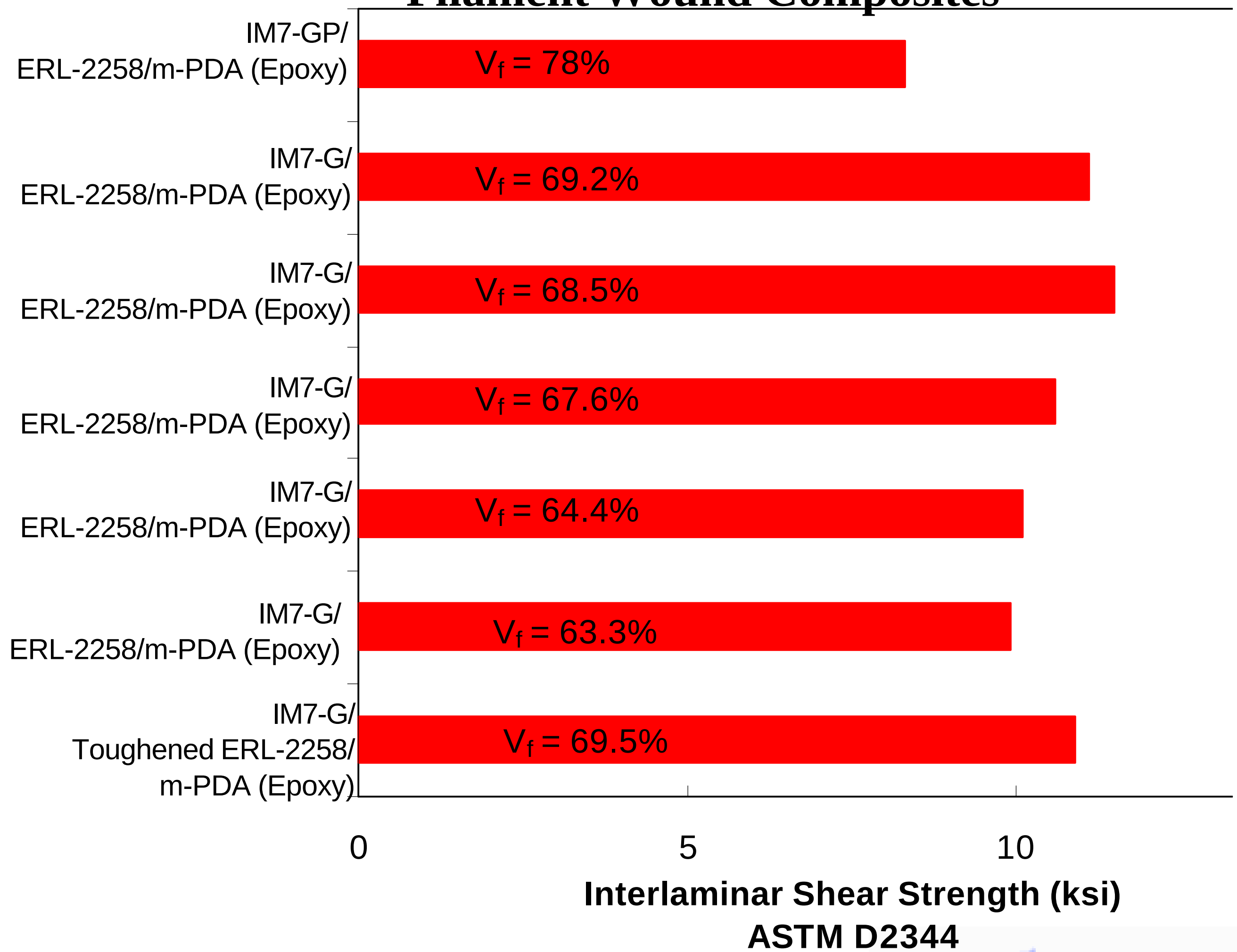
Project Objectives

- 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

A Puzzling Contradiction

- ILSS of hand laid-up vs. filament wound, EB cured composites

ILSS of ORNL Thermal Cured Filament Wound Composites



Oven Cured

Conclusions & Follow-On Work

- ILSS of hand laid up, EB cured composites can be improved by using EB compatible fiber coatings, and there appears to be significant potential for further improvement
- A new, 3 year CRADA involving 15 government and industry organizations has recently been initiated to address and resolve the interfacial property deficiencies of EB cured composites
- No ILSS deficiency exists with wet filament wound, EB cured composites