Properties Of Electron Beam Cured vs. Autoclave Cured Composites & Adhesives

Presented At The 2nd Electron Beam Curing Of Composites Workshop
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Acknowledgements

THE EBEAM DOE-DP CRADA TEAM

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Presentation Outline

- EB-Curable Materials & Processing (USAF T-38 Composite Windshield Frame Project)
  - S-2 Woven Glass/Epoxy Laminate Processing & Properties
  - Adhesive Processing & Properties
- EB vs. Autoclave Cured IM7/Epoxy Composite Properties (From DOE CRADA)
- Conclusions

U.S. Air Force T-38 Composite Windshield Frame Project

- Goals
  - Develop EB & X-ray curable S-2 woven glass prepregs and paste adhesives that meet requirements for T-38 composite windshield frame
  - Develop lowest cost, hand layup and debulk process for producing composite laminates and for bonding laminated steel plies
    - *Full Papers Are To Be Published In SAMPE Conference Proceedings (October '97 & June '98 Conferences)*

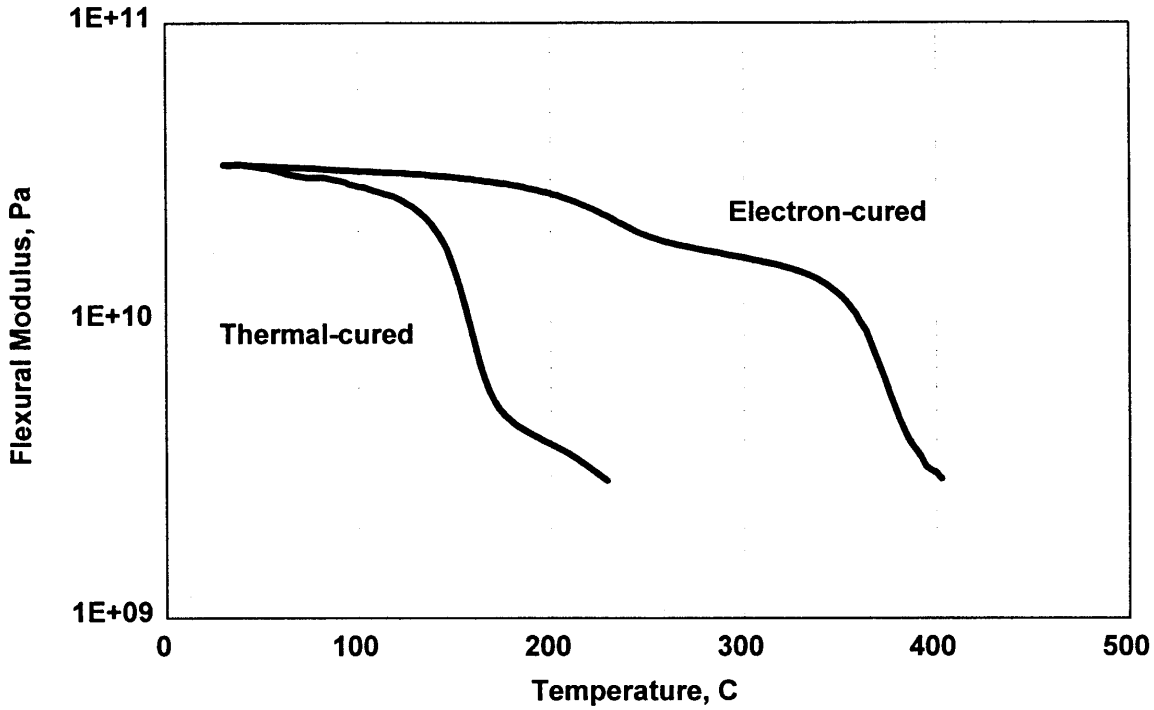
U.S. Air Force T-38 Composite Windshield Frame Project

- Current Materials
  - Aerospace-grade, Autoclave Cured S-2 Glass/Epoxy Prepreg
    - Style 6781, S-2 Woven Fiberglass & Cytec 919 Toughened Epoxy, Autoclave Cured For 4 hrs. @ 250°F under vacuum and 45 psi pressure
  - Aerospace-grade, Autoclave Cured Structural Film Epoxy Adhesive Used to Bond 36, 1.6 mm-Thick Stainless Steel Sheets (Surface Treated and Primed w/ Cytec BR-127 Primer)
    - Hysol EA 9628 NW Structural Film Epoxy Adhesive Autoclave Cured For 2 hrs. @250°F under vacuum and 45 psi pressure

U.S. Air Force T-38 Composite Windshield Frame Project

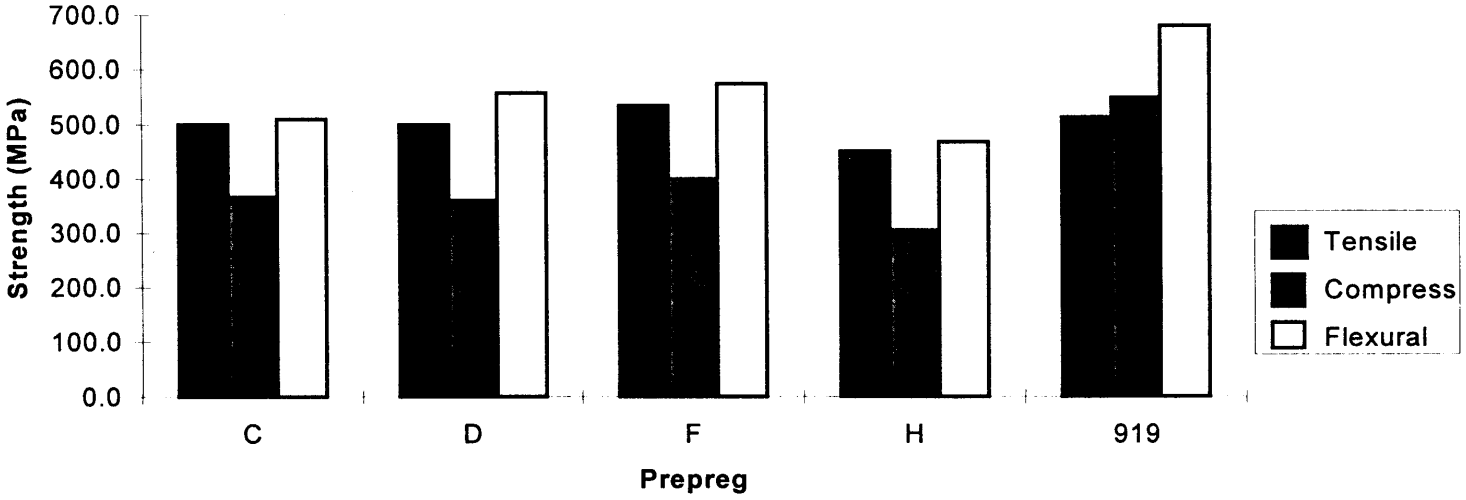
- Materials Evaluation Included:
  - 4 EB-Curable Cationic Epoxy Resins & 3 Fiber Sizings On 6781 S-2 Woven Glass Fabric
  - 18 EB & X-ray-Curable Cationic Epoxy Paste Adhesives and 4 Scrim Cloths

Comparison of glass transition temperatures for electron beam cured prepreg C and autoclave cured Cytec 919/6781



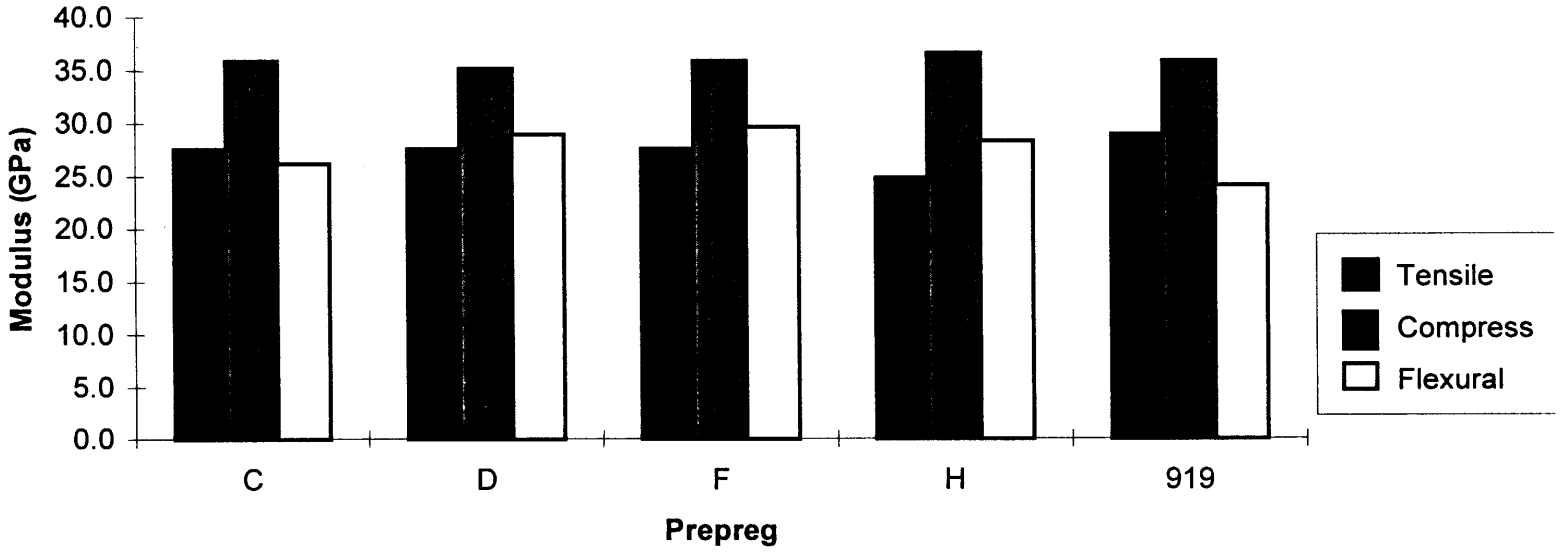
-DMA curves show substantial differences in thermomechanical properties of autoclave cured vs. electron beam cured epoxy resins.

Tensile, compressive, and flexural strengths of the electron beam prepregs compared to the autoclave cured Cytec 919 prepreg



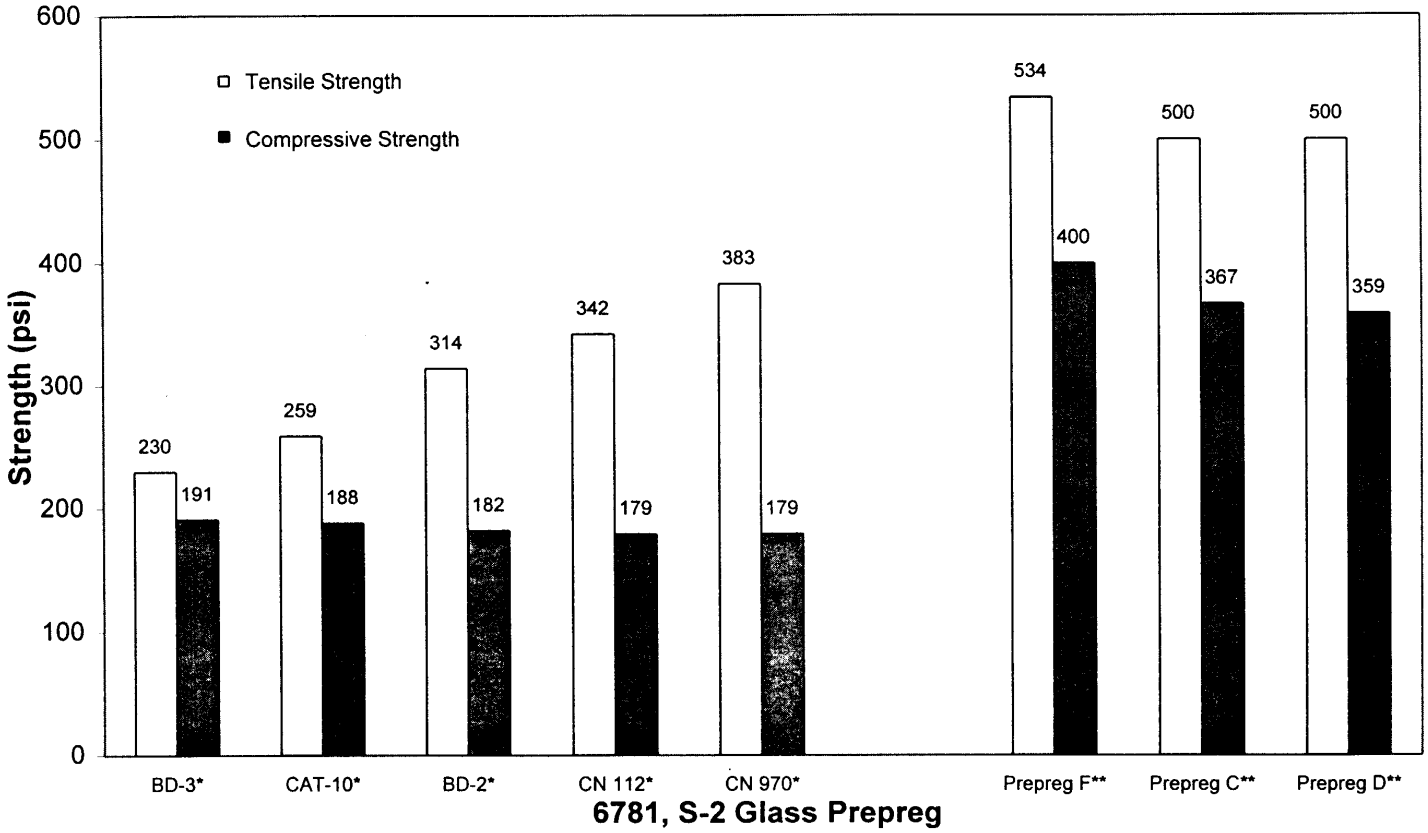
-Tensile strengths of prepregs C, D, and F are statistically equivalent to the 919 prepreg.
-Compressive strengths of prepregs C, D, and F are 23-30% lower than 919 prepreg.
-Flexural strengths of prepregs C, D, F are 15-25% lower than 919 prepreg.

Tensile, compressive, and flexural moduli of the electron beam cured prepregs compared to the autoclave cured Cytec 919 prepreg



-Tensile, compressive, and flexural moduli of prepregs C, D, and F are statistically equivalent to 919 prepreg.

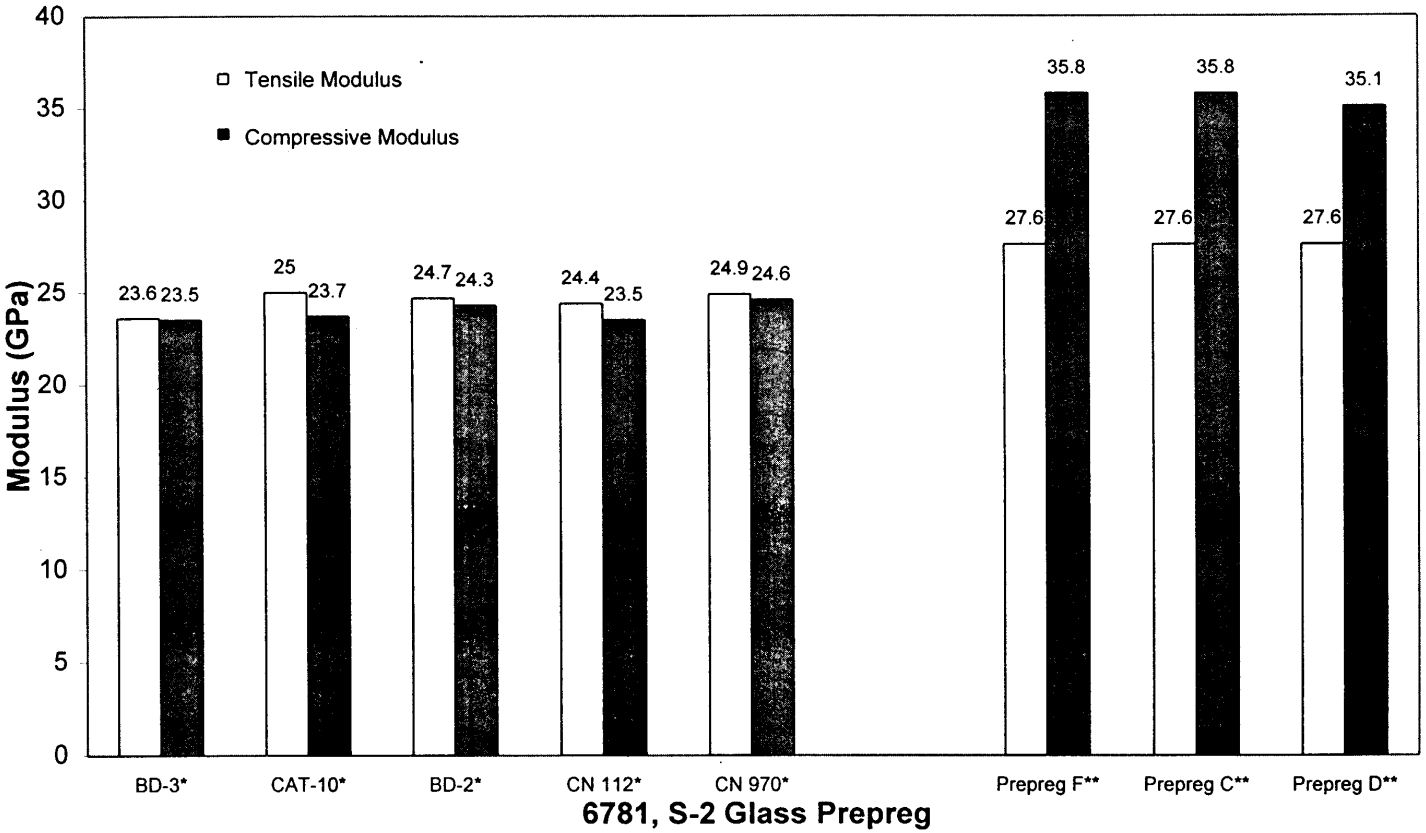
Comparative Published Data On Tensile & Compressive Strengths Of EB-Curable S-2 Woven Glass Laminates



(* Devney, et al., "Mech. Props. Of EB Cured FBG Laminates ", 28th Intl. SAMPE, Seattle, 1996 and; **Janke, et al., "The EB Cure Of FBG/Epoxy Prepregs", 29th Intl. SAMPE, Orlando, 1997.)

We Have Demonstrated > 40% Improvement In Tensile Str. And
> 100% Improvement in Compressive Str. Compared to a 1996 SAMPE Paper on S-2 Glass Laminates.

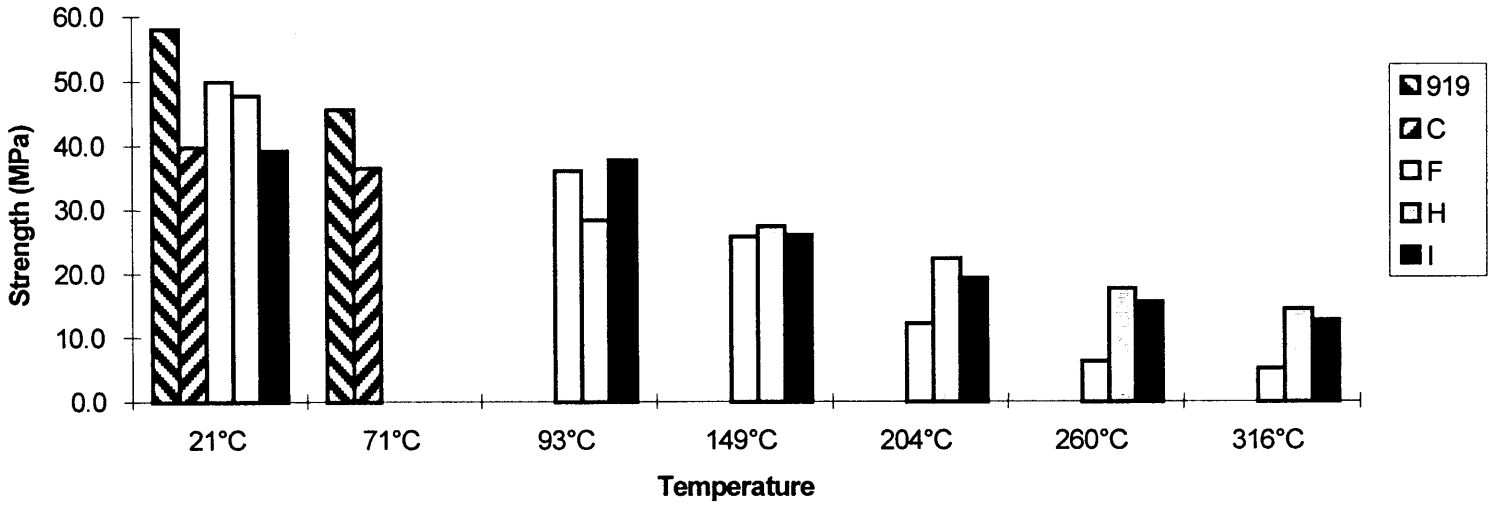
Comparative Published Data On Tensile & Compressive Modulus Of EB-Curable S-2 Woven Glass Laminates



(* Devney, et al., "Mech. Props. Of EB Cured FBG Laminates ", 28th Intl. SAMPE, Seattle, 1996 and; **Janke, et al., "The EB Cure Of FBG/Epoxy Prepregs", 29th Intl. SAMPE, Orlando, 1997.)

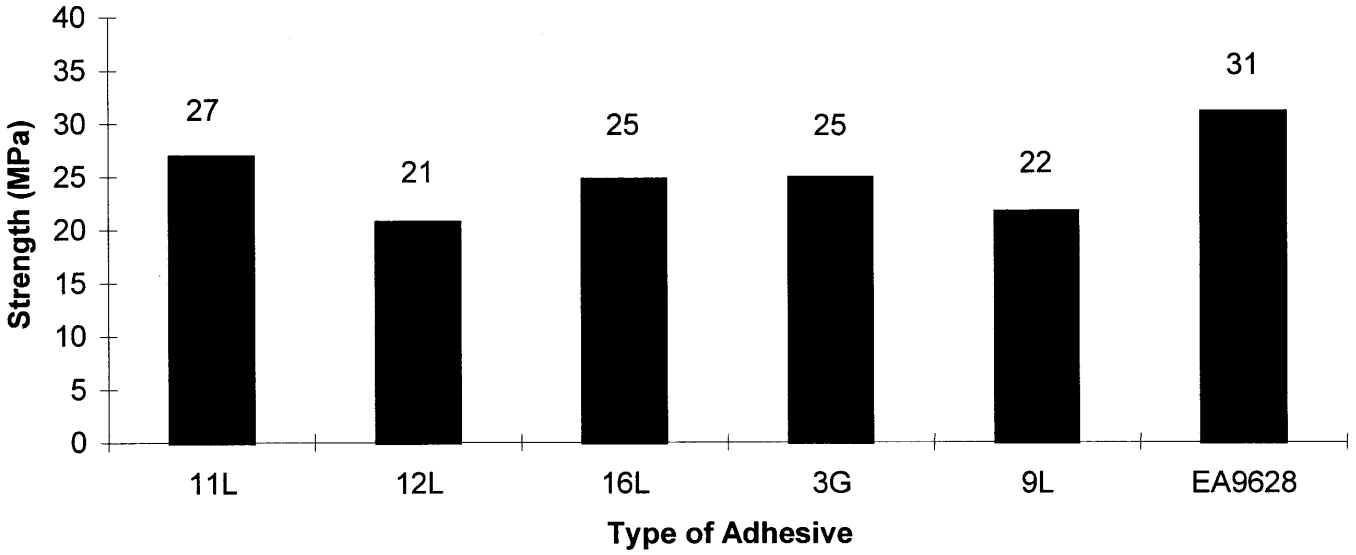
We have Demonstrated > 10% Improvement in Tensile Mod. and > 45% Improvement in Compression Mod. Compared to a 1996 SAMPE Paper on S-2 Glass Laminates.

Short-beam shear strength of electron beam prepregs compared to the autoclave cured Cytec 919/6781 prepreg



-Prepreg H and I exhibit very good elevated temperature, short-beam shear properties.

Adhesive lap shear strengths for electron beam curable cationic epoxies compared to autoclave cured Hysol EA 9628



-Adherends: 1.6 mm thick stainless steel, surface treated and primed with Cytec BR-127 primer.
-Bondline thickness: 5-7 mils.
-EA 9628 – autoclave cured, aerospace grade, structural epoxy adhesive (Hysol).
-Several adhesives exhibited shear properties above the required value of 21 MPa (3050 psi).

U.S. Air Force T-38 Composite Windshield Frame Project

- Conclusions
  - Using Low-Cost, Room Temperature, Vacuum Bag Pressure Debulks For The EB Materials vs. Autoclave Curing For The Cytec & Hysol Materials The Following Has Been Demonstrated:
    - Tgs of EB resins were significantly higher than Cytec 919
    - Room Temp. short-beam-shear strengths were within 18% of Cytec 919
    - High Tg EB resins exhibited good retention of short-beam-shear strength properties at elevated temperatures vs. Cytec 919
    - Tensile, Compressive, & Flexural Moduli were equivalent to Cytec 919
    - Tensile Strengths were equivalent to Cytec 919
    - Compressive & Flexural Strengths were 15-30% lower than Cytec 919
    - Significant improvements in properties vs. recently published paper has been demonstrated
    - Mechanical Properties Of EB & X-Ray Curable Paste Adhesives Exceeded Specifications
      - *Lap Shear Strength Requirement = 3050 psi or 21 MPa*
        - *"Best" EB Paste Adhesive > 3900 psi*

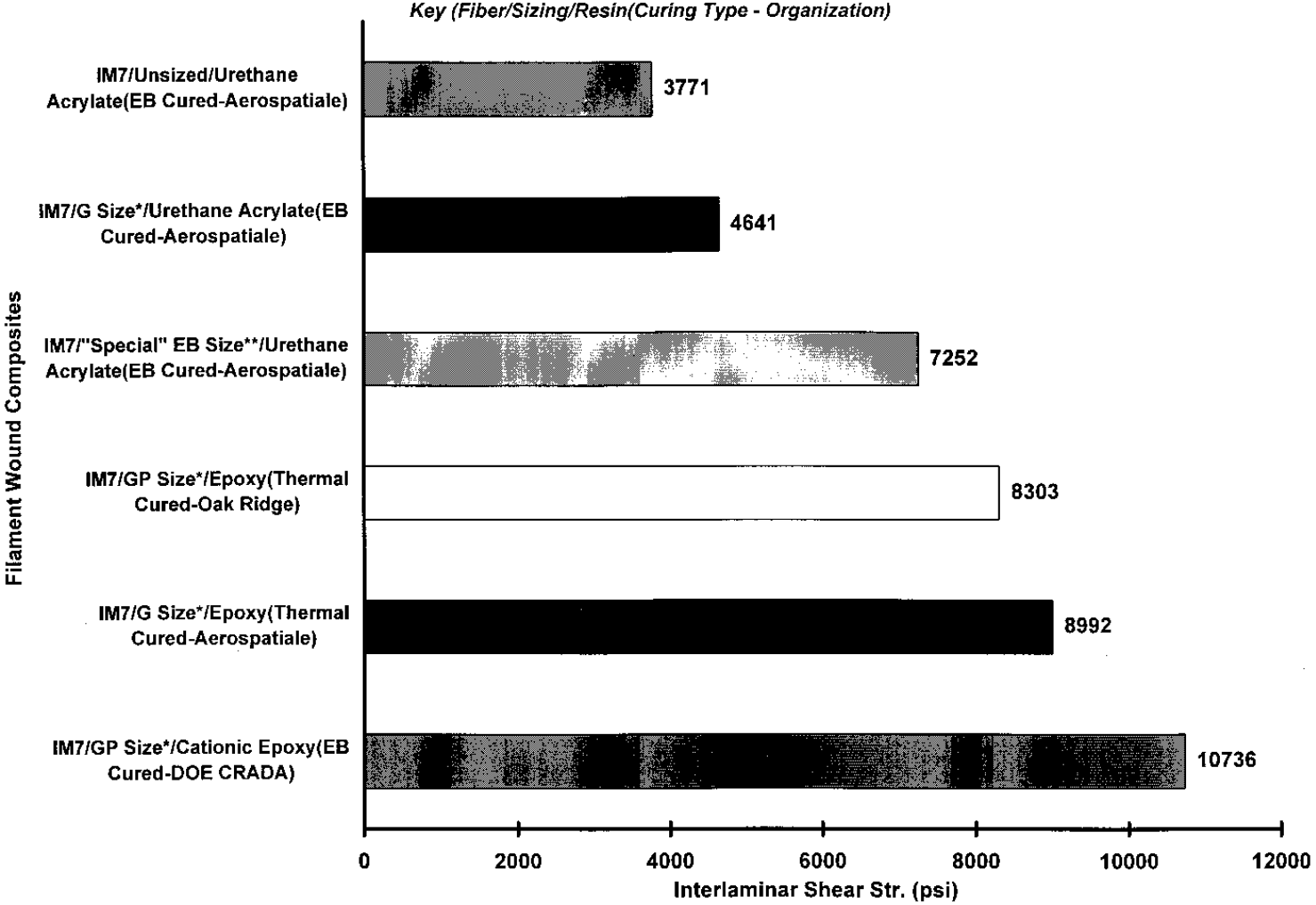
ELECTRON BEAM vs. OVEN CURED FILAMENT WOUND IM7/EPOXY LAMINATE PROPERTIES

Property Comparison Of Electron Beam Cured Versus Thermal Cured IM7-GP-12K/Resin (X) Filament Wound Laminates (15.24 cm dia.; 0.3175 cm thickness)

Resin Systems	Electron Beam Resin 6	Thermal Cured Resin 1 (Oven Cured)	Thermal Cured Resin 2 (Oven Cured)
Cure Conditions	150 kGy	3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C	3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C
Void Volume, %	< 1 %	< 1%	< 1%
Percent Fiber Content	75.8	77.8	74.6
Tg, °C (Tan Delta)	192	218	165
O° Tensile Strength, MPa (ksi) - Norm. to 75% F.V.	2358 (342)	1986 (288)	1538 (223)
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° Interlaminar Shear Strength, MPa (ksi)	73.8 (10.7)	57.2 (8.3)	47.6 (6.9)
O° Interlaminar Shear Strength, 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.

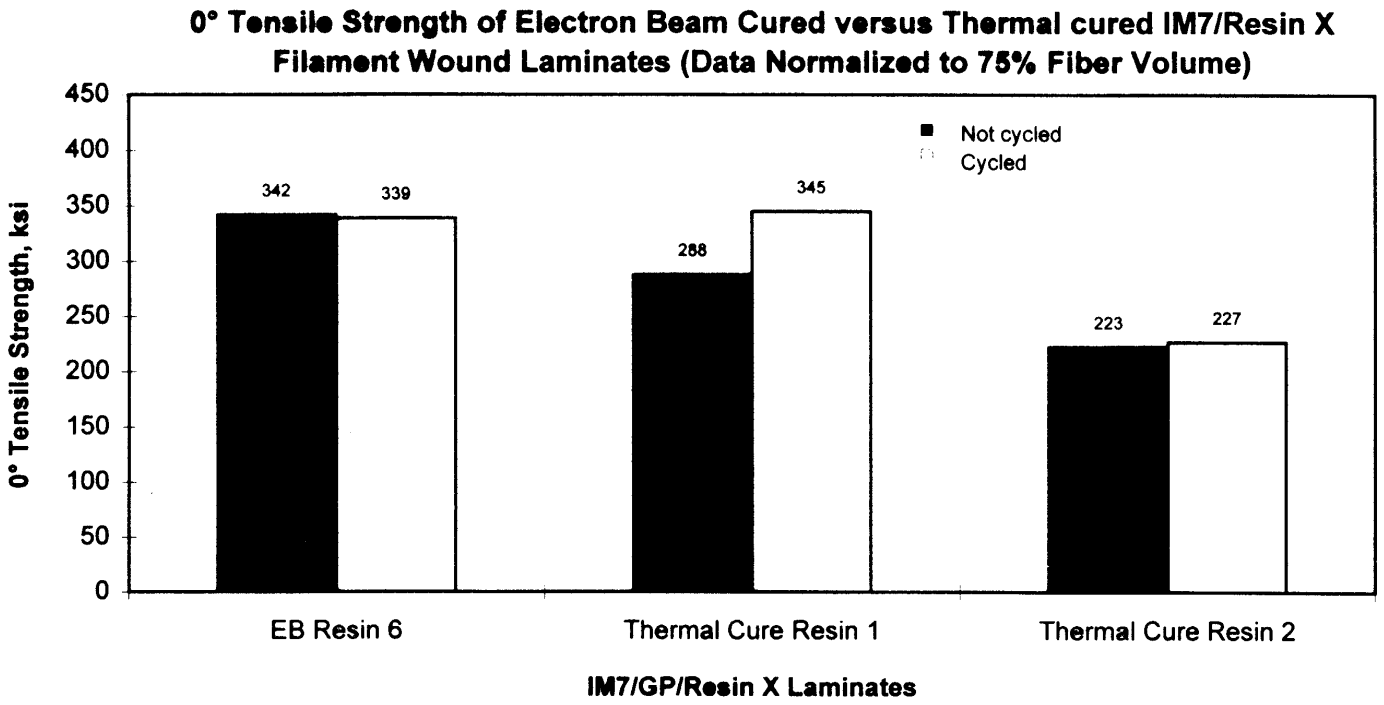
Effects of Fiber Sizings and Resin Chemistries on EBeam vs. Thermal Cured Filament Wound (5.75" dia. NOL rings, t = 0.124") Comp. Shear Props.



* Hercules G and GP Sizes are Standard Materials;

* *Aerospatiale's "Best" EB Size for Free Radical Acrylate Resins.

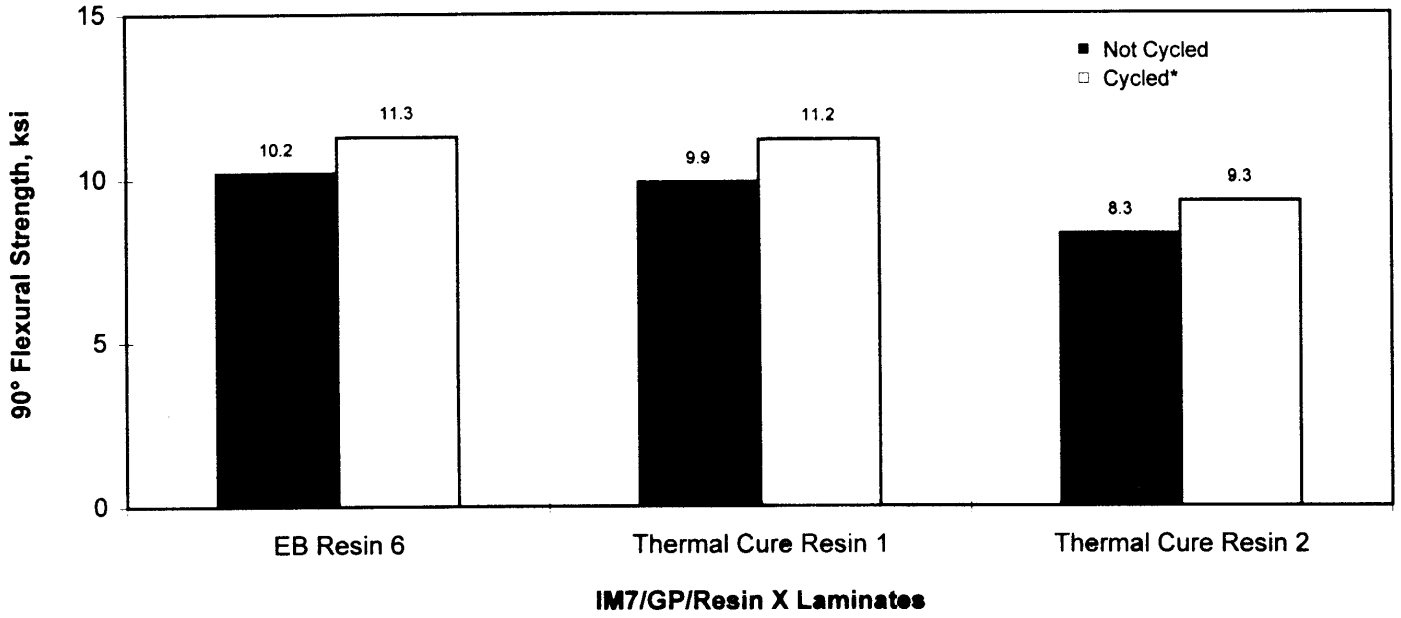
Data from Aerospatiale article in "Composites Science and Technology" 52 (1994) 299-307 and Recent EB DOE CRADA Data.



* Cycling procedure: Specimens placed in liquid nitrogen (-194°C) for 30 min; allowed to warm to room temperature for 30 min; placed in oven @ 121°C for 30 min; allowed to warm to room temperature for 30 min; cycle repeated 3 times.

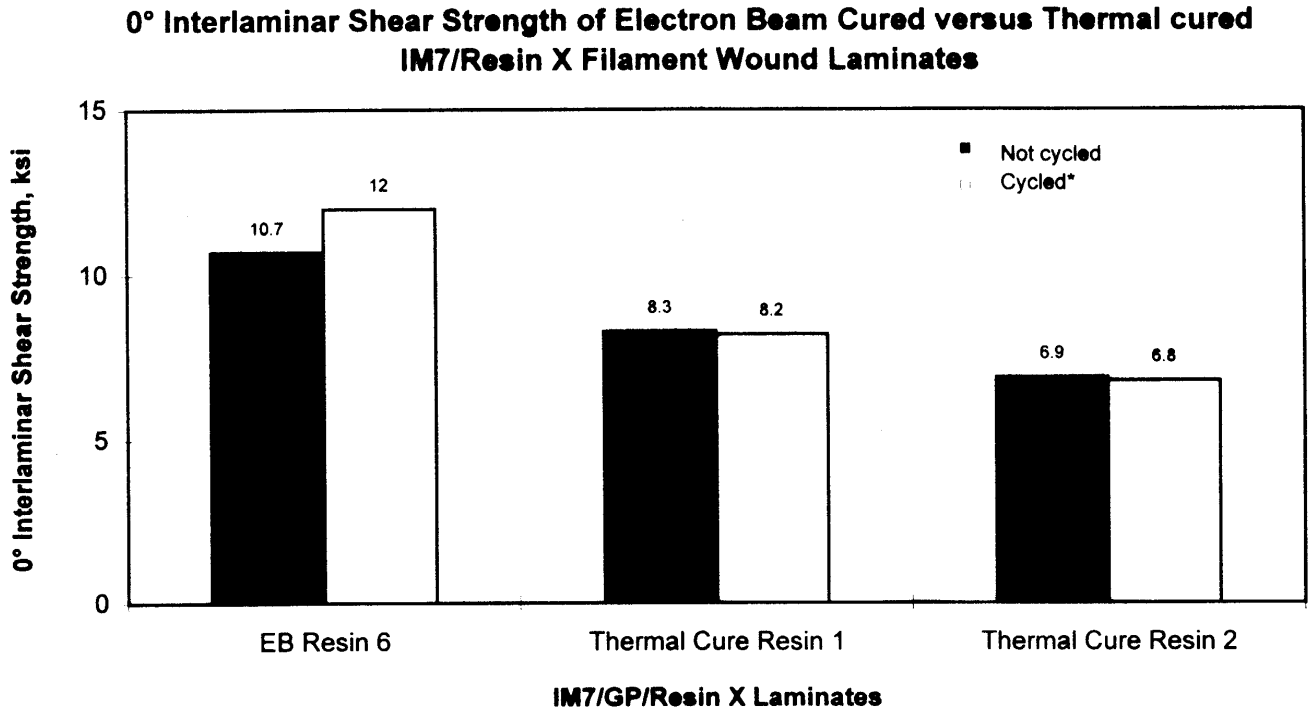
Thermal Cured Resin 1 oven cured 3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C
Thermal Cured Resin 2 oven cured 3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C

90° Flexural Strength of Electron Beam Cured versus Thermal cured IM7/Resin X Filament Wound Laminates (concave up)



* Cycling procedure: Specimens placed in liquid nitrogen (-194°C) for 30 min; allowed to warm to room temperature for 30 min; placed in oven @ 121°C for 30 min; allowed to warm to room temperature for 30 min; cycle repeated 3 times.

Thermal Cured Resin 1 oven cured 3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C
Thermal Cured Resin 2 oven cured 3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C



* Cycling procedure: Specimens placed in liquid nitrogen (-194°C) for 30 min; allowed to warm to room temperature for 30 min; placed in oven @ 121°C for 30 min; allowed to warm to room temperature for 30 min; cycle repeated 3 times.

Thermal Cured Resin 1 oven cured 3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C
Thermal Cured Resin 2 oven cured 3 hours @ 121°C, 3 hours @ 150°C, then 4 hours @ 177°C

EB* vs. Autoclave Cured Unidirectional IM7/Epoxy Laminate Properties

* EB laminates were prepared using *Room Temperature* intermediate *vacuum (15 psi) debulks* (every 4 plies) & final vacuum debulks *@ 160F*

vs.

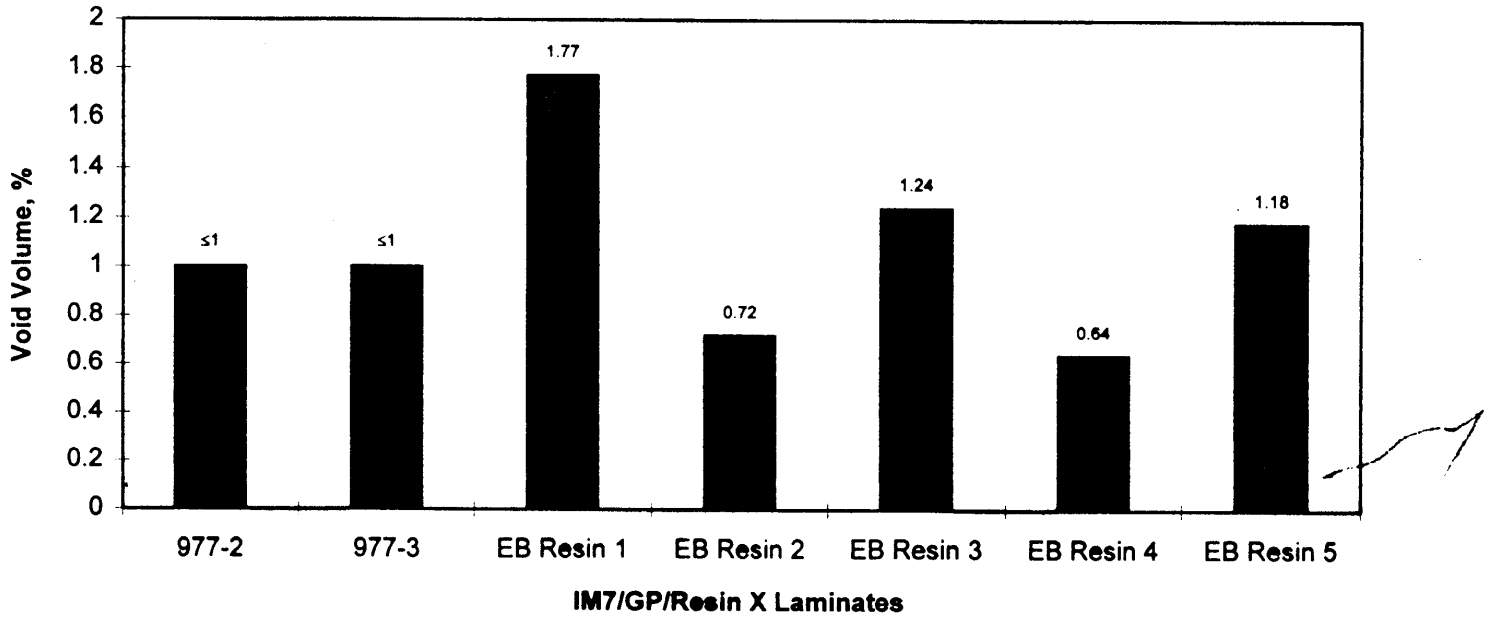
Autoclave - 85 psi & 350F

Property Comparison Of Electron Beam Cured vs Autoclave Cured IM7/Resin X Unidirectional Laminates (Data Normalized To 62% F.V.)

Resin Systems	Fiberite 977-2 (Fiberite Data)	Fiberite 977-3 (Fiberite Data)	EB Resin 1	EB Resin 2	EB Resin 3	EB Resin 4	EB Resin 5	EB Resin 6
Cure Conditions	Autoclave Cured (6 hrs. @ 350F @ 85 psi)	Autoclave Cured (3 hrs. @ 355F @ 85 psi)	250 kGy	150 kGy	150 kGy	150 kGy	150 kGy	150 kGy
Void Volume, %	Not Reported	Not Reported	1.77	0.72	1.24	0.64	1.18	1.7
Tg, °C (Tan Delta)	200	190/240	396	392	232	212	212	237/400
O° Tensile Str., MPa (ksi)	2537 (368)	2510 (364)	1869 (271)			2200 (319) Within 12%		2262 (328) Within 10%
O° Tensile Mod., GPa (msi)	166 (24.1)	162 (23.5)	168 (24.3)			157 (22.8)		164 (23.8)
180F Hot/Wet O° Tensile Str., MPa (ksi)	2362*** (343)		2282** (331)			2365** (343)		2386** (346)
180F Hot/Wet O° Tensile Mod., GPa (msi)	167*** (24.3)		172** (24.9)			177** (25.7)		166** (24)
O° Flex. Str., MPa (ksi)	1641 (238)	1765 (256)	1986 (288)	2006 (291)	1793 (260)	1765 (256)	1710 (248)	
O° Flex. Mod., GPa (msi)	147 (21.3)	150 (21.7)	196 (28.5)	163 (23.6)	163 (23.7)	154 (22.3)	150 (21.8)	
O° Comp. Str., MPa (ksi)	1580 (230)	1682 (244)	1683 (244)			1428 (207)		1524 (221)
O° Comp., Mod., GPa (msi)	152 (22)	154 (22.3)	149 (21.6)					
180F Hot/Wet O° Comp. Str., MPa (ksi)	1240*** (180)		1407** (204)			1324** (192)		1386** (201)
O° ILSS, MPa (ksi)	110 (16)	127 (18.5)	77 (11.2)	79 (11.5)	79 (11.5)	89 (12.9)	77 (11.2)	
Hot/Wet O° ILSS*, MPa (ksi)	72 (10.4)	89 (12.9)	61 (8.8)					
EB comps. were prepared using conventional lay-up techniques. Intermediate debulks were done under vacuum/4plies @ RT for 15 min. Final debulk under vacuum at 70C for 1 hr.								
* 1 wk. in H2O @ 160F, 977-3 & EB 1 tested @ 220F (977-2 tested @180F)	** 4 days in H2O @ 180F	*** 7 days in H2O @165F						

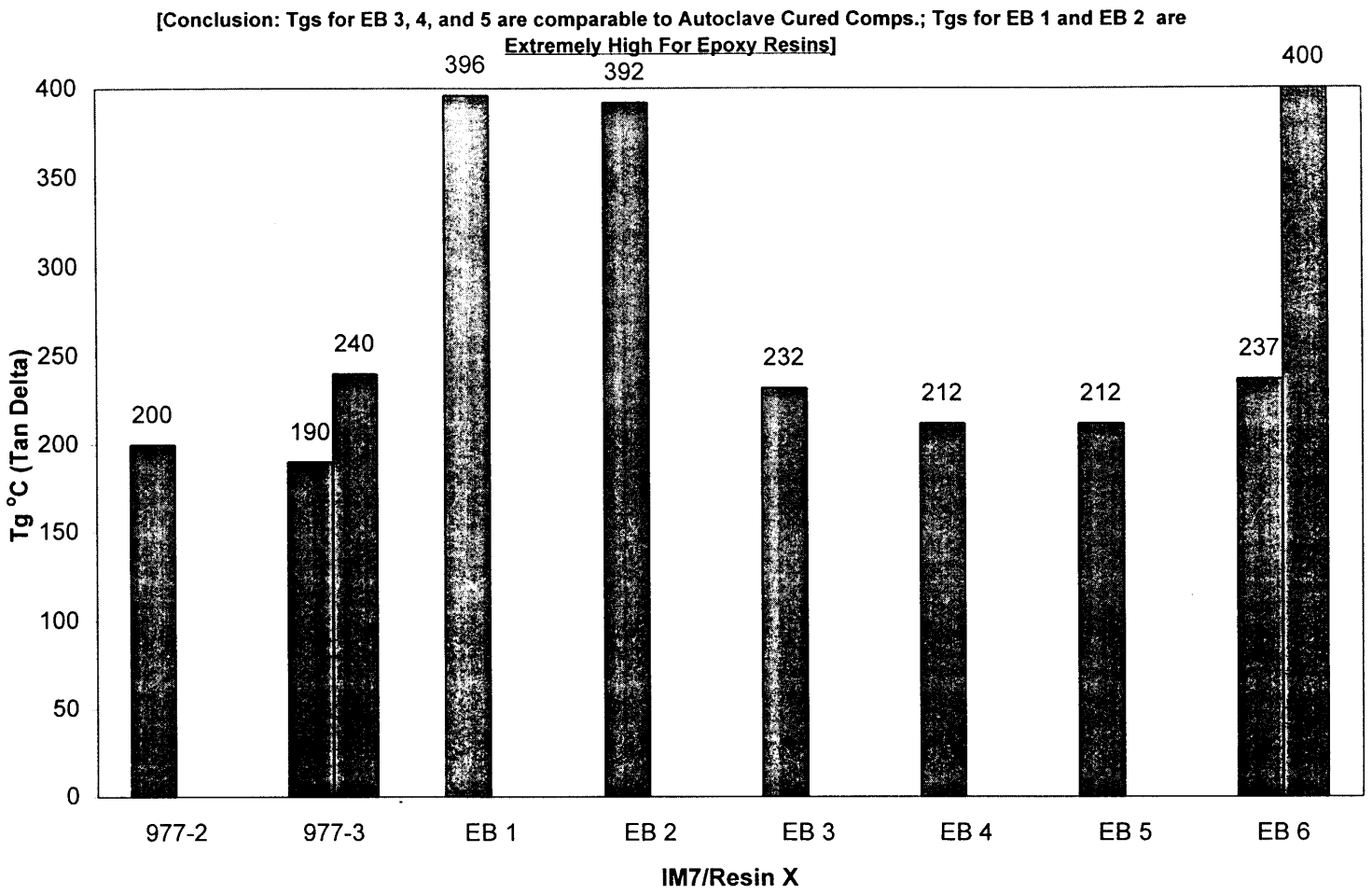
Shaded Boxes Indicate EB Composite Properties Which Were Essentially Equal To (Within 4%) Or Greater Than Fiberite's Autoclave Cured 977-2 And 977-3 Properties

Void Volume of Electron Beam Cured Versus Thermal Cured IM7/Resin X Laminates

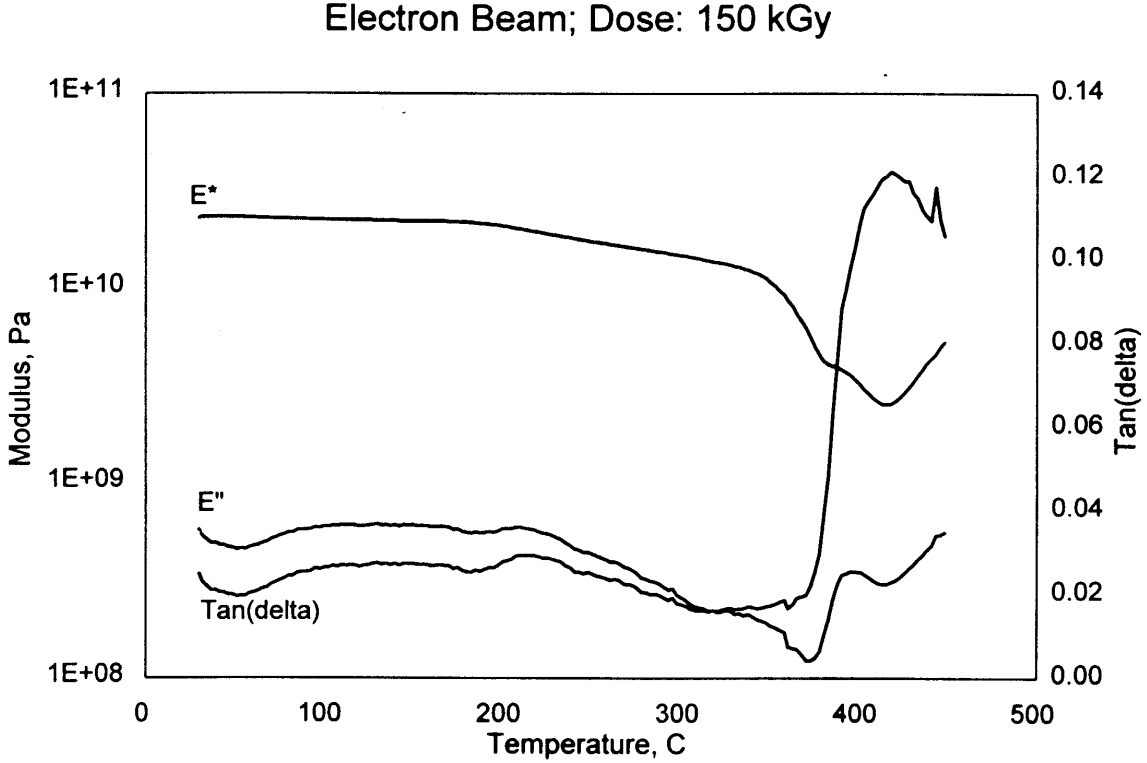


Fiberite 977-2 Autoclave Cured (6 hrs @ 350°F @ 85 psi)
Fiberite 977-3 Autoclave Cured (3 hrs @ 355°F @ 85 psi)

Tg °C (Tan Delta) Of Autoclave Cured vs. EBeam Cured IM7/Resin X Laminates



Fiberite 977-2 and 977-3 Autoclave Cured 3-6 hrs. @350F @85 psi. EB 1-6 Cured @ 150-250 kGy.

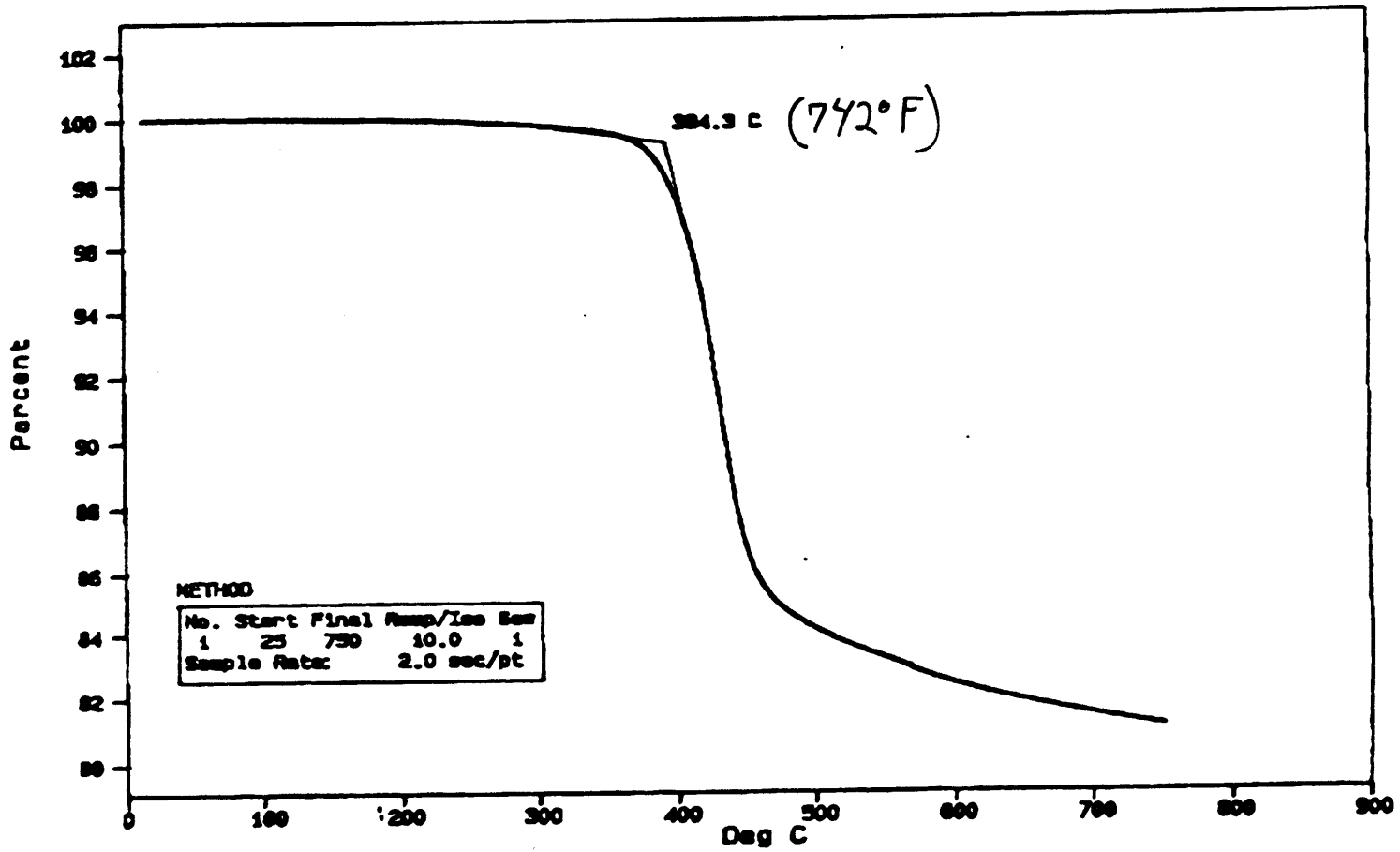

Electron Beam; Dose: 150 kGy
1E+11
1E+10
1E+09
1E+08
Modulus, Pa
E*
E"
Tan(delta)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Tan(delta)
0
100
200
300
400
500
Temperature, C

TGS-II

PL Thermal Sciences

SMPL ID : Panel 48 (8)
RUN ID : specimen 1
SIZE : 31.076 mg
OPERATOR: DAS

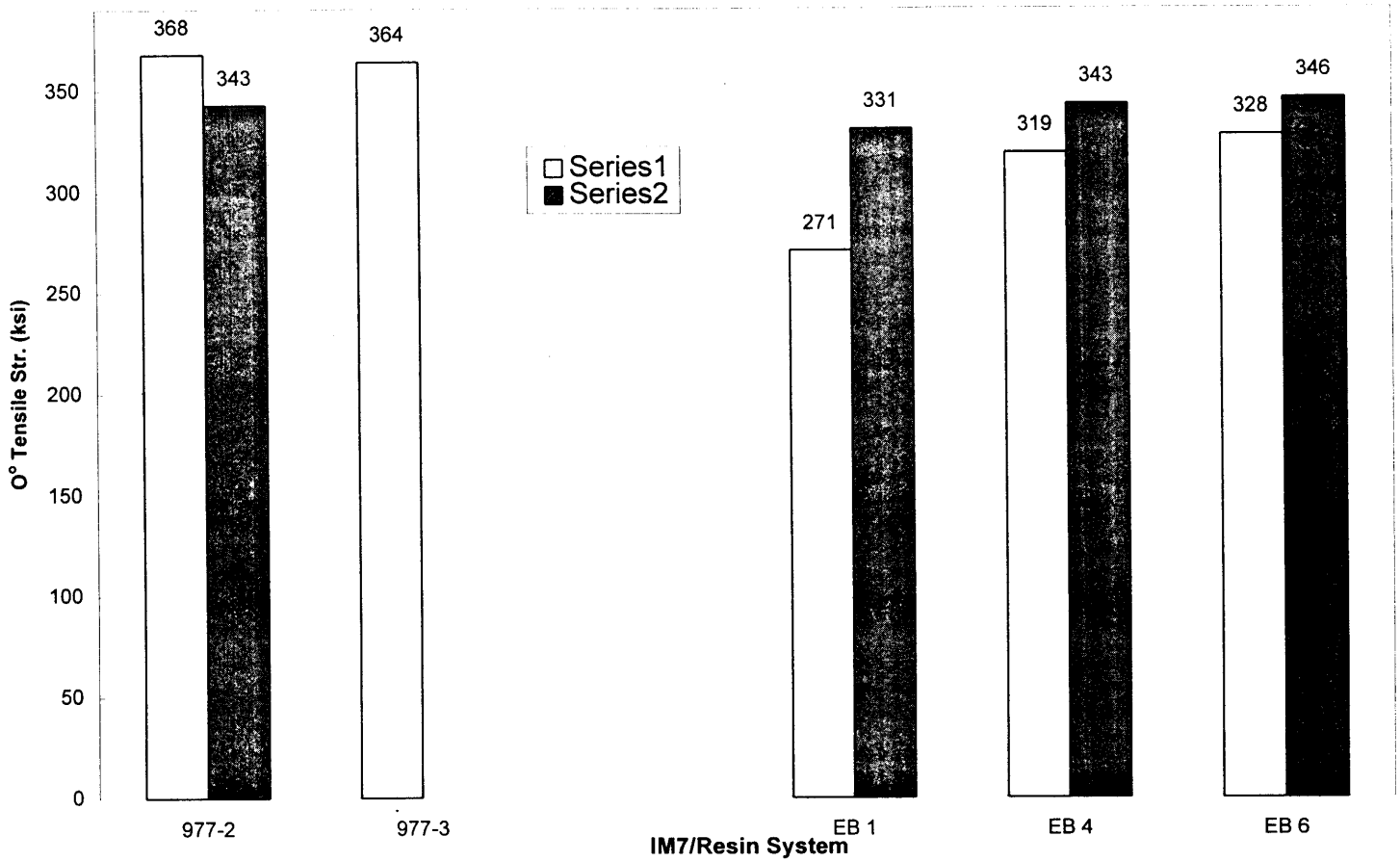
DATE RUN: Jan/17/1997
GASES : N2 purge
SOURCE : Demetrius
COMMENT :



VERSION: V4.30

O° Tensile Strength Properties (RT and 180F Hot/Wet) Of EBeam Cured vs. Autoclave Cured Unidirectional IM7 Laminates

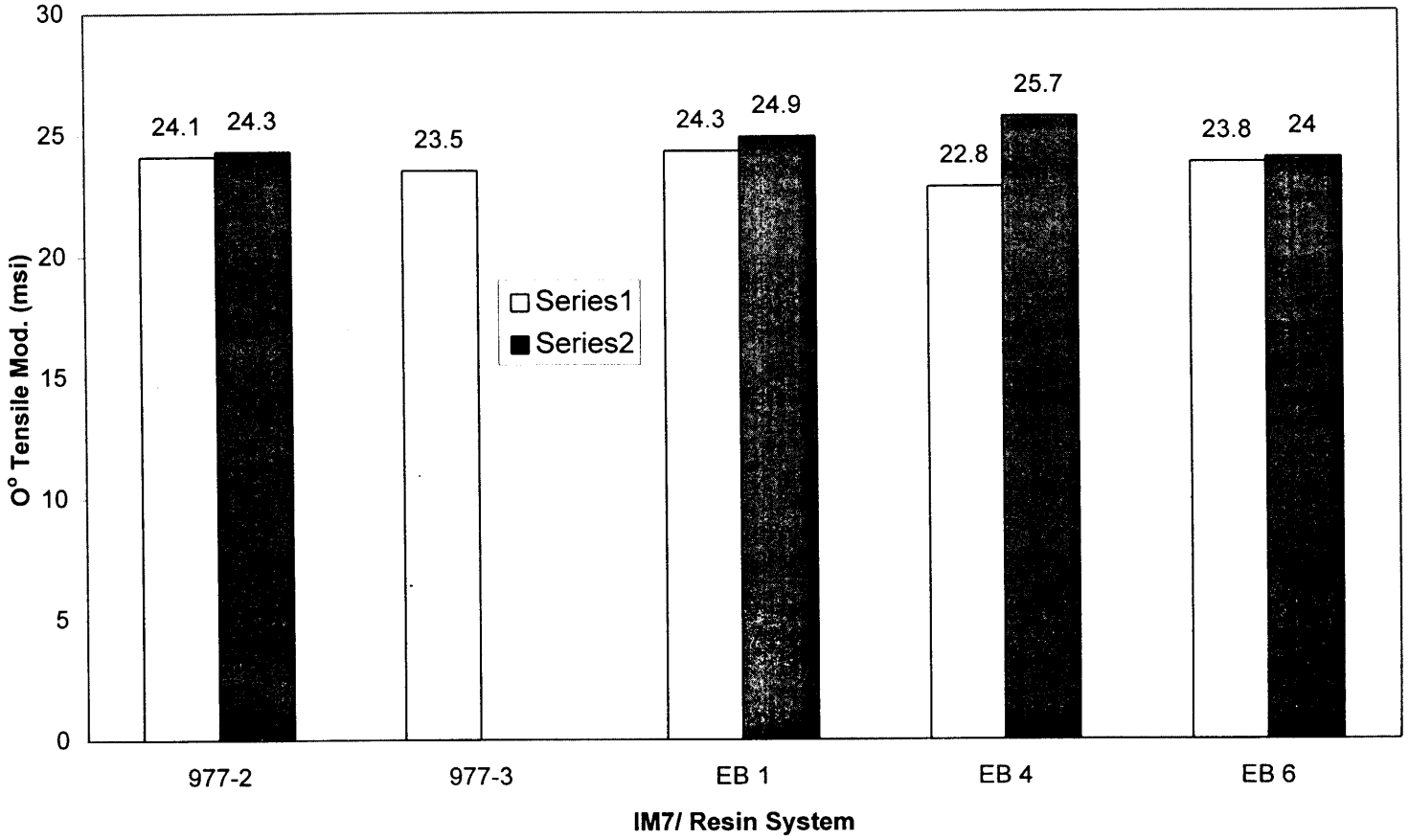
[Conclusion: 180F Hot/Wet Tensile Strength Properties Of Autoclave vs. EBeam Cured IM7 Composites Are Essentially Equal. RT Properties Of EBeam Comps.(EB 6) Are Only 10% Lower.]



Series 1: RT Properties; Series 2: 180F Hot/Wet Properties after 4-7 days in water @165-180F. Fiberite 977-2 and 977-3 Autoclave Cured @350F@85psi for 3-6 hrs.; EB 1,4,6 cured @150-250 kGy.

O° Tensile Modulus Properties (RT and 180F Hot/Wet) Of EBeam Cured vs. Autoclave Cured Unidirectional IM7 Laminates

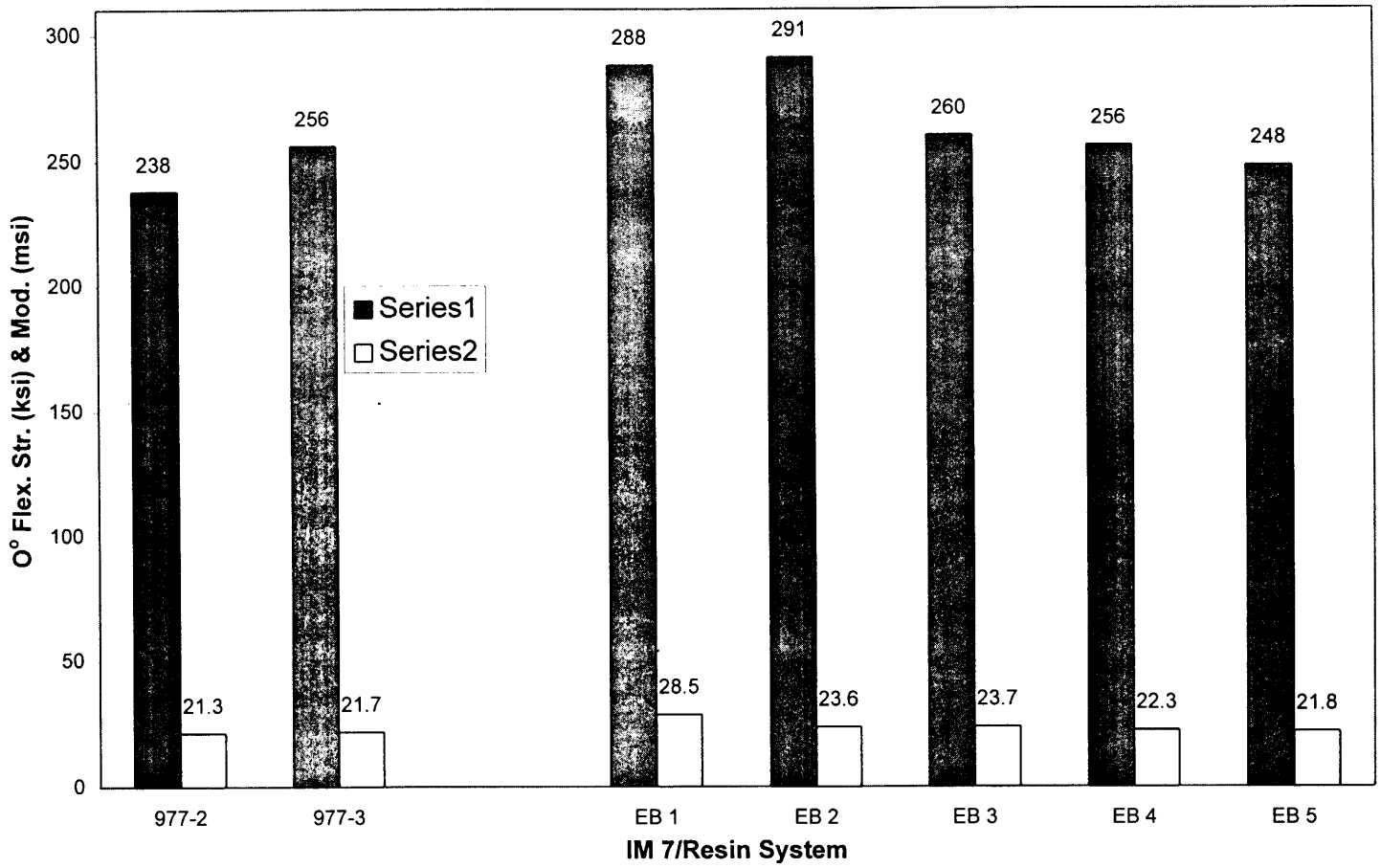
[Conclusion: RT and 180F Hot/Wet Tensile Modulus Properties Of EBeam vs. Autoclave Cured Comps. are Essentially Equal]



Series 1: RT Properties; Series 2: 180F Hot/Wet Properties after 4-7 days in water @165-180F. Fiberite 977-2 and 977-3 Autoclave Cured @350F@85psi for 3-6 hrs.; EB 1,4,6 cured @ 150-250 kGy.

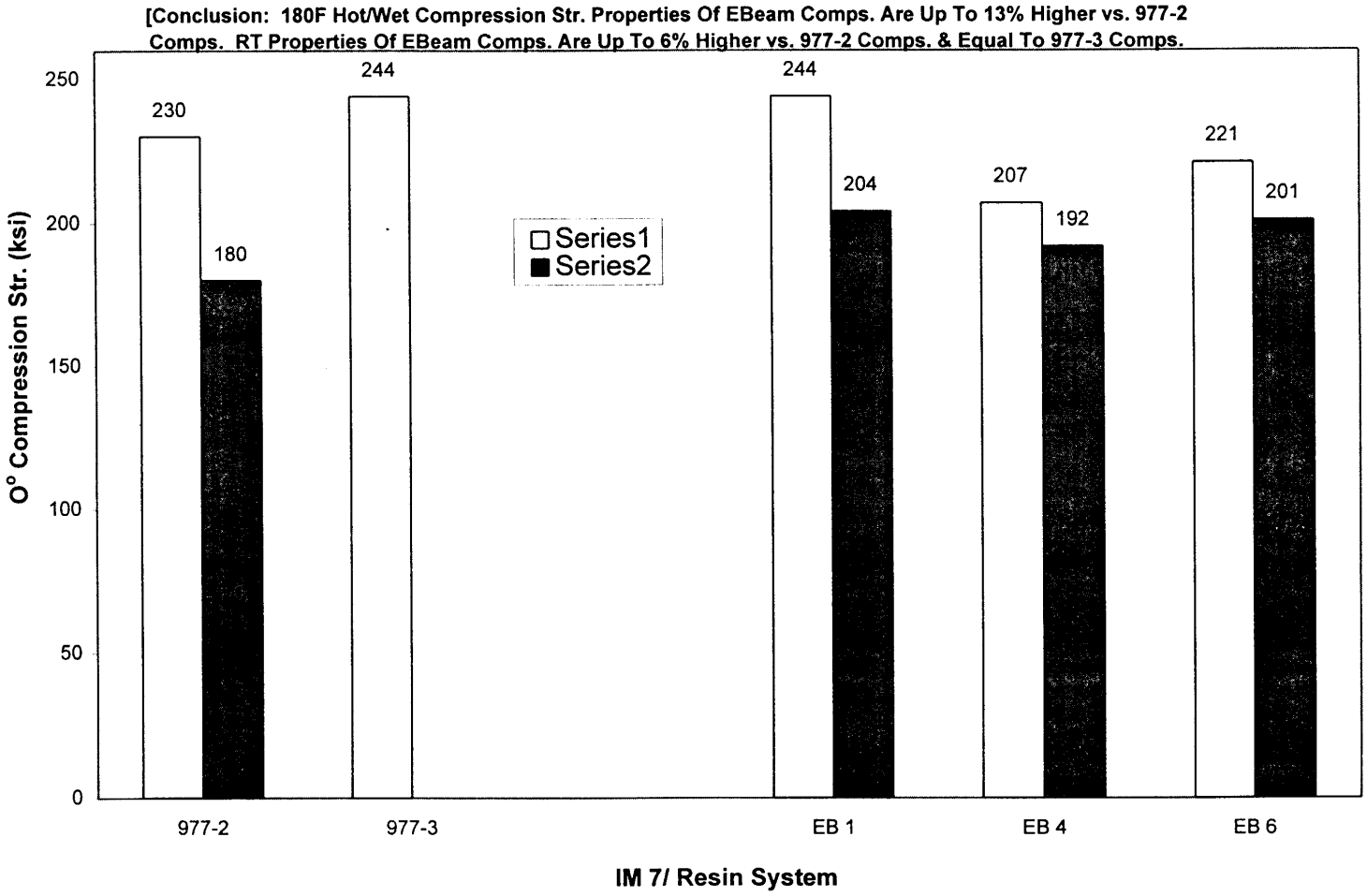
Room Temp. O° Flexural Strength and Modulus Properties Of EBeam Cured vs. Autoclave Cured Unidirectional IM7 Laminates

[Conclusion: Flex. Str. of EBeam Comps. are up to 14-22% Higher vs. 977-2 and 977-3 Comps. Flex. Mod. of EBeam Comps. are equal to or higher than 977-2 and 977-3 Comps.



Series 1: Flex. Str.; Series 2: Flex. Mod.; Fiberite 977-2 and 977-3 Autoclave Cured @350F@85psi for 3-6 hrs.; EB 1-5 cured @ 150-250 kGy.

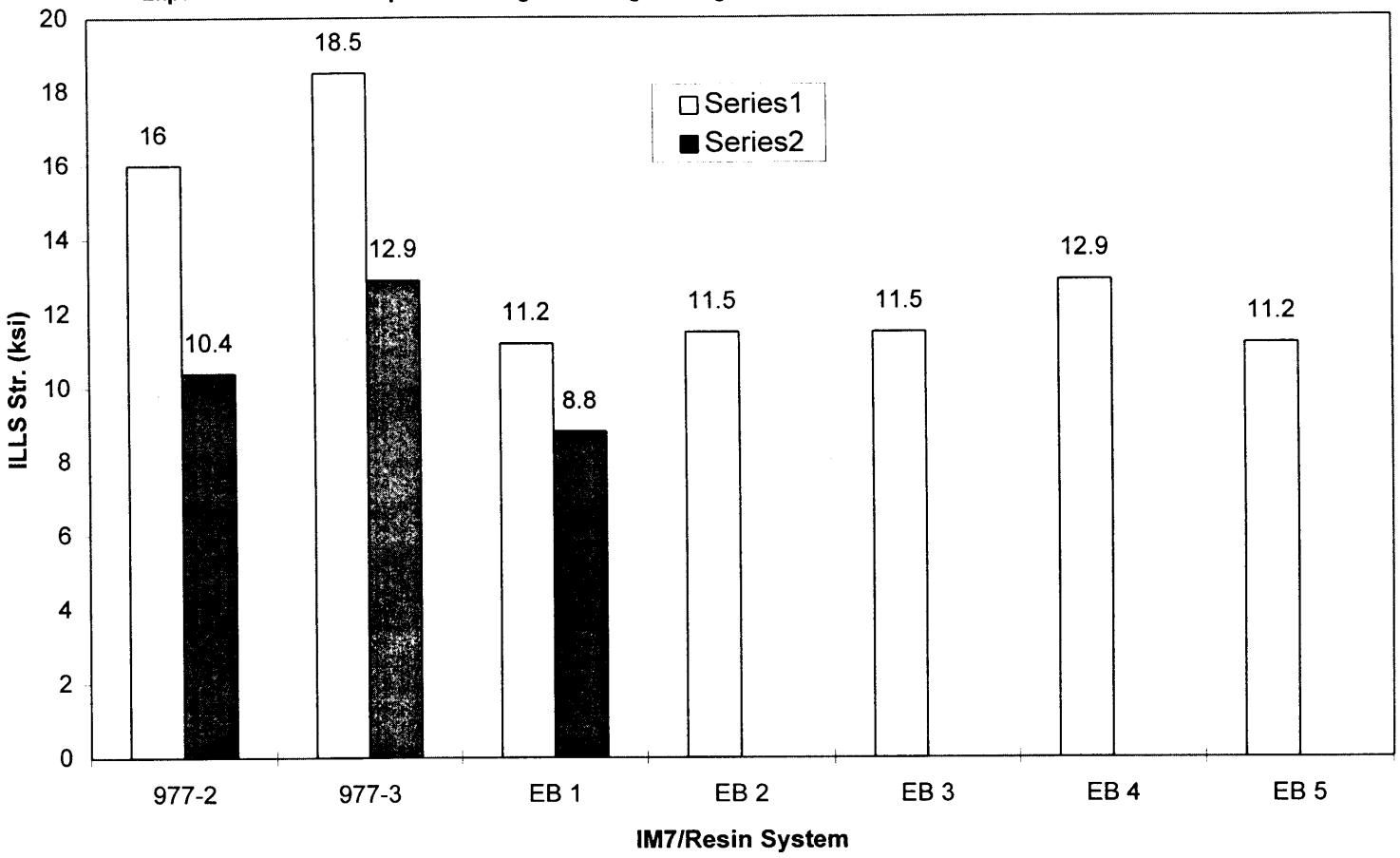
O° Compression Strength Properties (RT and 180F Hot/Wet) Of EBeam Cured vs. Autoclave Cured Unidirectional IM7 Laminates



Series 1: RT Properties; Series 2: 180F Hot/Wet Properties after 4-7 days in water @165-180F. Fiberite 977-2 and 977-3 Autoclave Cured @350F@85psi for 3-6 hrs.; EB 1,4,6 cured @ 150-250 kGy.

O° Interlaminar Shear Strength Properties (RT and Hot/Wet-SEE BELOW) Of EBeam Cured vs. Autoclave Cured Unidirectional IM7 Laminates

[Conclusion: RT ILSS Props. are 19% lower for EB vs. 977-2 Comps. Hot/Wet Props. for EB comps. Should Experience Less of a Drop-off in Strength Since Tgs are higher and % water absorp. is lower for the EB resins.]



Series 1: RT Properties; Series 2: All immersed in water 1 wk. @160F, 977-2 tested @180F; BUT 977-3 and EB 1 tested at 220F. Fiberite 977-2 and 977-3 Autoclave Cured @350F@85psi for 3-6 hrs.; EB 1-5 cured @ 150-250 kGy.

CONCLUSIONS

Property Results Of EB vs. Autoclave Cured IM7/Epoxy Unidirectional Laminates

- **The Following Properties Of EB Cured Composites Are Essentially Equal To (Within 4%) Or Greater Than (By 10% Or More) The Same Properties Of Fiberite's Autoclave Cured 977-2 And/Or 977-3 Composites:**
  - **Room Temperature Compression Strength**
  - **Room Temperature Compression Modulus**
  - **180F Hot/Wet Compression Strength (Some EB Composites Are Up To 13% Higher Than 977-2 Composites)**
  - **Room Temperature Flexural Strength (Some EB Composites Have Flexural Strengths 14% & 22% Higher Than 977-3 & 977-2 Composites, Respectively)**
  - **Room Temperature Flexural Modulus**
  - **180F Hot/Wet Tensile Strength**

CONCLUSIONS

Property Results Of EB vs. Autoclave Cured IM7/Epoxy Unidirectional Laminates

- The Following Properties Of EB Cured Composites Are Essentially Equal To (Within 4%) Or Greater Than (By 10% Or More) The Same Properties Of Fiberite's Autoclave Cured 977-2 And/Or 977-3 Composites:
  - 180F Hot/Wet Tensile Modulus
  - Room Temperature Tensile Modulus (Room Temp. Tensile Strengths Are Within 10% Of 977-2 & 977-3 Composites)
  - Tg (Some Tgs Significantly Exceed Those Of 977-2 & 977-3 Composites)
  - % Voids (Some EB Cured, Hand Laid-Up Composites Have Exhibited Void Contents Of <1%)

CONCLUSIONS

Property Results Of EB vs. Autoclave Cured IM7/Epoxy Unidirectional Laminates

- Hot/Wet Interlaminar Shear Strengths Are Within 15% Of 977-2 Composites
- Room Temperature Interlaminar Shear Strengths Are Within 19% Of 977-2 Composites