Electron Beam Curable Cationic Epoxy Resin Systems And Composites

Presented At The
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THE EBEAM DOE-DP CRADA TEAM

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Presentation Outline

- Introduction - Requirements, Epoxies, Tougheners, Initiators
- EB Curable Cationic Epoxy Resin Systems - Advantages And Highlights
- EB Cured Laminate Properties
- Variables Requiring Optimization For EB Curable Epoxy Resin Systems And Composite Properties

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EB Curable Cationic Epoxy Resin System Requirements

Must Have:

- Epoxy (Epoxies)
- Cationic Initiator
- EB Source

Optional Materials (for property enhancement and/or aid in processing):

- Tougheners
- Diluents
- Other Modifiers

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Evaluation Of EBeam Curable Epoxy Resin Families

- We have evaluated hundreds of epoxy resins & resin systems (Shell, Dow, Union Carbide, Ciba- Geigy) ;
- Including a large range of epoxide equivalent weights and viscosities:
  - Bisphenol A Liquid Epoxy Resins
  - Bisphenol F Epoxy Liquids
  - Epoxy Novolac Resins
  - Multifunctional Epoxy Resins
  - Cycloaliphatic Epoxy Liquids
  - Hydrocarbon Epoxies
  - Toughened Epoxies
  - Flexible Epoxies
  - Fusion Solid Epoxies
  - Multi-Epoxy Resins (Blends)
  - Diluted Liquid Epoxy Resins
  - Multifunctional Epoxy Diluents

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Evaluation of EB Curable Toughened Epoxy Resin Systems

- ***Over 85 Toughened Epoxy Resin Systems Have Been Evaluated Including Those Incorporating Tougheners Such As:***

  - **Engineering Thermoplastics**
  - **Hydroxy-Containing Thermoplastics**
  - **Reactive Flexibilizers**
  - **Rubbers/Elastomers**
  - **Undissolved Particles**
  - **Toughener Mixtures**
  - **Acrylates**

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Evaluation Of Initiators

– Over 25 Initiators Have Been Evaluated:

- Diaryliodonium Salts
- Triarylsulfonium Salts
- Diaryldiazonium Salts
- Iron Complexes
- Diaryldisulfones
- Triazine Compounds
- Others (Patents Pending)

- ***Several different non-nucleophilic anions with these initiators have been evaluated***

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Advantages of EB Curable Cationic Epoxies

- **No hardeners are required for EB cure**
- **Most Commercially available NON-AMINE containing epoxies successfully EB cure with no thermal postcure required *(if variables are optimized)***
- **Infinite number of resin systems and blends are possible**
- **Materials offer significant formulation and processing flexibility**

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Advantages of EB Curable Cationic Epoxies

- Indefinite storage at room temperature is possible *(as long as UV is not present)*
- No special care has been required in the handling, formulation, or EB curing of these systems
  - All epoxy resins were ordered off-the-shelf (No purified resins were required)
  - Resins were prepared in several different locations in the US and Canada under various temperature and humidity levels with no adverse effects on cure

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Advantages of EB Curable Cationic Epoxies

- No oxygen inhibition problems have been encountered during EB cure
- Materials are toughenable
- Requires relatively short cure times vs. thermal cure
- Relative cost of materials are comparable to thermally curable variants
- Materials yield excellent thermal, mechanical, and moisture resistance properties

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Highlights of EB Curable Cationic Epoxies Evaluated Thus Far

- **Resin viscosities are tailorable (10 cps - solid)**
- **Dry Tg Tan Delta (*data from hundreds of resin systems):* 54 - 435°C; (130 - 815°F)**
- **Wet Tg Tan Delta; after 48 hr. water boil; (*data from only 12 formulations):* 107 - 192°C; (225 - 378°F)**
- **DMA modulus, E': 170 - 581 ksi; (1.58 - 4 GPa);**
  - ***(Most were above 400 ksi)***

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Highlights of EB Curable Cationic Epoxies Evaluated Thus Far

- % Water absorption for untoughened and toughened epoxy systems *(after 48 hr. water boil):*
  - 0.93 - 10.64%; (Most cationic epoxies absorbed < 2.5%; The Bis A and Bis F epoxies absorbed only in the 1 - 2% range, while the cycloaliphatic epoxies absorbed the highest amounts of water; thermal cure epoxies are normally in the 3 - 6% range)

- % Shrinkage after EB cure:
  - Bis A and Bis F epoxies shrink in the range of 2.2 - 3.4%; Cycloaliphatics shrink about 4.8%; (Acrylates are notoriously high in the range of 8 - 20%; Thermal cure epoxies are generally in the range of 4 - 6%)

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Highlights of EB Curable Cationic Epoxies Evaluated Thus Far

- Room temperature toughness, K_{1c}:
  - 0.41 - 0.97 MPa $m^{0.5}$; (values are equal to 46% - 108% of the K_{1c} value of 0.90 for ICI's 3rd generation 977-3 toughened epoxy).
- Cold (-100°C) toughness, K_{1c} :
  - 0.46 - 1.26 MPa $m^{0.5}$
- Adhesive lap shear strengths
  - steel substrates with primer - recorded as high as 4800 psi;
  - composite substrates - no higher than 3600 psi;
  - aluminum substrates - no higher than 2600 psi

(values depended heavily on substrate and surface preparation).

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What Is The Bottom Line?

How Well Do The Laminate Properties Of EB Cured Cationic Epoxies Compare To Thermally Cured Epoxies?

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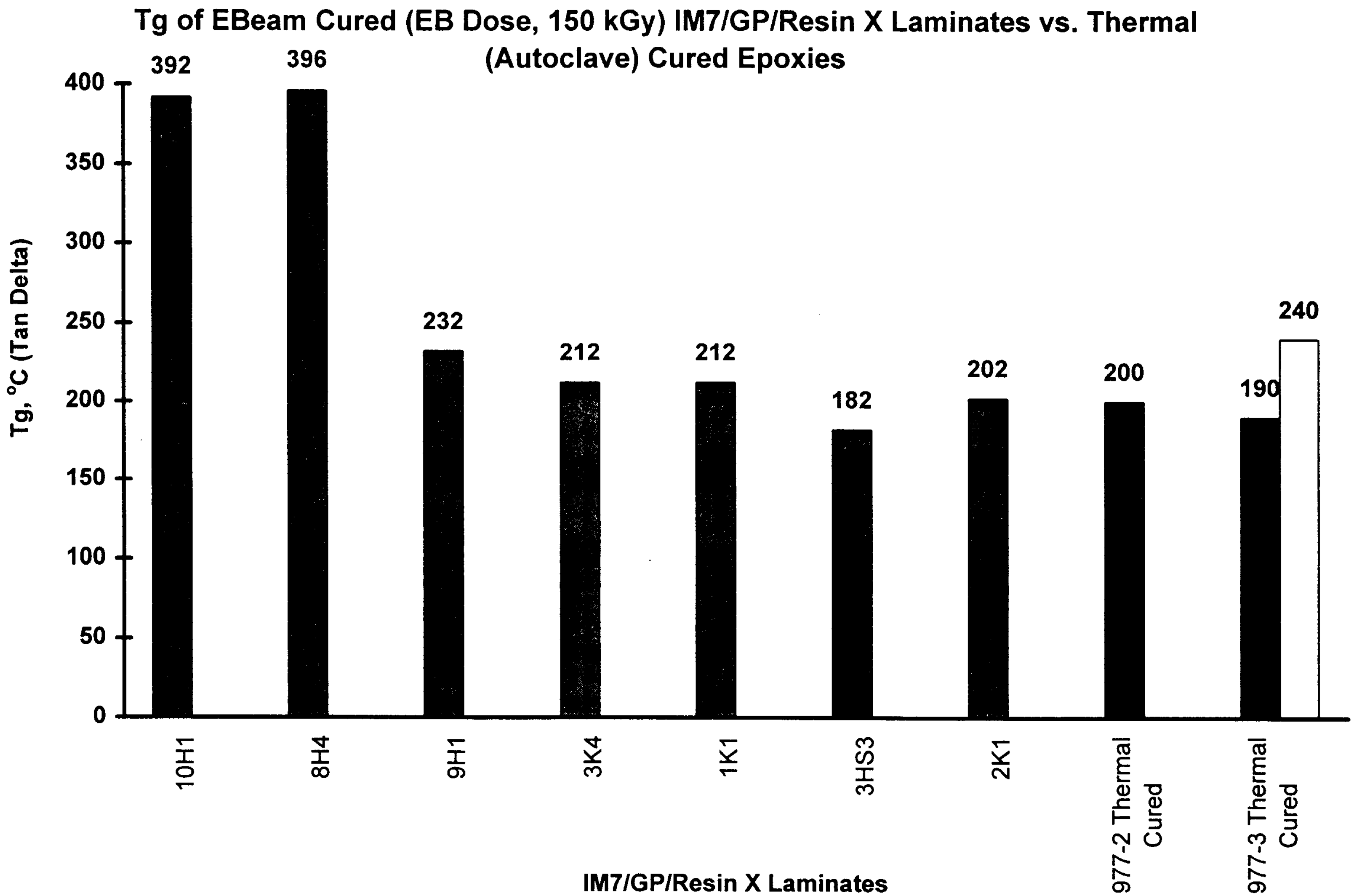

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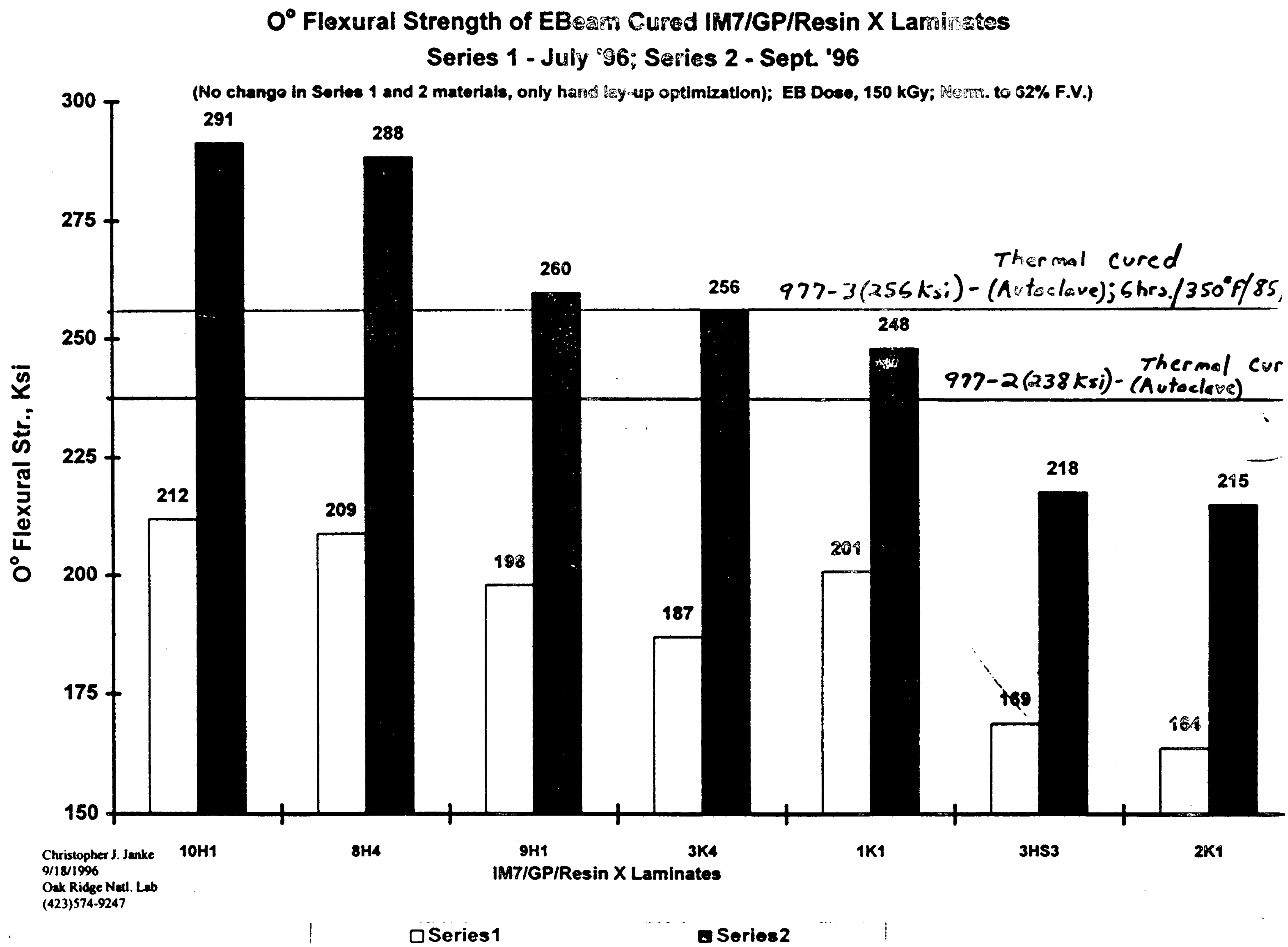

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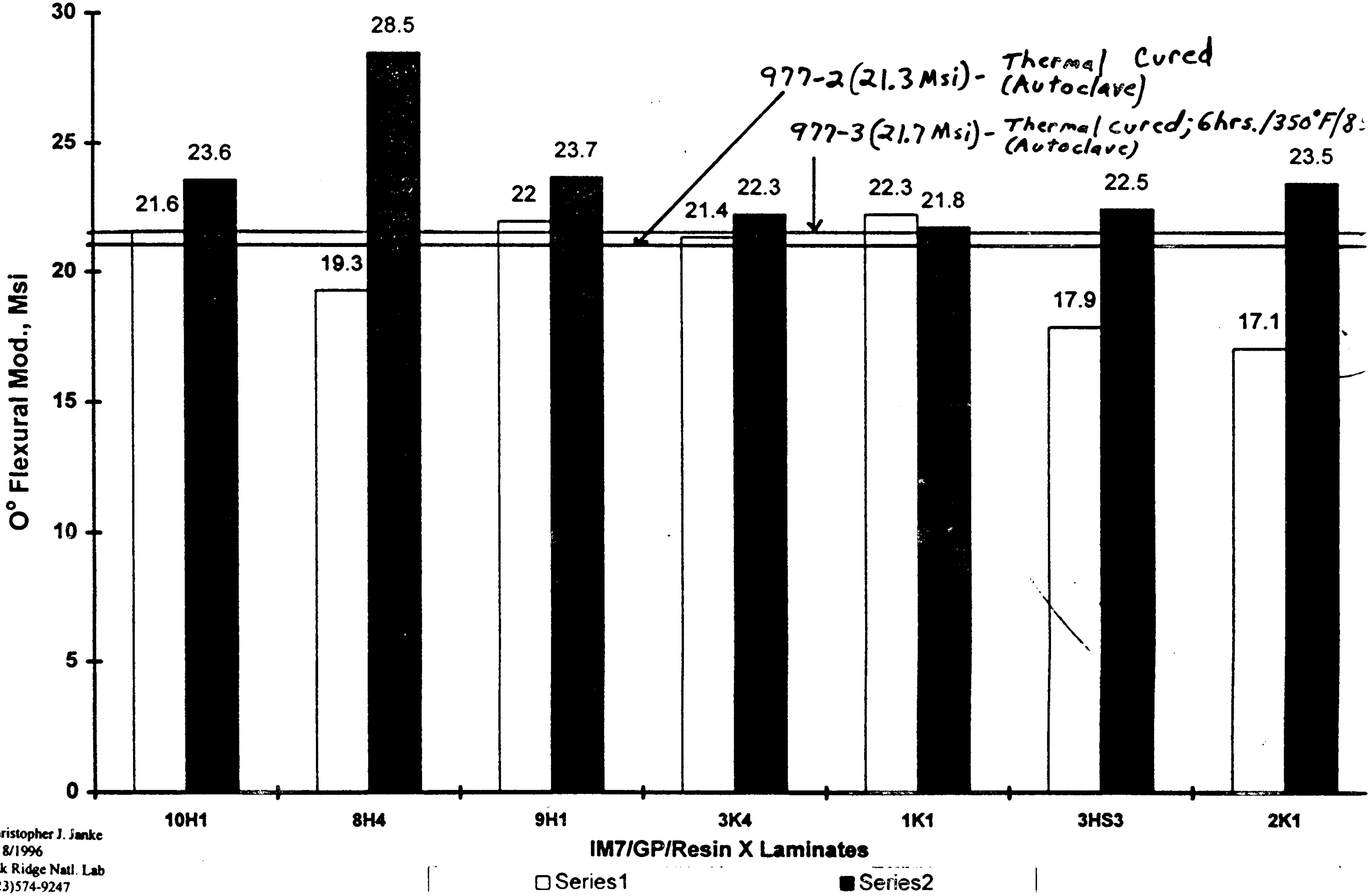
O° Flexural Modulus of EBeam Cured IM7/GP/Resin X Laminates

Series 1 - July '96; Series 2 - Sept. '96;

(No change in Series 1 and 2 materials, only hand lay-up optimization; EB Dose, 150 kGy; Norm. to 62% F.V.)



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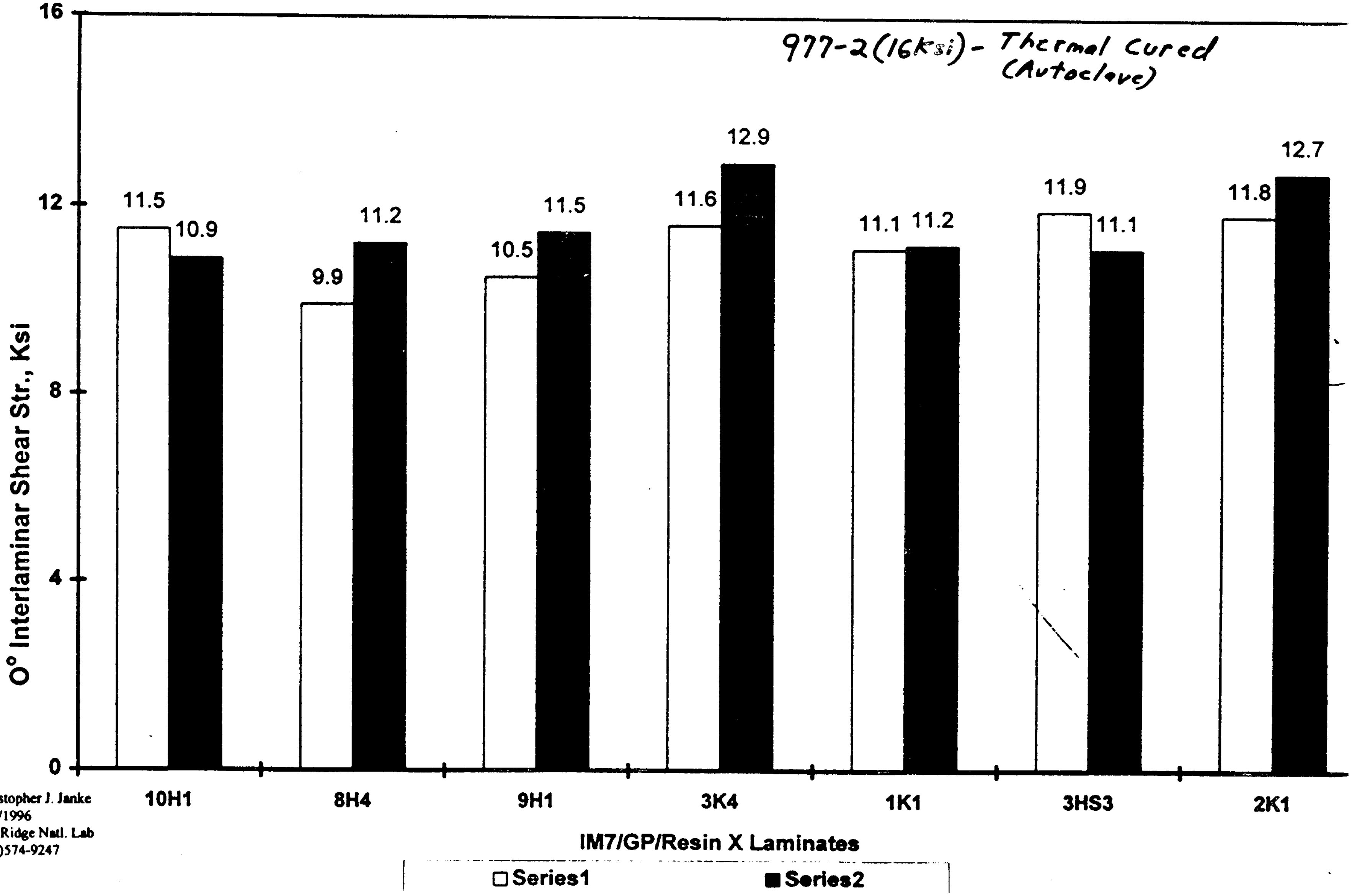
O° Interlaminar Shear Strength of EBeam Cured IM7/GP/Resin X Laminates
Series 1 - July '96; Series 2 - Sept. '96;
(No change in Series 1 and 2 materials, only hand lay-up optimization; EB Dose, 150 kGy)



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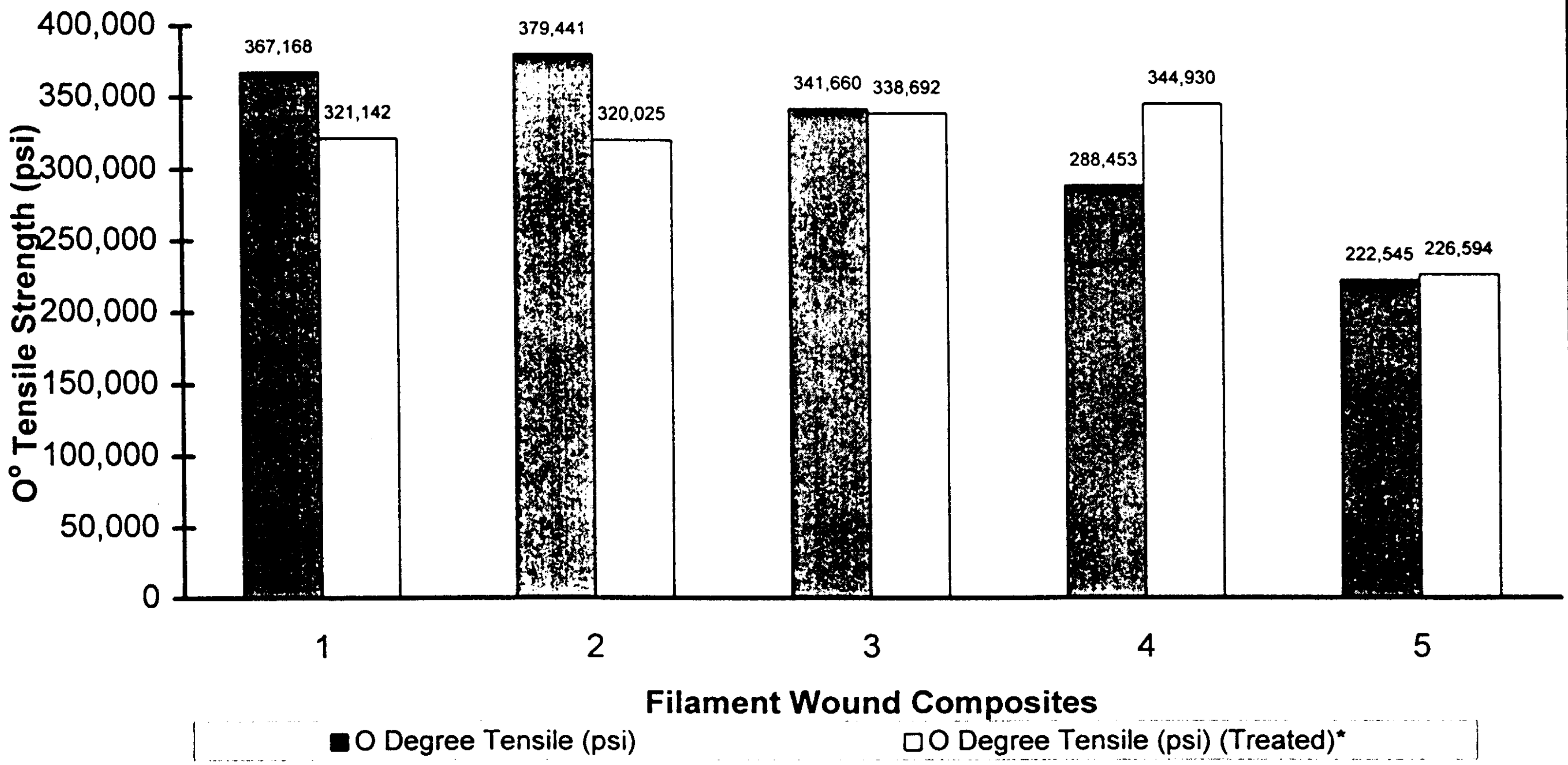
O° Tensile Strength Properties (Treated* and Untreated) of EBeam Cured vs. Thermal Cured Filament Wound Composites



Filament Wound Composite System: (Part Dia. - 6 in.; t - 0.125 inch; Fiber/Sizing/Tow Size - IM7/GP/12K; % Voids (Acid Digestion) - All < 1%)	1	2	3	4	5
Resin System	**EB Cured** Cationic Epoxy - Blend of Bis A and Cycloaliphatic Epoxies/3 phr Initiator A			**Thermal Cured:** Blend of Bis A & Cycloaliphatic Epoxies with Aromatic Amine Hardener	**Thermal Cured:** Bis A Epoxy w/3 phr BF3 MEA Catalyst
Cure Schedule	150 kGy	150 kGy	150 kGy	3 hrs. @250°F, 3 hrs. @300°F, 4 hrs. @350°F	3 hrs. @250°F, 3 hrs. @300°F, 4 hrs. @350°F
% Fiber Content (**Note: The Data is Normalized to 75% F.V.**)	75.80%	76.90%	75.80%	77.80%	74.60%

*Treated Procedure - Samples placed in liquid nitrogen dewar (-194°C or -317°F) for 30 min.; Allowed to warm to RT (30min.); Placed in oven @ 121°C (250°F) for 30 min.; Allowed to warm to RT (30min.); Cycle repeated 3 times.

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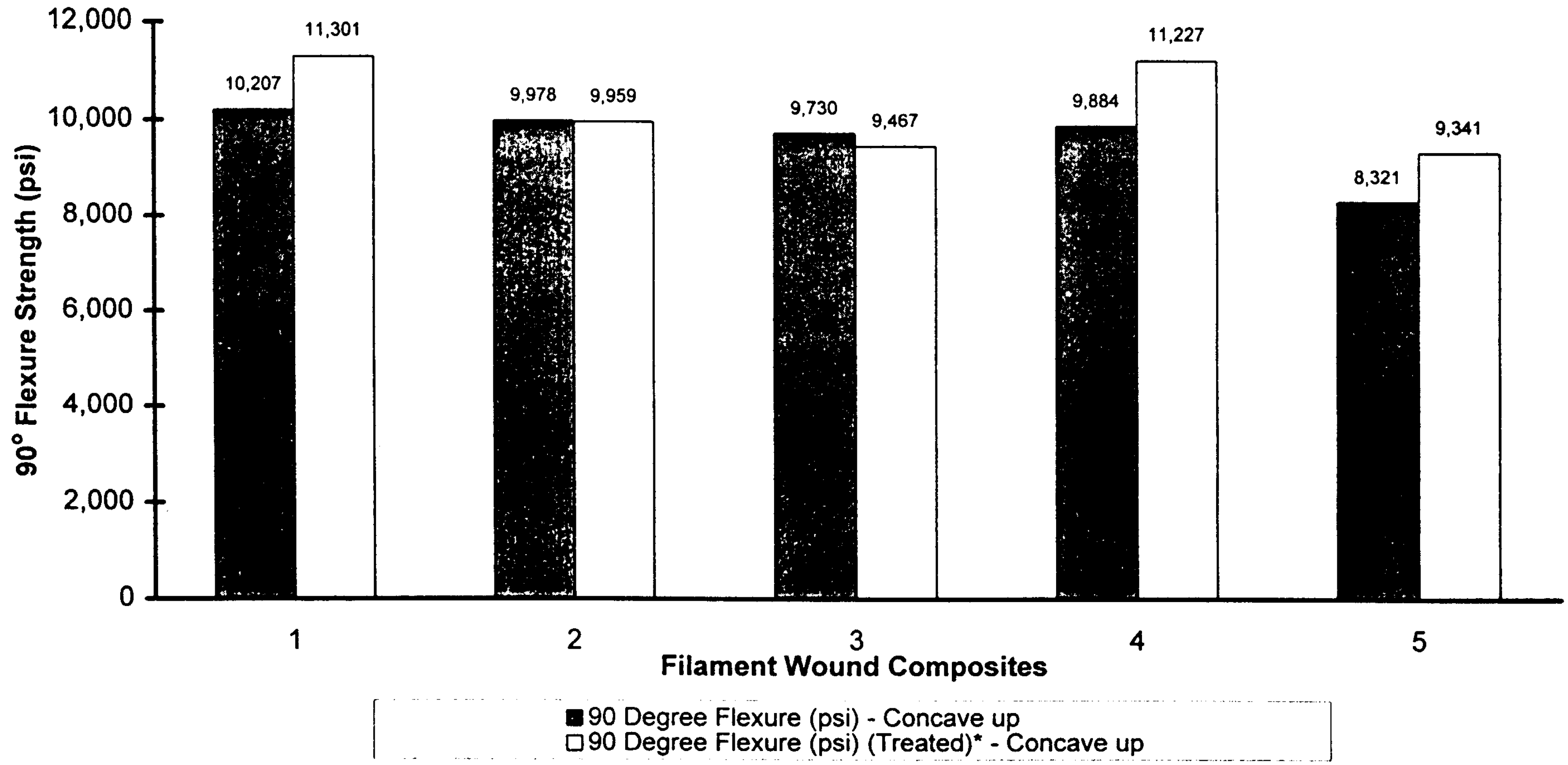
9O° Flexure Strength Properties (Treated* and Untreated) of EBeam Cured vs. Thermal Cured Filament Wound Composites



Filament Wound Composite System: (Part Dia. - 6 in.; t - 0.125 inch; Fiber/Sizing/Tow Size - IM7/GP/12K; % Voids (Acid Digestion) - All < 1%)	1	2	3	4	5
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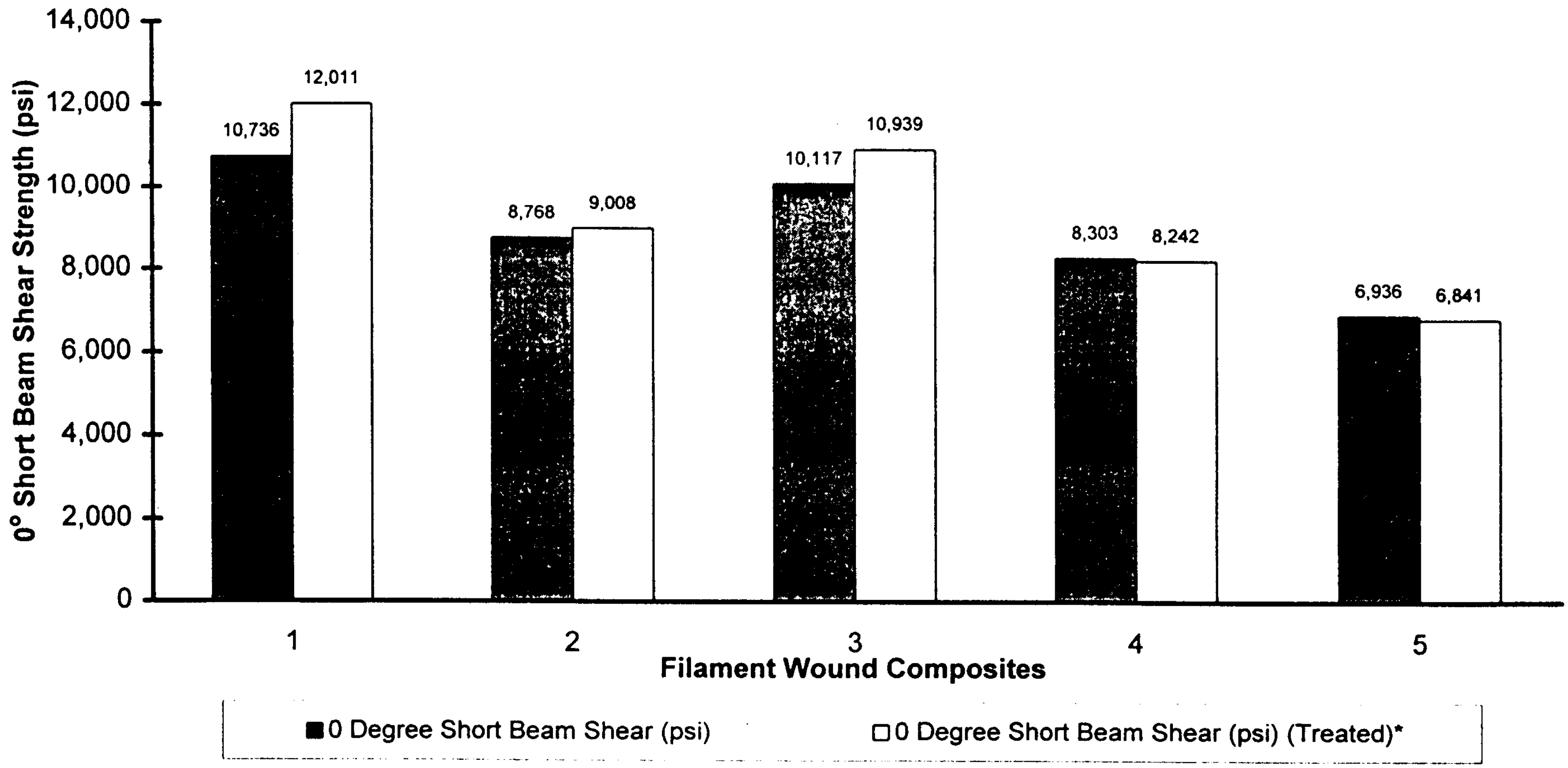
O° Short Beam Shear Strength Properties (Treated* and Untreated) of EBeam Cured vs. Thermal Cured Filament Wound Composites



Filament Wound Composite System: (Part Dia. - 6 in.; t - 0.125 inch; Fiber/Sizing/Tow Size - IM7/GP/12K; % Voids (Acid Digestion) - All < 1%)	1	2	3	4	5
Resin System	**EB Cured** Cationic Epoxy - Blend of Bis A and Cycloaliphatic Epoxies/3 phr Initiator A			**Thermal Cured:** Blend of Bis A & Cycloaliphatic Epoxies with Aromatic Amine Hardener	**Thermal Cured:** Bis A Epoxy w/3 phr BF3 MEA Catalyst
Cure Schedule	150 kGy	150 kGy	150 kGy	3 hrs. @250°F, 3 hrs. @300°F, 4 hrs. @350°F	3 hrs. @250°F, 3 hrs. @300°F, 4 hrs. @350°F
% Fiber Content	75.80%	76.90%	75.80%	77.80%	74.60%

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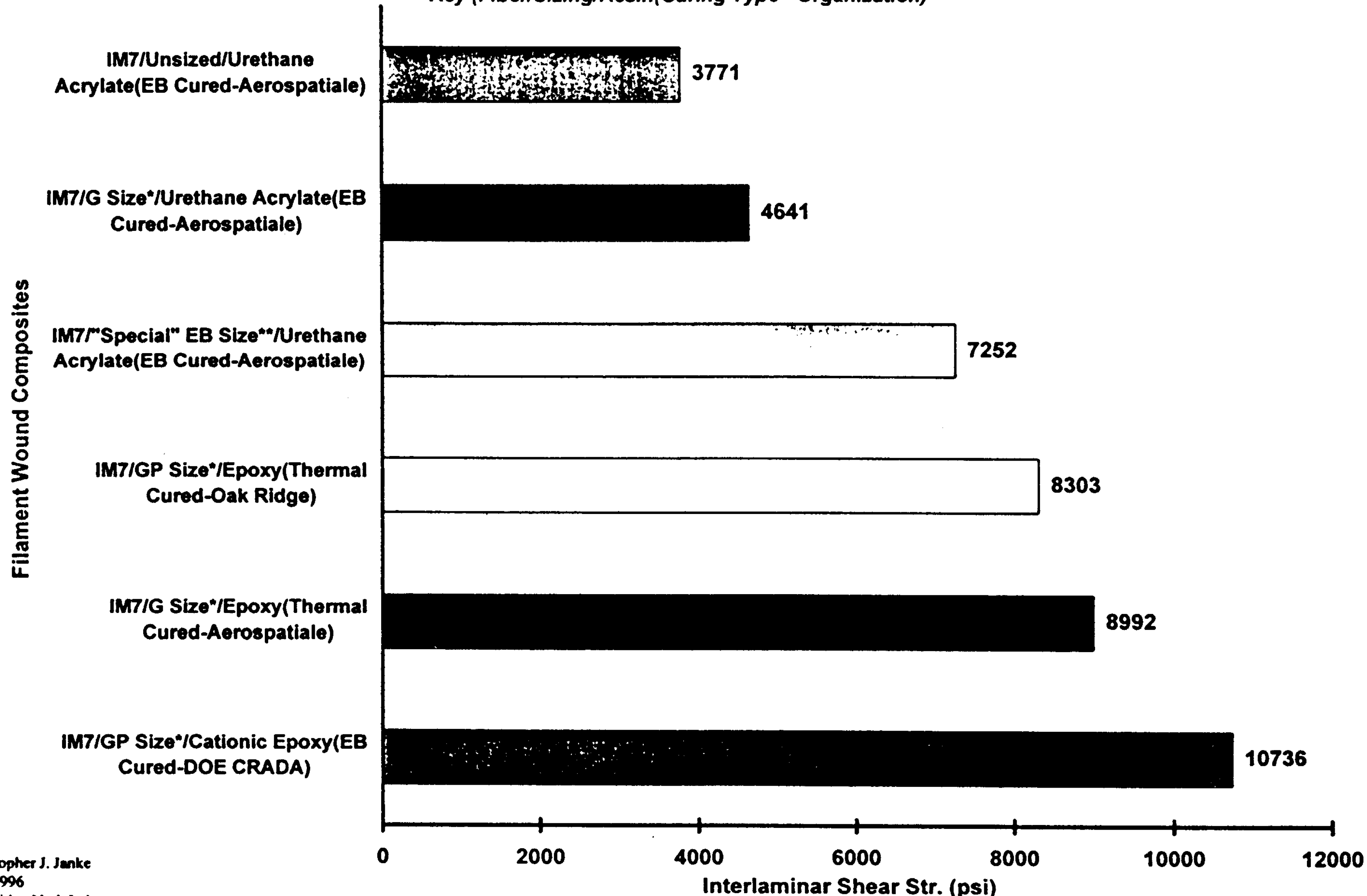
Effects of Fiber Sizings and Resin Chemistries on EBeam vs. Thermal Cured Filament Wound (5.75" dia. NOL rings, t = 0.124")
Comp. Shear Props.
Key (Fiber/Sizing/Resin(Curing Type - Organization)



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* 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.

Variables Requiring Optimization For EB Curable Epoxy Resin Systems And Composite Properties

- **Initiator Efficiency/Cure Effectiveness**
- **Effect Of Initiator Concentration On Tg**
- **Optimum Curing Dose**
- **Optimum Dose Rate**
- **Materials/Things to Avoid**
- **Fiber Sizings**

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Importance of Initiator Efficiency and EB Cure Effectiveness

Although the cationic epoxy UV cure mechanism is well known, the <u>curing mechanism for EB has not been established.</u>

(Solving the EB cure mechanism question could provide an answer as to why EB cured epoxies yield significantly higher thermal and mechanical properties than UV cured epoxies - Our work on UV or sun curing of commercially available epoxies contaning cationic PIs have yielded Tgs no higher than about 100°C, no matter how long they are exposed).

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Importance of Initiator Efficiency and EB Cure Effectiveness (Continued)

From Our Work General Trends Have Been Established Concerning the EB Cure Effectiveness of Initiators Including:

(These trends are also true in UV curing of cationic epoxy systems)

- **Diaryliodonium salts are more effective than triarylsulfonium salts assuming the same counteranion.**
- **Within the diaryliodonium (or triarylsulfonium) salt families, having the same counteranion, differences in cure effectiveness exist.**
- **PIs incorporating larger counteranions are generally more effective than smaller, more tightly bound counteranions**
- **We have identified four PIs (out of more than 25 evaluated) that are extremely efficient in terms of EB cure effectiveness and these materials have formed the basis of most of our work.**

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Importance of Initiator Efficiency and EB Cure Effectiveness (Continued)

- **Our studies have shown that there is indeed a significant difference in the thermal properties (Tg) of EB cured resin systems incorporating less efficient initiators versus those with highly efficient initiators.**

- **The Tgs of resin systems with <u>very efficient initiators</u> DO NOT change even after several thermal postcures.**

- **The Tgs of resin systems with <u>inefficient initiators</u> DO change after thermal postcure, and more importantly;**

The Tgs for resin systems incorporating <u>less efficient initiators</u> never approach the Tg of the same resin system with <u>highly efficient initiators</u> even after several thermal postcures.

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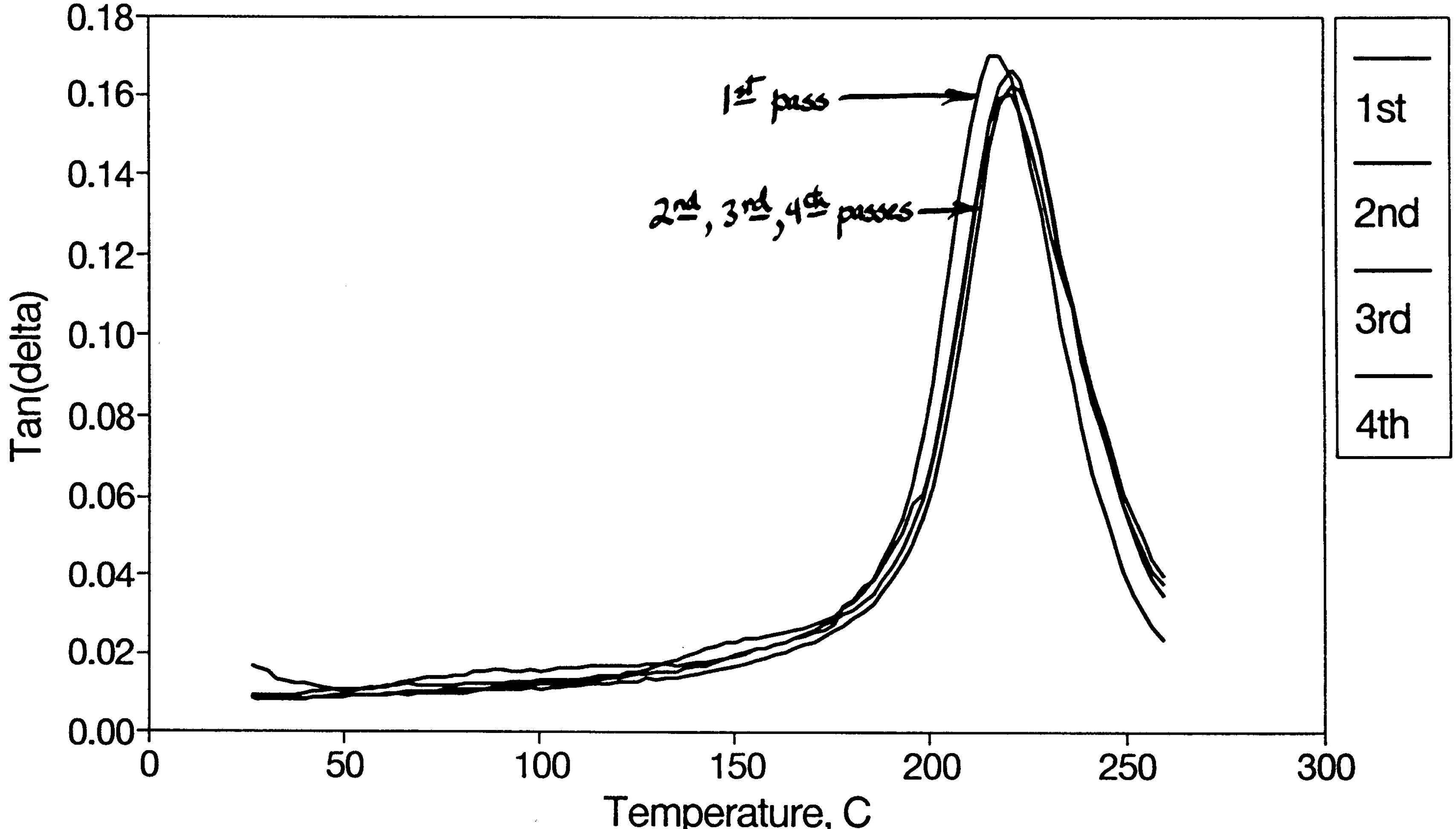
Effects of Thermal Cycling

Resin A/Init A(3 phr)/EB(150 kGy)



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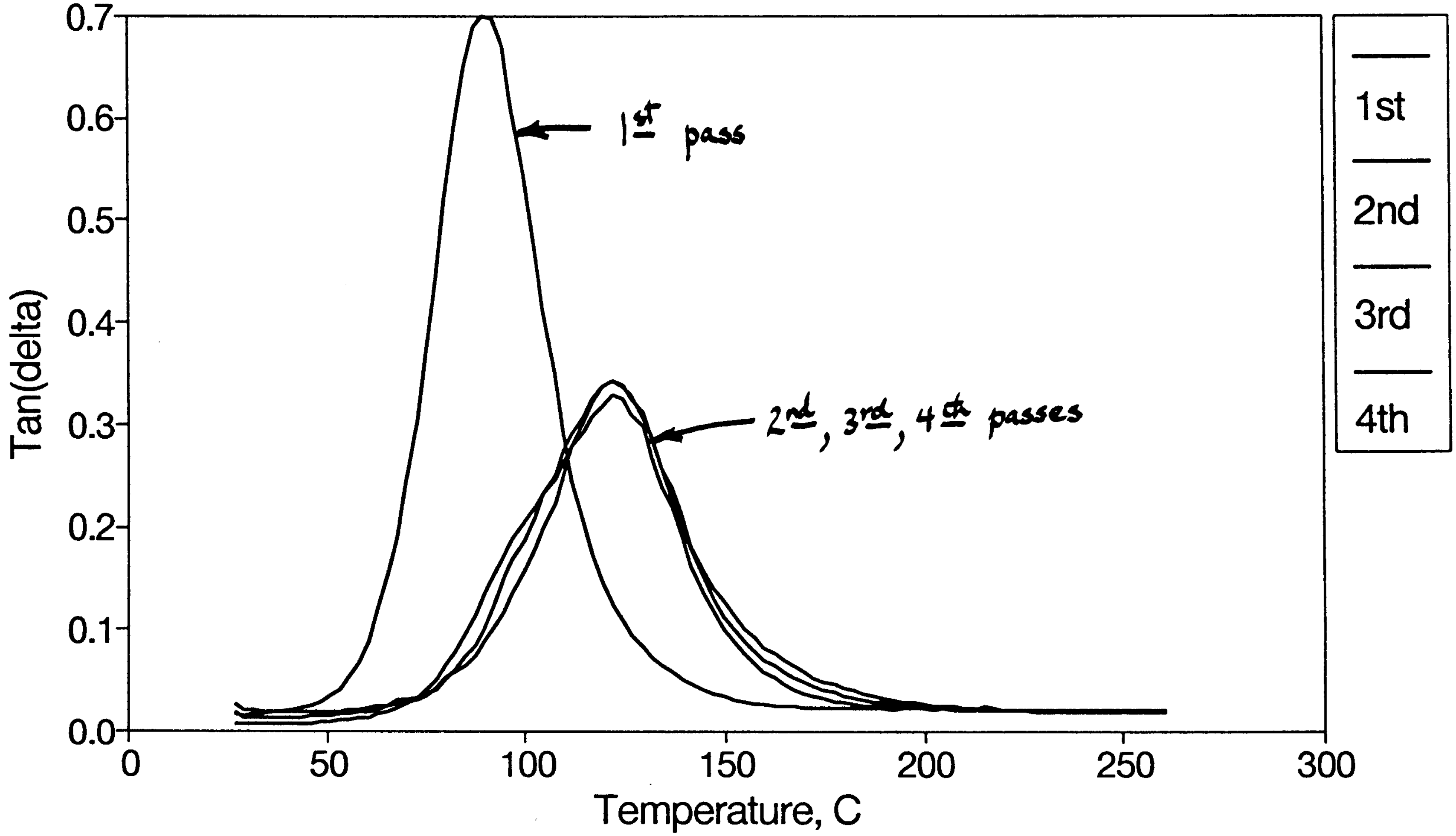
Effects of Thermal Cycling

Resin A/Init F(3 phr)/EB(150 kGy)



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Importance of Initiator Efficiency and EB Cure Effectiveness (Continued)

The Tgs of EB cured resin systems, studied thus far, with <u>very efficient initiators</u> have been equal to or exceed those same identical epoxy resin systems which have been <u>thermally cured</u> with BF_3 MEA catalyst.

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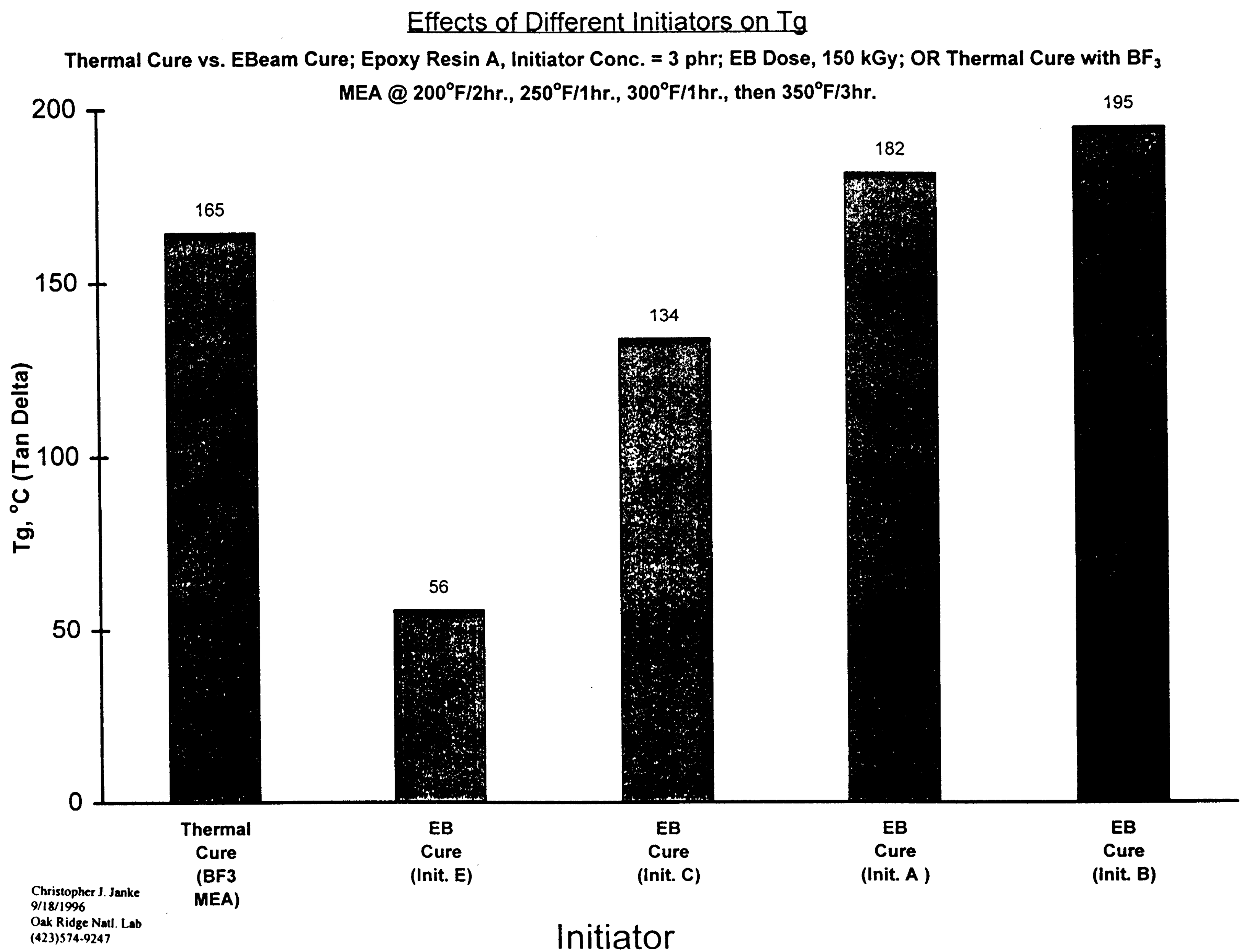
Effects of Different Initiators on Tg
Thermal Cure vs. EBeam Cure; Epoxy Resin A, Initiator Conc. = 3 phr; EB Dose, 150 kGy; OR Thermal Cure with BF3
MEA @ 200°F/2hr., 250°F/1hr., 300°F/1hr., then 350°F/3hr.
Tg, °C (Tan Delta)
200
150
100
50
0
165
56
134
182
195
Thermal Cure (BF3 MEA)
EB Cure (Init. E)
EB Cure (Init. C)
EB Cure (Init. A)
EB Cure (Init. B)
Initiator
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Optimum Initiator Concentration For EB Cure Effectiveness

Our work has shown that for most EB cured epoxies the optimum initiator concentration is in the range of 1 - 3 phr.

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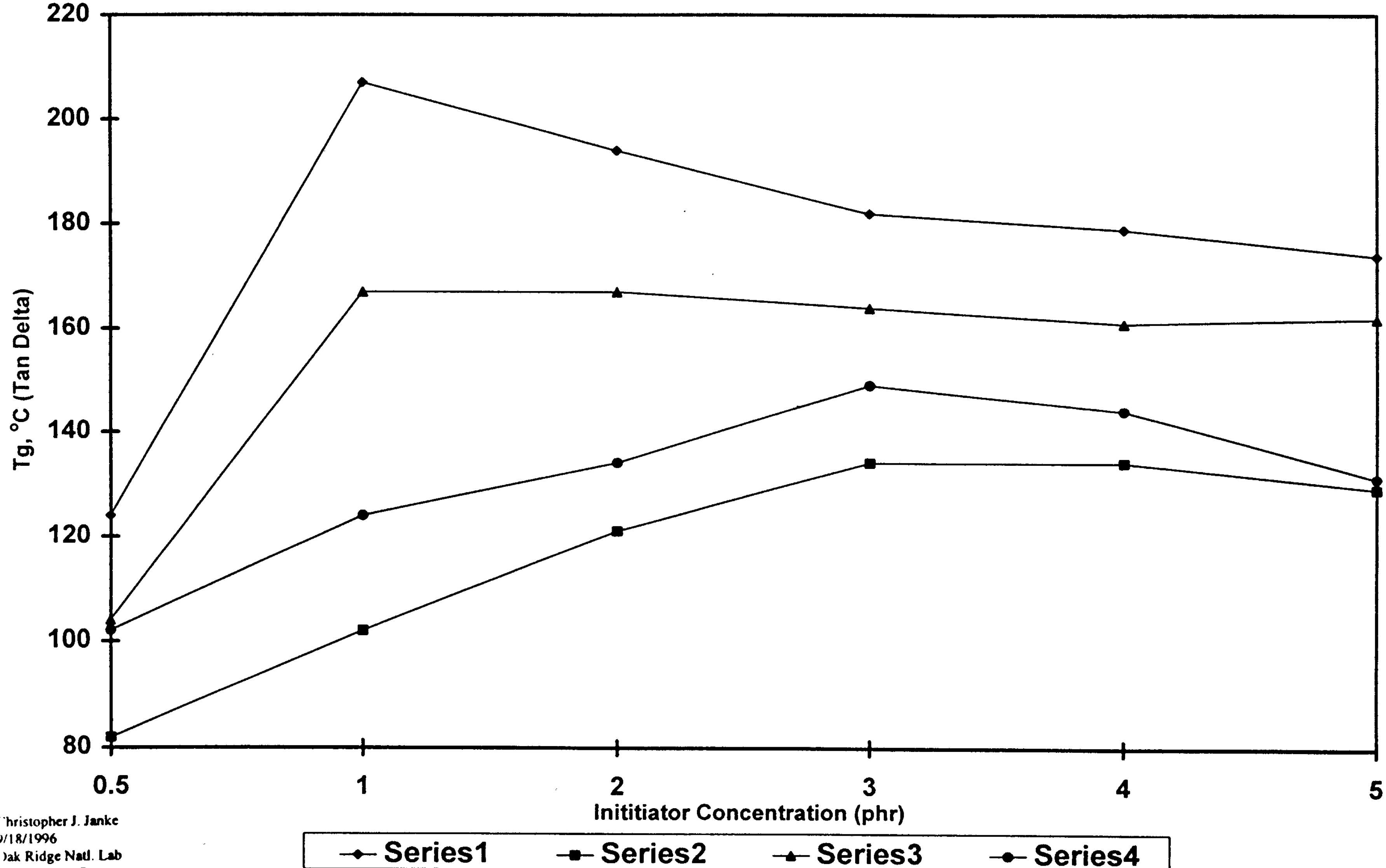
Effects of Initiator Concentration on Tg of Cationic Cure Epoxies; EB Dose, 150 kGy

Series 1 - Resin C/Initiator A; Series 2 - Resin C/Initiator C;
Series 3 - Resin D/Initiator A; Series 4 - Resin D/Initiator C



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Optimum EB Curing Dose

The majority Of Resin Systems, And Glass, Kevlar, Spectra, Or Carbon Composites Evaluated Thus Far Are EB Curable At Doses Ranging From:

70 - 250 kGy

(the specific dose depends on the resin system, fiber type, and % fiber content; normally 150 kGy is sufficient to cure most systems)

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Effects of Initiators on EB Curing Dose

Generally, the more efficient the initiator, the less EB dose is needed to cure the material

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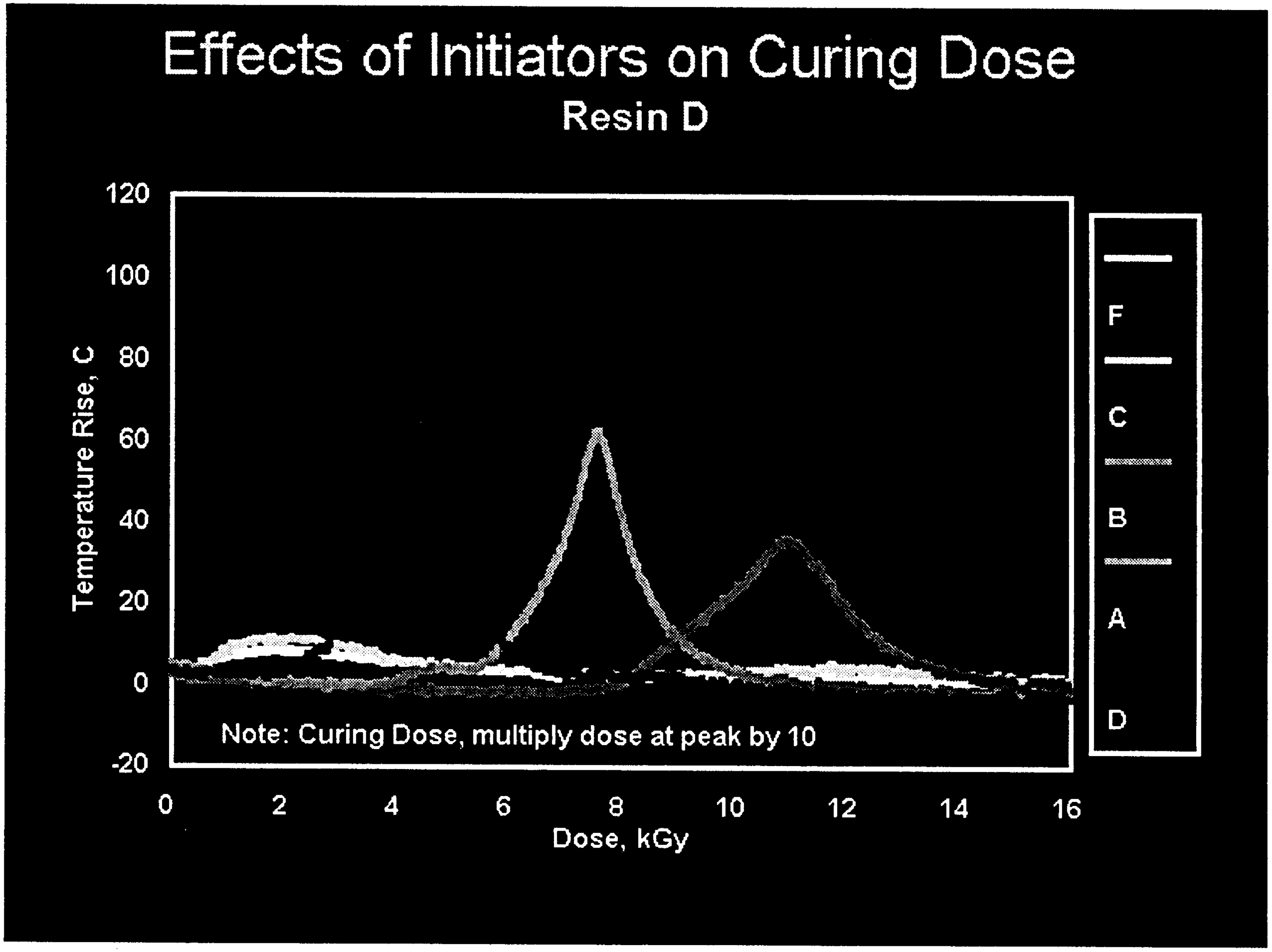

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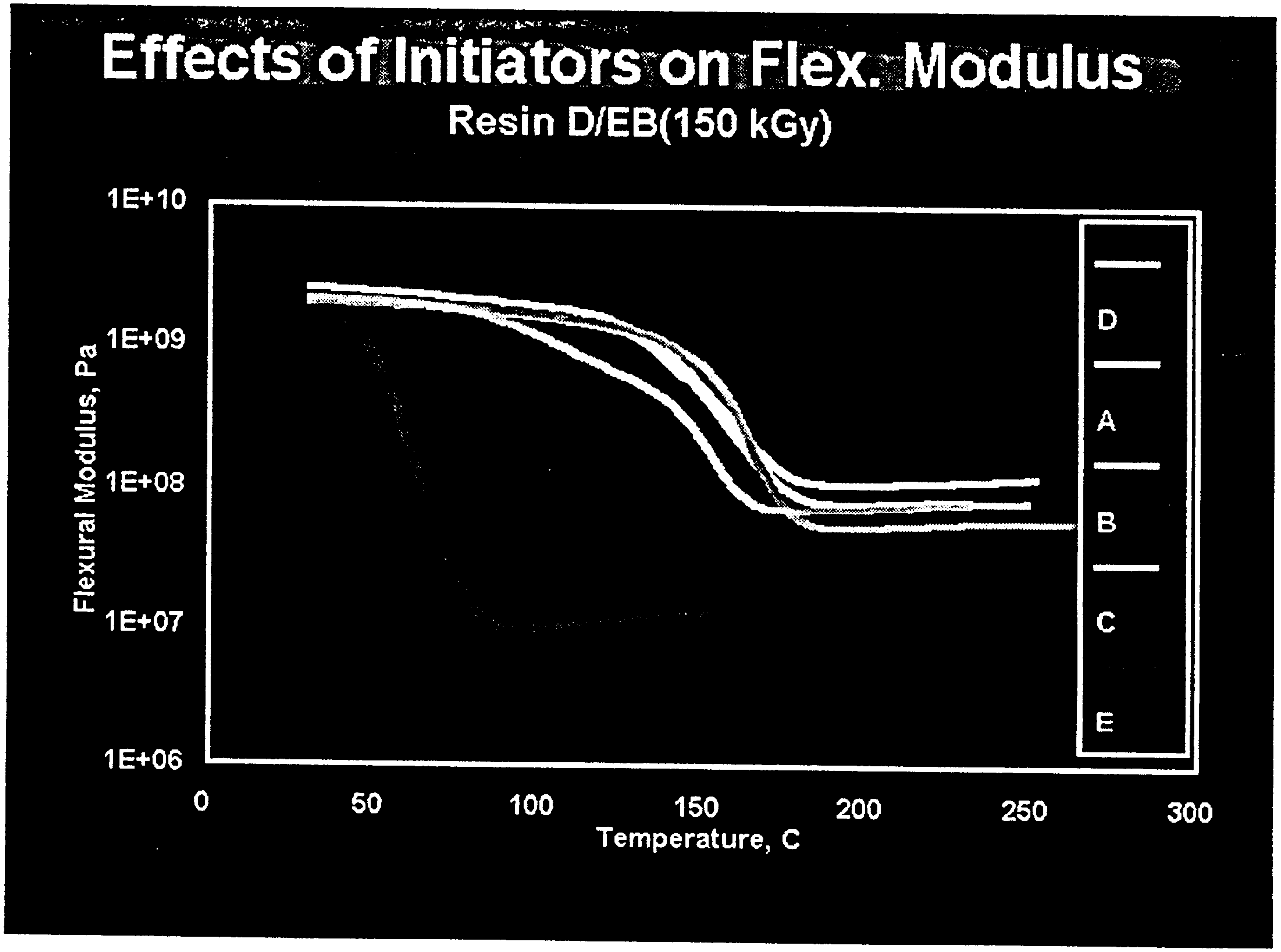

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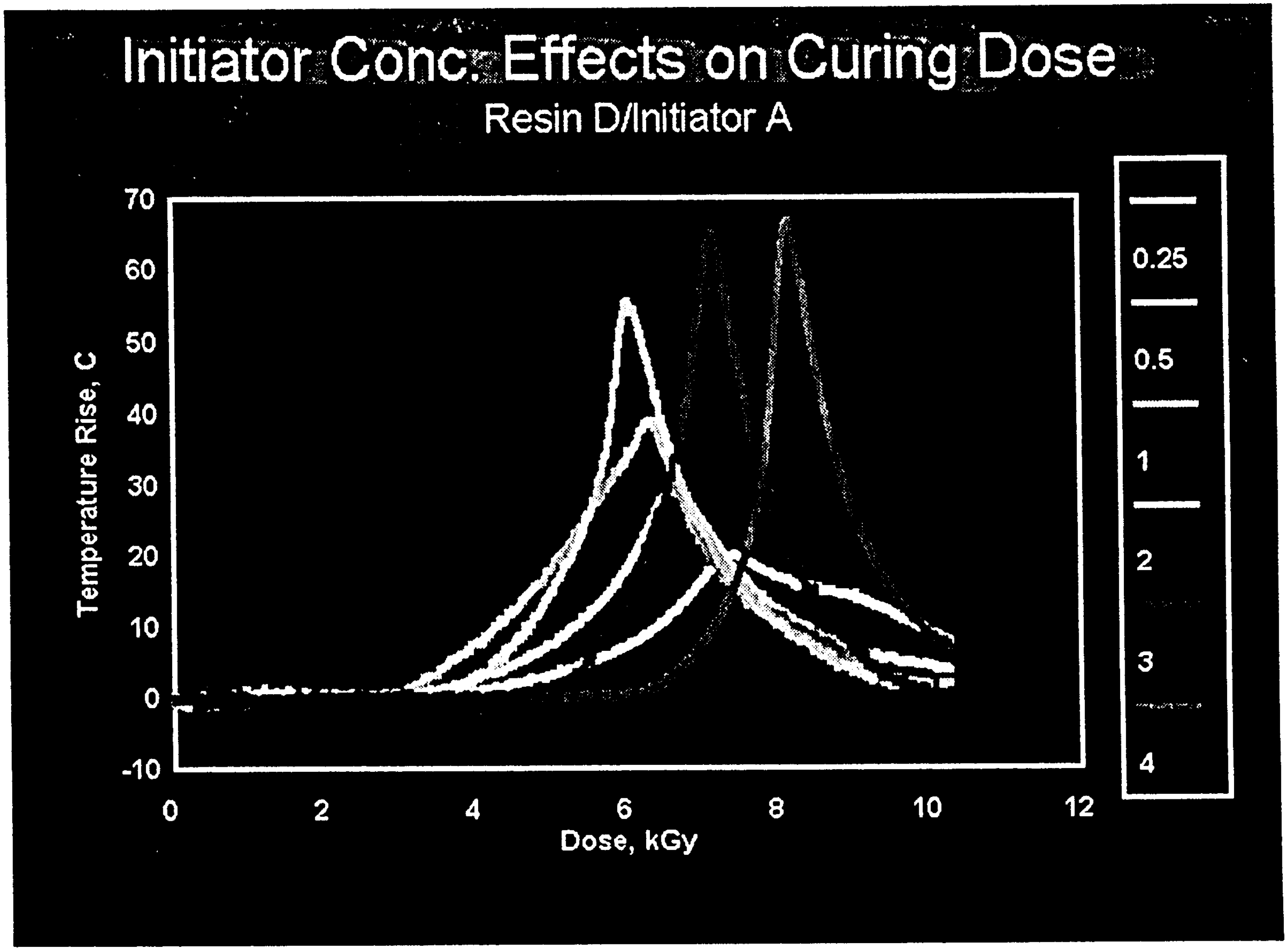

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EB Dose Effects

Overdosing (ie. up to 2-3 times the recommended EB dose) these materials has very little effect on the temperature at which the flexural modulus, E', decreases on the DMA Flexural Modulus vs. Temperature curve.

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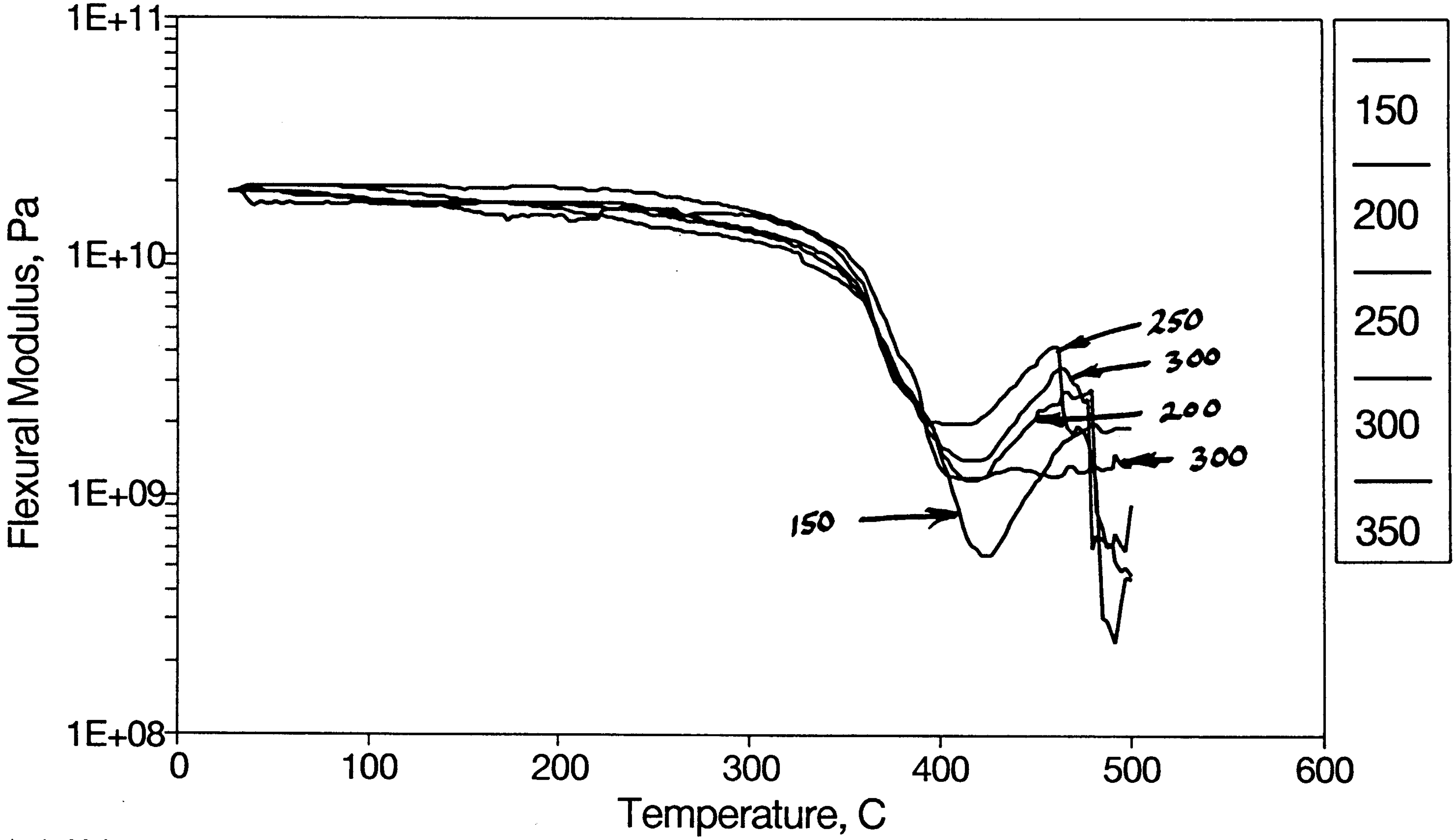
Dose Effects

Resin B/Init A(3 phr)/AS4/EB Curing



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Thermal Stability of Materials After EB Cure

The thermal stability of some of these cationic epoxies after EB cure has been very good

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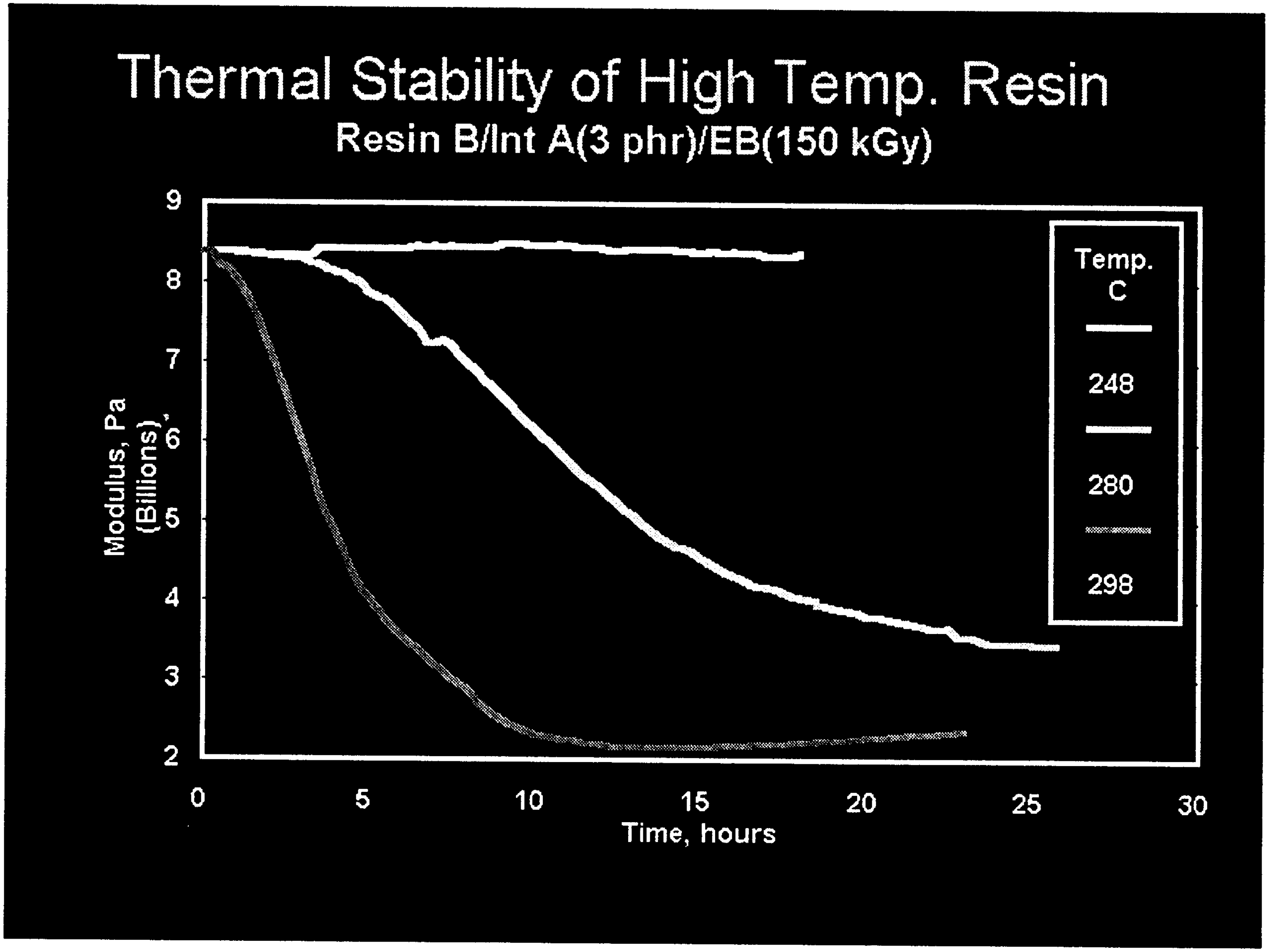

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Optimum EB Cure Dose Rate

- Studies of gamma dose rates of 90 Gy/min. versus EB dose rates of 90 MGy/min., on a limited number of epoxy resin systems studied thus far, do yield a difference in the Tg of the materials during the 1st pass of DMA; but after 1st pass, the Tg of these materials are comparatively equal.

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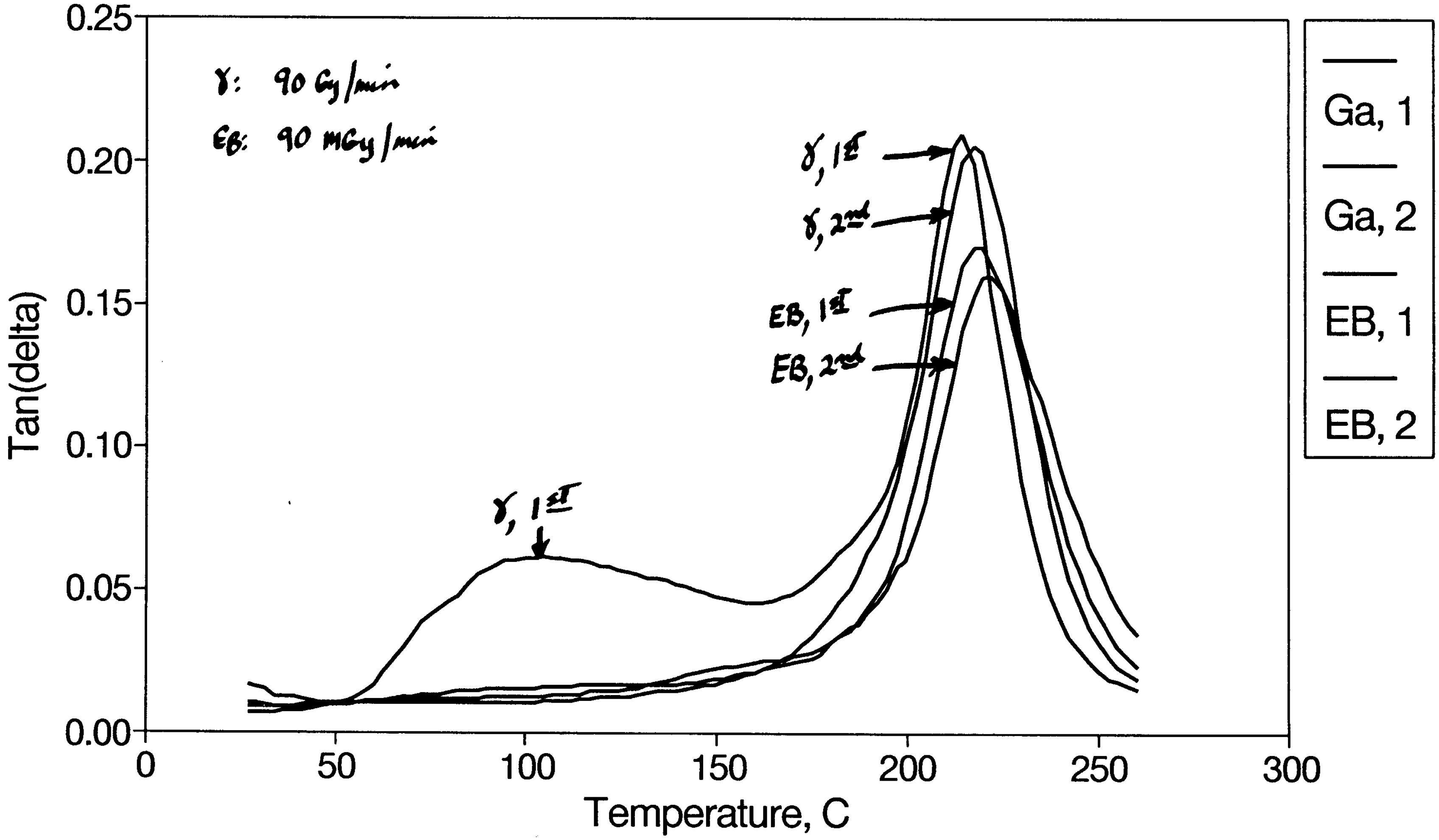
Dose Rate Effects

Resin A/Init A(3 phr)/Dose(150 kGy)



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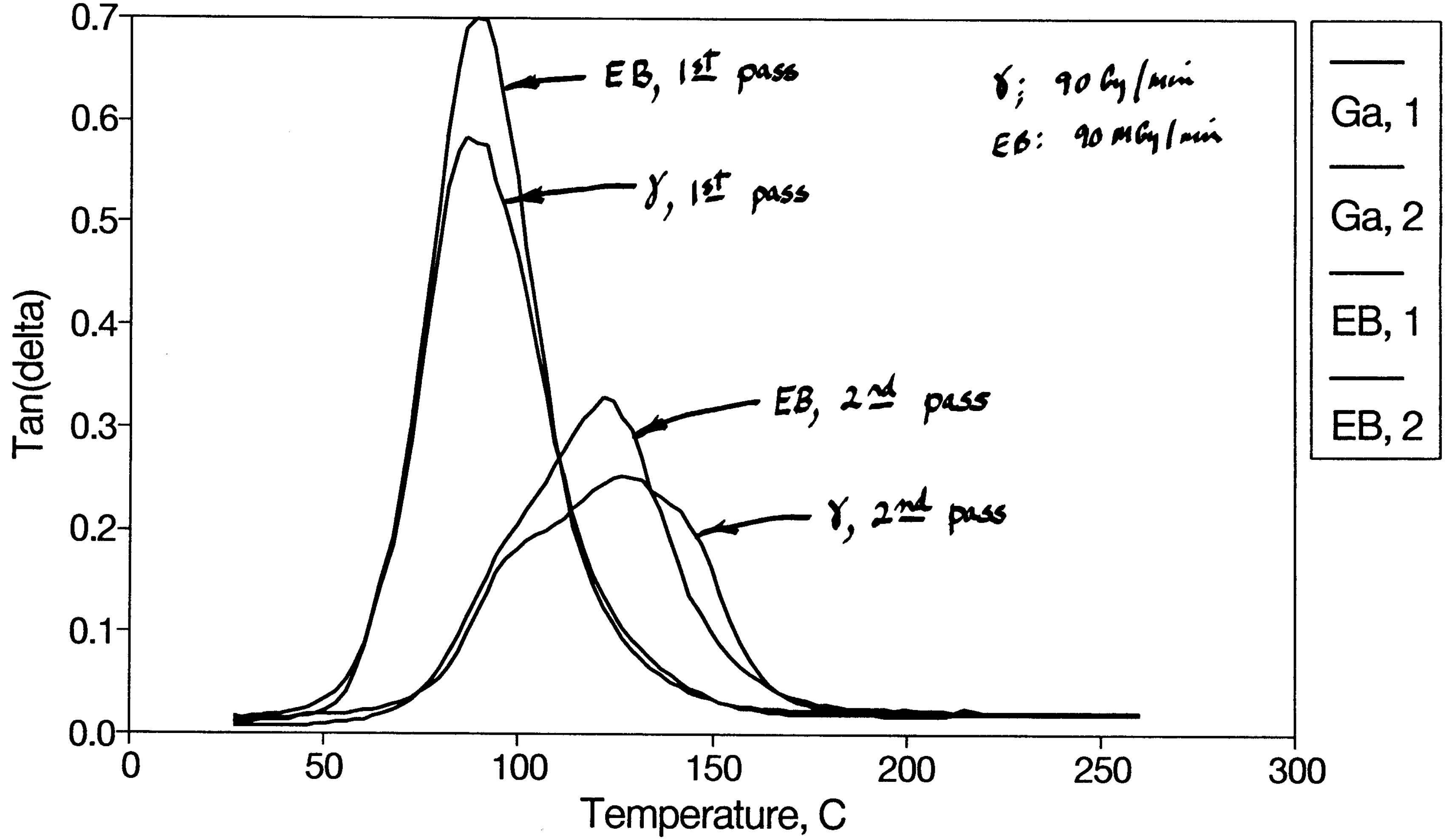
Dose Effects

Resin A/Init F(3 phr)/Dose(150 kGy)



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Materials/Things to Avoid

- Active Nitrogens (amines, hydrazines, etc.)
- Anionic Surfactants
- Calcium Carbonate and Basic Clays
- Alkaline Materials
- Strong Anions (Cl^-, Br^-, OH^-)
- UV or Solar radiation

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Fiber Sizings Evaluation On EB Cured Cationic Epoxies And Acrylate Systems

Fiber/Sizing/Resin	Conclusion
• Carbon/G & GP/Cationic	• No Cure Inhibition
• Carbon/UC 309/Cationic	• Large Cure Inhibition
• E-Glass/Several Evaluated/Cationic	• No Cure Inhibition
• S-2 Glass/Several Evaluated/Cat.	• No Cure Inhibition
• Kevlar Fiber/Cationic	• Slight Cure Inhibition
• Carbon/G & GP/Acrylate	• No Cure Inhibition, but requires “special” sizing for maximizing shear properties

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