ELECTRON BEAM CURED EPOXY RESIN COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS*

CHRISTOPHER J. JANKE
Oak Ridge Centers for Manufacturing Technology
Oak Ridge National Laboratory**
Oak Ridge, TN 37831-8048

George F. Dorsey
Lockheed Martin Energy Systems, Inc.***
Oak Ridge, TN 37831-8097

Stephen J. Havens
Oak Ridge Institute for Science and Education,
Oak Ridge, TN 37831-0117

Vincent J. Lopata
Atomic Energy of Canada Ltd. - Whiteshell Laboratories,
Pinawa, Manitoba, Canada ROE 1LO

Michael A. Meador
NASA Lewis Research Center
Cleveland, OH 44135

Introduction

Electron beam curing of Polymer Matrix Composites (PMCs) is a nonthermal, nonautoclave curing process that has been demonstrated to be a cost effective and advantageous alternative to conventional thermal curing. Advantages of electron beam curing include: reduced manufacturing costs; significantly reduced curing times; improvements in part quality and performance; reduced environmental and health concerns; and improvement in material handling. In 1994 a Cooperative Research and Development Agreement (CRADA), sponsored by the Department of Energy Defense Programs and 10 industrial partners, was established to advance the electron beam curing of PMC technology. Over the last several years a significant amount of effort within the CRADA has been devoted to the development and optimization of resin systems and PMCs that match the performance of thermal cured composites. This highly successful materials development effort has resulted in a board family of high performance, electron beam curable cationic epoxy resin systems possessing a wide range of excellent processing and property profiles. Hundreds of resin systems, both toughened and untoughened, offering unlimited formulation and processing flexibility have been developed and evaluated in the CRADA program.

---

*Cooperative Research and Development Agreement (CRADA) No. Y1293-0233.
**Managed by Lockheed Martin Energy Research Corporation for the U.S. Department of Energy under contract DE-AC05-96OR22464.
***Managed by Lockheed Martin Energy Systems for the U.S. Department of Energy under contract DE-AC05-84OR21400.

Our research has determined that conventional epoxy resins can be cured by exposure to electron beam radiation as provided by a high energy/power electron beam accelerator to provide materials with high glass transition temperatures and mechanical properties comparable to thermally cured epoxies (1-3). A cationic photoinitiator at a concentration of 1-3 parts per hundred of the epoxy resin is required for this process. These cationic photoinitiators are triaryl sulfonium and diaryliodonium salts of weakly nucleophilic anions. Diaryliodonium salts of the hexafluoroantimonate anion have been found to be the most effective commercially available photoinitiators. The cationic photoinitiator decomposes when subjected to irradiation from ultraviolet light or high energy electrons to produce a Bronsted acid (proton) which catalyzes the ring opening polymerization of the epoxy group. The weakly nucleophilic anion from the initiator is not strongly attracted to the cation that is generated, nor does it interfere with the growing polymer chain (4). Properties of the electron beam cured cationic epoxies include: glass transition temperatures (T_g's) ranging from 100-400°C (212-752°F), high flexural moduli [up to 4.0 GPa, (580 ksi)], low moisture absorption (<2%), good toughness obtained by the addition of toughening agents [0.41-0.92 $MPam^{1/2}$] (373-837 psi in $^{1/2}$); and low-moderate cost of the epoxy resin-photoinitiator compositions.

Several toughened and untoughened compositions were selected for evaluation as composite matrices. PMCs made from these easily processed resins have exhibited: low shrinkage after electron beam cure, low void content (0.6-1.8%) and good mechanical properties with IM7 carbon fiber [0° flexural strengths, 1.71-2.01 GPa (248-292 ksi); 0° flexural moduli, 150-196 GPa (21.8-28.4 msi; and 0° interlaminar shear strengths 77-89 MPa (11.2-12.9 ksi)]. Many composite parts manufactured via hand lay-up, tow/tape placement, filament winding, resin transfer molding (RTM), and vacuum assisted resin transfer molding (VARTM) have been produced using these materials, demonstrating their fabrication versatility.

Electron beam processing is potentially more economical than conventional thermal cure processing. Complex part shapes can be made with inexpensive tooling and part throughput is extremely high. Since electron beam curing is at near ambient temperatures, inexpensive, lightweight, and disposable fabrication tools or mold materials such as thermoplastics, foam plastics, plasters, waxes, and wood can be used instead of metals. Electron beam processing also allows the simultaneous curing of several different cationic epoxy resin compositions. Thus, a single composite structure fabricated from electron curable cationic epoxies with different thermal and mechanical properties can be cured in a single cycle. As electron beam curing can be conducted at room temperature or lower, stresses are reduced. This factor can be critical in the design of structures such as cryogenic tanks that must perform at low temperatures. Electron beam curable epoxy resins are friendly to the environment and greatly reduce the amount of waste generated in composite fabrication processes. No hardener such as an amine is required - only a few parts per hundred of a relatively nontoxic photoinitiator. Formulated and prepregged resin have essentially unlimited pot life and shelf life at room temperature provided that the resins are not exposed to ultraviolet or sunlight.

One particular epoxy resin-photoinitiator composition (designated Electron Beam Resin 8H) exhibited a very high glass transition temperature after electron beam curing; T_g, 396°C (745°F) from the peak of the DMA tan delta curve. This resin was extensively evaluated as a matrix resin for PMCs using Hercules IM7-GP-12K carbon fiber. Unidirectional prepreg of 8H with this fiber was manufactured by YLA, Inc. of Benicia, California. All test panels (16 plies unidirectional x 30.5

cm x 30.5 cm) were prepared using conventional lay-up techniques. Intermediate debulks were conducted under vacuum bag pressure every four plies at room temperature for 15 minutes. The final debulk and bleed cycle was performed under vacuum bag pressure at 70°C (158°F) for one hour. The panels were electron beam cured at the Whiteshell Laboratories of Atomic Energy of Canada Limited (AECL) using the AECL I10/1 Electron Linear Accelerator. Curing was performed under vacuum bag pressure while the panels were at room temperature at a dose per pass of 50 kGy for a total dose of 250 kGy.

In a thermal cure cycle there is a considerable decrease in resin viscosity as temperature increases, followed by an abrupt increase in viscosity with the onset of gelation. This factor combined with autoclave pressures may allow poorly laid-up laminates to be well consolidated. Since electron beam curing occurs at near ambient temperature, there is no viscosity decrease before gelation and curing. Thus, lay-up technique is critical in obtaining, good laminate properties. To date the best series of panels had a void volume of 1.77% by acid digestion, with the following room temperature mechanical properties: 0° flexural strength, 1.99 GPa (288 ksi); 0° flexural modulus, 196 GPa (28.4 msi); 0° compressive strength, 1.57 GPa (228 ksi); 0° compressive modulus, 149 GPa (21.6 msi); and 0° interlaminar shear strength, 77 MPa (11.2 ksi). Long term aging studies were conducted on early specimens of these laminates at NASA Lewis Research Center (LeRC). Weight loss in air after 1000 hours at 232°C (450°F) was only 4.25% but 18.4% after 1000 hours at 288°C (550°F). Mechanical properties were not significantly changed after 1000 hours at 232°C, but noticeably deteriorated on aging at 288°C.

Future efforts in the area of electron beam cured PMC's for high temperature applications will focus on improving the quality of electron beam resin 8H laminates and more extensive testing. Research efforts will also be directed toward the development of electron beam curable polyimides as part of a project sponsored by NASA LeRC.

References

1. Janke, C. J.; Dorsey, G. F.; Havens, S. J.; and Lopata, V. J.: Electron Beam Curing of Epoxy Resins by Cationic Polymerization. SAMPE International Symposium, vol. 41, 1996, pp. 196-206.

2. Janke, C. J.; Dorsey, G. F.; Havens, S. J.; and Lopata, V. J.: Toughened Epoxy Resins Cured by Electron Radiation. SAMPE International Technical Conference, vol. 28, 1996, pp. 877-889.

3. Lopata, V. J.; Chung, M.; Janke, C. J.; and Havens, S. J.: Electron Curing of Epoxy Resins: Initiator and Concentration Effects on Curing Dose and Rheological Properties. SAMPE International Technical Conference, vol. 28, 1996, pp. 901-910.

4. Crivello, J. V.; Lam, J. H. W.; and Volante, C. N.: Photoinitiated Cationic Polymerization Using Diaryliodonium Salts. Journal of Radiation Curing, vol. 4, July 1977, pp. 1-16.

Acknowledgements

THE EBEAM CRADA TEAM

- **AECL Technologies, Inc.**
- **Applied Poleramic, Inc.**
- **The Boeing Company**
- **Ciba-Geigy Corporation**
- **E-BEAM Services, Inc.**
- **Lockheed Martin Aero and Naval Systems**
- **Lockheed Martin Energy Systems, Inc.**
- **Lockheed Martin Tactical Aircraft Systems**
- **Nicolet Imaging Systems**
- **Northrop Grumman Corporation**
- **Sandia Corporation**
- **UCB Chemicals Corporation**
- **Department of Energy Defense Programs**
- **YLA, Inc. - Sean Johnson, Susan Robataille and Steve Smith**

Presentation Outline

- Introduction
- Electron Beam Curable Cationic Epoxy Resins & Composites - Advantages and Highlights
- High Temperature Composite Properties
  - Weight Loss
  - Flexural Properties
  - Interlaminar Shear Properties
- Conclusions
- Future Research Areas

Introduction

- **Electron Beam Curing is a Very Fast, Nonthermal, Nonautoclave curing method that uses High-Energy, High-Power Radiation to cure polymer matrix composites.**

ADVANTAGES OF PMC ELECTRON BEAM CURING OVER THERMAL CURING

- Shorter cure times
- Amenable to high production rates
- Lower overall energy requirements
- Reduced thermal stresses in cured part
- Effective with thick PMC parts
- Lower tooling costs
- Reduced environmental, safety, and health concerns
- Improved material handling
- Reduced overall manufacturing costs (25% - 65% Cost Savings vs. Thermal Curing)

The CRADA Has Developed Hundreds Of EB Curable Cationic Epoxy Resin Systems (Toughened and Untoughened)

Epoxies

- 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

Cationic Initiators (w/ Various Anions)

- Diaryliodonium Salts
- Triarylsulfonium Salts
- Iron Complexes
- Diaryldisulfones
- Triazine Compounds

Tougheners

- Engineering Thermoplastics
- Hydroxy-Containing Thermoplastics
- Reactive Flexibilizers
- Elastomers
- Rubbers
- Undissolved Thermoset Particles
- Undissolved Thermoplastic Particles
- Polyarylates

Advantages of Electron Beam Curable Cationic Epoxies

- Most Commercially Available (Non-Amine Containing) Epoxies EB Cure
- Unlimited Variety Of Epoxy Resin Systems Can Be Formulated
- No Hardeners Required (less environmental/health concerns)
- Indefinite Shelf Life (must be kept away from UV)
- No Oxygen Inhibition Problems During Cure
- Resin System Costs Are Comparable To Thermally Curable Epoxy Variants

Advantages of Electron Beam Curable Cationic Epoxies (Resin Properties Only)

- **Minimal Volatile Emissions During Cure; (< 0.1%)**
- **Wide Range Of T_gs (tan delta); 130 to >395°C; (T_g - T_{cure}) ranged from 100 to > 370°C**
- **Very Low Water Absorption After 48 hr. H_2O boil; some < 1% most < 2%: vs. thermal cured epoxies 3-6%**
- **Low Shrinkage; 2 - 3% vs. thermal cured epoxies 4-6% vs. EB cured acrylates 8-20%**
- **Resins Are Toughenable; RT K_{1c}s ranged from 0.41-0.97 MPa $m^{0.5}$ vs. 0.90 for Fiberite 977-3; -100°C K_{1c}s surpass RT values**
- **Low Total Mass Loss; 0.05-1.00% for resins after vacuum oven aging @125°C/5days vs. goal of <1% for composites**

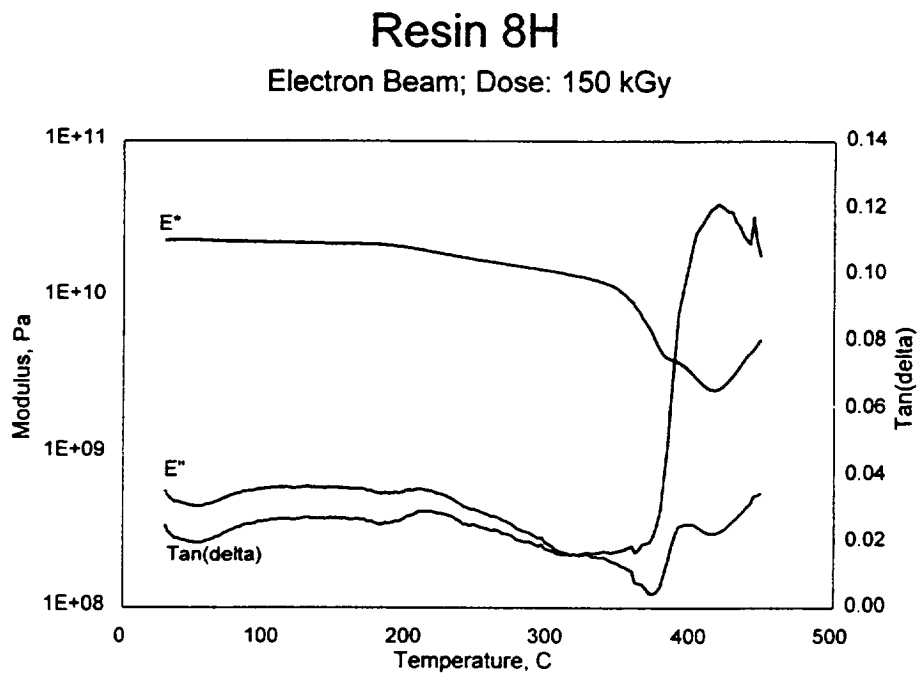
Highlights of EB Curable Cationic Epoxy Containing Composites

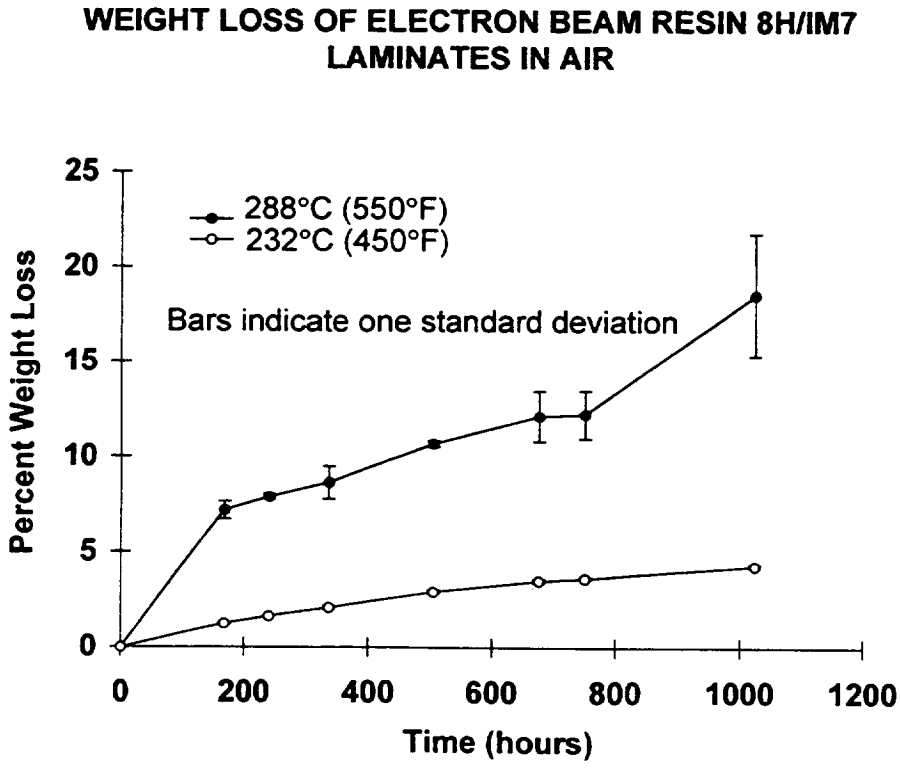
- **Many Cat. Epoxies Have Been Successfully Prepregged**
  - Numerous prepregs have been made via solution dip, direct hot melt coating, and film calendering methods
- **Many Cat. Epoxies Have Been Processed Using Several Fabrication Methods**
  - Many PMC parts have been manufactured via hand lay-up, tow placement, filament winding, RTM, and VARTM processes
- **Void Contents Are Comparable To Autoclave Cured PMCs**
  - Many PMCs fabricated using hand lay-up and filament winding processes have less than 1% void contents
- **Improved Mechanical Properties Compared To Autoclave Cured PMCs**
  - PMCs exhibit some mechanical properties exceeding those of Fiberite's, autoclave cured, 977-2 and 977-3 toughened epoxy PMCs
- **Cryogenic & Thermal Cycling Of PMCs Showed Excellent Retention Of Properties**
  - Mechanical properties of PMCs after cryogenic & thermal cycling were unaffected and in some cases increased in value

Property Comparison Of Electron Beam Cured Versus Thermal Cured IM7/Resin (X) Unidirectional Laminates (Data Normalized to 62% fiber volume)

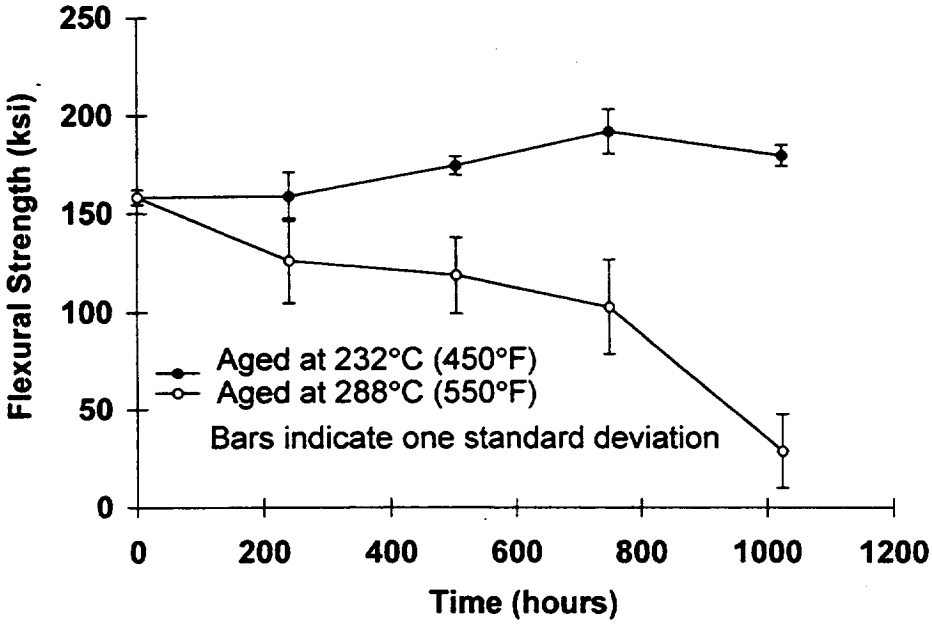
Resin Systems	Fiberite 977-2 (Fiberite Marketing Literature Data)	Fiberite 977-3 (Fiberite Marketing Literature Data)	EB Resin 8H	EB Resin 2	EB Resin 3	EB Resin 4	EB Resin 5
Cure Conditions	Autoclave Cured (6 hrs. @ 350°F @ 85 psi)	Autoclave Cured (3 hrs. @ 355°F @ 85 psi)	250 kGy	150 kGy	150 kGy	150 kGy	150 kGy
Void Volume, %	Not Reported	Not Reported	1.77	0.72	1.24	0.64	1.18
Tg, °C (Tan Delta)	200	190/240	396	392	232	212	212
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)	1680 (244)	1565 (227)				
O° Comp., Mod., GPa (msi)	152 (22)	154 (22.3)	149 (21.6)				
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)		89 (12.9)	61 (8.8)				

* 1 wk. in H_2O @ 160°F, tested @ 220°F

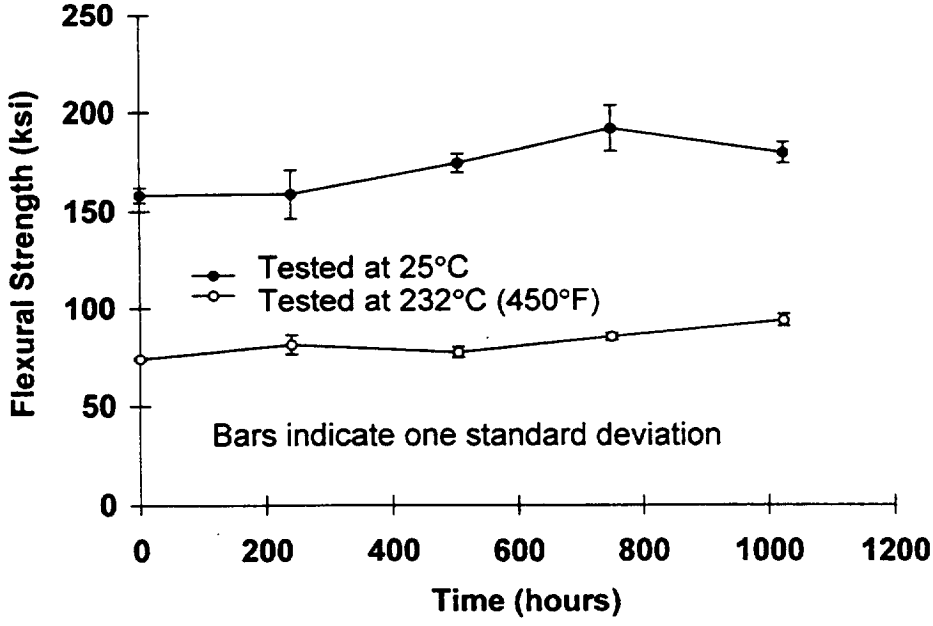

Resin 8H
Electron Beam; Dose: 150 kGy
1E+11
1E+10
1E+09
1E+08
Modulus, Pa
E*
E"
Tan(delta)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Tan(delta)
0
100
200
300
400
500
Temperature, C


WEIGHT LOSS OF ELECTRON BEAM RESIN 8H/IM7
LAMINATES IN AIR
288°C (550°F)
232°C (450°F)
Bars indicate one standard deviation
Percent Weight Loss
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Time (hours)

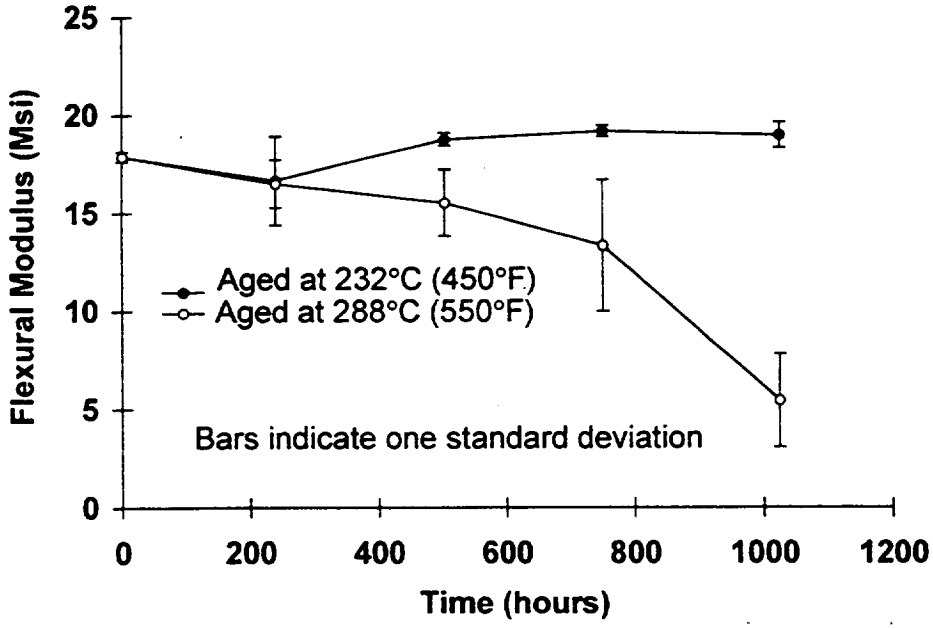
FLEXURAL STRENGTH OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR-TESTED AT 25°C



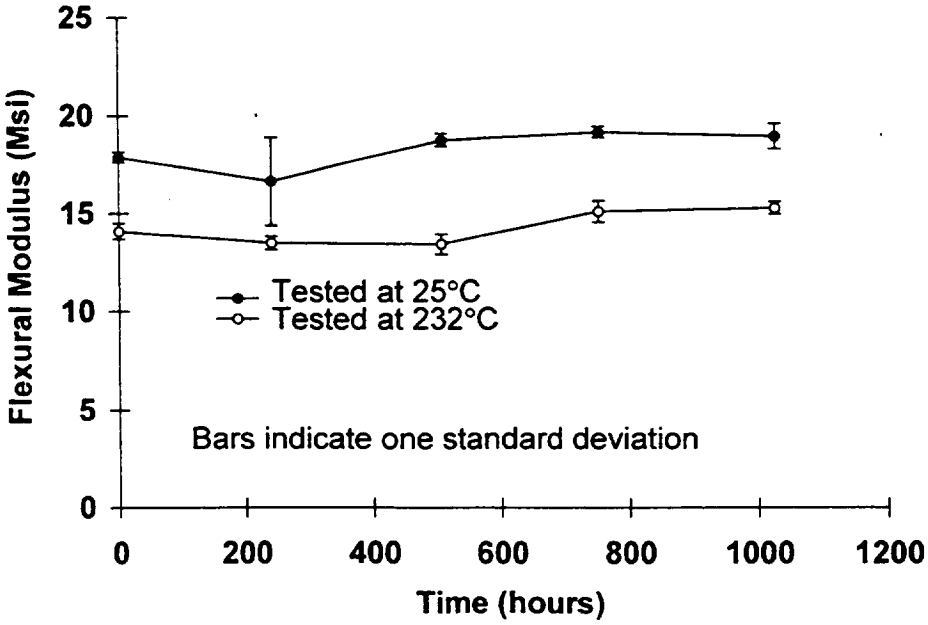
FLEXURAL STRENGTH OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR AT 232°C (450°F)



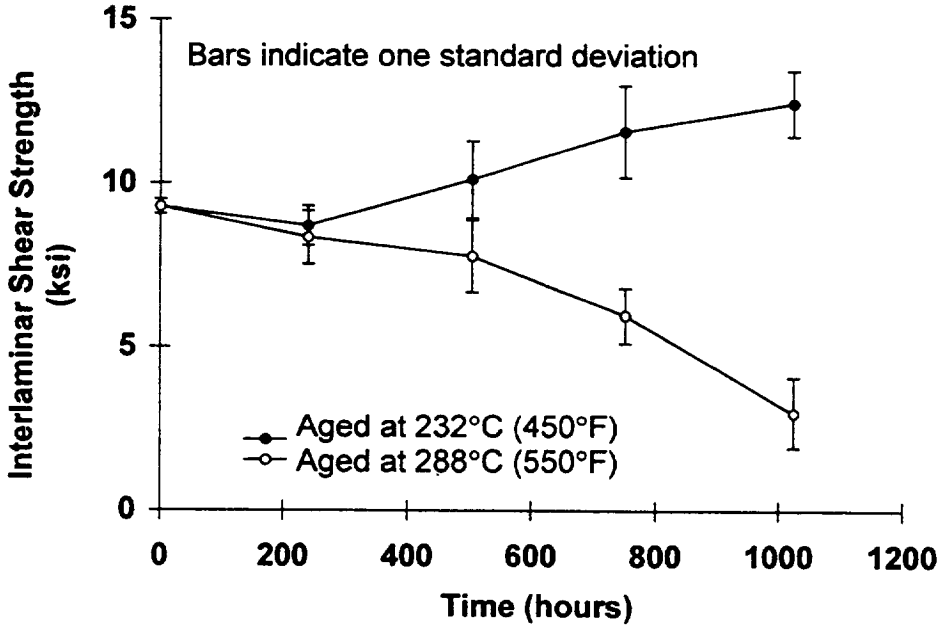
FLEXURAL MODULUS OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR - TESTED AT 25°C



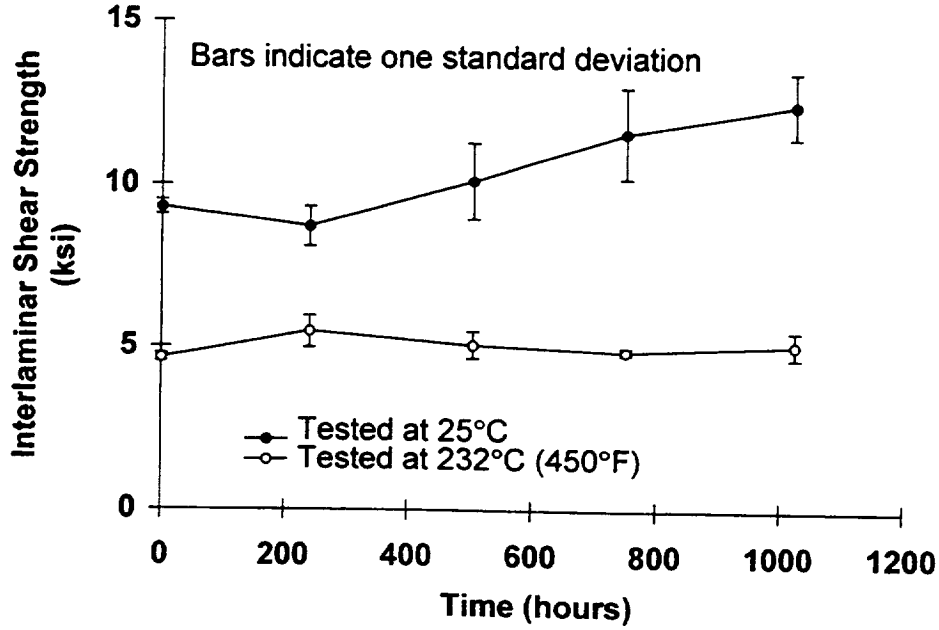
FLEXURAL MODULUS OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR AT 232°C (450°F)



INTERLAMINAR SHEAR STRENGTH OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR - TESTED AT 25°C



INTERLAMINAR SHEAR STRENGTH OF ELECTRON BEAM RESIN 8H/IM7 UNIDIRECTIONAL LAMINATES VERSUS AGING TIME IN AIR AT 232°C (450°F)



SUMMARY AND CONCLUSIONS

- Electron Beam Resin 8H exhibited a glass transition temperature of 396°C (745°F) after electron beam cure at room temperature
- Electron Beam Resin 8H/IM7 laminates exhibit good mechanical properties at 25°C
- Weight loss for the laminates is 4.25 and 18.4% after 1000 hours in air at 232°C (450°F) and 288°C (550°F), respectively
- Mechanical properties of Electron Beam Resin 8H are not affected by aging at 232°C, but are degraded by aging at 288°C

FOCUS OF FUTURE HIGH TEMPERATURE ELECTRON BEAM RESIN RESEARCH

- Optimize Electron Beam Resin 8H/IM7 fabrication to maximize mechanical properties
- Rerun aging tests on optimized laminates
- Explore feasibility of electron beam curable polyimides by screening of model compounds