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The ultimate objective of this program was to develop a fundamental understanding of the relations between the processing parameters, the resultant physical and chemical structure and the performance of E-beam cured polymer matrix composites for cryogenic fuel containment structures for future Air Force space operations vehicles. The E-beam induced cure mechanisms for cationic polymerized epoxides and free radical polymerized bismaleimides (BMI) were characterized in terms of processing variables, dissociation chemistry of the catalytic initiators, and inherent absorbed moisture. A general E-beam resin and composite cure model was developed as a function of E-beam processing variables. Stress-thermal cycling of BMI-Carbon fiber composites under cryogenic fuel simulated environments revealed that there is a high probability of microcracking with increasing number of thermo-cycles, higher pre-strain and humidity.

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# FINAL REPORT

# THE CHARACTERIZATION OF THE STRUCTURE-PROPERTY RELATIONS OF ELECTRON BEAM CURED COMPOSITES

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MARCH 2004

AFOSR CONTRACT NO.:
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# EXECUTIVE SUMMARY

## • SUMMARY

The ultimate objective of this program was to develop a fundamental understanding of the relations between the processing parameters, the resultant physical and chemical structure and the performance of E-beam cured polymer matrix composites for cryogenic fuel containment structures for future Air Force space operations vehicles. Such an understanding will guide processing conditions and materials development optimization to produce enhanced, reliable, durable composite structures.

The E-beam induced cure mechanisms for cationic polymerized epoxides and free radical polymerized bismaleimides (BMI) were characterized in terms of processing variables, dissociation chemistry of the catalytic initiators, and inherent absorbed moisture.

The epoxy resin glass transition temperatures were considerably lower than the thermally-cured glass transition temperatures of 170°C because of $H_2O$ termination reactions at the lower E-beam cure temperatures that result in a poor crosslinked network. Low intensity E-beam doses cannot induce curing of BMI but in the presence of N-vinylpyrrolidone, a reactive diluent, low temperature curing can readily occur.

An E-beam resin and composite cure model has been developed as a function of time and sample geometry on the effects of:
- temperature rise and cool down rates
- $T_g$ increase and associated resin yield stress rise
- any moisture-induced vapor pressure

as a function of E-beam processing variables. The objective of this study was to develop the processing tool that will guide and optimize the E-beam-cure process in order to achieve:
- full and uniform resin cure
- minimum residual stress that results from the temperature gradient in the resin
- the avoidance of moisture blistering induced by the vapor pressure-induced cavitation within the resin

Stress-thermal cycling of BMI-Carbon fiber composites under cryogenic fuel simulated environments revealed that there is a high probability of microcracking with increasing number of thermo-cycles, higher pre-strain and humidity. The principle findings were that the full cycles from -196°C up to 250°C cause the most significant microcrack development. Observations indicate that the high temperature portion of the cycle under load causes fiber-matrix interface failure. Subsequent exposure to high stresses in the cryogenic temperature region results in composite matrix microcracking due to the additional stresses associated with the fiber-matrix thermal expansion mismatch.

Initial structure-processing-performance studies of AFR-PEPA-N polyimides indicate oligomer crystals only melt in the 355-360°C range and can cause microcrack initiated defects in the cured resins and composites.

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# • <u>PUBLICATIONS</u>

1. Y. Li, R. J. Morgan, F. Tschen, H. -J. Sue, and V. Lopata, "Electron Beam Curing of Bismaleimide-Reactive Diluents Resins", Journal of Applied Polymer Science. (Submitted).

2. R. Ribeiro, R. J. Morgan, L. Bonnaud, J. Choi, V. Lopata, J. Lu and H.-J. Sue, "Characterization of the Electron Beam Curing of Cationic Polymerization of Diglycidylether of Bisphenol A Epoxy Resin", Journal of Composite Materials. (Submitted).

3. Y. Li, R. J. Morgan, F. Tschen, H. -J. Sue, and V. Lopata, "Electron Beam Curing Kinetics of Reactive Diluents Containing Bismaleimide", Proceedings of SAMPE 2004, Long Beach, CA, May, (2004). (In press).

4. J. Ju and R. J. Morgan, "Water Diffusion Based Non-Destructive Evaluation (NDE) of PMR II-50 / M60J 4-HS Weave Carbon Fabric Composite Materials Under Stress-Thermal Cycling", Proc. of ANTEC Technical Conference, Chicago, Illinois, May (2004). (In Press)

5. S. W. Moon, R. J. Morgan, and S. C. Lau, "Hygrothermal Modeling of Thick Thermoset Resin during Electron Beam Cure – Part I: Methodology and Modeling Cure Kinetics, Journal of Composite Materials, 38, 357 (2004).

6. S. W. Moon, R. J. Morgan, and S. C. Lau, "Hygrothermal Modeling of Thick Thermoset Resin during Electron Beam Cure – Part II: $T_g$-$\sigma_y$-$P_v$ Variations and Optimization, Journal of Composite Materials, 38, 375 (2004).

7. J. Ju and R. J. Morgan, "Characterization of BMI-Carbon Fiber Composite Microcrack Development under Stress – Thermal Cycling", Proc. of ANTEC Technical Conference, Nashville, TN, May (2003) pp. 2059-2062. ( Also Journal of Composite Materials, In press).

8. Y. Li, R. J. Morgan, F. Tschen, J. Ju, H.-J. Sue, and V. Lopata, "Investigation of Electron Beam Curing of Bismaleimide (BMI) and BMI/NVP Resins", Proc. of ANTEC Technical Conference, Nashville, TN, May, pp. 808-812, (2003).

9. J. Ju, M. Prochazka, B. Ronke, R. J. Morgan, E.E. Shin, J. Lincoln, and D. Curliss, "Damage Assessment of Stress-Thermal Cycled High Temperature Polymer Matrix Composites", $23^{rd}$ *High Temple Workshop Proceedings,* Jacksonville, FL, February, Paper D, (2003).

10. J. Ju, Y. Li, J .Lu, S. W. Moon, R. Ribeiro, B. Ronck, F. Tschen, and R. J. Morgan, "Fundamental Materials Structure-Properties Studies for Electron Beam Cured Composites", *Proc. SAMPE 2003,* Long Beach, CA, May, pp. 1969-1980, (2003).

11. R. J. Morgan, D. Li, J. Lu, S. W. Moon and R. Ribeiro, "Development and Characterization of Non-Autoclave Processes for Composites", Proceedings of the 47th International SAMPE Symp., Long Beach, CA, May, pp. 585-599 (2002).

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12. R. J. Morgan, J. Lu, D. Li, R. Ribeiro and S. W. Moon, "Development and Properties of Enhanced Thermal and Cryogenic Resistant Resins", Proceedings of High Temple Workshop XXII, Santa Fe, NM, January, Paper Q, (2002).

13. R. J. Morgan, E.E. Shin, J. Lincoln and J. Zhou, "Overview of Polymer Matrix Composites Performance and Materials Development for Aerospace Applications", SAMPE Journal, 37, No. 2, 102 (2001).

- **THESIS**

1. L. A. Murphy, "Morphological Investigation of AFR-PEPA-N Imide Oligomers and Their Cured Polyimides and the Remodification of AFR-PEPA-N to Achieve Liquid Crystalline Behavior", M. S. Thesis, Texas A&M University, (2003)

# COMPREHENSIVE TECHNICAL SUMMARY

## OBJECTIVES AND ACHIEVEMENTS

- The ultimate objective of this program was to develop a fundamental understanding of the relations between the processing parameters, the resultant physical and chemical structure and the performance of E-beam cured polymer matrix composites for cryogenic fuel containment structures for future Air Force space operations vehicles. Such an understanding will guide processing conditions and materials development optimization to produce enhanced, reliable, durable composite structures.

- A hygrothermal composite cure model was developed, in conjunction with experimental data, for the E-beam processing of composites in terms of E-beam dose-time sequences in order to achieve full resin cure, minimum residual stresses and avoidance of moisture-induced cavitation within the composite.

- The E-beam induced cure mechanisms for cationic polymerized epoxides and free radical polymerized bismaleimides was characterized in terms of processing variables, dissociation chemistry of the catalytic initiators, and inherent absorbed moisture.

- Resin toughness and composite microcrack resistance upon thermal cycling from the cryogenic temperature range to ~250 °C were monitored and correlated with their chemical and physical structure.

- Study the structure-processing-performance relations of phenylethynyl phthalic anhydride crosslinked fluorinated polyimides (AFR-PEPA-N).

## TECHNICAL TASKS

### TASK (1) CHARACTERIZATION OF THE ELECTRON BEAM CURING OF CATIONIC POLYMERIZATION OF DIGLYCIDYLETHER OF BISPHENOL A EPOXY RESIN

The characterization of the electron beam (E-beam) curing of diaryliodonium hexafluoroantimonate-diglycidylether of bisphenol A epoxy resin-initiator system was reported as a function of (i) diarylodonium hexafluoroantimonate catalyst (initiator) concentrations of 0.1 to 10 parts per hundred (phr) and total electron beam doses of 5 to 150 kilogray (kGy). The in-situ E-beam temperature of the resin was monitored as a function of dose-time characteristics. The degree of cure was monitored after radiation exposure by Fourier transform infra red spectrometry (FTIR) and the glass transition temperatures ($T_g$) by differential scanning calorimetry (DSC). The degree of cure and cure rate increased with total dose exposure and initiator concentration (Figure (1)). The

maximum cure rate occurred at 5kGy exposure and, thereafter, decreased as reactive species concentration decreased. The maximum in-situ E-beam temperature of 76°C was recorded for the resin containing 10 phr initiator, with a maximum degree of cure of 94% and glass transition temperature of 86°C, indicating that the cure reactions under E-beam are glassy-state diffusion controlled (Figure (2)).

The resin glass transition temperatures were considerably lower than the thermally cured glass transition temperatures of 170°C because of $H_2O$ termination reactions at the lower E-beam cure temperatures that result in a poor crosslinked network. In addition, evidence was presented that the diaryliodonium hexafluoroantimonate catalytic activity for epoxide cationic polymerization is retarded by $H_2O$.

E-beam exposure causes the diaryliodonium hexafluoroantimonate to dissociate into active catalytic species, such as $HSbF_6$, well below 100 °C compared to catalytic thermal-induced dissociation near 200 °C.

The E-beam cure reaction rate was modeled as a function of degree of cure and dose exposure by a standard autocatalytic kinetic model.
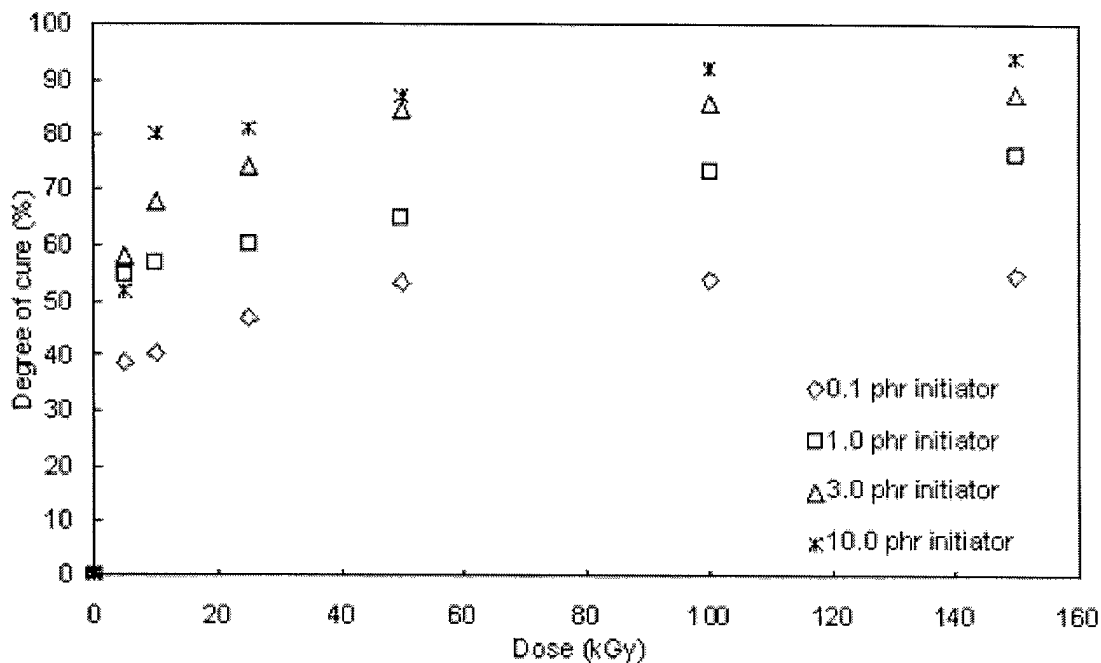


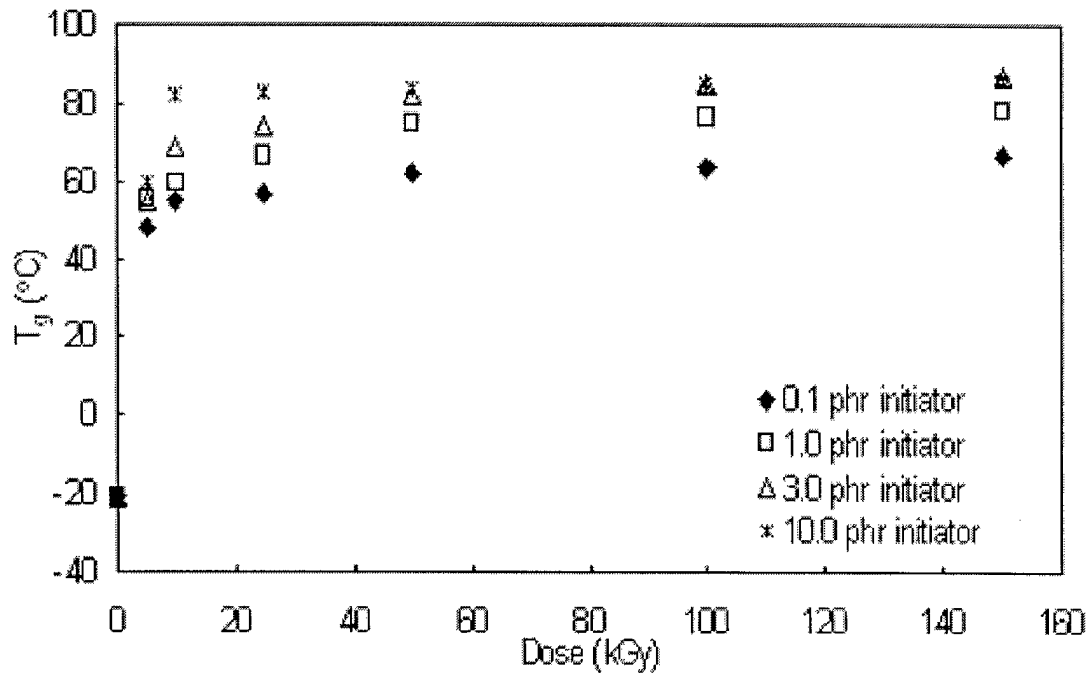*Figure (1).* Degree of cure of epoxy versus dose

*Figure (2)*. Glass transition temperature versus dose for different initiator concentrations

## ● PUBLICATIONS

1.  R. J. Morgan, E.E. Shin, J. Lincoln and J. Zhou, "Overview of Polymer Matrix Composites Performance and Materials Development for Aerospace Applications", SAMPE Journal, 37, No. 2, 102 (2001).
2.  R. J. Morgan, J. Lu, D. Li, R. Ribeiro and S. W. Moon, "Development and Properties of Enhanced Thermal and Cryogenic Reistart Resins", Proceedings of High Temple Workshop XXII, Santa Fe, NM, January, Paper Q, (2002).
3.  R. J. Morgan, D. Li, J. Lu, S. W. Moon and R. Ribeiro, "Development and Characterization of Non-Autoclave Processes for Composites", Proceedings of the 47th International SAMPE Symp., Long Beach, CA, May, pp. 585-599 (2002).
4.  R. Ribeiro, R. J. Morgan, L. Bonnaud, J. Choi, V. Lopata, J. Lu and H.-J. Sue, "Characterization of the Electron Beam Curing of Cationic Polymerization of Diglycidylether of Bisphenol A Epoxy Resin", Journal of Composite Materials. (Submitted).

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# TASK (2) HYGROTHERMAL MODELING OF THICK THERMOSET RESINS AND COMPOSITES DURING ELECTRON-BEAM CURING

An E-beam resin and composite cure model has been developed as a function of time and sample geometry on the effects of:

- temperature rise and cool down rates
- $T_g$ increase and associated resin yield stress rise
- any moisture-induced vapor pressure

as a function of the processing variables in conjunction with experimental data developed for the epoxy resin in Task (1). The objective of this study was to develop the processing tool that will guide and optimize the e-beam-cure process in order to achieve:

- full and uniform resin cure
- minimum residual stress that results from the temperature gradient in the resin
- the avoidance of moisture blistering induced by the vapor pressure-induced cavitation within the resin

Part I of this study summarized the modeling procedure of E-beam-induced cure kinetics, and the results of local temperature and degree of cure rise within the sample as a function of dose (Figure (3)).
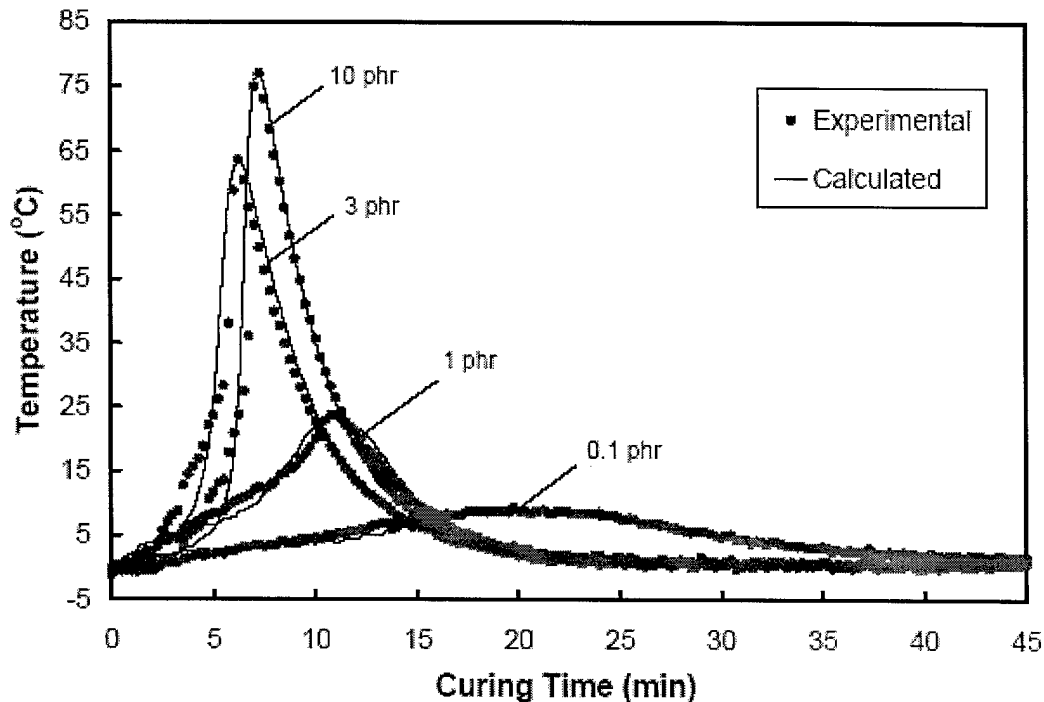


*Figure (3).* Predicted temperature evolution vs. curing time for different initiator concentrations

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In Part II of the study, dynamic characteristics of $T_g$ - $\sigma_y$ - $P_v$ rise and their modeling procedures together with an attempt at optimizing the e-beam-cure process were modeled.

Glass transition temperature of the resin during cure was predicted using the phenomenological equations from the experimental curve $T_g = f(\alpha)$. The generic model, which is a function of $T_g$ and temperature, was proposed for the estimation of the local yield stress of the resin, $\sigma_y$, during cure. Predicted results of dynamic changes in temperature, $T_g$, $P_v$, and associated $\sigma_y$ revealed that for initiator concentration of 3 and 10 phr, most parts of the sample with constant moisture concentration (2 wt. %) reached the critical condition for about 1 min during cure ( Figure (4)). In the critical condition, where the water vapor pressure exceeds the resin yield stress, possible damage from moisture blistering is expected. For 0.1 and 1 phr, cases, however, $\sigma_y$ was expected always greater than $P_v$ throughout e-beam treatment because of the low cure temperature (less than 30 °C).

One simulation was performed to optimize the E-beam-cure process by controlling the thermal history of the sample via adjusting thermal boundary conditions. The results showed that the cure temperature thus, the temperature gradient in the resin was reduced significantly and the critical condition could be avoided during cure, while obtaining the same degree of cure as before.
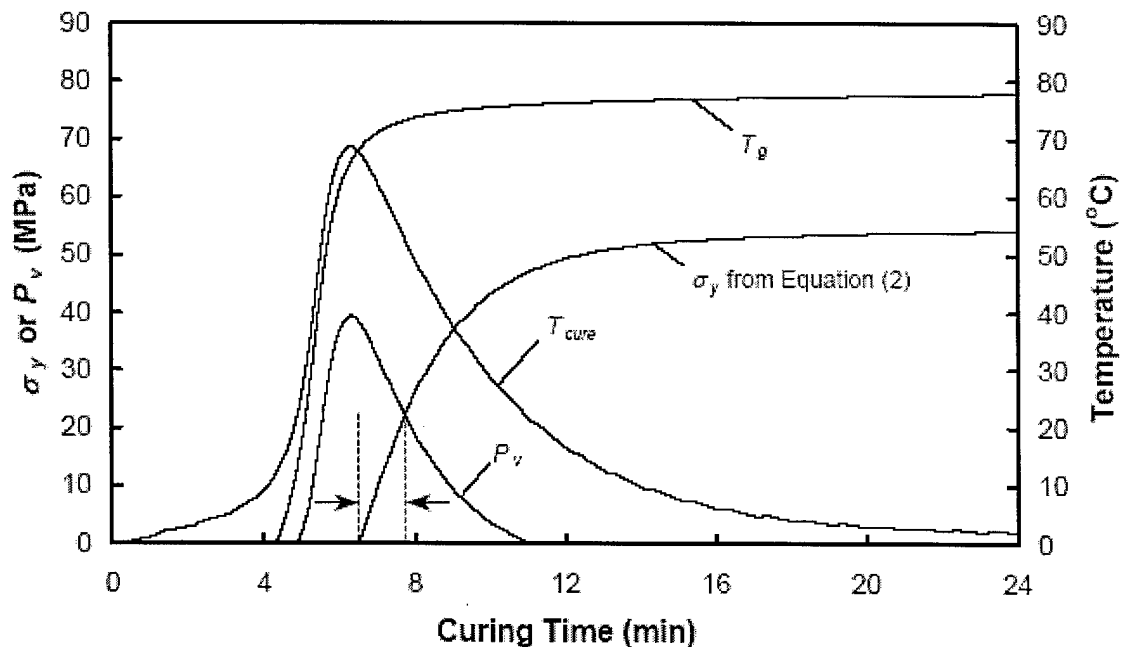


*Figure (4).* Predicted T- $\sigma$y-Pv vs. curing time at the center of the sample for an initiator concentration of 3 phr

● <u>PUBLICATIONS</u>

1. S. W. Moon, R. J. Morgan, and S. C. Lau, "Hygrothermal Modeling of Thick Thermoset Resin during Electron Beam Cure – Part I: Methodology and Modeling Cure Kinetics, Journal of Composite Materials, 38, 357 (2004).
2. S. W. Moon, R. J. Morgan, and S. C. Lau, "Hygrothermal Modeling of Thick Thermoset Resin during Electron Beam Cure – Part II: $T_g$-$\sigma_y$-$P_v$ Variations and Optimization, Journal of Composite Materials, 38, 375 (2004).

## TASK (3) ELECTRON BEAM CURING OF REACTIVE DILUENTS CONTAINING BISMALEIMIDE

Electron-beam (E-beam) curing of 4,4'-Bismaleimidodiphenylmethane (BMPM) / BMI-1,3-tolyl / o,o'-diallylbisphenol A (DABPA) based bismaleimide (BMI) systems and their mixing with various reactive diluents, such as N-vinylpyrrolidone (NVP) and styrene, were investigated to elucidate how temperature, electron-beam dosage and diluent concentration affect the cure extent. The effect of free radical initiators on the cure reactions was also studied. It was found that low intensity E-beam doses cannot cause the polymerization of BMI. High intensity E-beam exposures give high reaction conversions due to high temperature rise, which induced thermal curing. It was shown that NVP is a good reactive diluent for BMI. BMI/NVP can be initiated easily by low intensity E-beam without thermal curing. FT-IR studies indicate that about 70% of the reaction is complete for BMI/NVP with 200kGy dosage exposure at 10kGy per pass (Figure (5)). The sample temperature only reaches about 75°C. The $T_g$ of the product was 180°C. Free radical initiator, dicumyl peroxide, can accelerate the reaction rate at the beginning of E-beam exposure, but does not affect final reaction conversion. The increase of the concentration of NVP in the BMI/NVP systems increases the reactive conversions almost linearly (Figure (6)). The dilution and activation of NVP in BMI make the BMI reaction more complete under E-beam radiation. Unfortunately, only up to 60 weight percent BMI is soluble in the NVP diluent.

● <u>PUBLICATIONS</u>

1. Y. Li, R. J. Morgan, F. Tschen, J. Ju, H.-J. Sue, and V. Lopata, "Investigation of Electron Beam Curing of Bismaleimide (BMI) and BMI/NVP Resins", Proc. of ANTEC Technical Conference, Nashville, TN, May, pp. 808-812, (2003).
2. Y. Li, R. J. Morgan, F. Tschen, H. -J. Sue, and V. Lopata, "Electron Beam Curing Kinetics of Reactive Diluents Containing Bismaleimide", Proceedings of SAMPE 2004, Long Beach, CA, May, (2004). (In press).
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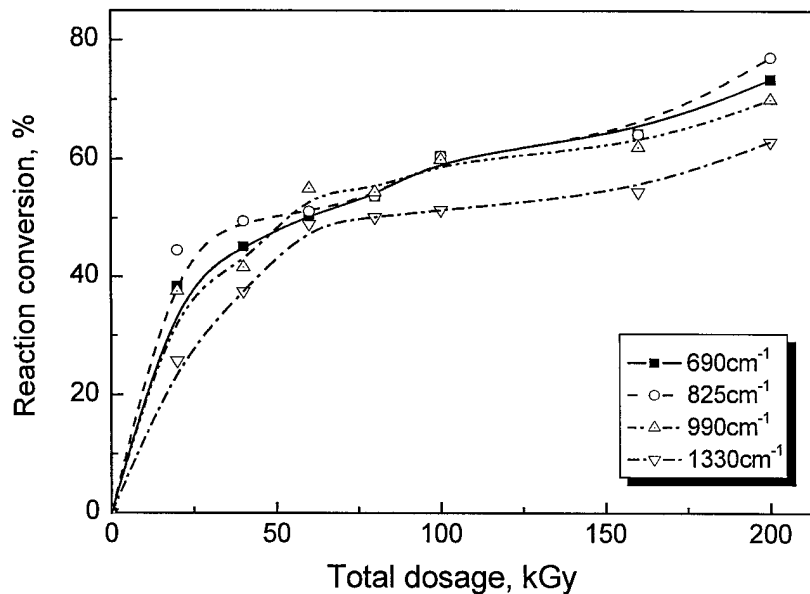
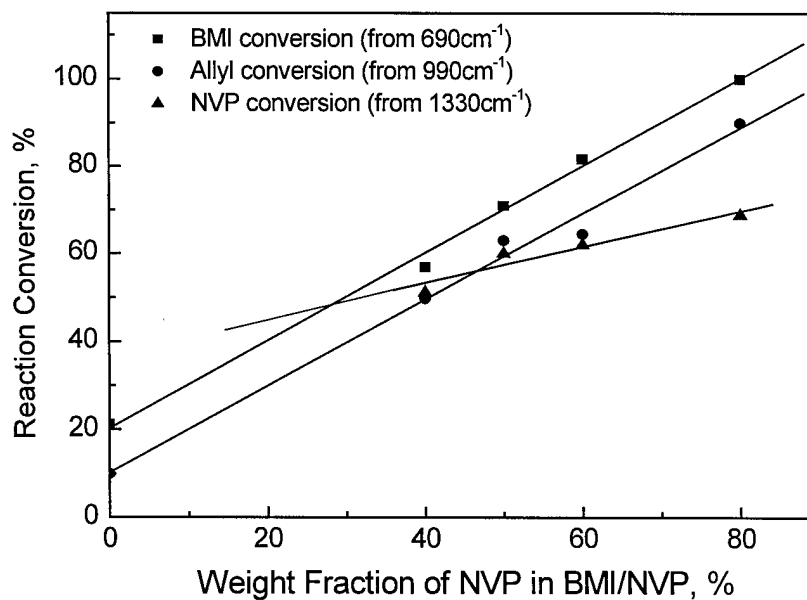**Figure (5).** The dependence of reaction conversion of BMI/NVP 50/50 on applied E-beam dosage (10kGy per pass)



**Figure (6).** The dependence of reaction conversion of BMI/NVP system on concentration of NVP (Dosage applied: 200kGy at 10kGy per pass)

## TASK (4) CHARACTERIZATION OF MICROCRACK DEVELOPMENT IN BMI-CARBON FIBER COMPOSITE UNDER STRESS AND THERMAL CYCLING

The objective of this research was to determine the effect of thermal cycling on the development of microcracks in BMI-carbon fiber composites (5250-4 RTM / IM7 4-harness satin weave fabric). By clamping composite specimens on the radial sides of half cylinders having two different radii (78.74mm and 37.96mm), two different strain conditions with respect to the neutral axis (-0.406 to 0.406 % and -0.843 to 0.843 %) were applied to the composites. Three different thermal cycling experiments, 1) –196ºC to 250ºC, 2) 23ºC to i)150ºC ii) 200ºC iii) 250ºC, and 3) -196ºC to 23ºC were performed as a function of stress, number of thermal cycles, heating or cooling rate, and humidity conditions. An in-situ monitoring microscope was used to observe the microcrack development during the experiment. The results indicate that there is a higher probability of microcracking with increasing number of thermo-cycles, higher pre-strain and humidity (Figure (7)). The principle findings are that the full cycles from -196ºC up to 250ºC cause the most significant microcrack development (Figure (8)). Observations indicate that the high temperature portion of the cycle under load causes fiber-matrix interface failure. Subsequent exposure to higher stresses in the cryogenic temperature region results in composite matrix microcracking due to the additional stresses associated with the fiber-matrix thermal expansion mismatch.
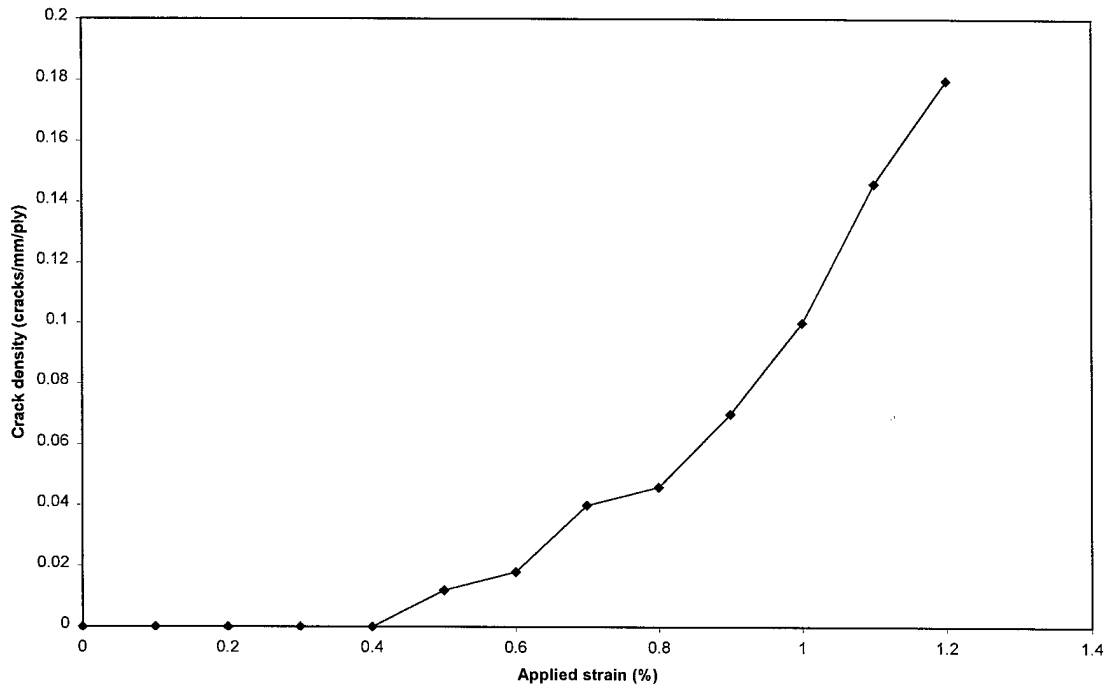


*Figure (7).* IM7-5250-4 RTM's transverse crack-densities as a function of applied strain at room temperature
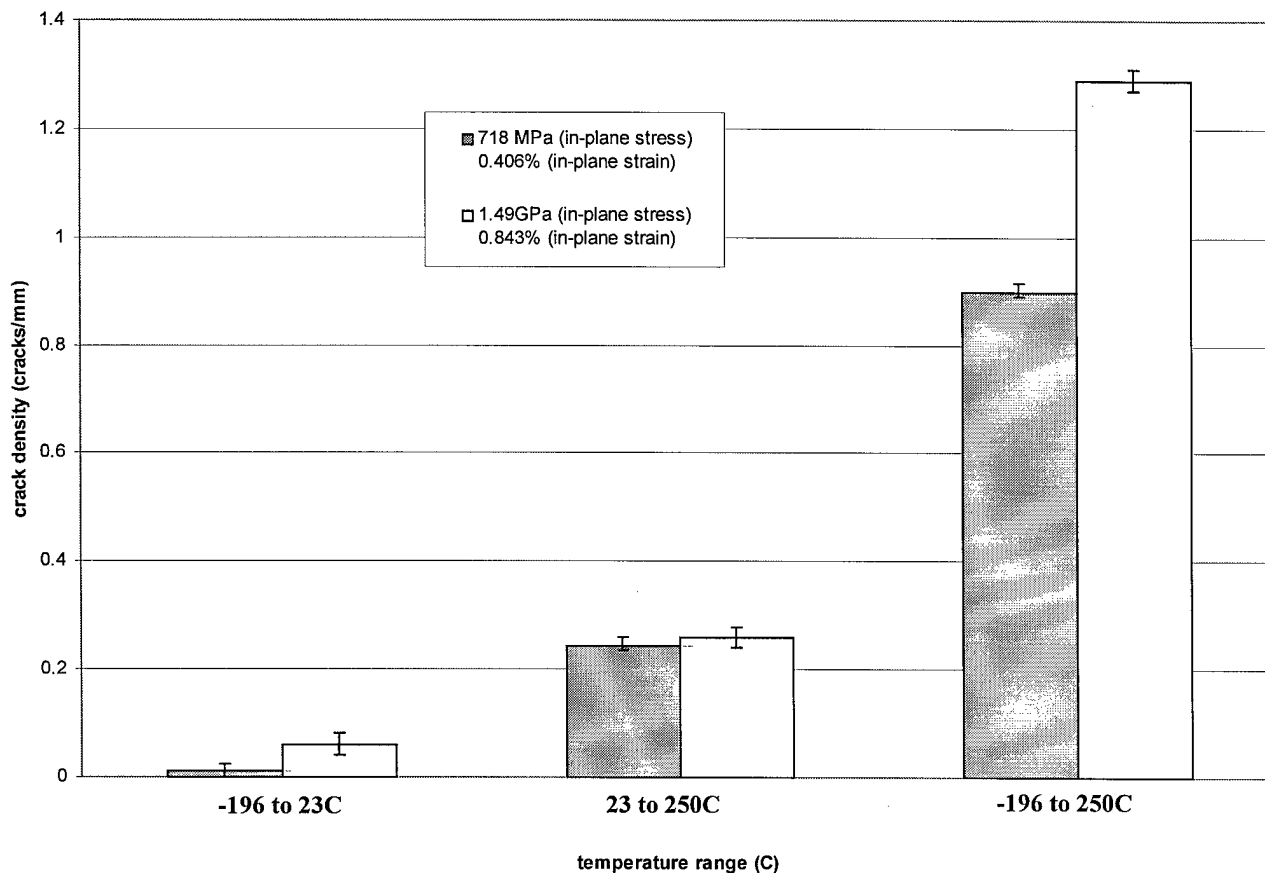
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**Figure (8).** Microcrack densities of 5250-4 RTM composite (3ply) for two different pre-strain and three different temperature types of thermo-cycling for two thermo-cycles

- ## PUBLICATIONS

1. J. Ju, M. Prochazka, B. Ronke, R. J. Morgan, E.E. Shin, J. Lincoln, and D. Curliss, "Damage Assessment of Stress-Thermal Cycled High Temperature Polymer Matrix Composites", *23rd High Temple Workshop Proceedings*, Jacksonville, FL, February, Paper D, (2003).
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3. J. Ju and R. J. Morgan, "Characterization of BMI-Carbon Fiber Composite Microcrack Development under Stress – Thermal Cycling", Proc. of ANTEC Technical Conference, Nashville, TN, May (2003) pp. 2059-2062. ( Also Journal of Composite Materials, In press).
4. J. Ju and R. J. Morgan, "Water Diffusion Based Non-Destructive Evaluation (NDE) of PMR II-50 / M60J 4-HS Weave Carbon Fabric Composite Materials Under Stress-Thermal Cycling", Proc. of ANTEC Technical Conference, Chicago, Illinois, May (2004). (In Press)

## TASK (5) STRUCTURE-PROCESSING-PERFORMANCE RELATIONS OF PHENYLETHYNYL PHTHALIC ANHYDRIDE CROSSLINKED FLUORINATED POLYIMIDES (AFR-PEPA-N PI's)

We have addressed the issue of inherent oligomer crystals and their melting temperature relative to onset of crosslinking and as such unmelted crystals are the initiators of massive microcrack development during deformation and failure of AFR-PEPA-N PI's. The imide oligomer crystals were formed in films during the synthesis-imidization process for AFR-PEPA-2 and AFR-PEPA- 4 but not with higher molecular AFR-PEPA- 8. In these AFR-PEPA-2 films (~0.2 mm thick) it was found the oligomer crystals only melted between 355°C to 360°C (Figure (9)). At 355°C for 15 min, the degree of cure is 50%, hence it is vital that the oligomer crystal defects are eliminated in the synthesis- imidization stages of these PI's. The oligomer crystals were found to dissolve in N-methyl pyrollidone, NMP, after 24 hours at 100°C.
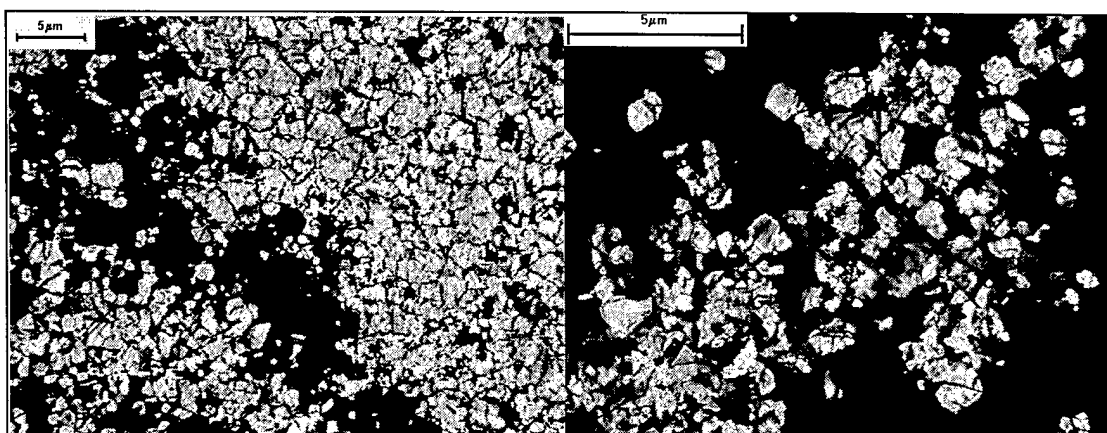
- ## PUBLICATIONS

1. L. A. Murphy, "Morphological Investigation of AFR-PEPA-N Imide Oligomers and Their Cured Polyimides and the Remodification of AFR-PEPA-N to Achieve Liquid Crystalline Behavior", M. S. Thesis, Texas A&M University, (2003)
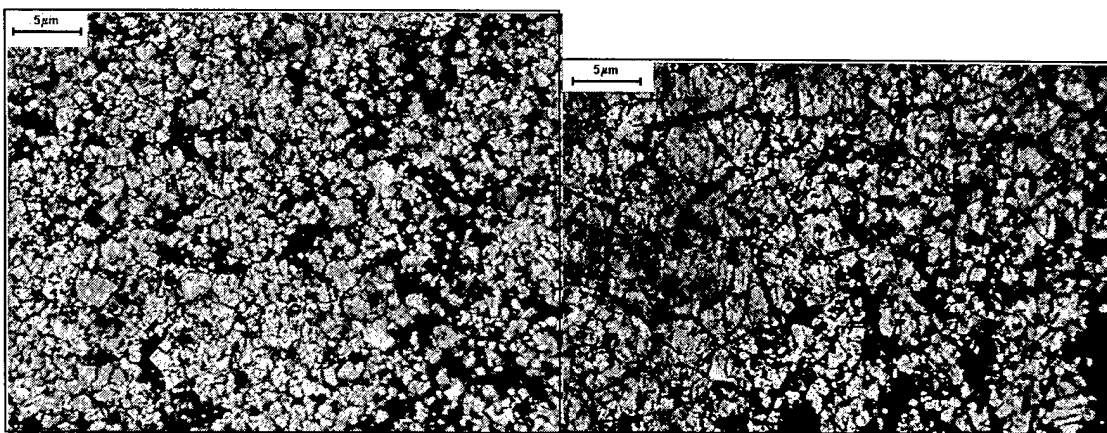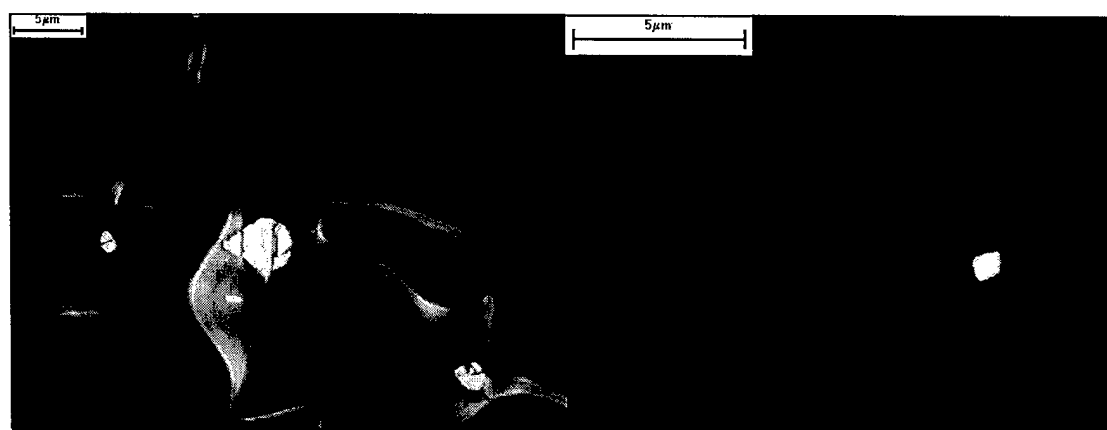
(a) No Anneal / Cure: Film cast at 150°C.

(b) Cure at 325°C, 15 minutes.

(c) Cure at 350°C, 15 minutes.

(d) Cure at 355°C, 15 minutes.

(e) Cure at 360°C, 15 minutes.

(f) Cure at 375°C, 15 minutes.

*Figure (9)*. Polarized Optical Micrographs of Oligomer Crystals in AFR-PEPA-2 PI Films as a Function of 15 minute Anneal Temperature

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