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14. ABSTRACT The overall goals of this program were to conduct fundamental characterization and development studies of the structure-processing-performance relations of phenylethynyl phthalic anhydride crosslinked fluorinated polyimides (AFR-PEPA-N) and their carbon fiber composites for applications for future Air Force vehicles and associated propulsion systems. The technical areas that were primarily pursued and documented in this final report are i) The stress-thermal cycling of polyimide composites in extreme thermal environments; ii) Cure characterization of the phenylethynyl oligomer end caps, oligomer morphology and chemical modification of oligomer end groups; iii) Characterization of optimum cure conditions versus onset of network degradation; and iv) Development of failure modeling methodology of composites in extreme service environments.					
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FINAL REPORT

CHARACTERIZATION OF THE STRUCTURE – PROCESSING - PERFORMANCE RELATIONS OF PHENYLETHYNYL PHTHALIC ANHYDRIDE CROSSLINKED FLUORINATED POLYIMIDES (AFR-PEPA-N) AND THEIR CARBON FIBER COMPOSITES

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MARCH 2007

AFOSR CONTRACT NO.:-
FA 9550-04-1-0137

EXECUTIVE SUMMARY

SUMMARY

The overall goals of this program were to conduct fundamental characterization and development studies of the structure-processing-performance relations of phenylethynyl phthalic anhydride crosslinked fluorinated polyimides (AFR-PEPA-N) and their carbon fiber composites for applications for future Air Force vehicles and associated propulsion systems. Such applications include light weight engine components for stealth aircraft, and primary structures for space aer propulsion cryogenic fuel containment structures and future hypersonic vehicles.

The principal technical areas studied were:-

- (i) The stress-thermal cycling of polyimide composites in extreme thermal environments;
- (ii) Cure characterization of the phenylethynyl oligomer end caps, oligomer morphology and chemical modification of oligomer end groups;
- (iii) Characterization of optimum cure conditions versus onset of network degradation;

and

- (iv) Development of failure modeling methodology of composites in extreme service environments.

Stress-thermal cycling experiments of BMI-carbon fiber composites that simulate cryogenic containment environments during launch and re-entry of future space vehicles revealed full cycles from -196°C up to 250°C cause the most significant microcrack development as a result of fiber-matrix interface failure at high temperatures that initiates matrix microcracking at high stresses in the cryogenic temperature region. Progressive laminate damage modeling for launch conditions, also, revealed thermal residual stresses are the principal causes of complete laminate microcracking with fuel seepage through the microcracks accelerating the failure process.

The thermal cure reactions and associated kinetics of AFR-PEPA-4 oligomer and an model compound N-phenyl-[4-(phenylethynyl) phthalimide] were characterized by FTIR and DSC measurements in the 350-410C temperature range. The cure reactions involve a fast first-order reaction stage with the formation of polymers from the phenylethynyl end caps followed by a slow diffusion-controlled crosslinking. Modification of the oligomer end caps to produce lower cure temperatures was also achieved.

The crystal morphology of the AFR-PEPA-N oligomer was characterized and shown to produce network inhomogeneities during cure.

Full cure of AFR-PEPA-4 polyimides is achieved at 437.2°C, however for cure times of over an hour at 440-450°C major network chemical degradation also takes place.

The methodology to model the progressive composite laminate sequential failure paths of polyimide-carbon fiber composites for future hypersonic service environments has been developed. This modeling involves rapid sequential physical, chemical, thermal and mechanical overlapping degradation mechanisms.

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PUBLICATIONS

1. Y. Li and R. J. Morgan, "Thermal Cure of Phenylethynyl-Terminated AFR-PEPA-4 Imide Oligomer and a Model Compound", *Journal of Applied Polymer Science*, 111, 4446-4453 (2006).
2. Y. Li, N. Obando, F. Tschen, and R.J. Morgan, "Thermal Analysis of Phenylethynyl End-Capped Fluorinated Imide Oligomer AFR-PEPA-4", *Journal of Thermal Analysis and Calorimetry*, 85, 125-129 (2006).
3. J. Ju, R.J. Morgan, E.E. Shin, and T. Creasy, "Characterization of Micro-cracking in M40J/PMR-II-50 under Thermal Cycling Combined with Mechanical Loading: Part I - Investigation of Main and Interactive Effects using Design of Experiment", *Journal of Composite Materials*, In print (2006).
4. J. Ju, R.J. Morgan, E.E. Shin, and T. Creasy, "Characterization of Micro-cracking in M40J/PMR-II-50 under Thermal Cycling Combined with Mechanical Loading: Part II – Failure Analysis", *Journal of Composite Materials*, In print (2006).
5. Y. Li, L.A. Murphy, J.E. Lincoln, and R.J. Morgan, "Phenylethynyl End-Capped Fluorinated Imide Oligomer AFR-PEPA-N: Morphology and Processability Characteristics", *Macromolecular Materials and Engineering*, Accepted (2006).
6. J. Ju, B.D. Pickle, R.J. Morgan, and J.N. Reddy, "An Initial and Progressive Failure Analysis for Cryogenic Composite Fuel Tank Design", *Journal of Composite Materials*, Accepted (2006).
7. Y. Li, L.A. Murphy, and R.J. Morgan, "Morphology Investigation of AFR-PEPA-N Imide Oligomer and Their Cured Polyimides", *Proceedings of 51st ISSE, SAMPE 2006, Long Beach, CA, 2006*.
8. J. Ju, R.J. Morgan, and E.E. Shin, "Transverse Interface Failure of M40J/PMR-II-50 Composites under High Temperature Exposure", *Proceedings of 51st ISSE, SAMPE 2006, Long Beach, CA, 2006*.
9. J. Ju, R.J. Morgan and E.E. Shin, "Transverse Interface Failure of M40J/PMR-II-50 Composites under High and Low Temperature Exposure, *Proceedings of ANTEC 2006 of Society of Plastics Engineering, Charlotte, NC, 2006*.
10. R.J. Morgan, Y. Li, J. Ju, E.E. Shin, L.A. Murphy, and N. Obando, "Structure-Property Relations of High Temperature Polyimide-Carbon Fiber Polymers", *Proceedings of High Temple Workshop XXVI, Austin, TX, 2006*.
11. Y. Li, G.S. Payette, N. Obando, J. O'Neal, J. Ju, R.J. Morgan, and J.N. Reddy, "Evaporative Cooling of Moisture Bearing Epoxy Composite Plate", *Proceedings of SAMPE 2006 Fall Technical Conference, Dallas, TX, 2006*.
12. Y. Li, F. Tschen, J.E. Lincoln, and R.J. Morgan, "Structure-Property Relations of Siloxane Modified Polyimide Composites", *Proceedings of SAMPE 2006 Fall Technical Conference, Dallas, TX, 2006*.
13. J. Ju, R.J. Morgan, and J.N. Reddy, "Multiphysics Based Progressive Failure Analysis for Cryogenic Composite Fuel Tank Design", *Proceedings of ANTEC 2007 of Society of Plastics Engineering, Cincinnati, Ohio, 2007 (accepted)*.
14. J. Ju, R.J. Morgan, and J.N. Reddy, Thermo-Mechanical Analysis of Composites under Combined Conduction Heating and Large Deflection Bending, *IMECE 2005-81262, ASME International Mechanical Engineering Congress & Exposition, November 5-11, 2005, Orlando, Florida*.
15. Y. Li, R.J. Morgan, and F. Tschen, "Structure-Property Relations of Phenylethynyl Terminated Imide Oligomers", *Proceedings of High Temple Workshop XXV, Paper EE, Point Clear, AL, 2005*.

16. R.J. Morgan, T. Creasy, Y. Li, J. Ju, F. Tschen, N. Obando, O. Enuwi and J.E. Lincoln, "Composite Thermal-Induced Degradation Mechanisms and Protection for Future Aerospace Vehicles", Proceedings of 27th High Temple Workshop, Sedona, AZ, February, 2007.
17. J. Ju, and R.J. Morgan, "Water Diffusion Based Non-destructive Evaluation of PMR-II-50/M60J 4HS Weave Carbon Fabric Composite Materials under Stress-Thermal Cycling", ANTEC 2004 of Society of Plastics Engineering, Chicago, Illinois, 687, May 2004.
18. R.J. Morgan, Y. Li, F. Tschen, and L. Murphy, "Structure – Processing – Performance Relations of High Temperature Polymers", 24th High Temple Workshop Proceedings, Paper G, Sacramento, CA, February, 2004.
19. Y. Li, and R.J. Morgan, "Structure-Property Relations of a Phenylethynyl Terminated Imide Oligomer (AFR-PEPA-4)", Proceedings of 33rd NATAS Conf., pp. 10, Universal City, CA, 2005.
20. Y. Li, R.J. Morgan, and F. Tschen, "A Study of Thermal Cure of a Phenylethynyl Terminated Imide Oligomer (AFR-PEPA-4)", Proceedings of 50th ISSE, SAMPE 2005, Long Beach, CA, 2005.
21. J. Ju, R.J. Morgan, T.C. Creasy, S. Hafernik, and E.E. Shin, "Statistical Approach to Evaluate Composite Damage", Proceedings of ANTEC 2005, Boston, MA, 2005.

THESIS

1. Y. Li, "Synthesis and Cure Characterization of High Temperature Polymers for Aerospace Applications", Ph.D. Thesis, Texas A&M University (2004).
2. B. Pickle. "Modeling Damage Growth Mechanisms of Composites During Stress-Thermal Cycling", M.S. Thesis, Texas A&M University (2004).
3. J. Ju, "Characterization of Composite Performance under Cryogenic Conditions", Ph.D. Thesis, Texas A&M University (2005).
4. J. O'Neal, "Thermal Protection of High Temperature Polymer-Matrix Carbon Fiber Composites", M.S. Thesis, Texas A&M University (2005).
5. F. Tschen, "Synthesis of Novel Polyimides for Testing of Structure-Processing and Property Relations When Used to Form High Temperature Polymer Matrices", M.S. Thesis, Texas A&M University (2005).

COMPREHENSIVE TECHNICAL SUMMARY

OBJECTIVES AND ACHIEVEMENTS

- The overall goals of this program were to conduct fundamental characterization and development studies of the structure-processing-performance relations of phenylethynyl phthatic anhydride crosslinked fluorinated polyimides (AFR-PEPA-N) and their carbon fiber composites for applications for future Air Force vehicles and associated propulsion systems.
- Study the effects of stress-thermal cycling conditions in extreme thermal environments on the microcrack initiation and propagation in polyimide composites.
- Characterize the cure kinetics and mechanisms of phenylethynyl imide oligomer end caps and their chemical modifications, together with oligomer crystal morphology, upon crosslinked network structure.
- Ascertain optimum imide oligomer degree of cure versus onset of network degradation.
- Develop failure modeling methodology of composites in extreme service environments.

TECHNICAL TASKS

TASK (I) STRESS-THERMAL CYCLING OF COMPOSITES IN EXTREME THERMAL ENVIRONMENTS

One objective of this task was to ascertain the critical controlling parameters for microcrack initiation and propagation from stress-thermal cycling. Parameters studied were i) mechanical strain; 0%, 0.175~0.350%, and 0.325~0.650%, ii) temperature profile of thermal cycling; 1)23°C to -196°C to 250°C, 2) 23°C to 250°C, and 3)23°C to -196°C, iii) number of thermal cycles; one to eight, and iv) heating rate; 1°C/min and 4°C/min.

The results indicate that the number of thermal cycles was the primary controlling factor (41%) while the thermal cycling temperature amplitude (25%) and-mechanical strain (22%) were secondary as shown in Figure (1). The number of thermal cycles also exhibited a significant interaction effect on the development of microcracks when it is combined with either temperature profile of thermal cycling (7%) or mechanical strain (5%).

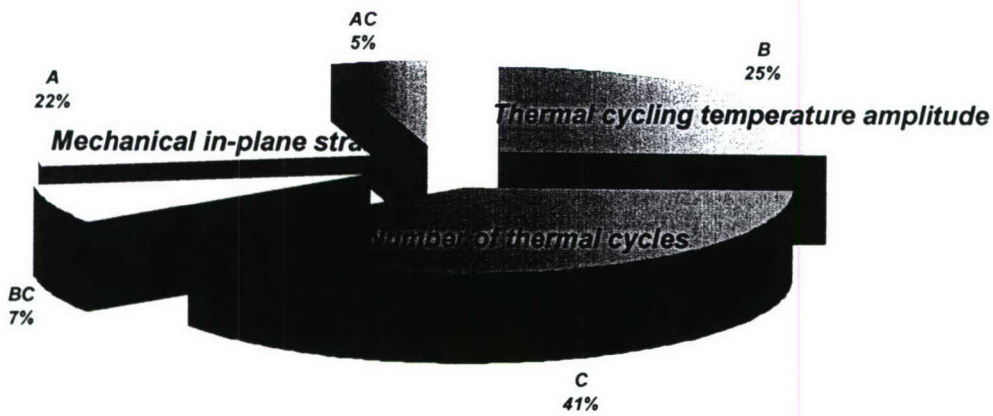


Figure (1). Quantified Significant Effects

In Figure (2), we show the crack density after one thermo-cycle as a function of thermal cycling profile. Cryogenic and high temperature combined thermo-cycling profile (room temperature to -196°C to 250°C and back to room temperature) showed the highest crack density and 40 to 44% increase compared to the other temperature profiles.

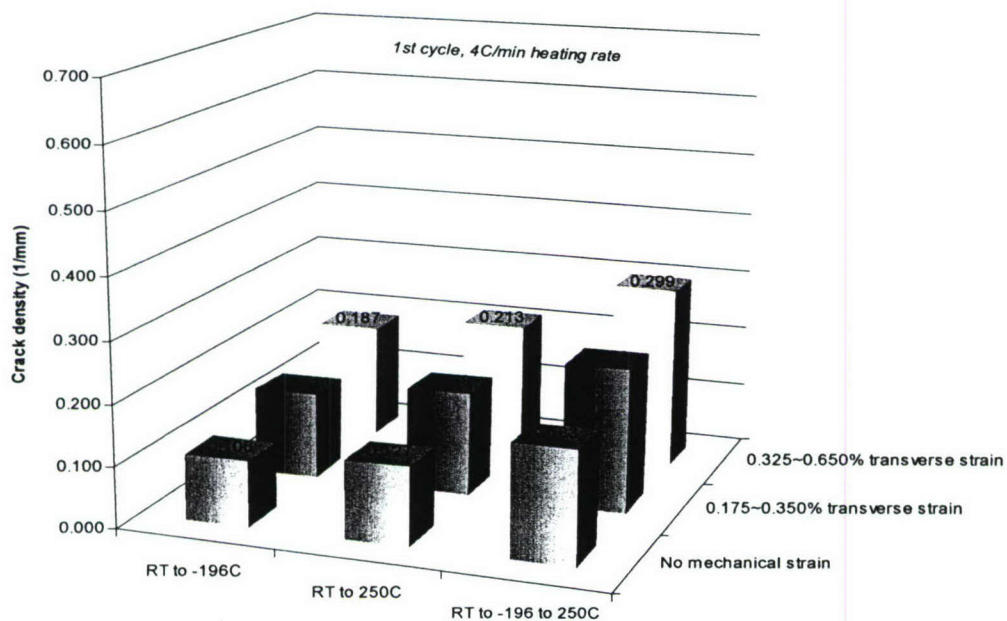


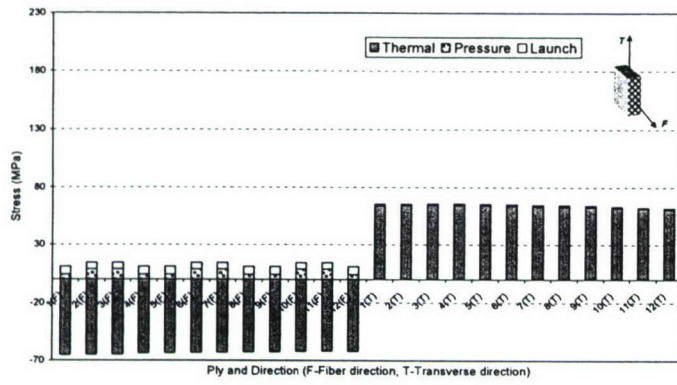
Figure (2) Crack Densities with Three Different Thermal-Cycling Temperature Profiles and Transverse Mechanical Strains after 1 Cycle

Full thermal cycles and their number from -196°C up to 250°C cause the most significant microcrack development as a result of fiber-matrix interface failure at high temperatures that initiate matrix cracking at high stresses in the cryogenic temperature region.

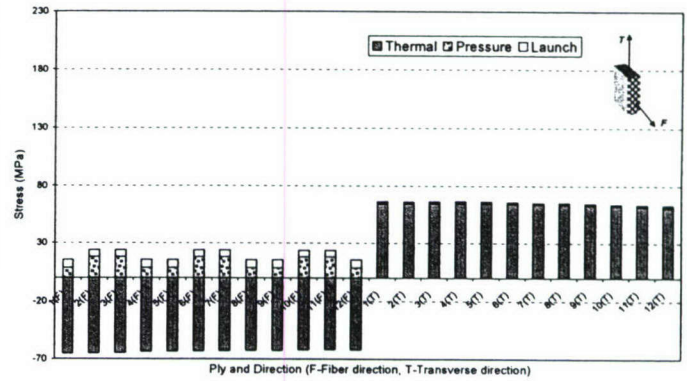
Composite cryogenic fuel containment structures experience the highest stress during launch of future space transportation vehicles.

We have developed a methodology to model the progressive laminate sequential failure paths in these service environments. This methodology involves the following steps. (i) application of classical laminate plate theory, together with thermodynamic procedures (ii) maximum failure stress criteria and (iii) incorporation of combined fundamental damage mechanisms on each ply versus time. The resultant model characterizes the loss of strength and stiffness versus time for each ply and, also, the whole laminate.

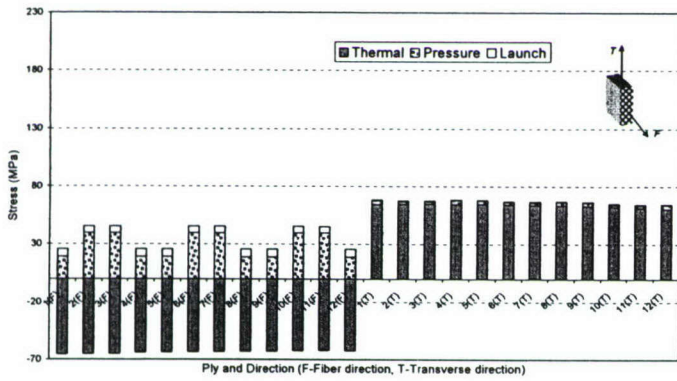
Stress analyses on each ply incorporated thermal residual stresses, internal pressure stresses and acceleration launch stresses. Thermal gradients through the composite thickness for time after fuel fill and fuel transportation though microcracks were, also, incorporated into the model. The thermal, pressure and launch induced stresses in the fiber and transverse directions at -253°C under various pressures for both the graphite-epoxy and -BMI laminates are shown in Figure (3) and (4), respectively.



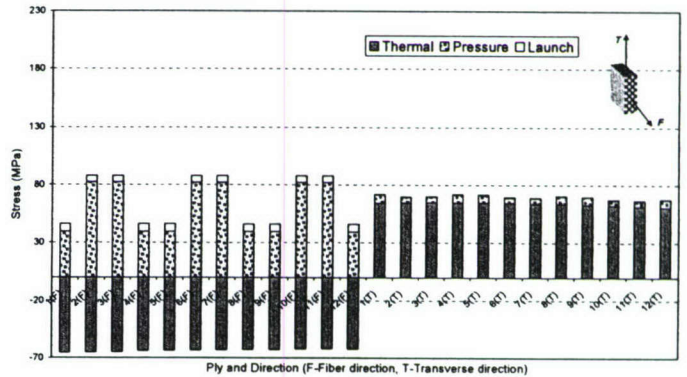
(a) at -253C and 65 KPa (IM7/977-2)



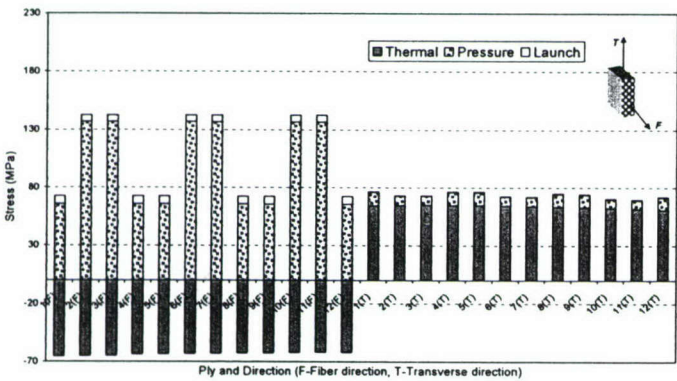
(b) at -253C and 132 KPa (IM7/977-2)



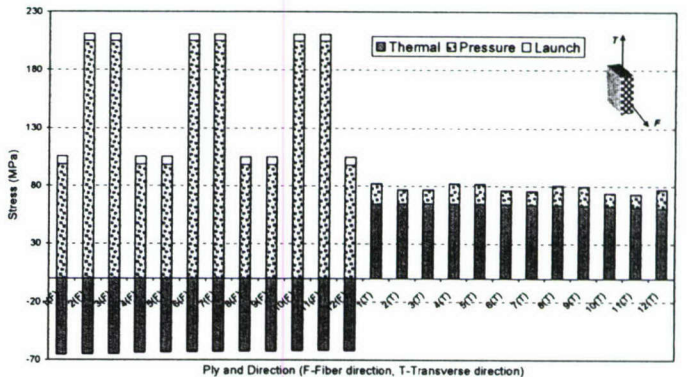
(c) at -253C and 290KPa (IM7/977-2)



(d) at -253C and 600 KPa (IM7/977-2)

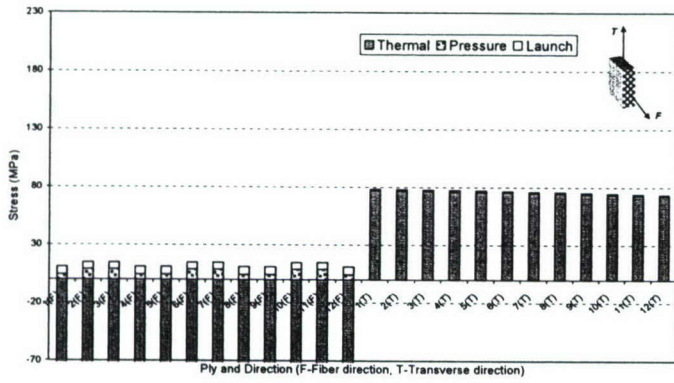


(e) at -253C and 1000 KPa (IM7/977-2)

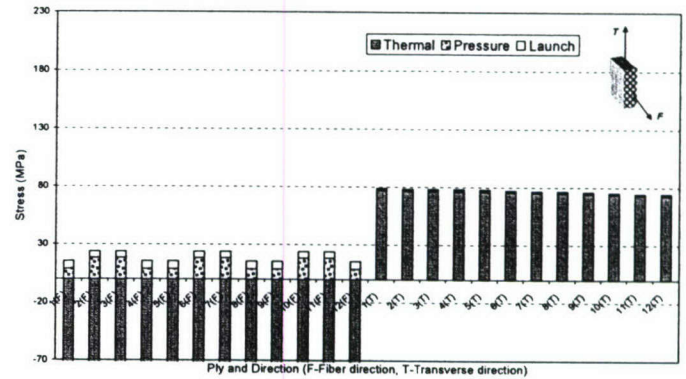


(f) at -253C and 1500 KPa (IM7/977-2)

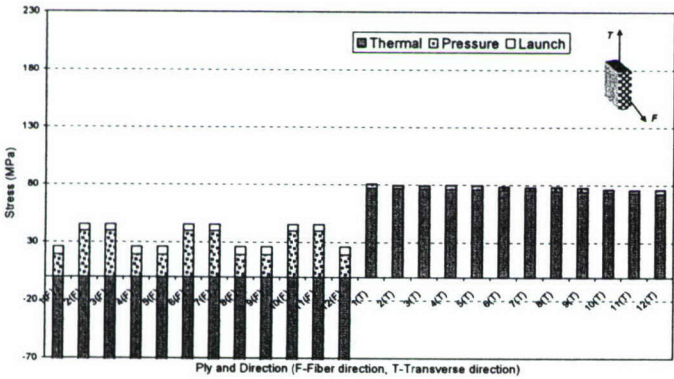
Figure (3). Thermal, pressure, and launch induced stresses of IM7/977-2 $[0/90/90/0/0/90]_s$ composite in fiber and transverse directions in the principal material coordinate at -253°C under various pressures.



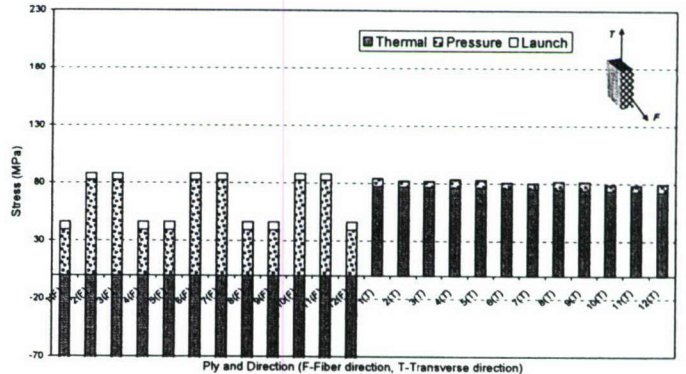
(a) at -253C and 65KPa (IM7/5250-4)



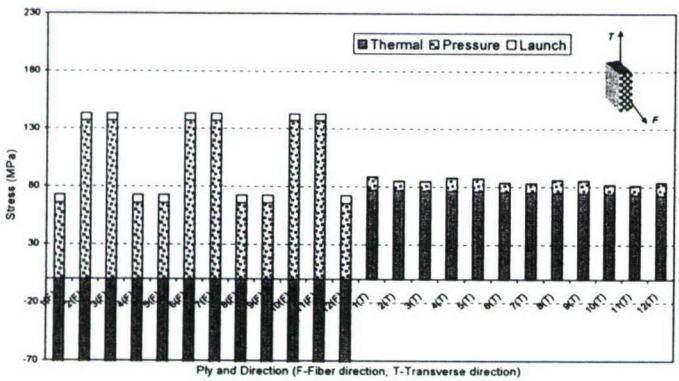
(b) at -253C and 132KPa (IM7/5250-4)



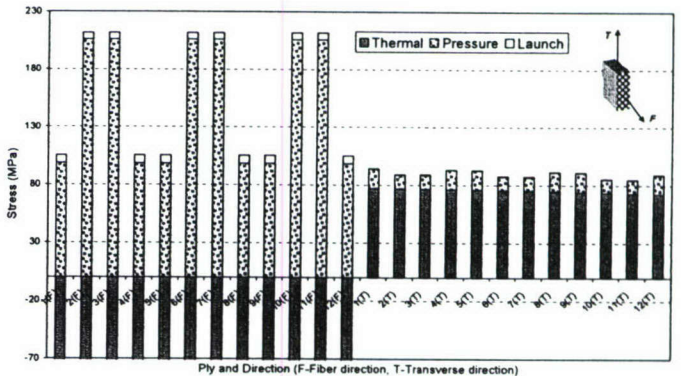
(c) at -253C and 290KPa (IM7/5250-4)



(d) at -253C and 600KPa (IM7/5250-4)



(e) at -253C and 1000KPa (IM7/5250-4)



(f) at -253C and 1500KPa (IM7/5250-4)

Figure (4). Thermal, pressure, and launch induced stresses of IM7/5250-4 $[0/90/90/0/0/90]_s$ composite in the fiber and transverse directions at -253°C under various pressures.

Our principal findings were as follows:-

- Thermal residual stresses applied on IM7/977-2 and IM7/5250-4 laminates are the most significant source (80-98% of the total stresses) to determine initial ply transverse matrix cracking and complete laminate matrix cracking.
- Once cracks initiate, causing ply stiffness decreases, the fuel pressure plays an important role in the progressive failure by raising pressure stresses on undamaged plies.
- Instantaneous temperature and temperature gradient updates caused by fuel transportation through microcracks, as well as laminate stiffness matrix updates, significantly affect the progressive failure behavior of laminates.
- For IM7/5250-4 at -253°C and 1500KPa fuel seepage based progressive analysis shows that an initial stage of ply failure may cause a complete laminate cracking which does not occur using the conventional laminate stiffness matrix update analysis.

PUBLICATIONS

1. J. Ju, R.J. Morgan, and J.N. Reddy, "Multiphysics Based Progressive Failure Analysis for Cryogenic Composite Fuel Tank Design", *Proceedings of ANTEC 2007 of Society of Plastics Engineering*, Cincinnati, Ohio, 2007 (accepted).
2. J. Ju, R.J. Morgan, E.E. Shin, and T. Creasy, "Characterization of Micro-cracking in M40J/PMR-II-50 under Thermal Cycling Combined with Mechanical Loading: Part I - Investigation of Main and Interactive Effects using Design of Experiment", *Journal of Composite Materials*, In print (2006).
3. J. Ju, R.J. Morgan, E.E. Shin, and T. Creasy, "Characterization of Micro-cracking in M40J/PMR-II-50 under Thermal Cycling Combined with Mechanical Loading: Part II – Failure Analysis", *Journal of Composite Materials*, In print (2006).
4. J. Ju, B.D. Pickle, R.J. Morgan, and J.N. Reddy, "An Initial and Progressive Failure Analysis for Cryogenic Composite Fuel Tank Design", *Journal of Composite Materials*, Accepted (2006).
5. J. Ju, R.J. Morgan, and, E.E. Shin, "Transverse Interface Failure of M40J/PMR-II-50 Composites under High Temperature Exposure", *Proceedings of 51st ISSE, SAMPE 2006*, Long Beach, CA, 2006.
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7. J. Ju, R.J. Morgan, and J.N. Reddy, Thermo-Mechanical Analysis of Composites under Combined Conduction Heating and Large Deflection Bending, *IMECE 2005-81262, ASME International Mechanical Engineering Congress & Exposition*, November 5-11, 2005, Orlando, Florida.
8. J. Ju, R.J. Morgan, T.C. Creasy, S. Hafernik, and E.E. Shin, "Statistical Approach to Evaluate Composite Damage", *Proceedings of ANTEC 2005*, Boston, MA, 2005.
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THESIS

1. B. Pickle. "Modeling Damage Growth Mechanisms of Composites During Stress-Thermal Cycling", M.S. Thesis, Texas A&M University (2004).
2. J. Ju, "Characterization of Composite Performance under Cryogenic Conditions", Ph.D. Thesis, Texas A&M University (2005).

TASK (II) CHARACTERIZATION OF AFR-PEPA-N IMIDE OLIGOMERS

The thermal cure reactions and associated kinetics of AFR-PEPA-4 oligomer and an model compound N-phenyl-[4-(phenylethynyl) phthalimide] were characterized by FTIR and DSC measurements in the 350-410C temperature range. The cure reactions involve a fast first-order reaction stage with the formation of polymers from the phenylethynyl end caps followed by a slow diffusion-controlled crosslinking. Modification of the oligomer end caps to produce lower cure temperatures was also achieved.

The crystal morphology of the AFR-PEPA-N oligomer was characterized and shown to produce network inhomogeneities during cure.

Full cure of AFR-PEPA-4 polyimides is achieved at 437.2°C, however for cure times of over an hour at 440-450°C major network chemical degradation also takes place.

AFR-PEPA-4 imide oligomer exhibits an early degradation in the 350°C to 440°C cure range with an associated 1-1.5% weight loss obtained by TGA analyses (10°C/min in air) (Figure(5)). The principal degradation and associated weight loss does not occur until above 500°C in this TGA analyses as illustrated in Figure (5). Greg Schoeppner, AFRL, has reported the early loss of fluorine in AFR-PEPA-4 imide oligomer [1].

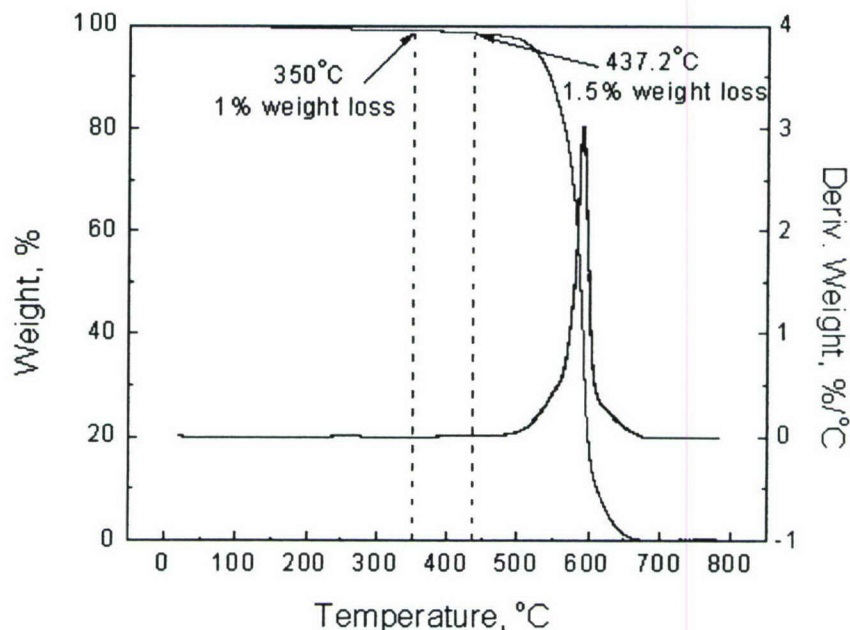


Figure (5) TGA Analyses of AFR-PEPA-4 Imide Oligomer (10°C/min in Air)

We studied the thermal degradation of AFR-PEPA-N imide oligomers by combined TGA-FTIR studies under a N₂ atmosphere (Figure (6)). From difference spectra analyses the principal chemical degradation changes involved the formation of aromatic isocyanate species (ArNCO) at 2284 cm⁻¹ wave-numbers, CO₂ at 2176cm⁻¹ wave-numbers and CHF₃ species at 1150cm⁻¹ wave-numbers. The appearance of these degradation species as a function temperature at a heating rate of 20°C/min is shown in Figure (6). The IR band intensities of the degradation species are shown in both tabular form and plots as a function of temperature in Figure (7). The CHF₃ degradation species are evolved in the 500-600°C, whereas the ArNCO and CO₂ degradation species are evolved at higher temperature in the 600-700°C range.

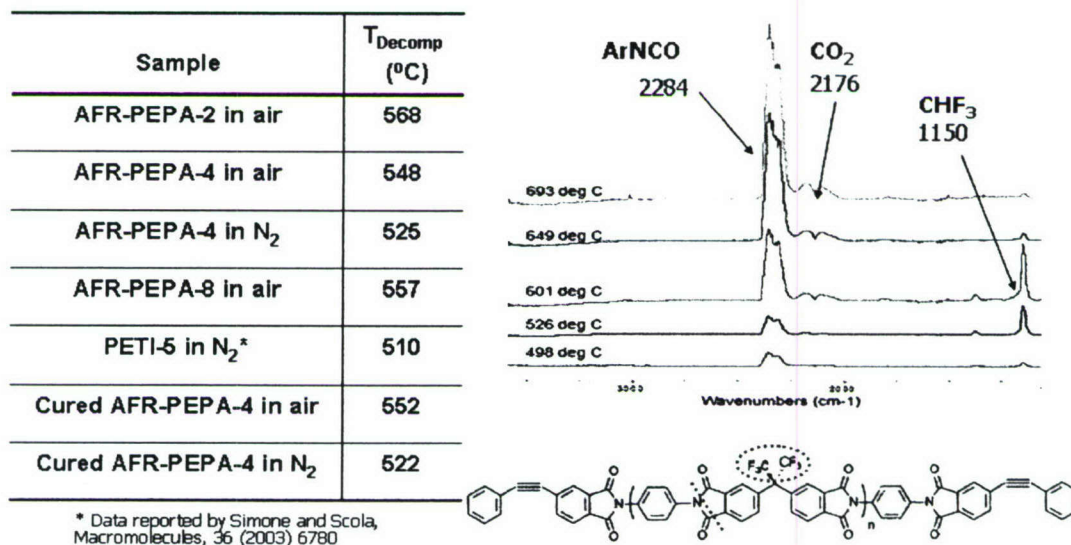


Figure (6). TGA-FTIR Analyses of AFR-PEPA-N Imide Oligomer at a Heating Rate of 20°C/min in an N₂ Atmosphere (T_{decomp} is the onset Major Weight Loss Temperature).

Isothermal Temperature(C)	ArNCO		CO ₂		CHF ₃	
	2284 Int. (mm)	%	2176 Int. (mm)	%	1150 Int. (mm)	%
498	3	7	0	0	1	8
526	4	10	0	0	7	54
601	17	42	1	50	13	100
649	30	73	1	50	1	8
693	41	100	2	100	1	8

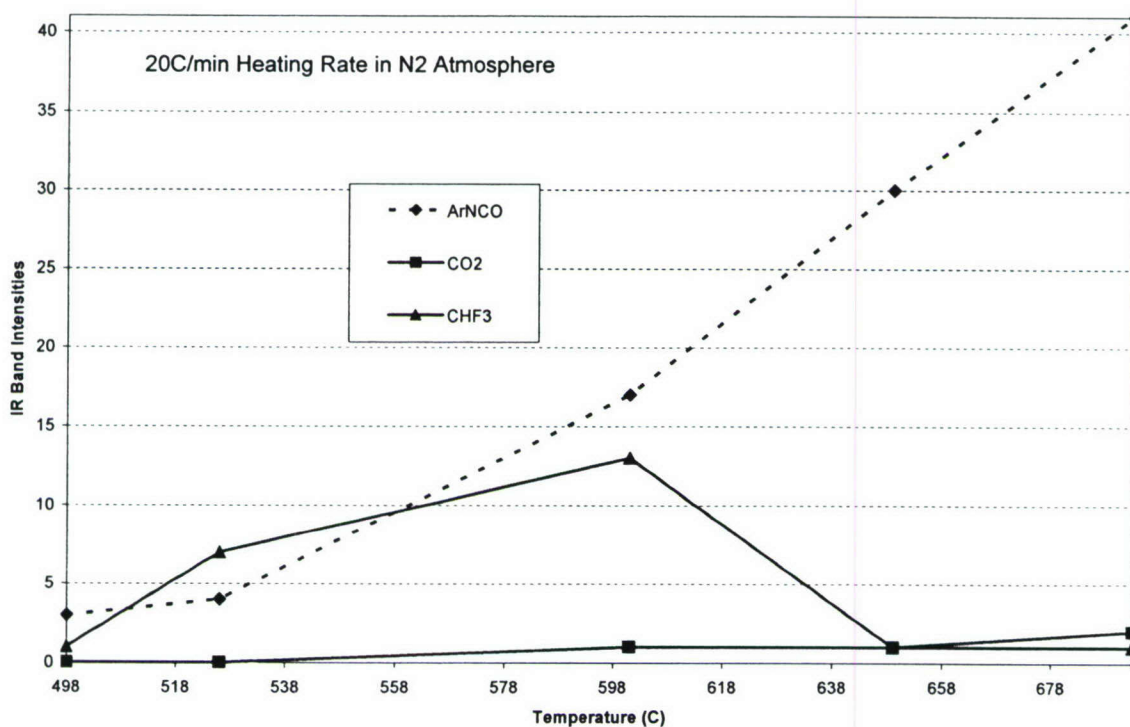


Figure (7) IR Band Intensities of ArNCO, CO₂ and CHF₃ Degradation Species of AFR-PEPA-N Imide oligomer as a Function of Temperature.

The early degradation weight loss spike of 1-1.5% weight loss observed in the 350-400°C range by TGA analyses maybe a result of the metal sample holder catalyzing early fluorine loss. Certainly, only 20% of the total imide fluorine content is lost at these low temperatures.

TGA analyses of the imide oligomer (initially uncured) and a 390°C, 1 hour cured polyimide in air and N₂ atmospheres are compared in Table (1). Weight loss at a specific temperature in the 500-600°C range is slightly greater in air than N₂. Char yields at 800°C are zero in air compared to 57-58% in N₂ indicating complete loss of the more volatile oxidation-induced degradation species.

Table (1). TGA Data of AFR-PEPA-4 and Its Cured Polyimide (Heating rate: 10°C/min)

Sample	T _d 5% (°C)	T _d 10% (°C)	Char yield at 800 °C (%)
AFR-PEPA-4 in air	524	544	0
AFR-PEPA-4 in N ₂	527	549	57.9
Cured AFR-PEPA-4 in air	524	544	0
Cured AFR-PEPA-4 in N ₂	529	553	57.4

FTIR and DSC studies as a function of isothermal cure for AFR-PEPA-4 polyimides reveal full cure at 410°C for 8 hours is not achieved. In Figure (8), a plot of T_g versus reaction conversion is shown and that full cure can be achieved at 437.2°C by extrapolation of this plot. For cure times at 440-450°C of over an hour the major degradation regime will be shifted into the cure zone (Figure (8)). The combined effects of crosslink density, T_g and degradation mechanisms upon the mechanical properties of the AFR-PEPA-N polyimides as a function of temperature and cure conditions have not as yet been ascertained.

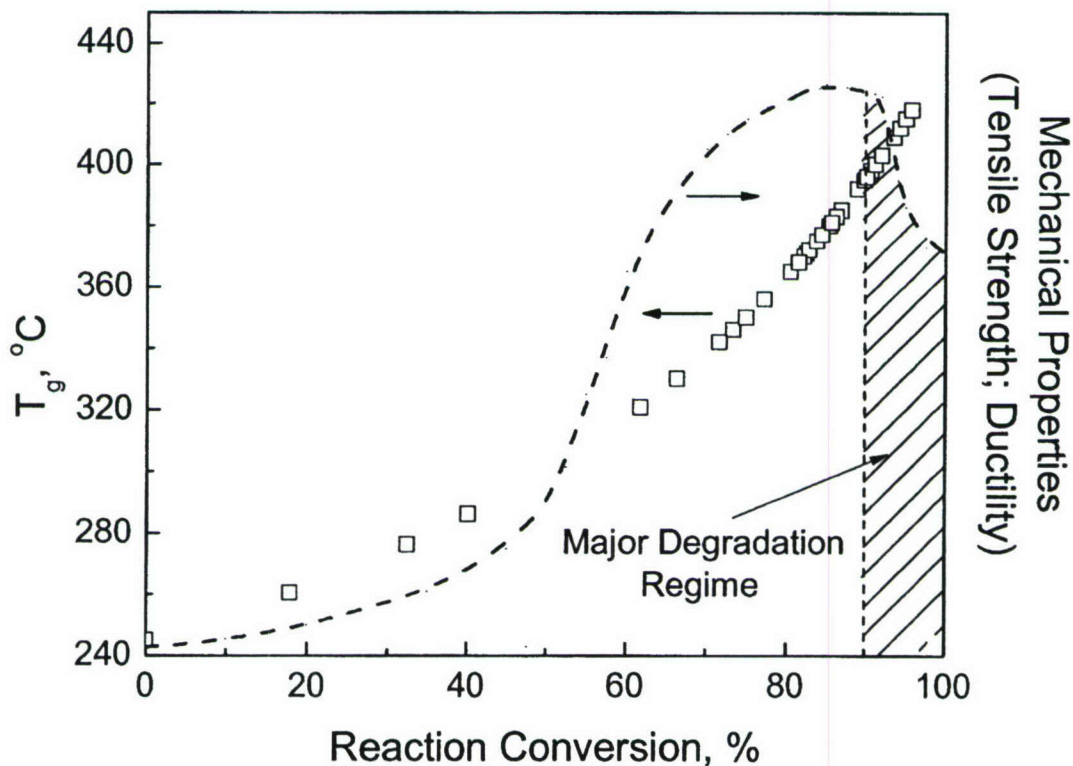


Figure (8) T_g versus Reaction Conversion for AFR-PEPA-4 Polyimide

PUBLICATIONS

1. Y. Li and R. J. Morgan, "Thermal Cure of Phenylethynyl-Terminated AFR-PEPA-4 Imide Oligomer and a Model Compound", Journal of Applied Polymer Science, 111, 4446-4453 (2006).
2. Y. Li, N. Obando, F. Tschen, and R.J. Morgan, "Thermal Analysis of Phenylethynyl End-Capped Fluorinated Imide Oligomer AFR-PEPA-4", Journal of Thermal Analysis and Calorimetry, 85, 125-129 (2006).
3. Y. Li, L.A. Murphy, J.E. Lincoln, and R.J. Morgan, "Phenylethynyl End-Capped Fluorinated Imide Oligomer AFR-PEPA-N: Morphology and Processability Characteristics", Macromolecular Materials and Engineering, Accepted (2006).
4. Li, Y., L.A. Murphy, and R.J. Morgan, "Morphology Investigation of AFR-PEPA-N Imide Oligomer and Their Cured Polyimides", Proceedings of 51st ISSE, SAMPE 2006, Long Beach, CA, 2006.
5. R.J. Morgan, Y. Li, J. Ju, E.E. Shin, L.A. Murphy, and N. Obando, "Structure-Property Relations of High Temperature Polyimide-Carbon Fiber Polymers", Proceedings of High Temple Workshop XXVI, Austin, TX, 2006.
6. Y. Li, R.J. Morgan, and F. Tschen, "Structure-Property Relations of Phenylethynyl Terminated Imide Oligomers", Proceedings of High Temple Workshop XXV, Paper EE, Point Clear, AL, 2005.

THESIS

1. Y. Li, "Synthesis and Cure Characterization of High Temperature Polymers for Aerospace Applications", Ph.D. Thesis, Texas A&M University (2004).
2. F. Tschen, "Synthesis of Novel Polyimides for Testing of Structure-Processing and Property Relations When Used to Form High Temperature Polymer Matrices", M.S. Thesis, Texas A&M University (2005).

TASK (III) METHODOLOGY TO MODEL PROGRESSIVE COMPOSITE FAILURE IN FUTURE HYPERSONIC SERVICE ENVIRONMENTS

The methodology to model the progressive composite laminate sequential failure paths of composites as cryogenic containment structures has been initially applied for polyimide-carbon fiber composites in future hypersonic vehicle service environments, where there will be rapid sequential overlapping physical, chemical, thermal and mechanical degradation mechanisms as illustrated in Figure (9). The mechanisms to be addressed together with the associated kinetics include:-

- Further AFR-PEPA-4 polyimide cross-linking;
- Oxidative surface degradation of AFR-PEPA-4 – carbon fiber composites;
- Composite strength and modulus decreases with increasing thermal exposure, that includes resin, fiber and fiber-matrix interface deterioration in mechanical properties;
- Moisture-induced composite blistering;
- Ablation/spalling – induced composite damage as a result of shock waves.

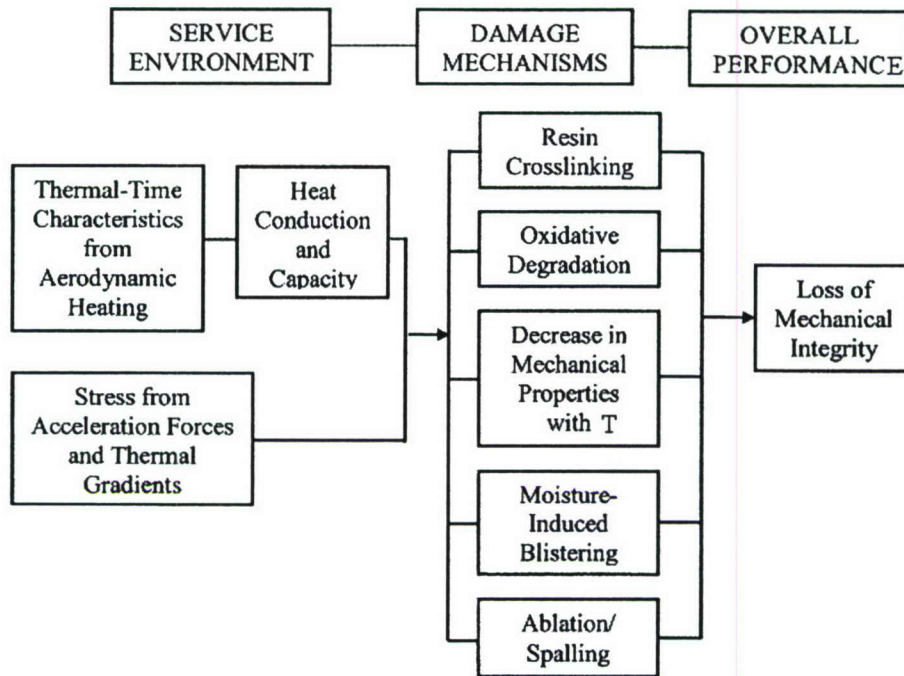


Figure (9). Future Hypersonic Vehicle Primary Structure Composite Failure Modeling

PUBLICATIONS

1. R.J. Morgan, T. Creasy, Y. Li, J. Ju, F. Tschen, N. Obando, O. Enuwi and J.E. Lincoln, "Composite Thermal-Induced Degradation Mechanisms and Protection for Future Aerospace Vehicles", Proceedings of 27th High Temple Workshop, Sedona, AZ, February, 2007.