Project Title:

CONSTITUTIVE MODELING AND TESTING OF POLYMER MATRIX COMPOSITES INCORPORATING PHYSICAL AGING AT ELEVATED TEMPERATURES

Grant No.:

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$196,614

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Technical Monitor: Dr. Thomas S. Gates

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Technical Objectives:

1. Advanced polymer matrix composites (PMC's) are desirable for structural materials in diverse applications such as aircraft, civil infrastructure and biomedical implants because of their improved strength-to-weight and stiffness-to-weight ratios. For example, the next generation military and commercial aircraft requires applications for high strength, low weight structural components subjected to elevated temperatures. A possible disadvantage of polymer-based composites is that the physical and mechanical properties of the matrix often change significantly over time due to the exposure of elevated temperatures and environmental factors. For design, long term exposure (i.e. aging) of PMC's must be accounted for through constitutive models in order to accurately assess the effects of aging on performance, crack initiation and remaining life. One particular aspect of this aging process, physical aging, is considered in this research. Physical aging is a thermoreversible process that causes the polymer matrix to become stiffer, more brittle, and the creep and stress
relaxation rates to be reduced. Due to the explicit time dependence of viscoelasticity, creep and recovery tests are a natural choice for studying the time dependent aging process. While a great deal of research has been performed detailing the effects of physical aging on polymers, very little information is available for high temperature PMC’s. The ultimate goal is to develop accurate analytical models and accelerated test methods needed to engineer advanced polymer matrix composites to ensure long-term structural integrity over the design life-time.

2. Adhesives and adhesive joints are widely used in various industrial applications to reduce weight and costs, and to increase reliability. Joints, in particular, have been and continue to be areas in which weight can be trimmed from an airframe through the use of novel attachment techniques. In order to save weight over traditional riveted designs, to avoid the introduction of stress concentrations associated with rivet holes, and to take full advantage of advanced composite materials, engineers and designers have been specifying an ever-increasing number of adhesively bonded joints for use on airframes. It is believed that the key to develop advanced adhesive joints to meet future challenges of elevated temperature, environmental exposure, and durability is to understand the mechanics of the adhesive joints based on the adhesive’s microstructure and the physics of interfacial adhesion. To obtain this understanding is the rational for a comprehensive study aimed at 1) establishing a correlation between the microstructural changes and the long term bond strength in adhesive joints by the use of interfacial fracture mechanics to characterize interfacial toughness as a function of the mode mixity at the debonding crack-tip and 2) developing finite element computations to obtain a calibration between the applied load and the crack tip stress intensity factor (or energy release rate) based on the load and specimen geometry.

3. The hybrid titanium composite laminate (HTCL) is a material system that merits attention because of its capability to operate in structures at higher temperatures. In this system, thin plies of titanium are adhesively laminated together using a high temperature resin with high modulus fibers included in the bondline. In laminated systems such as these, several researchers have shown improvements in fracture toughness and fatigue life over monolithic metals. Material systems such as the ARALL (Aramid Reinforced Aluminum Laminates) and GLARE laminates have essentially the same concept of the HTCL’s and are now flying on several commercial and military aircraft. The history of laminated metals has shown definite mechanical advantages that can translate to weight savings in commercial and military aircraft applications. The objective of this study is to investigate the laminated/hybrid technology applied to high temperature titanium alloys, and a graphite fiber reinforced high temperature thermoplastic polyimide adhesive, in hopes of demonstrating that these systems will be useful in the next generation high speed aircraft.

4. Processing is an important issue in the selection and design of high temperature PMC’s for structural applications. High performance polyimides have been selected as the polymer matrix for polymeric composites, and these materials are expected to exhibit time dependent, viscoelastic properties in high temperature environments. In addition, it is imperative that the cost of processing polyimides in the melt be reduced to make polyimides cost efficient in aerospace and other applications. In general, polyimides are difficult to process due to the rigid rod structure in their backbone and this limits their applications. This problem can be
addressed by the use of additives. Additives are materials which are physically dispersed in a polymer to enhance certain properties, thus making the polymer more suitable for industrial and consumer applications. An example of the use of additives in polymers is the incorporation of silicone additives in thermoplastics to improve the fire performance properties of plastics without negatively affecting processing and molding characteristics. It is hoped that these novel additives will reduce the melt viscosity of these polyimides for easier processing (i.e., resin transfer molding).

In response to the four aforementioned technical challenges, the overall objective of this research project is to characterize the effects of elevated temperature aging on the mechanical properties of polymer matrix composites. Specifically, the objectives are:

(A) To establish the viscoelastic behavior of IM7/K3B composites using creep compliance, strain recovery and the effects of physical aging on the time dependent response at several isothermal conditions below the glass transition temperature.

(B) To conduct an experimental study to obtain fracture toughness parameters (Gf) for a predictive scheme to estimate remaining life of a bonded joint.

(C) To assess the improvement in mechanical properties achieved by the influence of the titanium layer in HTCL’s by comparing the uniaxial tensile results of static strength at room temperature and to predict the laminate strength and load-deformation behavior based on the constituent material properties by performing an analytical study.

(D) To compare the rheological effects of blending polyimides with bisamic acid and bisimide additives aimed at reducing the melt viscosity.

**Technical Approach:**

1. **Physical Aging in Composites at Elevated Temperatures**

Micromechanical analyses and the finite element method were used to develop a model to predict the long term behavior of the graphite reinforced thermoplastic polyimide composite IM7/K3B. An analytical study was also undertaken to investigate the effects of the aging-time reference used in the time/aging-time superposition technique that provided the material properties required to make long term compliance predictions of the composite.

The IM7/K3B composite is a graphite reinforced thermoplastic polyimide with a glass transition temperature \( T_g \) of approximately 240°C. Along with micromechanical analyses and the finite element method, experimental results from neat K3B resin provided short term (momentary) creep compliance curves which allowed for evaluation of the long-term compliance behavior of the composite. The momentary sequenced creep/aging curves were collapsed (using time/aging-time superposition) through a horizontal (time) shift using the shortest, middle and longest aging time curve as the reference curve. Two matrix dominated loading modes, shear and transverse, were investigated in tension or compression. Creep compliance and the effects of physical aging on the time dependent response was measured for uniaxial loading at several isothermal conditions below \( T_g \) and compared to the model.
2. Durability of Adhesive Joints

The adhesive system used for the study was comprised of Ti-6Al-4V titanium adherends bonded with an adhesive (FM®x5) based on a polyimide developed at the NASA-Langley Research Center (LaRC™-PETI-5). Room temperature Mode I, Mode II and Mixed-Mode I and II fracture toughness results were obtained from Double Cantilever Beam (DCB), End Notched Flexure (ENF), and Cracked Lap Shear (CLS) tests, respectively. Testing was performed on specimens with no environmental exposure (as-received), as well as isothermally exposed for 5,000 hours at 177°C, and isothermally exposed to a hot/wet environment (80°C, 90%+ relative humidity). The fracture surfaces of the adhesive joints were also analyzed to determine the method by which the crack propagated (i.e. cohesive, interfacial, or both).

3. Hybrid Titanium Laminate System

Four unidirectional hybrid titanium composite systems were fabricated with different titanium alloys and titanium layer thicknesses. Two of the four HTCL systems were fabricated with the titanium Ti-15-3 alloy, while the other two systems were fabricated with the titanium Timetal β-21S alloy. Each HTCL system consisted of either three plies or four plies of the titanium alloy. Dog-bone specimens per ASTM D3552-77 were machined and tested statically to failure in tension using a servo-hydraulic test frame at room temperature.

4. Processible Polyimide Additives

Structural and thermal characterization of bisamic acid and bisimide additives were performed by elemental analysis, Fourier transform infrared spectroscopy (FTIR), nuclear magnetic spectroscopy (NMR), mass spectrometry, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The two test materials, NASA Langley Research Center’s phenylethynyl terminated imide LaRC™-PETI-5, and Dupont’s Avimid® KIII polymer K3B, were chosen because of their high stiffness, toughness, high thermal and thermooxidative stability, good damage resistance, environmental resistance, and retention of mechanical properties at high temperatures. These properties allow K3B and PETI-5 to be utilized in a variety of applications such as structural resins for advanced aircraft vehicles, missiles, coatings for electronic devices, and automotive frames.

The structural and thermal properties of the additives were determined. The melt viscosity was determined by a torque rheometer with digital control and data acquisition. The polyimides were blended with 5%, 10%, and 15% additives by weight. The effect of the additives on the melt viscosity of the polyimides were also determined. Direct comparisons between the amount of the additives and the reduction of the melt viscosity are made.

Research Accomplishments:

1. Physical Aging in Composites at Elevated Temperatures

In a composite, the two matrix dominated compliance terms associated with time dependent behavior occur in the transverse and shear directions. Layups selected to provide material properties for these two modes are the unidirectional 12-ply [90] and the angle-ply 8-ply [±45]
for the in-plane transverse and shear respectively. Rectangular test specimens measuring 20.32 cm. by 2.54 cm. of approximately 0.0135 cm. thickness were cut from laminated panels, as shown in Figure 1. Strain in the gage section is measured with high temperature foil strain gages applied in the center of the specimen.

![Specimen configuration and gage location for creep compliance tests.](image)

Figure 1. Specimen configuration and gage location for creep compliance tests.

In this study, a unidirectional composite was modeled and a square array packing of circular cross-section fibers was assumed. A schematic of the cross-section of the unidirectional fiber reinforced composite is shown in Fig. 2a, and for a normal load applied in the $x_2$-direction, the composite is subjected to plane strain deformation. Furthermore, due to symmetry and the periodicity of fiber spacing, the state of stress and deformation in the composite was completely defined by the stresses and strains in a quarter region of a unit cell as shown in Fig. 2b. Experimental data from momentary creep tests of K3B was used as the input for modeling the matrix, and the fibers were modeled as isotropic, linear elastic solids.

![Schematic of cross-section of composite](image)

Figure 2. (a) Transverse cross-section of the composite and (b) the quarter unit cell.
The long term viscoelastic behavior of a unidirectional composite can be modeled using the momentary creep compliance experimental results from the neat matrix material. When a polymeric composite is loaded transversely in compression, the effect of using different reference curves with time/aging-time superposition is most sensitive to the physical aging shift rate at lower test temperatures. Depending on the loading mode, the reference curve used can result in a more accurate long term prediction, especially at lower test temperatures. When longer loading times are considered, certain reference curves used with time/aging-time superposition can result in predictions that do not diverge from test data, as shown in Figure 3.

![Figure 3. Test versus predictions for long term transverse creep tests.](image)

2. **Durability of Adhesive Joints**

The focus of this phase of the research was to conduct an experimental study to obtain fracture toughness parameters (Gc) for a predictive scheme to estimate remaining life of a bonded joint. The adhesive system used for the study was comprised of Ti-6Al-4V titanium adherends bonded with an adhesive (FM®x5) based on a polyimide developed at the NASA-Langley Research Center (LaRC™-PETI-5). Room temperature Mode I, Mode II and Mixed-Mode I and II fracture toughness results were obtained from Double Cantilever Beam (DCB), End Notched Flexure (ENF), and Cracked Lap Shear (CLS) tests, respectively. Testing was performed on specimens with no environmental exposure (as-received), as well as isothermally exposed for 5,000 hours at 177°C, and isothermally exposed to a hot/wet environment (80°C, 90%+ relative humidity). The fracture surfaces of the adhesive joints were also analyzed to determine the method by which the crack propagated (i.e. cohesive, interfacial, or both). The test apparatus, ENF specimen configuration, and fracture toughness results are shown in Figures 4-6, respectively. In all loading cases, the threshold strain energy release rates were reduced as a result of 5,000 hours of isothermal exposure at 177°C, and further reduced due to 5,000 hours of exposure to 80°C and 90%+ relative humidity. In this case, the mode of failure depended on the particular type of loading and was virtually unaffected by the environmental exposure.
Figure 4. Elevated temperature servohydraulic test frame with long focal length microscope.

Figure 5. Schematic for the Ti-6Al-4V/FM®x5 end notch flexure specimen.

Figure 6. Effect of environmental exposure on Mode II fracture toughness.
3. Hybrid Titanium Laminate System

A schematic of the HTCL system used in this research is shown in Figure 7. The experiments showed that the titanium layer in these HTCL systems influences the mechanical properties. Higher yield strength in the titanium alloys results in HTCL's with greater ultimate strength. However, stiffer titanium alloys did not result in a HTCL with a higher elastic modulus. The yield strength of the titanium layer had no significant effect on the yield strength of the HTCL. If systems with higher strength-to-weight-ratios are of primary concern, as in applications for future high speed aircraft, HTCL systems that are fabricated with many thinner titanium plies show improvement over systems with fewer, thicker titanium plies.

![Figure 7. Schematic of the Hybrid Titanium Composite Laminate (HTCL).](image)

Good agreement was achieved between the analytical laminate analysis performed in this study and experimental values obtained for the Young's modulus and the strength of HTCL systems, as shown in Figure 8. The stress-strain curves and the stress level at which the titanium layers fail are predicted using Classical Lamination Theory and the Tsai-Hill failure criterion. The thermal residual stresses due to the curing cycle have been accounted for in the predictions. It was found that the nonlinear behavior before laminate failure did not significantly affect the analytical predictions, thus the use of an elastic-plastic laminate analysis is not required to predict the strength from constituent properties.

4. Processible Polyimide Additives

In this work, low molecular weight compounds, as shown in Figure 9, were used as additives for K3B and LARC-PETI-5. The symbol X in the figure represents 2 to 10 carbon chains (i.e., 6 for hexylaniline, 8 for octylaniline, or 10 for decylaniline). The melt viscosity was determined by a torque rheometer with digital control and data acquisition. The rheological studies showed that as the amount of additive incorporated into the polyimide is increased, there was a reduction of the melt viscosity (See Figures 10-13). The polyimide K3B showed an onset of reduction in melt viscosity at 281°C. For PETI-5, an onset of reduction in melt viscosity was shown at 243°C until 267°C. Above 267°C, the viscosity of the PETI-5 began to increase due to what is believed to be crosslinking. Some of the additives reduced the melt viscosity during the crosslinking, while others increased the melt viscosity. After crosslinking, the blends with larger amounts of additives showed a greater decrease in melt viscosity. At temperatures greater than 300°C, there was no advantage in increasing the concentration of additive. In general, the additives exhibited a minor effect on the glass transition temperature of the polyimides.
Figure 8. The stress-strain response of the 11 mils thick Titanium Ti-15-3 specimens.

Figure 9. Synthesis of bisamic acid and bisimide additives.
Figure 10. Viscosity plot for the octylaniline bisimide additive with K3B.

Figure 11. Viscosity for the octylaniline bisamic acid and bisimide additive with K3B at 330°C.
Figure 12. Viscosity plot for the octylaniline bisimide additive with PETI-5.

Figure 13. Viscosity for the octylaniline bisamic acid and bisimide additive with PETI-5 at 347°C.
Impact, Uniqueness, Benefits to Society, and Relevance to the Aeronautics Enterprise:

This funding enabled Dr. Veazie and several graduate and undergraduate students to conduct experimental and analytical research to explore the viscoelastic constitutive relationship between elevated temperature exposure and the change in mechanical properties that will lead to improved high-performance, high temperature structural polymer matrix composite materials. The funding allowed Dr. Veazie's mainstream research to focus on the development of accelerated test methods and life prediction methodology for the long term durability of polymer matrix composites for potential use on commercial aircraft, high-speed aircraft, and military vehicles.

Methods unique to this research include the use of a finite element micromechanics model to predict the long term viscoelastic behavior of PMC’s using the time dependent properties of the matrix material as input. Also unique is the use of interfacial fracture mechanics to establish a correlation between the microstructural changes and the long term bond strength in adhesive joints to characterize interfacial toughness as a function of the mode mixity at the debonding crack-tip.

The High Speed Civil Transport, envisioned to have a lifetime of over 60,000 flight hours at operating temperatures near 188°C and to travel at speeds of Mach 2, is the impetus for intensive design and development studies at NASA and major airframe developers. The results of this work is needed in demonstrating that these systems will be useful in this next generation high speed aircraft. The long term viscoelastic behavior of a unidirectional composite can be modeled using the momentary creep compliance experimental results from the neat matrix material. When a polymeric composite is loaded transversely in compression, the effect of using different reference curves with time/aging-time superposition is most sensitive to the physical aging shift rate at lower test temperatures. Depending on the loading mode, the reference curve used can result in a more accurate long term prediction, especially at lower test temperatures. When longer loading times are considered, certain reference curves used with time/aging-time superposition can result in predictions that do not diverge from test data.

In applications for future high speed aircraft, it was found that if systems with higher strength-to-weight-ratios are of primary concern, HTCL systems that are fabricated with many thinner titanium plies show improvement over systems with fewer, thicker titanium plies. Overall, the HTCL systems tested provide stronger alternatives to their corresponding monolithic metals. The nonlinear behavior before laminate failure did not significantly affect the analytical predictions, thus the use of an elastic-plastic laminate analysis is not required to predict the strength from constituent properties.

Interactions/collaborations with NASA Center Investigators:

Collaborations:  Dr. Thomas S. Gates
NASA Langley Research Center

Dr. Gates has been influential in the experimental methods and modeling efforts of Dr. Veazie for several years. Collaborations on projects including Durability Modeling Development for the
HIGH SPEED RESEARCH PROGRAM and Micromechanics Modeling and Computational Materials for the AIRCRAFT MORPHING PROGRAM has been ongoing.

Collaborations: Mr. Shannon C. Arnold
NASA Langley Research Center

Mr. Arnold has collaborated with Dr. Veazie on the processing of polymer matrix composites including resin transfer molding of composites. Mr. Arnold has also provided some of the composite materials used in this research.

Collaborations: Dr. Joycelyn Simpson
NASA Langley Research Center

Dr. Simpson has been instrumental in providing direction for graduate researchers under Dr. Veazie’s supervision in the processing of advanced polyimides. These graduate students have visited NASA-LaRC to work with Dr. Simpson in her laboratory.

Interactions/collaborations with U.S. Industry Investigators:

Collaborations: Mr. Ronald Zabora
The Boeing Commercial Airplane Group

Collaborations with Mr. Zabora include issues concerning the materials, experimental methods and procedures for durability modeling development for Boeing projects including the HIGH SPEED CIVIL TRANSPORT. Topics including fracture mechanics and viscoelastic properties of laminated composites, bonded joints, and hybrid composite laminates have been studied.

Collaborations: Dr. Jim Criss
Lockheed/Martin

Dr. Criss has collaborated with Dr. Veazie on the resin transfer molding of advanced polyimide resins and composites.

Interactions/collaborations with other NASA PIs:

Interactions: Dr. C. T. Sun
Purdue University

Interactions with Dr. Sun has been ongoing for the past few years. Dr. Sun recently organized a special ASTM Symposium on Time-Dependent and Nonlinear Effects in Polymers and Composites of which the Dr. Veazie was a presenter. Dr. Sun’s project DYNAMIC AND NONLINEAR RESPONSE AND FAILURE IN THICK-SECTION COMPOSITES AND LAMINATES has been influential in the development and progression of Dr. Veazie’s project.
Transitions (Accomplishments being used by others, especially Government Laboratories and U.S. Industries)

NASA Langley Research Center
Dr. Thomas S. Gates

Experimental methods and modeling efforts from this research has been useful on projects including Durability Modeling Development for the HIGH SPEED RESEARCH PROGRAM. Also, results from this research has been useful on Micromechanics Modeling and Computational Materials projects for the AIRCRAFT MORPHING PROGRAM.

The Boeing Commercial Airplane Group
Mr. Ronald Zabora
Mr. Ronan Cunningham

Composite material characterization, experimental methods and procedures from this research has been influential for composite structures and durability modeling development for the Boeing project HIGH SPEED CIVIL TRANSPORT.

Lockheed/Martin Aerospace Systems
Dr. Jim Criss

Processing methods to improve the durability of advance polymer matrix composite materials have been collaborated with Dr. Criss. Durability testing was performed in the hopes of demonstrating that resin transfer molded composites will be useful as structures for the F22 Fighter Aircraft.

Awards, Honors:


2. Dr. David R. Veazie: Publications Editor (Mechanical and Industrial Engineering), National Technical Association (NTA), appointed 1997.


Refereed Publications (Students):


**Publications (Students)/Presentations (by Students):**


Participants in research grant: (PI, Grad Students, Undergraduate Students; specify minority/female participants)

Principal Investigator: David R. Veazie (Minority – African American)
Graduate Student: Lanetria Garrett (Female, Minority – African American)
Graduate Student: Christie Gooch (Female, Minority – African American)
Graduate Student: Josiah Scott Lindsay (Minority – African American)
Undergraduate Student: Charmin Roundtree (Female, Minority – African American)
Undergraduate Student: Kerry Davis (Minority – African American)
Undergraduate Student: Ron Grover (Minority – African American)
Undergraduate Student: Genine Bryant (Female, Minority – African American)
Undergraduate Student: Keva Vaughn (Female, Minority – African American)

Other Grants/Contracts during Funding Period: (agency, title, period, budget)

P.I. Veazie
  Fracture Toughness Testing of Aged Bonded Joints Under Fatigue for Titanium Graphite Hybrid Laminates
  Grant No. 0375538 Boeing 7/15/98-5/14/99 $15,000

P.I. Veazie
  Computational Materials Research
  Grant No. NCC-1-270 NASA 12/15/97-12/14/98 $20,964

P.I. Veazie
  Impact Damage and Residual Strength of Structural Composites
  Grant No. N00014-97-1-0832 ONR 07/01/97-7/01/99 $230,000

P.I. Veazie
  Computational Materials - Macro-Level Composite Modeling
  Grant No. NAG-1-1919 NASA 05/01/97-12/01/97 $13,591