Graphite/Polyimide Composites Subjected to Biaxial Loads at **Elevated Temperatures**

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Abstract

- accomplishments from a five year study concerned First, we will review our most important research unidirectional and woven graphite/polyimide composites based on T650-35, M40J and M60J fibers embedded in either PMR-15 or PMR-II-50 with the prediction of mechanical properties of polyimide resins.
- experimentally verified on an eight harness satin (8HS) woven T650-35/PMR-15 composite aged in composites aged in nitrogen will be proposed and Then, an aging model recently developed for the nitrogen at 315°C for up to 1500 hours.
- The study was supported jointly between 1999 and 2005 by the AFOSR, the NASA Glenn Research Center, and the National Science Foundation.

We Were a Part of These Efforts!!!



Rocket Based Combined Cycle Combustion Chamber Support Structure

NASA Glenn Announcement, March 2004.

UEET (Ultra-efficient Engine Program). The support structure was prepared from a between NASA Glenn and Boeing to design, fabricate and test the support structure support chamber for a Rocket Based Combined Cycle engine successfully survived "A lightweight high temperature polymer matrix composite (HTPMC) combustor hot-fire testing at ATK-GASL. This testing concludes a three year collaboration and fulfills a GPRA (Government Performance Reform Act) milestone for the high temperature composite material, PMR-II-50"

4HS M40J/PMR-II-50 and 4HS M60J/PMR-II-50 Shear Testing of 8HS T650-35/PMR-15,

both (T650-35) and high (M40J and M60J) modulus graphite fibers with PMR-15 and PMR-II-50 polyimide resins tested under biaxial shear Mechanical behavior of unidirectional and woven graphite/polyimide composites based on medium dominated stress conditions over a temperature range of 20°C to 316°C under dry and wet been investigated experimentally and numerically. conditions has

M. Kumosa et al., Comparison of the 45° off Axis and Iosipescu Shear Tests for Woven Fabric Composite Materials, Composites Technology & Research, Vol. 24 (2002) pp. 3-16.

Temperatures Determined from the ±45° Tensile and Iosipescu Shear Tests, *Journal of Composites* M. Gentz et al., Mechanical Behavior of a Woven Graphite/PMR-15 Composite at Room and Elevated Technology & Research, Vol. 25, Issue 1 (2003) pp. 22-34.

M. Gentz, et al., In-Plane Shear Testing of Woven Graphite/Polyimide Composites with Medium and High Modulus Graphite Fibers at Room and 316°C Temperatures, *Composites Science and Technology*, Vol. 64 (2004) pp. 203-220.

Graphite/Polyimide Composites



Woven composite systems; plain (left) and eight harness satin 8HS (right)

A major limitation of woven fiber/polymer matrix composite systems is the inability of these materials to resist intralaminar and interlaminar damage initiation and propagation under sheardominated biaxial loading conditions. **Biaxial Shear Dominated Strength of** 8HS T650-35/PMR-15 System

- There are numerous shear test methods for woven fabric composites, each with its own advantages and disadvantages.
- and tensile tests. The application of these two graphite/polyimide composites at room and elevated temperatures was evaluated in Two techniques, which show much tests for the shear testing of woven potential, are the losipescu shear and ±45° this project both experimentally numerically.





Composites under Shear-Dominated Biaxial Loads, Mechanics of Composite Materials and Structures, Vol. 7 (2000) pp. 129-152.

SEM Analysis (Stages of Damage in 8HS T650-35/PMR-15)







Stages of crack initiation and propagation in 8HS T650-35/PMR-15 at room temperature under shear dominated in-plane loads. G. Odegard, K. Searles and M. Kumosa, Nonlinear Analysis of Woven Fabric-Reinforced Graphite/PMR-15 Composites under Shear-Dominated Biaxial Loads, Mechanics of Composite Materials and Structures, Vol. 7 (2000) pp. 129-152

Axis and losipescu Shear Tests for Woven Fabric Composite Materials, J. Composites Technology & M. Kumosa, G. Odegard, D. Armentrout, L. Kumosa, K. Searles and J. K. Sutter, Comparison of the ±45° Off-Research, Vol. 24, No. 1 (2002) pp.3-16. M. Gentz, D. Armentrout, P. Rupnowski, L. Kumosa, J. K. Sutter and M. Kumosa, Mechanical Behavior of a Woven Graphite/PMR-15 Composite at Room and Elevated Temperatures Determined from the \pm 45° Tensile and losipescu Shear Tests, Composites Technology & Research, Vol. 25 (2003) pp. 22-34

Iosipescu VS. ±45° Tensile Tests 8HS T650-35/PMR-15;

maximum loads from the ±45° and losipescu tests at room and Shear stresses at the onset of intralaminar damage and at the 316°C temperatures for the 8HS T650-35/PMR-15 system.

T650/PMR-15	Shear Stre	sses at the	Shear Stresse	s at Maximum
	Onset of li Damag	ntralaminar e [MPa]	Loads	[MPa]
Test	±45°	losipescu	±45°	losipescu
	(biaxial)	(shear)	(biaxial)	(shear)
at RT	56.6 ± 2.0	94.8 ± 1.3	82.0 ± 0.15	105.8 ± 2.6
at 315°C	37.3 ± 5.2	59.9 ± 1.2	50.8 ± 6.0	71.8 ± 4.2

G. Odegard, K. Searles and M. Kumosa, Nonlinear Analysis of Woven Fabric-Reinforced Graphite/PMR-15 Composites under Shear-Dominated Biaxial Loads, Mechanics of Composite Materials and Structures, Vol. 7 (2000) pp. 129-152.. M. Kumosa, G. Odegard, D. Armentrout, L. Kumosa, K. Searles and J. K. Sutter, Comparison of the ±45° Off-Axis and losipescu Shear Tests for Woven Fabric Composite Materials, J. Composites Technology & Research, Vol. 24, No. 1 (2002) pp.3-16. M. Gentz, D. Armentrout, P. Rupnowski, L. Kumosa, J. K. Sutter and M. Kumosa, Mechanical Behavior of a Woven Graphite/PMR-15 Composite at Room and Elevated Temperatures Determined from the ±45° Tensile and losipescu Shear Tests, Composites Technology & Research, Vol. 25 (2003) pp. 22-34.

Modeling of 8HS T650-35/PMR-15 Visco-Elastic Meso- & Micro-

dominated loads on the failure process of eight harness satin (8HS) T650-35/PMR-15, 3D models of the meso- and micro- unit cells were built. The magnitude of residual meso- and micro-stresses in the warp and fill tows and the stresses caused by purely mechanical shear and biaxial loads were numerically determined as a function of the cooling To understand the effect of biaxial and shear rate. B. Benedikt, P. Rupnowski and M. Kumosa, Visco-Elastic Stress Distributions and Elastic Properties in Unidirectional Graphite/Polyimide Composites with Large Volume Fractions of Fibers, Acta Materialia, Vol. 51, No. 12 (2003) pp. 3483-3493

Composite Subjected to Biaxial In-Plane Loads at Room Temperature, Composites Science and Technology, P. Rupnowski and M. Kumosa, Meso- and Micro-Stress Analyses in an 8HS Graphite/Polyimide Woven Vol. 63 (2003) pp. 785-799.

Visco-Elasto-Plastic Meso- Micro Modeling of 8HS T650-35/PMR-15



graphite/polyimide composites for visco-elasto-plastic micro- and meso-stress Finite element representations of unidirectional (left) and 8HS woven (right) analyses. P. Rupnowski, M. Gentz and M. Kumosa, Mechanical Response of a Woven Graphite/Polyimide Composite to In-Plane Shear Dominated Biaxial Loads at Room and Elevated Temperatures, Acta Materialia, Vol. 52, No. 19 (2004) pp. 5603-5613. Meso- & Micro- Stress Distributions in 8HS T650-35/PMR-15

Meso- and micro-stresses in the center of the tow in the undulation region of 8HS T650/PMR-15 for various external in-plane loads at room temperature.

			-			-
		Mes	o-Stresses [MPa	[]		Micro-Stresses [MPa]
\smile	(trans.	σ_{YY}	σ_{zz} (trans.	$\sigma_{\rm XZ}$ (in-	Failure	σ ₁ (max.
	olane)	(longi. in-	out of plane)	plane '	Index	principal stress
		plane)		shear)	T'sai-Hill	in the matrix)
	4	-119	18	-1	0.6	94
	6	-129	16	-1	1.1	107
	8	145	20	-1	0.7	102
	6	-98	19	108	3.9	208
	3	136	17	0	1.2	111
	1	-107	17	109	4.4	222
	0	167	20	109	4.0	216
		158	18	110	4.6	230

∆T residual stresses, TX(Z) applied in-plane tensions along the warp and fill tows, S in-plane shear with TX=TZ=S=100MPa

Visco-Elasto-Plastic Meso- Micro Modeling of 8HS T650-35/PMR-15



loads if the actual composite architecture as well as the fiber and matrix The macro-response of the composite to shear could be accurately predicted as a function of temperature and in-plane shear dominated properties are considered.

In-Plane Shear Dominated Biaxial Loads at Room and Elevated Temperatures, Acta Materialia, Vol. 52, No. 19 P. Rupnowski, M. Gentz and M. Kumosa, Mechanical Response of a Woven Graphite/Polyimide Composite to

(2004) pp. 5603-5613.

Critical Issues

- The weakest fracture mode in the 8HS T650/PMR-15 composite is the combined state of stress consisting of in-plane shear and biaxial Under biaxial shear dominated loads ($\pm 45^{\circ}$ off-axis), the tow cracks tension along the warp and fill tows. In shear (losipescu test), transverse tow cracks initiate at approximately 95 MPa shear stress. initiate at 57 MPa shear stress. This can be explained numerically.
- Linear elastic macro- and micro- stress analyses cannot explain the very complex fracture/failure process in woven graphite/polyimide linear macro-approaches are not suitable to explain the effect of laminates subjected to in plane shear dominated loads. Also, nonbiaxial loads and residual stresses on the damage initiation stresses.
- Visco-elasto-plastic analytical and FEM stress analyses are needed. In particular, the effect of manufacturing residual stresses on the failure process must be considered.
- The type of fracture and the critical loads will be affected by physical and chemical aging.

Residual Stresses and Tow Micro-Cracking



Cross-sections of woven 8HS T650-35/PMR-15 (left), 4HS M40J/PMR-II-50 (middle) and 4HS M60J/PMR-II-50 (right) composites after manufacturing and post curing

- depend composites graphite/polyimide ₽. **Residual** stresses primarily on:
 - Visco-elasto-plastic stiffness properties and CTEs of polyimide resins
- Fiber elastic properties (longitudinal, transverse, shear)
- CTEs of fibers (both longitudinal and transverse)
- Manufacturing conditions
- Aging conditions
- Fiber/matrix interfaces
- Composite architecture,
 - etc., etc, etc.

A methodology has been suggested for the evaluation of coefficients of thermal expansion (both longitudinal and transverse) of medium (T650-35) and high (M40J and M60J) modulus graphite fibers. The methodology was subsequently used to determine the stiffness and thermal properties of the fibers from the macroscopic input data of unidirectional and stiffness properties (longitudinal, transverse and shear) and woven composites based on the same fibers embedded either in PMR-15 or PMR-II-50 polyimide resins. P. Rupnowski, M. Gentz, J.K. Sutter and M. Kumosa, An Evaluation of Elastic Properties and Coefficients of Thermal Expansion of Graphite Fibers from Macroscopic Composite Input Data, *Proceedings of the Royal* Society, Vol. 461 (2005) pp. 347-369

Expansion Coefficients of Medium and High Modulus Graphite Fibers, Composites Part A; Applied Science P. Rupnowski, M. Gentz, J. K. Sutter and M. Kumosa, An Evaluation of the Elastic Properties and Thermal *and Manufacturing*, Vol. 36 (2004) pp. 327-338. T650-35, M40J, M60J; Elastic Properties

the temperature the fiber properties were resonance resins were obtained by properties of the T650-35, systems were measured using the three-component length dilatometry. Then, (re-calculated macrothermal M40J and M60J fiber composites and their neat of of The room for T650-35) coefficients calculated expansion oscillator method. Lhe



Expansion Coefficients of Medium and High Modulus Graphite Fibers, Composites Part A; Applied Science and P. Rupnowski, M. Gentz, J. K. Sutter and M. Kumosa, An Evaluation of the Elastic Properties and Thermal Manufacturing, Vol. 36 (2004) pp. 327-338.

Eshelby/Mori-Tanaka Approach

$$C_{f} = \left[\left(\frac{1}{f_{v}} - 1 \right) C_{m} (I - S) (C_{m}^{-1} - C_{c}^{-1}) + I \right] \left[C_{m}^{-1} - (S - f_{v} (S - I)) (C_{m}^{-1} - C_{c}^{-1}) \frac{1}{f_{v}} \right]^{-1}$$

$$\alpha_{f} = \frac{1}{f_{v}} C_{f}^{-1} \left[(C_{m} - C_{f}) (S - f_{v} (S - I)) - C_{m} \right] (\alpha_{m} - \alpha_{c}) + \alpha_{m}$$

where

 C_{p} $C_{c'}$ C_{m} are the stiffness matrices of the fibers, composite and resin, respectively

S is the Eshelby tensor and / is the identity matrix

 $lpha_{f}$, $lpha_{m}$, and $lpha_{c}$ are the column vectors of the CTEs for the fibers, matrix and composite, respectively

 f_{ν} is the volume fraction of fibers

Macro- to Micro-Approach

employed to compute the uncertainty of indirect evaluation of Classical error analysis based on the Monte Carlo method applied to the inverse Eshelby/Tanaka-Mori model was graphite fiber properties.



P. Rupnowski, M. Gentz, J.K. Sutter and M. Kumosa, An Evaluation of Elastic Properties and Coefficients of Thermal Expansion of Graphite Fibers from Macroscopic Composite Input Data, Proceedings of the Royal Society, Vol. 461 (2005) pp. 347-369. T650-35, M40J, M60J; "Final" Estimates

-	E _{f11} [GPa]	E _{f22} [GPa]	G _{f12} [GPa]	G _{f23} [GPa]	Vf12	CTE (long.) 10 ⁻⁶ /K	CTE (trans.) 10 ⁻⁶ /K
T650-	224	15.4	21.1	5.8	0.44	-1.16	13.3
35	% +	± 0.5	± 1.1	± 0.4	± 0.02	± 0.05	± 0.8
	(243)	(13.8)	(23.1)	(2.0)	(0.29)	(84)	(1.8)
M40J	325	10.8	20.8	3.9	0.22	-2.0	8.7
	± 19	± 0.3	± 2	± 0.1	± 0.05	± 0.1	± 1.6
	(377)					(83)	
M60J	500	9.4	I	I	I	-2.0	18.0
	± 2	± 0.5				± 0.2	± 4
	(588)					(-1.1)	

() from literature

- methodology is extremely sensitive to the accuracy of the input macro-data, especially in The newly developed experimental/numerical the case of the elastic properties.
- However, using the macro composite input length dilatometry in conjunction with EMT and FEM, high quality estimates of fiber data from the oscillator resonance method and properties were obtained.
- The methodology also works very well with thermal expansions of graphite fibers.

process. Numerous XRD measurements were made embedded AI and Ag inclusions placed in four ply 8HS woven and 6 ply unidirectional graphite/PMRcomposites were determined both experimentally to determine residual strains and stresses in unidirectional and woven (8HS) T650-35/PMR-15 and numerically as a function of the manufacturing Interlaminar residual thermal stresses 15 composites. B. Benedikt, M. Kumosa, P.K. Predecki, L. Kumosa, M.G. Castelli and J.K. Sutter, An Analysis of Residual Thermal Stresses in a Unidirectional Graphite/PMR-15 Composite Based on the X-ray Diffraction Measurements, *Composites Science and Technology*, Vol. 61, No. 14 (2001) pp. 1977-1994.

B. Benedikt, P. Rupnowski, L. Kumosa, J. K. Sutter, P.K. Predecki and M. Kumosa, Determination of Interlaminar Residual Thermal Stresses in a Woven 8HS Graphite/PMR-15 Composite Using X-Ray Diffraction Measurements, *Mechanics of Advanced Materials and Structures*, Vol. 9 (2002) pp. 1-20.

X-Ray Diffraction Tests on T650-35/PMR-15 **Composites with Embedded Inclusions**



X-Ray Diffraction Tests on T650-35/PMR-15 **Composites with Embedded Inclusions**



Aluminum inclusion



unidirectional plies



NORE THIS

Intel T650	-lamin -35/P	ar Res MR-15	5 Comp	Stress(Dosite	es in 8	HS
 Residual 35/PMR-1 	5 compo	s in unid osites we	lirectiona ere deter	il and 8H imined	HS T650	
 just o 	n cooling	(no exterr	nal loads a	pplied)		
 with e 	external be	ending loa	ds (small	and large)		
 after a 	aging in N	₂ and air				
	X-ray with	Eshelby/Mo	ori-Tanaka		Plate theory	
	σ11 [MPa]	σ 22 [MPa]	σ 33 [MPa]	σ 11 [MPa]	σ 22 [MPa]	σ 33 [MPa]
Linear elastic	70.7 ± 17	71.1 ± 17	36.7 ± 16	94.0	94.0	0
Visco-elastic	67.3 ± 17	67.6 ± 16	33.0 ± 16	63.1	63.1	0
Residual interl	aminar stre	esses in 8H and n	IS T650-35, o aging)	/PMR-15 (I	no externa	l loads

Fiber/Polyimide Composites Subjected to Aging X-Ray Diffraction Experiments on Graphite

15 composites subjected to aging either in air or nitrogen and (XRD) measurements of residual strains in embedded aluminum interlaminar stresses in unidirectional and woven 8HS T650/PMRspherical inclusions were performed to evaluate the residual external bending loads.





Unidirectional T650-35/PMR-15 system aged in nitrogen (left) and in air (right) for 1170 hours.

Composite Using X-ray Diffraction Measurements, Mechanics of Advanced Materials and Structures, Vol. 9 B. Benedikt et al. Determination of Interlaminar Residual Stresses in a Woven 8HS Graphite/PMR-15 (2002) pp. 375.

B. Benedikt et al., , Analysis of Stresses in Aluminum Particles Embedded Inside Unidirectional and Woven Graphite/Polyimide Composites Subjected to Large Bending Loads, Mechanics of Advanced Materials and Structures, Vol. 11, No. 1 (2004) pp. 31-49.

B. Benedikt et al., X-Ray Diffraction Experiments on Aged Graphite Fiber/Polyimide Composites with Embedded Aluminum Inclusions, Composites Part A, Vol. 35 (2004) pp. 667-681.

Our New Model of Aging in Nitrogen

Based on:

(8HS) Woven T650-35/PMR-15 Aged in Nitrogen" "The Mechanical Response of Eight Harness Satin :>q

P. Rupnowski, M. Gentz, D. Armentrout, J. K. Sutter and , M. Kumosa

Acta Materialia, Vol. 53, No. 17 (2005) pp. 4555published in: 4565.

Our model has not yet been presented to this community.

- The mechanical response of an eight harness aging in nitrogen at 315°C for up to approximately 1500 hours was investigated satin woven T650-35/PMR-15 composite to both experimentally and numerically.
- The aging stresses in the composite were numerically predicted on a meso-scale using the concept of a unit cell.

- shrinkage effects were considered in the Viscoelastic, age stiffening, and volumetric simulations to describe the mechanical behavior of the neat PMR-15 polyimide in the composite subjected to aging at 315°C.
- To verify the numerical predictions, the strength and stiffness of the composite were measured as a function of aging time using the ±45° tensile test.

Viscoelastic Properties of PMR-15

(upper right). Subsequently, long relaxation tests at 275, $\epsilon(t)$). Then, an optimization technique was employed to shift factors were obtained. and the horizontal thermal A series of mechanical 2 h performed under constant modulus E(t) for each test function of time ($\sigma(t)$ and 300, 325 and 350°C were constructed (lower right) determine the relaxation stresses and strains as a displacement to obtain a master curve was



•••

Age Stiffening & Shrinkage of PMR-15

ah in the previous constutive equation is a J.M., and Rabzak, C., (1997), "Physical and Chemical Aging Effects in PMR-15 Neat [Kamvouris, J. E., Roberts, G. D., Pereira, horizontal aging shift factor taken from Resin", *ASTM ŠTP 1302*, pp. 243-258.]

was determined for times ranging from 0 to The aging shrinkage strain rate for PMR-15 The same rate was assumed in the aging 300 h and was found to be -23.4.10⁻⁶/h. simulations of the composite for up to 1000h.



Aging Experiments

- Twenty-two specimens with the fibers aligned at ± composite panel. The dimensions of the specimens were 153.5 x 25.4 x 5.34 mm. Following waterjet 45° from their long axis were waterjet cut from a cutting the specimens were dried in a vacuum at 110°C for 24 h.
- The specimens were placed in an oven in a static nitrogen atmosphere at room temperature. The temperature of the oven was ramped at 5°C per minute until 315°C was reached.
- Once the isothermal aging temperature was achieved, the aging time started. From the twenty specimens four specimens each were aged at 288, 624, 958, 1296, and 1535 h.

Aging Experiments

- room temperature at a rate of 1 mm/min. The ± 45° tensile tests were performed at until failure.
- of three room temperature tensile tests at all aging time were performed and a minimum Two room temperature tensile tests at 0 other aging times was performed.
- During the ±45° tests, acoustic emission (AE) was monitored by a D9215 sensor from Physical Acoustic Corp. (PAC)



Results from the ±45° experiments on the aged composite specimens included:

(2) stress at the initiation of intralaminar (1) the ultimate strength of the damage as determined by AE, (3) the shear modulus ±45°specimens,

All as a function of aging time at 315°C.



Modeling

properties and shrinkage of Then, the properties of the tows were simulated using the unitand strains in the composite Eshelby/Mori-Tanaka model was employed to viscoelastic meso unit-cell representing the Subsequently, aging was 3 right). cell and the meso- stresses as introduced into a (see were determined function of time. the tows. the composite obtain The



Modeling Results



Numerical in- and out-of-plane shrinkage strains (*) as a function of aging at 315°C *) not yet experimentally verified).

Shear stress vs. shear strain diagrams and the shear moduli at 315°C before and after aging for 1000 hours. **Modeling Results**



The maximum transverse stress in the tows (above) after aging for 1000 hours at 315°C, as determined from the model, was approximately 85 PMa (upper limit, could be even lower!). After cooling without aging the stress is appr. 64 MPa.

Conclusions

- intralaminar damage, and the shear modulus of 8HS Aging in nitrogen at 315°C for up to 1500 hours had a very small effect on the strength, onset of T650-35/PMR-15.
- The stress relaxation in PMR-15 that takes place at elevated temperature substantially reduces aging stresses in the composite.
- The aging stresses inside the tows were much smaller than the cooling stresses after the manufacturing cycle.
- Our numerical predictions agreed well with the experimental results.