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14. ABSTRACT
The goal of this research was to establish applicability and effectiveness of novel continuous carbon nanofibers as nanoreinforcement in advanced organic matrix composites. The specific objectives were: (1) demonstrate applicability of continuous carbon nanofibers for delamination suppression in advanced PMC laminates; (2) explore manufacturing and characterize mechanical behavior of carbon nanofiber reinforced epoxy matrix nanocomposites. Continuous carbon nanofibers were successfully manufactured and used to reinforce interfaces in specially designed aerospace grade carbon-epoxy laminates. Static and fatigue Mode I and II fracture mechanics and edge delamination testing were performed. Substantial improvements in delamination toughness, mechanical strength, and fatigue life were observed for the first time. Pioneering multilayered carbon nanofiber reinforced nanocomposites were manufactured and evaluated. It was demonstrated that continuous carbon nanofibers may provide unique advantages for structural nanocomposite applications.

15. SUBJECT TERMS

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AFOSR GRANT F49620-03-1-0142

FINAL REPORT 03/05/2003 – 05/18/2007

GRANT DATA

AFOSR Grant No. F49620-03-1-0142
"Novel Continuous Carbon Nanofibers for the Next Generation Lightweight Structural Nanocomposites"
Principal Investigator: Yuris Dzenis, Department of Engineering Mechanics, University of Nebraska-Lincoln
AFOSR Program Director: Dr. Charles Lee

EXECUTIVE SUMMARY

A strategic goal of the U.S. Air Force is to be able to deliver munitions to targets anywhere around the globe from the United States in 55 minutes. This will require very high speeds and novel, very lightweight and temperature resistant materials. Nanoscale materials technology has been recognized as critical for the defense needs in the 21st century. Nanocomposites are promising emerging materials for structural and functional applications due to unique properties of their nanoscale constituents. However, the currently available nanocomposites based mostly on nanoparticles lack the high strength and stiffness required for structural applications. The advent of high-performance fibers and their introduction to advanced composites produced a revolution in the area of lightweight structural materials in the last decades. Further dramatic improvement of fiber properties is expected with the reduction of their diameters into the nanometer range. Superstrong nanofibers can lead to new, revolutionary levels of performance of composites. A spectacular example of the emerging nanofibrous material is carbon nanotubes (CNTs). CNTs have been recently shown to possess extreme mechanical and physical properties. However, CNTs produced by the bottom-up synthetic methods are discontinuous and their applications in composites are hindered by the difficulties with their processing, alignment, and achievement of high volume fractions.

In this project, a new class of nanoscale reinforcement, i.e. continuous carbon nanofibers was explored for the first time. A novel nanomanufacturing technology based on the electrospinning technology was utilized. Continuous carbon nanofibers were produced from polyacrylonitrile (PAN). Newly developed methods of controlled nanofiber deposition and alignment were utilized to produce oriented nanofiber assemblies. Fabricated carbon nanofibers were used in structural organic matrix composites with specific objectives to: (1) demonstrate applicability of continuous carbon nanofibers for delamination suppression in advanced PMC laminates; (2) explore manufacturing and characterize mechanical behavior of carbon nanofiber reinforced epoxy matrix nanocomposites. Continuous carbon nanofibers were used to reinforce interfaces in specially designed aerospace grade carbon-epoxy laminates. Static and fatigue Mode I and II fracture mechanics and edge delamination testing was performed. Substantial improvements in delamination toughness, mechanical strength, and fatigue life were observed for the first time. Pioneering multilayered carbon nanofiber reinforced nanocomposites were manufactured and evaluated. It was demonstrated that continuous carbon nanofibers may provide unique advantages for structural nanocomposite applications.

This project provides an initial body of knowledge for the development of a new family of advanced nanoreinforcing materials, i.e. high-performance continuous nanofibers for the next generation lightweight structural nanocomposites. These nanofibers can be produced at a reasonable cost compared to other high-performance nanomaterials, such as carbon nanotubes. Nanofiber continuity dramatically reduces the cost of their handling and processing into nanocomposites. Utilization of newly developed methods of nanofiber alignment makes possible fabrication of nanofibers with superior anisotropic properties. In addition, these methods enable fabrication of nanocomposites with higher volume fractions and complex nanoreinforcement architectures. The resulting continuous nanofibers and their organic matrix nanocomposites are expected to be usable in many DoD and civilian applications.

STATEMENT OF THE PROBLEM STUDIED

The goal of this research was to establish applicability and effectiveness of novel continuous carbon nanofibers as nanoreinforcement in advanced organic matrix composites. Two major objectives of this project were: (1) to demonstrate the effects of nanofibers on delamination toughness and durability of laminates by comparative static and fatigue fracture mechanics and edge delamination studies on composites with and without carbon nanoreinforcement at interfaces; (2) to explore manufacturing and characterize mechanical behavior of carbon nanofiber reinforced epoxy matrix nanocomposites.

SUMMARY OF THE MOST SIGNIFICANT RESULTS

Carbon Nanofiber Manufacturing

Continuous carbon nanofibers were manufactured from commercial PAN precursors utilizing electrospinning process. The nanofibers were stabilized (cross-linked) and carbonized at different carbonization temperatures. The as-spun, stabilized, and carbonized nanofibers were studied by SEM and XRD. The electrospun PAN and carbon nanofibers were uniform in diameter. The nanofiber samples did not require expensive purification, unlike VGCF or carbon nanotubes. XRD studies on the carbon nanofibers fired at different temperatures showed that higher temperature resulted in better nanostructure.

Manufacturing and Evaluation of Advanced PMC Laminates with Carbon Nanofiber Reinforcement at Interfaces – 1. Fracture Mechanics Evaluation

Continuous nanofibers manufactured from commercial PAN precursor were used to reinforce interlaminar interfaces in aerospace grade carbon-epoxy composites. Panels were manufactured with as-spun PAN, stabilized PAN, and carbon nanofibers inserted between plies of aerospace grade carbon-epoxy composites. Care was taken to eliminate warpage of nanofiber sheets during stabilization and carbonization. A specialized constrained thermal treatment system was introduced and used for this purpose. Fracture mechanics specimens were manufactured and Mode I and II interlaminar fracture testing was performed utilizing DCB and ENF tests, respectively. Toughening effects of as-spun PAN, stabilized PAN and carbon nanofibers were examined. Substantial toughening was observed for the first time with continuous carbon nanofibers. Comparisons of carbon nanofiber systems with polymer nanofiber systems (reinforced with as-spun PAN and stabilized PAN nanofibers) showed that largest improvements in the interlaminar fracture toughness (200% improvement in GIC and 60% in GIIC) were achieved with carbon nanofibers. The latter effect is nontrivial and promising as carbon nanofibers could be expected to be brittle. All improvements were achieved with a negligible increase in composite weight. SEM fractographic analysis showed nanofiber pullout and crack bridging as the major nanomechanisms of toughening.

Manufacturing and Evaluation of Advanced PMC Laminates with Carbon Nanofiber Reinforcement at Interfaces – 1. Evaluation of Edge Delamination

Edge delamination in pioneering laminated composites with hierarchical continuous carbon nano and conventional microfiber reinforcement was studied for the first time. Continuous carbon nanofibers were manufactured from commercial PAN precursors using previously developed techniques. These nanofibers were used to reinforce interfaces in aerospace grade carbon-epoxy laminates. The optimal laminate lay-up was designed based on modeling using a newly developed model of edge stresses in advanced composite laminates. The $[12_2/-12_2/0_2]_s$ lay-up was selected to excite the interlaminar shear stresses at edges. Panels were manufactured with and without carbon nanofibers at interfaces. Care was taken to eliminate warpage of nanofiber sheets during stabilization and carbonization. A specialized constrained thermal treatment system was introduced and used for this purpose.

Edge delamination testing was performed under quasistatic and fatigue loadings. Probabilistic analysis of the effects of nanoreinforcement was performed. Effects of carbon nanofibers on delaminating edge stresses were studied for the first time. Substantial improvements in delamination onset stress and ultimate strength were observed. Probabilistic analysis on multiple specimens showed that these improvements were statistically significant. Fatigue analysis showed substantial improvements in fatigue life and durability of the nanomodified composites. The improvements were achieved with a negligible increase in composite weight. SEM fractographic analysis showed nanofiber pullout and crack bridging as the major nanomechanisms of toughening. Coupled with substantial Mode I and II toughening observed in the previous reporting period, the results demonstrate high efficiency of novel continuous carbon nanofibers for nanoreinforcement of interfaces in advanced composite laminates. Studies of edge delamination demonstrate that carbon nanoreinforcement is capable of suppression of (theoretically singular) edge stresses causing delamination in composite structures.

Manufacturing and Evaluation of Pioneering Layered Epoxy-Carbon-Nanofiber Nanocomposites

Pioneering multilayered carbon nanofiber reinforced nanocomposites were manufactured and evaluated for the first time. Continuous carbon nanofibers were manufactured from commercial PAN precursors. Nanofiber sheets were stacked, impregnated with epoxy resin and cured under controlled temperature, vacuum, and pressure. Composites were tested by dynamic mechanical analysis and modified fracture mechanics methods.

Analysis showed substantial anisotropy of mechanical and fracture properties in these novel materials. Feasibility of manufacturing of continuous carbon nanofiber nanocomposites demonstrated in this project for the first time opens up unique prospects for the next generation structural nanofiber-reinforced nanocomposites.

LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Principal Investigator:

Y. Dzenis

Graduate Students:

Y. Wen (Ph.D., May 2004)

L. Liu (Ph.D., January 2007)

X. Ren (Ph.D., January 2007)

Undergraduate Student:

C. Petersen

Post-docs:

X. Wu, Y. Wen

LIST OF PUBLICATIONS AND OTHER OUTCOMES

Graduated PhD Students

Y. Wen, "Novel Continuous Carbon and Ceramic Nanofibers and Nanocomposites", Ph.D. Dissertation, Department of Engineering Mechanics, University of Nebraska-Lincoln, 2004 (Advisor: Y. Dzenis)

L. Liu, "Numerical and Experimental Analysis of Nanofiber Deposition and Alignment in Electrospinning", Ph.D. Dissertation, Department of Engineering Mechanics, UNL, 2007 (Advisor: Y. Dzenis)

X. Ren, "Nanomanufacturing and Analysis of Novel Continuous Piezoelectric Nanofibers", Ph.D. Dissertation, Department of Engineering Mechanics, University of Nebraska-Lincoln, 2007 (Advisor: Y. Dzenis)

Journal Papers

Dzenis, Y, "Spinning Continuous Nanofibers for Nanotechnology", *Science*, 304, 25 June 2004, 1917-1919

Dzenis, Y. and Wen, Y., "Direct Fabrication of Highly Aligned Dense Yarns of Continuous Polymer, Carbon, and Ceramic Nanofibers", *Science* (submitted)

Yuya, P.A., Wen, Y., Li, Z., Turner, J.A., Dzenis, Y.A., "Determination of Young's Modulus of Individual Electrospun Nanofibers by Microcantilever Vibration Method", *Applied Physics Letters* 90, 111909 (2007)

Wu, X., Ghoshal, G., Kartashov, M., Aslan, Z., Turner, J., and Dzenis, Y., "Experimental Characterization of Impact Damage Tolerance of a Cross-Ply Graphite Fiber/Epoxy Laminate", *Polymer Composites*, 2007 (in press)

Wu, X., Dzenis, Y., and Strabala, K., "Wrinkling of a Charged Elastic Film on a Viscous Layer", *Meccanica*, 2007 (in press)

Chiew, S.Y., Wen, Y., Dzenis, Y., and Leong, K.W., "The Role of Electrospinning in the Emerging Field of Nanomedicine", *Current Pharmaceutical Design*, special issue on Nanomedicine and Drug Delivery (invited review), 2006, 12, 4751-4770

Wu, X. and Dzenis, Y., "Droplet on a Fiber: Geometrical Shape and Contact Angle", *Acta Mechanica* 185, 215-225 (2006)

Wu, X. and Dzenis, Y., "Wave Propagation in Nanofibers", *Journal of Applied Physics* 100, 124318 (2006)

Wu, X. and Dzenis, Y., "Guided Self-Assembly of Diblock Copolymer Thin Films on Chemically Patterned Substrates", *Journal of Chemical Physics* 125, 174707 (2006)

Ren, X. and Dzenis, Y., "Novel Continuous Poly(vinylidene fluoride) Nanofibers", MRS Symp. Proc. Vol. 920 2006 Materials Research Society 0920-S03-03

Wu, X.-F. and Dzenis, Y., "Electrohydrodynamic instability of thin conductive liquid films", *Journal of Physics D: Applied Physics* 2005, 38 (16): 2848-2850

Wu, X.-F., Dzenis, Y., "Elasticity of Nanofiber Networks", *J. Appl. Physics*, 98, 093501 (2005)

Wu, X.-F. and Dzenis, Y., "Experimental determination of probabilistic edge-delamination strength of a graphite-fiber composite," *Composite Structures*, 2005, 70(1): 100-108

Wu, X.-F. and Dzenis, Y., "Determination of dynamic delamination-initiation toughness of a graphite-fiber/epoxy composite using Hopkinson pressure bar," *Polymer Composites*, 2005, 26(2): 165-180

Wu, X.-F. and Dzenis, Y., "Antiplane surface acoustic waves (SAWs) propagating in elastic half-plane coated with an anisotropic laminate," *Composite Science & Technology*, 2005, 65(11-12): 1761-1768

Kwon, O. Y. and Dzenis, Y., "Embedded PVDF Film Sensor for In-Situ Monitoring of Structural Integrity of Laminated Composites", *Key Engineering Materials*, 2004, no. 270/273, pp. 1929-1934

Wu, X.-F., Dzenis, Y., and Gokdag, E., "Edge-cracked orthotropic bimaterial butt joint under anti-plane singularity," *International Journal of Nonlinear Sciences and Numerical Simulation*, 2004, 5(4): 347-354

Wu, X.-F., Dzenis, Y., and Rinschen, B.D., "Screw dislocation interacting with interfacial edge-cracks in piezoelectric bimaterial strips," *International Journal of Nonlinear Sciences and Numerical Simulation*, 2004, 5(4): 341-346

Dzenis, Y., Qin, M., and Pagano, N., "A Method of Evaluation of Transverse Critical Energy Release Rate (Fiber Failure Mode) in Advanced Composites", *International Journal of Fracture*, 2003, Vol. 118, No. 1, pp. 11-16

Wu, X.-F., Dzenis, Y., and Fan, T.-Y., "Two Semi-Infinite Interfacial Cracks Between Two Bonded Dissimilar Elastic Strips", *International Journal of Engineering Science*, 2003, Vol. 41, No. 15, pp. 1699-1710

Wu, X.-F., Dzenis, Y., and Zou, W.-S., "Interfacial Edge Crack between two Bonded Dissimilar Orthotropic Strips under Antiplane Point Loading", *ZAMM*, 2003, Vol. 83, No. 6, pp. 419-422

Dzenis, Y.A., "Cycle-based Analysis of Damage and Failure in Advanced Composites Under Fatigue. 1 - Experimental Observation of Damage Development Within Loading Cycles", *International Journal of Fatigue*, 2003, Vol. 25, No. 6, pp. 499-510

Dzenis, Y.A., "Cycle-based Analysis of Damage and Failure in Advanced Composites Under Fatigue. 2 - Stochastic Mesomechanics Modeling", *International Journal of Fatigue*, 2003, Vol. 25, No. 6, pp. 511-520

Books Edited

"Progress in Non-Destructive Evaluation", S. Joshi, Y. Dzenis, Eds., Proceedings of the NDE Symposium, 2004 ASME International Engineering Congress and Exposition (IMECE2004), American Society of Mechanical Engineering, 2004

"Progress in Non-Destructive Evaluation", Y. Dzenis, C. Cetinkaya, Eds., Proceedings of the NDE Symposium, 2003 ASME International Engineering Congress and Exposition (IMECE2003), American Society of Mechanical Engineering, 2003

Honors / Awards

Principal Investigator:

2007	Sigma Xi 2007 Outstanding Scientist Award
2004	Invited perspective on continuous nanofibers in *Science* (first paper on electrospinning or continuous nanofibers in *Science/Nature*)
2004	Fellowship and Visiting Professorship, Laboratory of Modeling and Structural Optimization, University of Paris-VI, France
2004	UNL College of Engineering Faculty Research Award in the rank of Full Professors (one per year per College)
2003	Endowed McBroom Chair and Professor, University of Nebraska-Lincoln
2003	UNL College of Engineering Faculty Service Award
	Multiple invited plenary and keynote lectures at national and international conferences (2003-2007)

INTERACTIONS/TRANSITIONS

Conference Presentations

Dzenis, Y., "Novel Continuous Carbon Nanofibers and Nanocomposites", 2006 AFOSR Polymer Matrix Composite Review, Long Beach, April 2006

Dzenis, Y., "Novel Continuous Carbon Nanofibers and Nanocomposites", 2005 AFOSR Polymer Matrix Composite Review, San Diego, August 2005

Dzenis, Y., "Next Generation Structural Supernanocomposites", International Conference on Composite Materials ICCM-15, Durban, 2005 (invited plenary lecture)

Dzenis, Y., "Nanomanufacturing of Continuous Nanofibers and Products", International IUPAC Conference 2005, Mauritius, 2005 (invited plenary lecture)

Dzenis, Y., "Novel Continuous Nanofibers: Nanomanufacturing and Properties", International Conference NanoInsight-2005, Luxor, 2005 (invited plenary lecture)

Dzenis, Y., "Advanced Continuous Nanofibers and Nanocomposites", World Forum Nanocomposites'2005, San Francisco, 2005 (invited lecture)

Dzenis, Y., "Advanced Continuous Nanofibers for Structural Nanocomposites", International Conference MCM-13, Riga, Latvia, 2004 (invited plenary lecture)

Dzenis, Y., "Manufacturing of Continuous Ceramic Nanofibers", 3rd DoD U.S.-Korea Workshop on Nanotechnology, 2004, Seoul (sponsored by AFOSR; organizer – Dr. Les Lee, AFOSR) – invited expert-speaker and member of US government delegation

Dzenis, Y., "Novel Advanced Continuous Nanofibers as Next Generation Reinforcement for Composites", European Conference ECCM-11, Rhodes, Greece, 2004, Vol II, p. 26

Dzenis, Y., "NDE Monitoring of Cracks in Adhesive Composite Joints", ASME IMECE 2004-61305, Anaheim, CA, Nov 2004

X. Wu and Y. Dzenis, "Experimental study on dynamic delamination toughness of a graphite-fiber/epoxy composite with interface modified by nanofibers", The 41st Annual SES Technical Meeting, Lincoln, NE, 2004

Y. Wen and Y. Dzenis, "Advanced Laminated Composites with Nanofiber Reinforced Interfaces", The 41st Annual SES Technical Meeting, Lincoln, NE, 2004

X. Wu and Y. Dzenis, "Elasticity of planar random fiber networks", The 41st Annual SES Technical Meeting, Lincoln, NE, 2004

X. Wu and Y.Dzenis, "Surface Acoustic Solitons in Elastic Half-Space Coated with Piezoelectric Film", The 41st Annual SES Technical Meeting, Lincoln, NE, 2004

X. Wu and Y. Dzenis, "Surface acoustic wave (SAW) propagation in anisotropic-coated solids", The 41st Annual SES Technical Meeting, Lincoln, NE, 2004

L. Liu and Y. Dzenis, "Electric Field-Assisted Nanofabrication of Highly Oriented Electrospun Nanofibers", The 41st Annual SES Technical Meeting, Lincoln, NE, 2004

Dzenis, Y., "Modeling and Mechanical Behavior of Continuous Ceramic Nanofibers", NSF Nanoscale science and Technology Grantees Conference, Washington, D.C., December 2004

Dzenis, Y., "Electrospinning of Nanofibers for Composite Laminates", 2004 Polymer Matrix Composite Review, Long Beach, CA, May 2004 (Presented by Dr. X. Wu)

Dzenis, Y., "Next Generation Nanofibers", AFOSR Panel, Dayton, Oct 2003 (organizer - Dr. Charles Lee, AFOSR) as part of SAMPE Meeting in Dayton, OH. This Workshop was attended by researchers from AFRL, academia, and aerospace industry

Dzenis, Y.A., "High-Performance Nanofibers and Nanocomposites", ICMAT, Singapore, Dec 2003 (Invited Plenary Lecture)

Petersen, B. and Dzenis, Y., "Novel Composites with Nanoparticle Reinforced Interfaces", SES 40th Tech Meeting, Ann Arbor, October 2003

Dzenis, Y.A., "Research on High-Performance Continuous Nanofibers", NSF Rushmore Workshop on Nanotechnology, Aug 2003 (Invited Expert Presentation)

Dzenis, Y.A., "Nanofibers and Structural Nanocomposites", 5th International Conference on Advanced Composites, Corfu, Greece, May 2003 (Invited Keynote Lecture)

Dzenis, Y., Qin, M., and Pagano, N., "Evaluation of Transverse Critical Energy Release Rate (Fiber Failure Mode) in Advanced Composites", 9th International

Conference on The Mechanical Behavior of Materials, Geneva, Switzerland, May 2003

Interactions with AFRL and Private Sector

Multiple lectures and participations by the PI in technology reviews on organic matrix composites, nanocomposites, nanotechnology at AFRL

Invited presentation at AFOSR US-Korea workshop on Nanomanufacturing in Seoul, 2004

Discussions with two aerospace companies on technology transfer

Other Interaction / Dissemination Activities

A unique new course EM 491/891 "Nanocomposites" was developed and taught by the PI (Spring 2005)

The PI continued development of $2.1M Advanced Nanomaterials and Nanomanufacturing Laboratories (Director – Y. Dzenis): among other things obtained external funding ($330,000, DURIP/AFOSR) for acquisition of ultrafast digital imaging system. The laboratories were extensively used in this project.

The PI developed a winning NRI proposal to establish a unique National Nanofiber User Facility at UNL. The facility will be available for use by DoD researchers.

APPENDIX: METHODS, PROCEDURES, AND DATA OUTCOMES

Novel Continuous Carbon Nanofibers and Nanocomposites: Methods, Procedures, and Results

AFOSR Grant F49620-03-1-0142

PI: Yuris Dzenis
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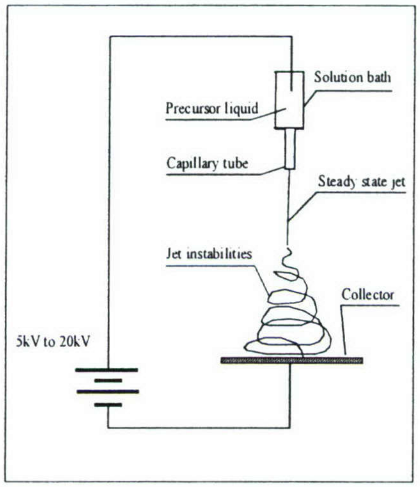
(402) 472-0713, ydzenis@unl.edu

AFOSR Program Director: Dr. Charles Lee

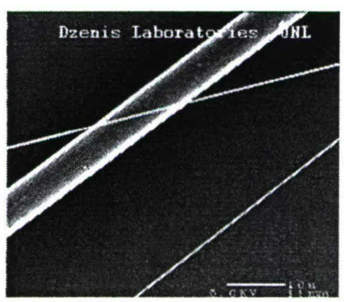
Project Objectives

- Explore feasibility and further develop nanomanufacturing methods for novel continuous carbon nanofibers and their nanocomposites
- Demonstrate applicability of continuous carbon nanofibers for delamination suppression in advanced polymer matrix composite laminates
- Explore manufacturing and characterize mechanical behavior of carbon nanofiber reinforced epoxy matrix nanocomposites

Nanofiber Manufacturing

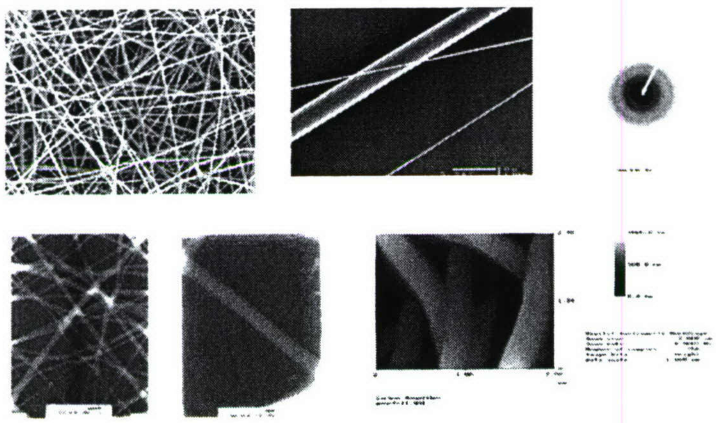


Example of Continuous Nanofiber

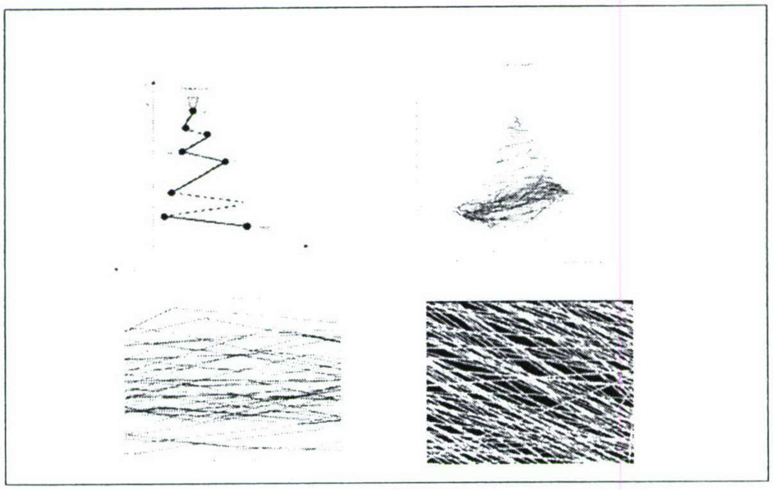


Commercial and electrospun
carbon fibers

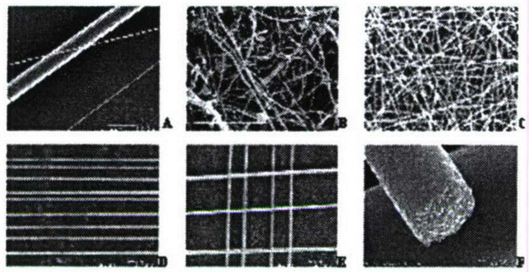
Fabricated Carbon Nanofibers



Modeling-Based Development of Methods of Nanofiber Alignment



Invited Perspective on Continuous Nanofibers in *Science*



Y. Dzenis, "Spinning Continuous Nanofibers for Nanotechnology", *Science*, 2004, 1917-1919

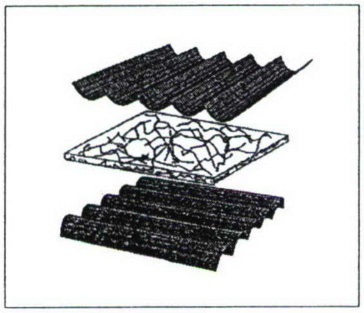
Next Big Nanotech - Comparison of commercial advanced carbon fiber, one of the smallest advanced fibers available, and electrospun continuous nanofiber (A). Comparison of vapor grown commercial carbon nanofibers (B) and electrospun carbon nanofibers (C) showing substantially improved nanofiber uniformity and sample purity. Examples of highly aligned and spaced linear and orthogonal assemblies of continuous nanofibers produced by the gap method of alignment developed by the PIs group at UNL (D, E). Cross-section of pioneering continuous nanocrystalline zirconia nanofiber produced at UNL for potential applications in supertough ceramics (F).

Problem of Delamination

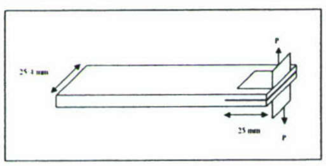
- Fracture along interfaces between plies in advanced composite laminates
- Theoretical singularity of peel and shear stresses near edges caused by ply properties mismatch
- Straight, non-reinforced interlaminar plane with low fracture resistance in laminates

Proposed Solution

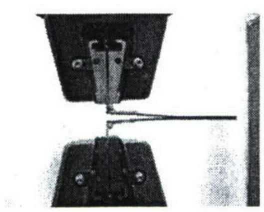
- Nanofiber reinforcement at interfaces (UNL patents awarded and pending)



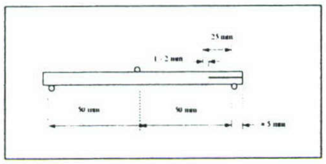
Evaluation of Mode I Fracture Toughness



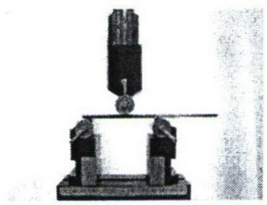
$$G_{IC} = \frac{\int_0^{\delta_B} P(\delta)d\delta - \frac{1}{2}P_B\delta_B}{w(a_B - a_0)}$$



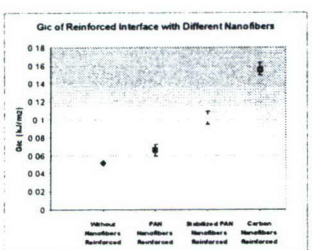
Evaluation of Mode II Fracture Toughness



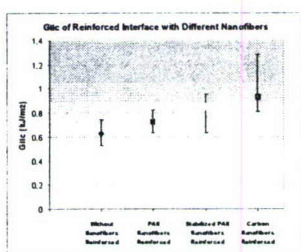
$$G_{IIC} = \frac{9P_C \delta_C a^2}{2W(2L^3 + 3a^3)}$$



Toughening with Nanoreinforcement

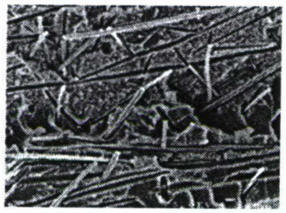


Mode I

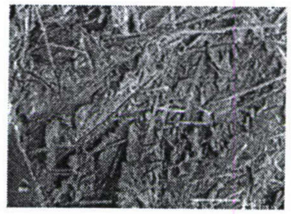


Mode II

Nanomechanisms



Mode I

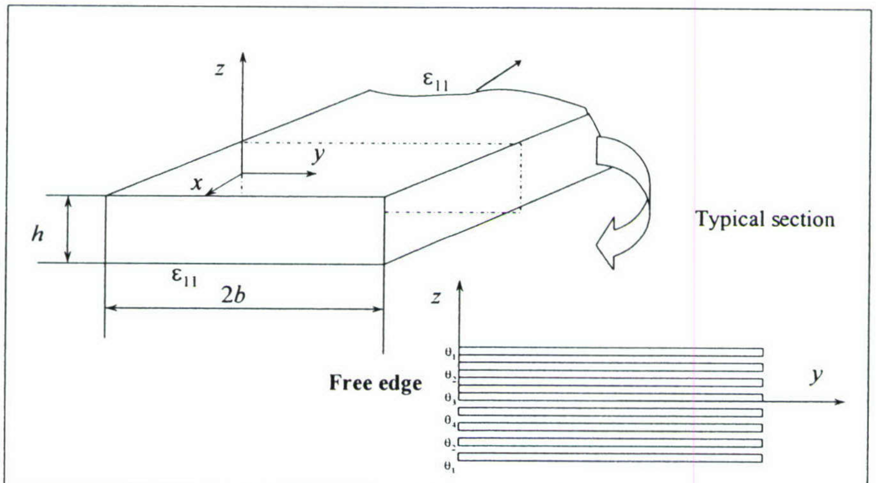


Mode II

Edge Delamination Analysis

- Free edge stress analysis and laminate design
- Experimental evaluation
- Evaluation of nanomechanisms

Free Edge Stress Analysis



Free Edge Stress Analysis

$$\begin{Bmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\\ \varepsilon_5\\ \varepsilon_6\end{Bmatrix}=\begin{bmatrix}S_{11} & S_{12} & S_{13} & 0 & 0 & S_{16}\\ S_{12} & S_{22} & S_{23} & 0 & 0 & S_{26}\\ S_{13} & S_{23} & S_{33} & 0 & 0 & S_{36}\\ 0 & 0 & 0 & S_{44} & S_{45} & 0\\ 0 & 0 & 0 & S_{45} & S_{55} & 0\\ S_{16} & S_{26} & S_{36} & 0 & 0 & S_{66}\end{bmatrix}\begin{Bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6\end{Bmatrix}+\begin{Bmatrix}\alpha_1\\ \alpha_2\\ \alpha_3\\ 0\\ 0\\ \alpha_6\end{Bmatrix}\Delta T$$

Boundary Conditions

$\sigma_2 = \sigma_4 = \sigma_6 = 0$, at $y=0, b$

$\sigma_3 = \sigma_4 = \sigma_5 = 0$, at $z=\pm h/2$

Laminate is assumed to be in a state of plane strain in the x-direction, and ε_1 is constant

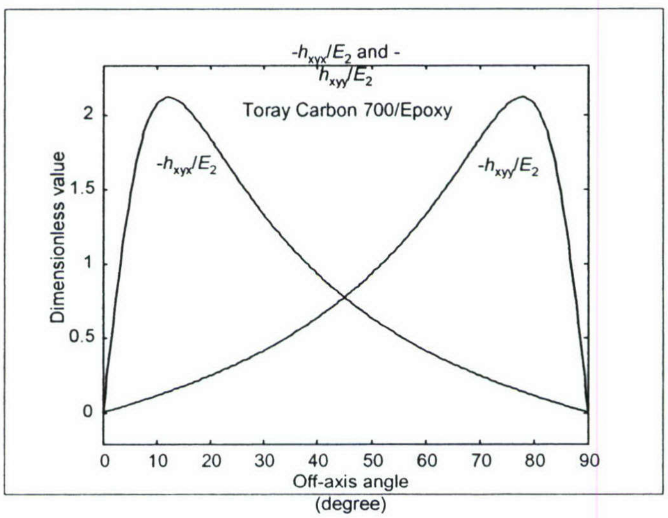
Analysis

- Ply thickness: 0.125 mm
- Unidirectional ply properties (P7951S-20-1000)

  E_1= 135.0 GPa, E_2=8.5 GPa, G_{12}=6.17 GPa
  ν_{12}=0.34, ν_{23}=0.40

- Constant tensile strain ε_{11}=0.02

Coupling Coefficients



Stress Functions

$$\sigma_2 = \frac{\partial^2 F}{\partial^2 z}, \quad \sigma_3 = \frac{\partial^2 F}{\partial^2 y}, \quad \sigma_4 = -\frac{\partial^2 F}{\partial y \partial z},$$
$$\sigma_5 = -\frac{\partial \Psi}{\partial y}, \quad \sigma_6 = \frac{\partial \Psi}{\partial z}$$

- Stress functions in i^{th} ply

$$F^{(i)}(y,\eta) = (1-3\eta+2\eta^3)F_{i-1}(y) + (\eta-2\eta^2+\eta^3)G_{i-1} + (3\eta^2-2\eta^3)F_i(y) + (\eta^3-\eta^2)G_i(y)$$
$$\Psi^{(i)} = (1-\eta^2)\Psi_{i-1}(y) + \eta^2 G_{i-1} + (\eta-\eta^2)H_{i-1}(y)$$

F_{i-1}, $G_{i-1,}$ $H_{i-1,}$ Ψ_{i-1} are stress functions and corresponding derivatives in the (i-1)-th ply, while F_i, $G_{i,}$ $H_{i,}$ Ψ_i are stress functions in the i-th ply, and $\eta=(y-y_{i-1})/(y_i-y_{i-1})$

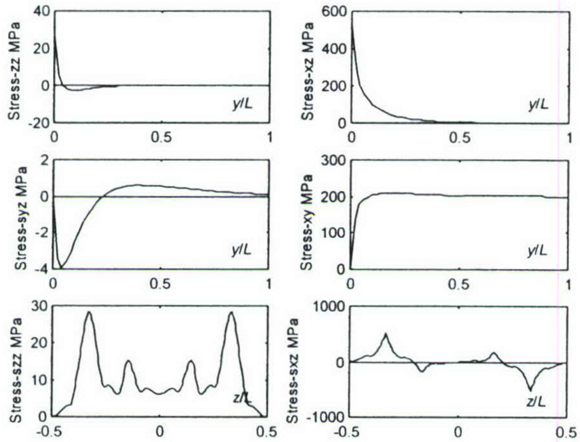
Minimum Complementary Strain Energy

$$\delta U = \iint_A \varepsilon \delta \sigma dydz$$
$$= \iint_A \sigma_i \hat{S}_{ij} \delta \sigma_j + (\varepsilon_1 S_{i1}/S_{11} + \hat{\alpha}_i)\delta\sigma_i dydz = 0$$

where

$$\sigma_1 = (\varepsilon_1 - \alpha_1 \Delta T - S_{1j}\sigma_j)/S_{11} \quad (j = 2,3,6)$$
$$\hat{S}_{ij} = S_{ij} - \frac{S_{i1}S_{1j}}{S_{11}}, \quad \hat{\alpha}_1 = \alpha_i - \frac{S_{1i}}{S_{11}}\alpha_1$$

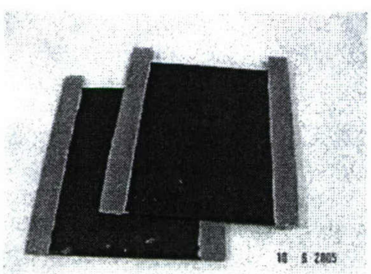
Edge Stresses

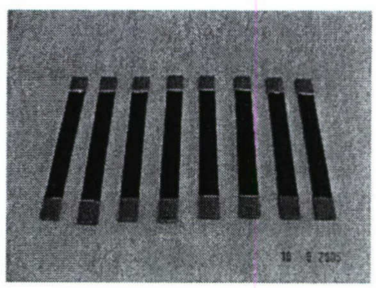


Lay-up: $[12_2/-12_2/0_2]_s$; strain: $\varepsilon_{11}=0.02$

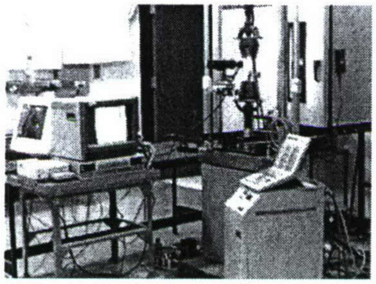
Experimental Analysis

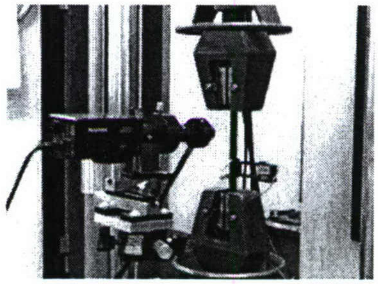
- Specimens with and without nanofiber reinforcement at interfaces





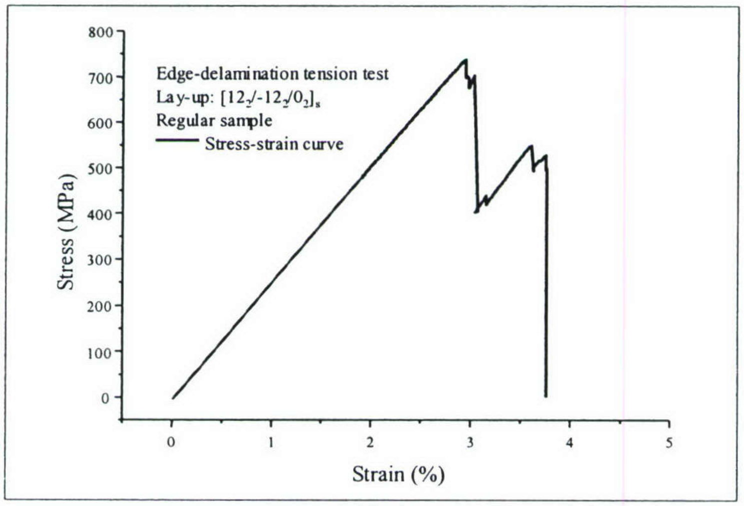
Test Setup





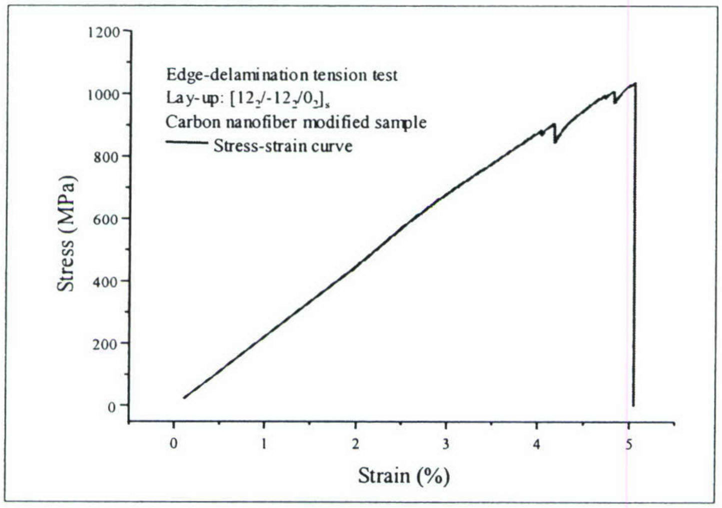
Typical Stress-Strain Curve

- Unmodified laminate

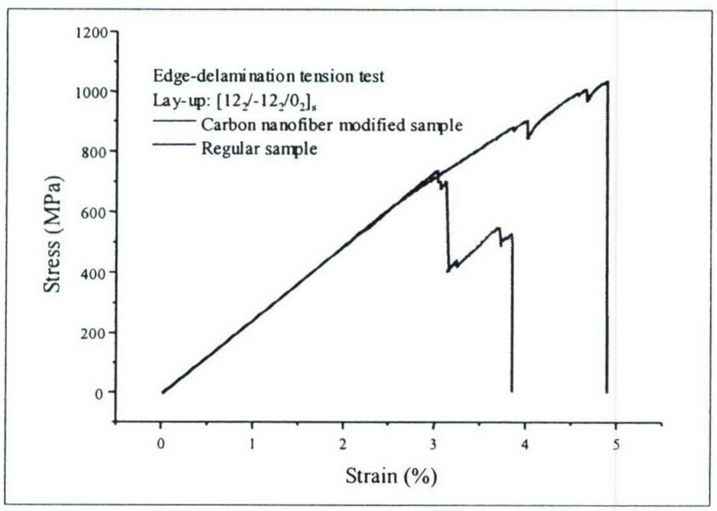


Typical Stress-Strain Curve

- Nanomodified laminate

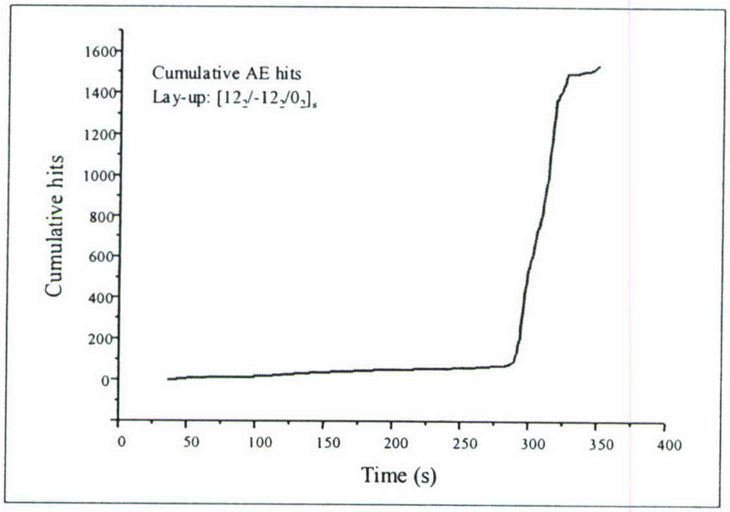


Comparison



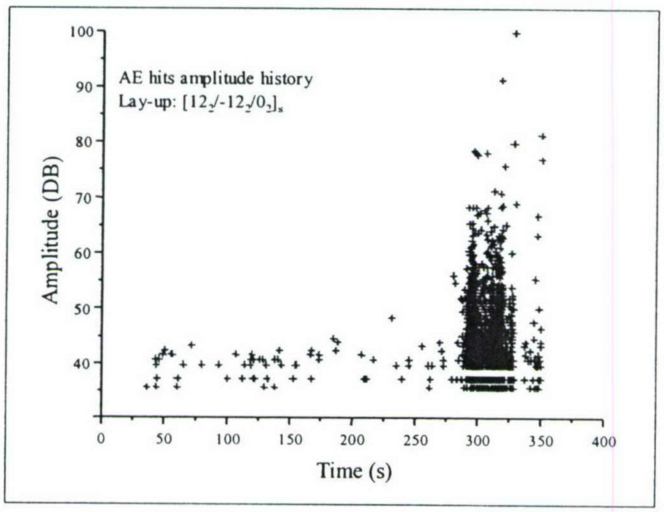
AE Accumulation

- Unmodified laminate



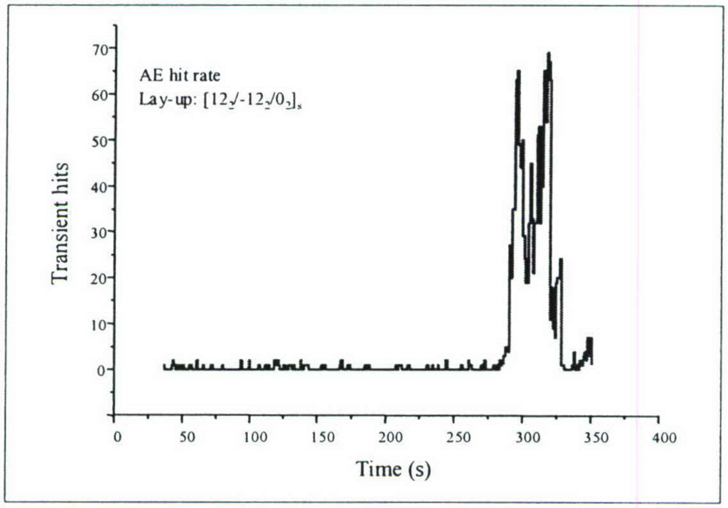
AE Accumulation

- Unmodified laminate



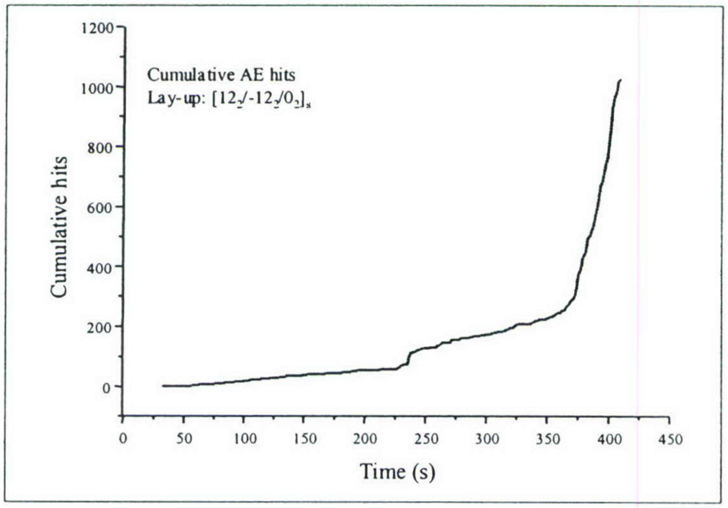
AE Accumulation

- Unmodified laminate



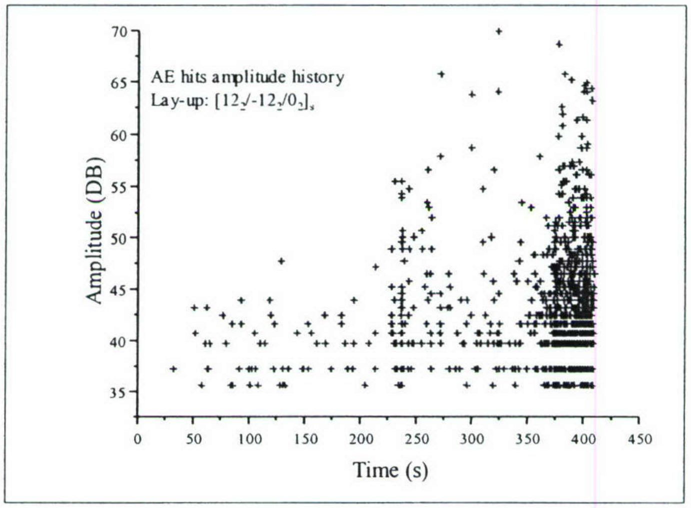
AE Accumulation

- Nanomodified laminate



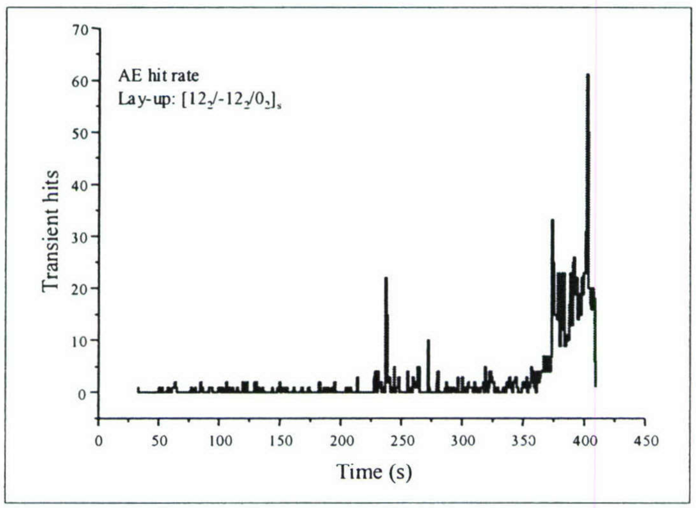
AE Accumulation

- Nanomodified laminate



AE Accumulation

- Nanomodified laminate



Probabilistic Analysis

Two-parameter Weibull model:

$$P(\sigma) = \exp[-(\frac{\sigma}{\sigma_0})^m]$$

Mean value:

$$\bar{\sigma} = \sigma_0[\Gamma(1+\frac{1}{m})]$$

where σ_0 and m are model parameters

Median rank formula for data reduction:

$$f(x) = 1 - \frac{i-0.3}{n+0.4}$$

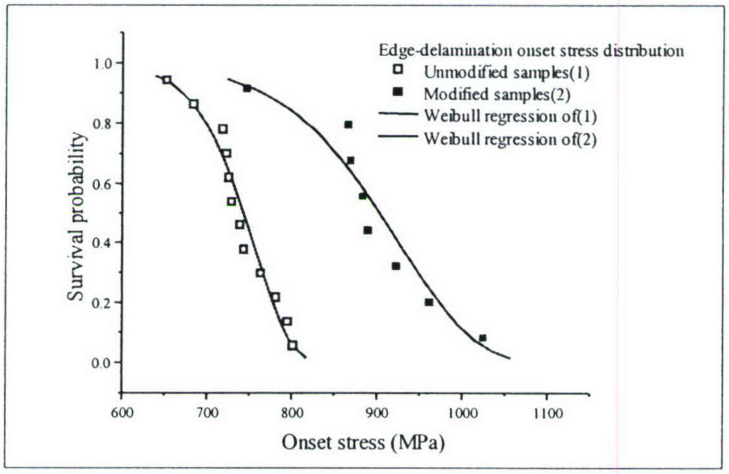
where i is the i-th specimen for a sample size of n specimens in the increasing strength sequence.

Results

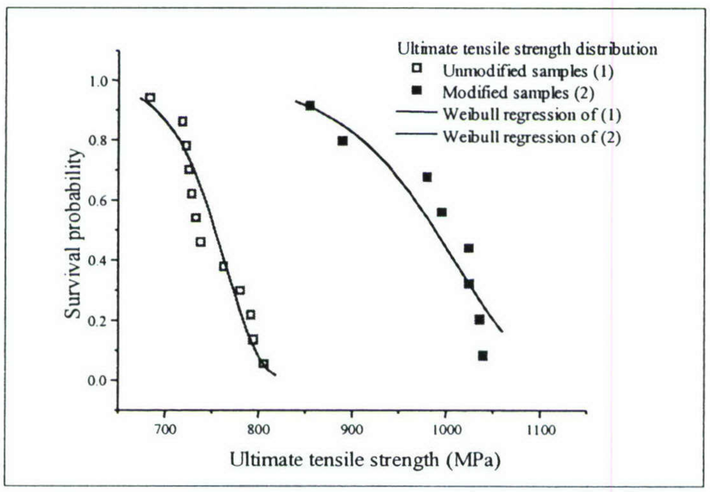
- 12 unmodified and 8 nanomodified specimens tested
- Weibull distribution parameters:

		Unmodified laminate	Modified laminate
Onset Stress	σ_0	757.40 (MPa)	932.97 (MPa)
	m	18.54	11.35
	Mean value	735.90 (MPa)	892.17 (MPa)
Ultimate Strength	σ_0	766.34 (MPa)	1014.96 (MPa)
	m	21.44	13.86
	Mean value	747.29 (MPa)	977.58 (MPa)

Delamination Onset Stress



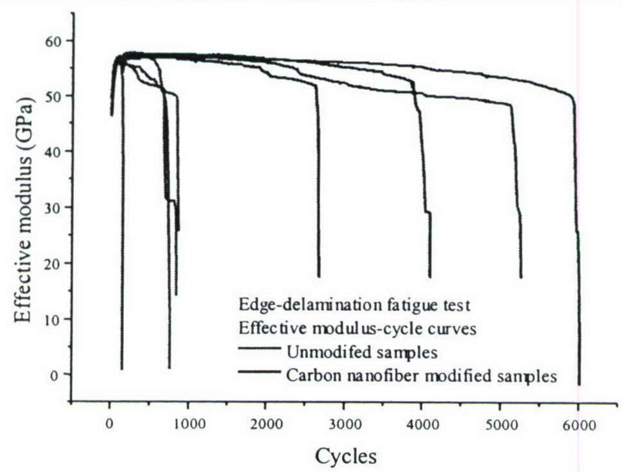
Ultimate Laminate Strength



Fatigue Analysis

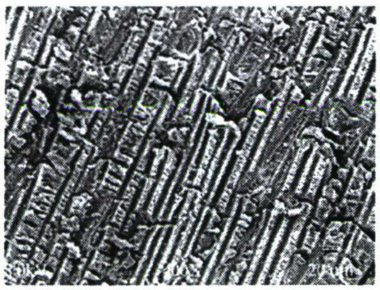
- Laminate lay-up: $[12_2/-12_2/0_2]_s$
- Prepreg: Toray P7951S-20-1000 (T700S fiber)
- Testing system: MTS 8500 with Instron software
- Specimen dimensions: ~140×20 ×2.27 mm
- Fatigue frequency: 3Hz
- Loading ratio: R=0.1
- Maximum stress: 0.8 of the average ultimate tensile strength
- Fatigue loading: sine – wave
- Control method: Load control

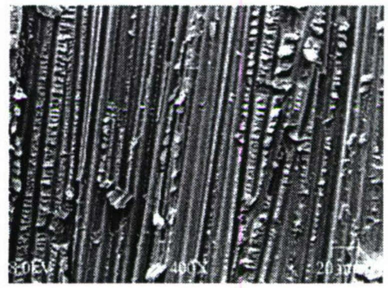
Fatigue Stiffness Degradation



Evaluation of Nanomechanisms

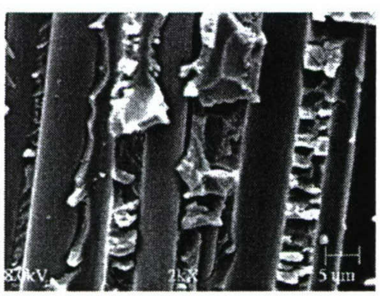
- Unmodified laminate

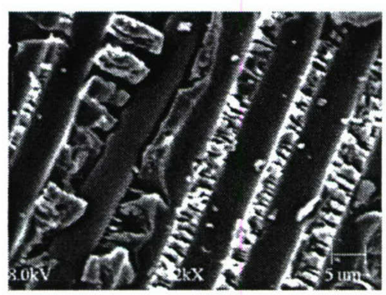




Evaluation of Nanomechanisms

- Unmodified laminate



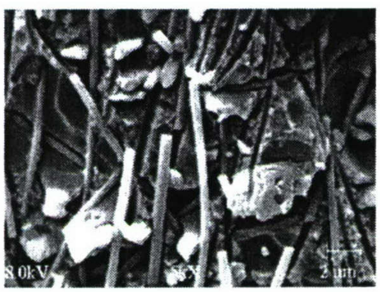


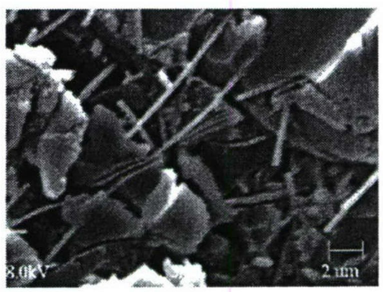
Evaluation of Nanomechanisms

- Nanomodified laminate

Evaluation of Nanomechanisms

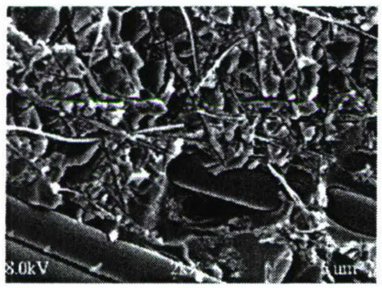
- Nanomodified laminate

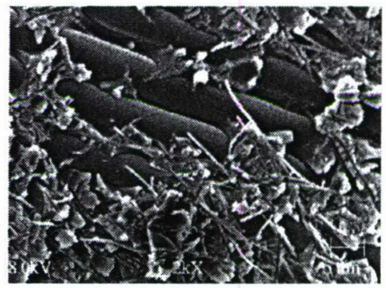




Evaluation of Nanomechanisms

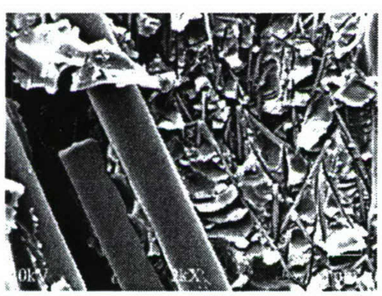
- Nanomodified laminate

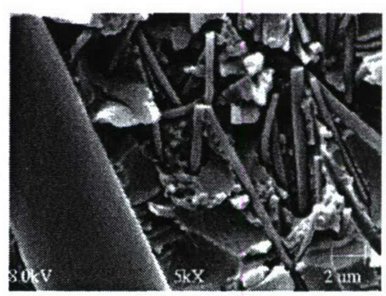




Evaluation of Nanomechanisms

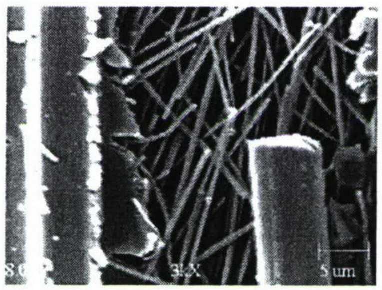
- Nanomodified laminate

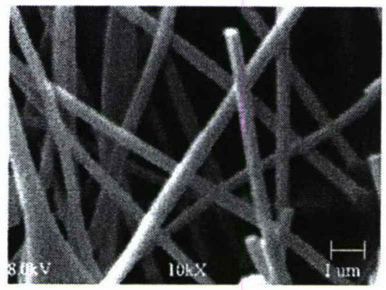




Evaluation of Nanomechanisms

- Nanomodified laminate



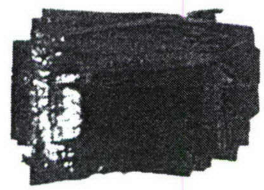


Carbon Nanofiber-Reinforced Epoxy Matrix Composites

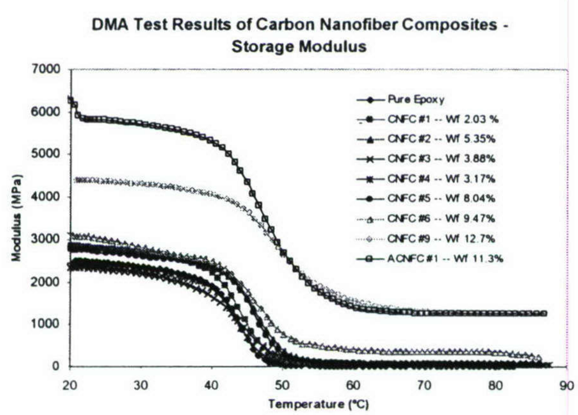
- Manufacturing of random and aligned carbon nanofiber sheets and nanocomposites
- DMA analysis
- Fracture mechanics analysis

World’s First Layered Continuous Nanofiber Nanocomposites

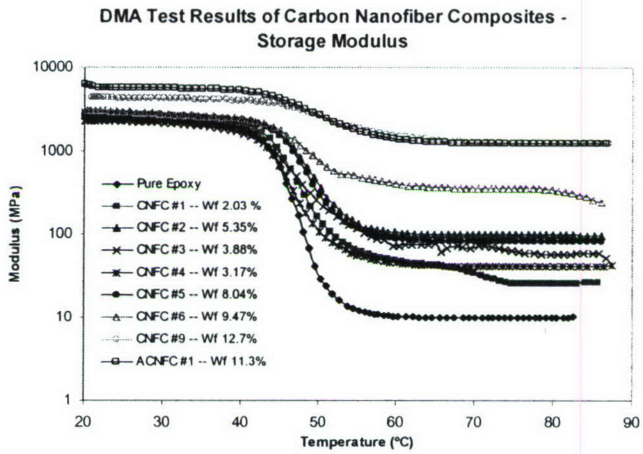
- Random and aligned carbon nanofiber sheets
- Impregnation with epoxy resin and stacking
- Curing under controlled pressure, temperature, vacuum



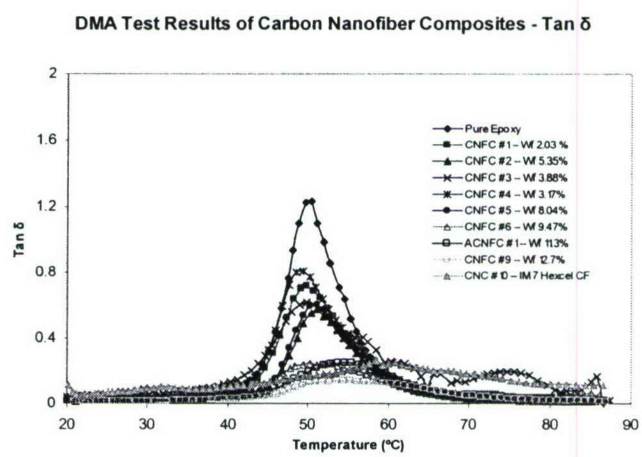
DMA Modulus



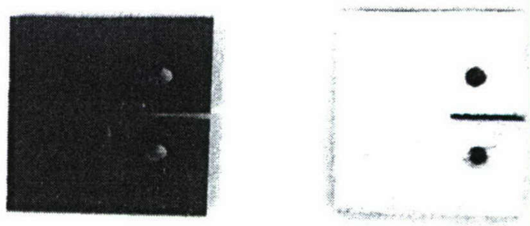
DMA Modulus



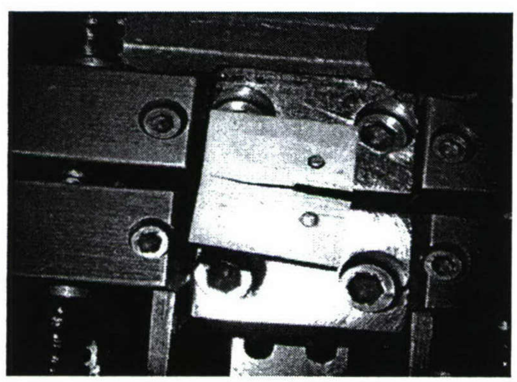
Loss Tangent



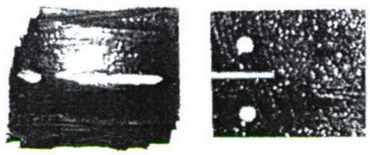
Fracture Mechanics: Random Carbon Nanofibers



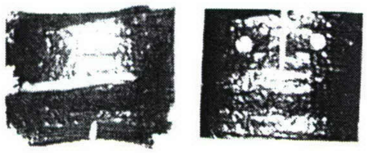
Fracture Mechanics Testing



Manufacturing of Aligned Nanofiber Composites for Evaluation of Fracture Toughness Anisotropy

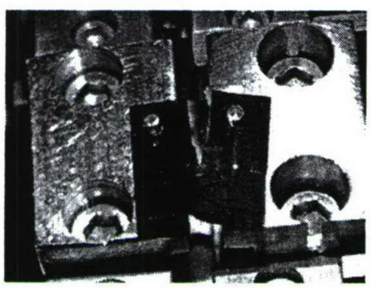


Fiber Direction

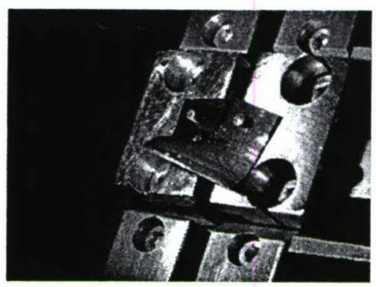


Fiber Direction

Fracture Mechanics Testing

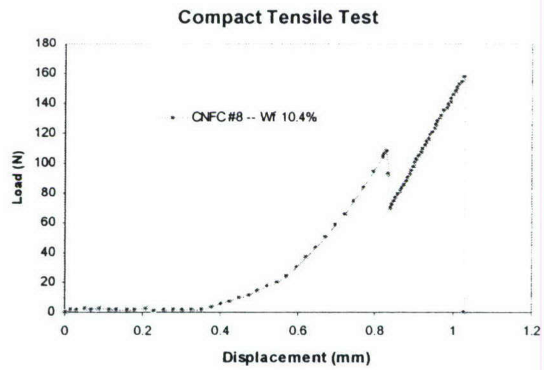


Specimen I

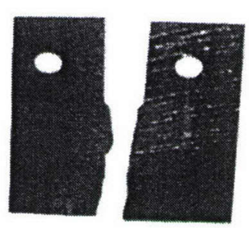


Specimen II

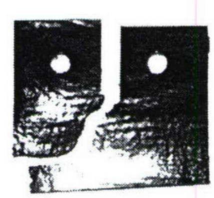
Typical Output



Failed Specimens



Specimen I



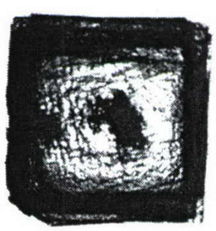
Specimen II

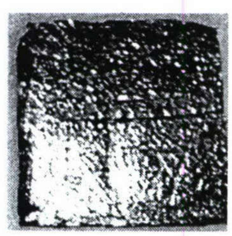
Improved Nanocomposite Preparation

- Manufacturing of higher volume fraction carbon nanofiber composites by modified methods
- DMA analysis
- Improved fracture mechanics testing

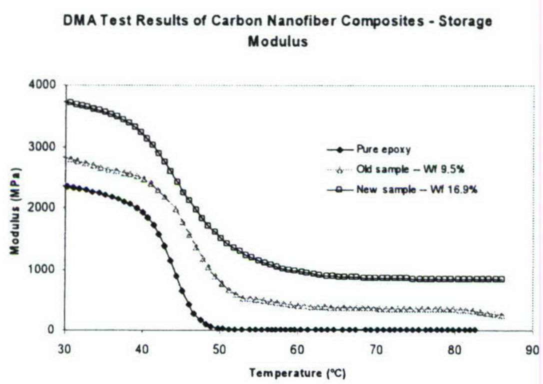
Modified Manufacturing of Carbon Nanofiber Nanocomposites

- Modification of resin impregnation
- Modification of curing conditions



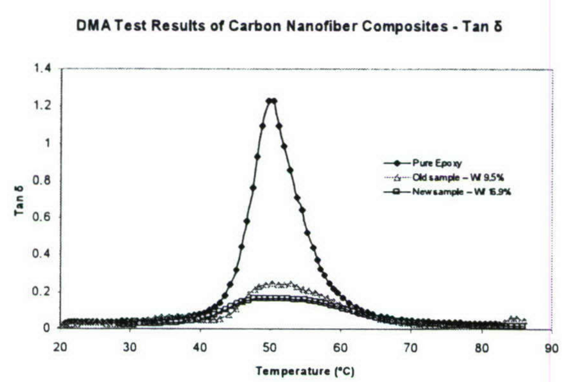


DMA Analysis

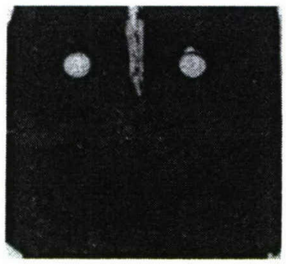


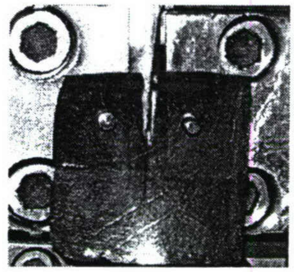
Note: Compared with Old sample #6, 40 layers, wf 9.5% only.

Loss Tangent

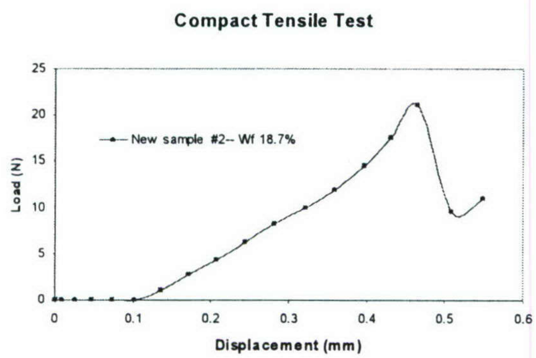


Fracture Mechanics Testing





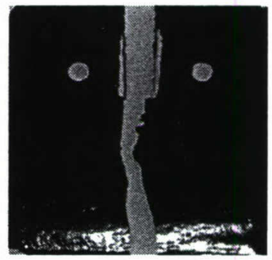
Output



Modified Compact Tension Specimen

Before test

After test

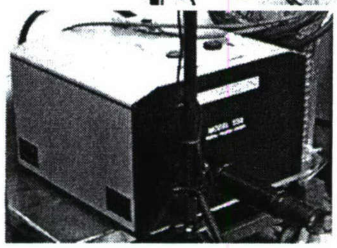


Use of Advanced New Instrumentation

- High-speed digital video observation system (AFOSR/DURIP)
  - Dynamic fracture testing
  - Nanomanufacturing process analysis

CORDIN Model 550-24 Rotating Mirror CCD Camera System (AFOSR/DURIP)

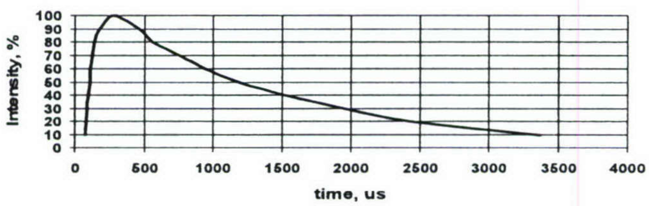
- 24 CCD sensors
- Rotating mirror redirects image to CCD sensors in continues fashion
- Gas driven turbine max rotation rate is 12500 rps
- Max framing rate is 1.5 million fps
- Shutter time (at max fps) is 350 ns
- CCD resolution is 1000x1000 pixels
- CCD Dynamic range is 10 bit
- Macro 28-200 mm, 1:3.5-5.6 Lenses (Sigma)



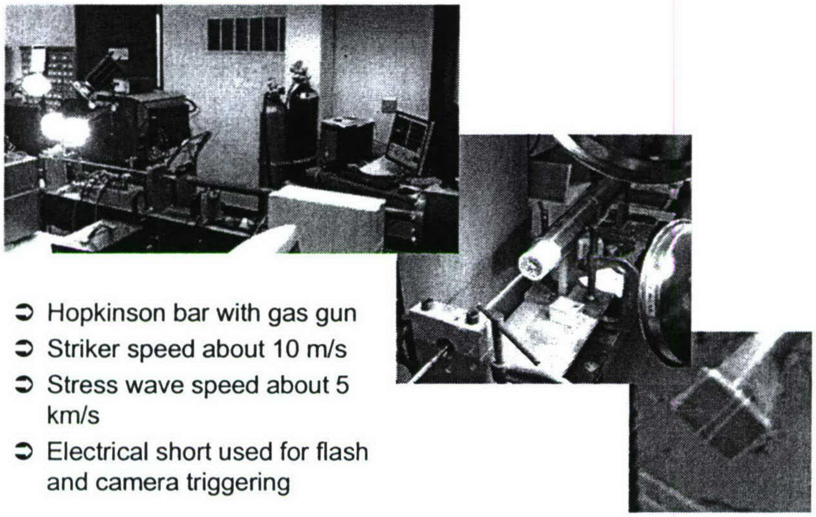
Advanced 2500 DR Flash Lights

- Flash Power is 1000 WS, 1000 Joules (2500 effective watt seconds)
- Flash duration is 1/770 second at full power (60%)
- Modeling Light Power is 250 Watt

Flash light intensity

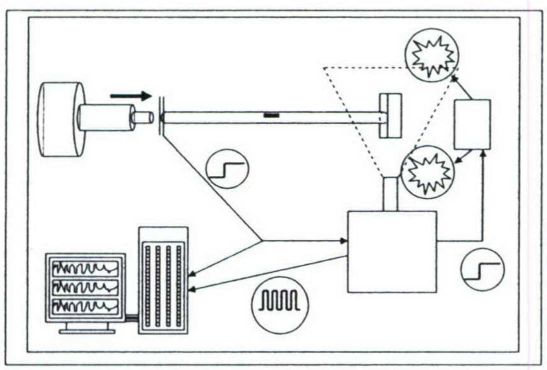


Dynamic Fracture Test Setup



- Hopkinson bar with gas gun
- Striker speed about 10 m/s
- Stress wave speed about 5 km/s
- Electrical short used for flash and camera triggering

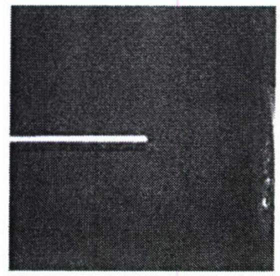
Hopkinson Bar Test Schematic



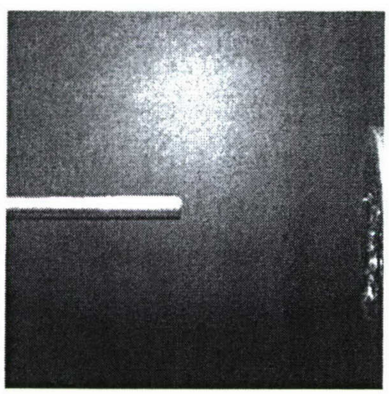
- Main trigger signal comes from short in front of the bar
- After trigger initiated, strain wave travel time through the bar is 270 us
- Flash lights triggered after 70 us to give 200 us for intensity rise time
- Camera triggered after 270 us
- Peak (90%) light intensity will be maintained within 300 us

Synchronization Optimization: High Speed Test

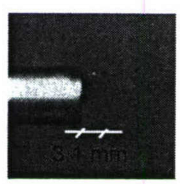
- "No motion" test for light synchronization purposes
- Frames per second: 200,000
- Image acquiring timeframe: 120us
- All frames are taken in max light intensity time frame
- Slight disposition of individual frames
- Slight light variation of individual frames



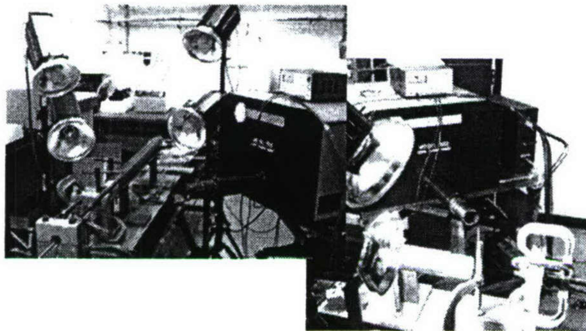
Slower Dynamic Test

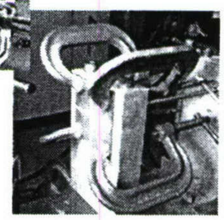


- Slow motion test of bar propagation (D=8mm)
- Frames per second : 14510
- Image acquiring timeframe: 1654 us.
- Most frames are taken out of a max light intensity time frame
- Within first 10 frames motion average speed is 4.5 m / s



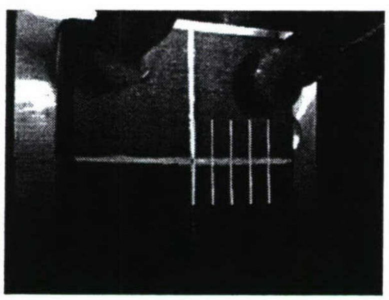
Composite Plate Impact Test Setup





- Four point clamping was used to hold plate
- View axis was inclined to plate with 45°

Observation and Evaluation



- Frames per second : 9836
- Image acquiring timeframe: 2440us.
- Only first two frames taken in max light intensity time frame
- Several oscillation were observed

Summary

- Continuous carbon nanofibers were manufactured and used to reinforce interfaces in advanced composite laminates for the first time
- Substantial improvements in strength and fatigue life were recorded
- Nanofiber-reinforced laminated composites were produced and tested for the first time
- Continuous carbon nanofibers provide unique advantages for structural nanocomposite applications

Interactions/Transitions

- Commercial development and use of advanced composites with nanofiber-reinforced interfaces is being discussed with two aerospace companies
- National Nanofiber Facility has been funded by NRI and is being developed at UNL (Director: Y. Dzenis)