Abstract

Carbon Nanotubes for Human Space Flight

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Single-wall carbon nanotubes offer the promise of a new class of revolutionary materials for space applications. The Carbon Nanotube Project at NASA Johnson Space Center has been actively researching this new technology by investigating nanotube production methods (arc, laser, and HiPCO) and gaining a comprehensive understanding of raw and purified material using a wide range of characterization techniques. After production and purification, single wall carbon nanotubes are processed into composites for the enhancement of mechanical, electrical, and thermal properties. This "cradle-to-grave" approach to nanotube composites has given our team unique insights into the impact of post-production processing and dispersion on the resulting material properties. We are applying our experience and lessons-learned to developing new approaches toward nanotube material characterization, structural composite fabrication, and are also making advances in developing thermal management materials and electrically conductive materials in various polymer-nanotube systems. Some initial work has also been conducted with the goal of using carbon nanotubes in the creation of new ceramic materials for high temperature applications in thermal protection systems. Human space flight applications such as advanced life support and fuel cell technologies are also being investigated. This discussion will focus on the variety of applications under investigation.

Carbon Nanotubes for Human Space Flight

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ES4/Materials and Processes Branch

at

University of Oklahoma

May 14, 2003

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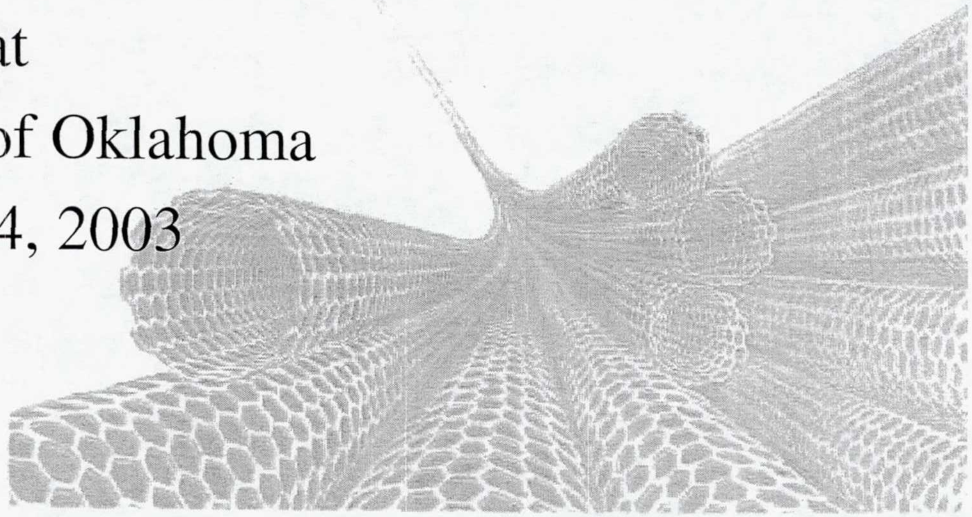
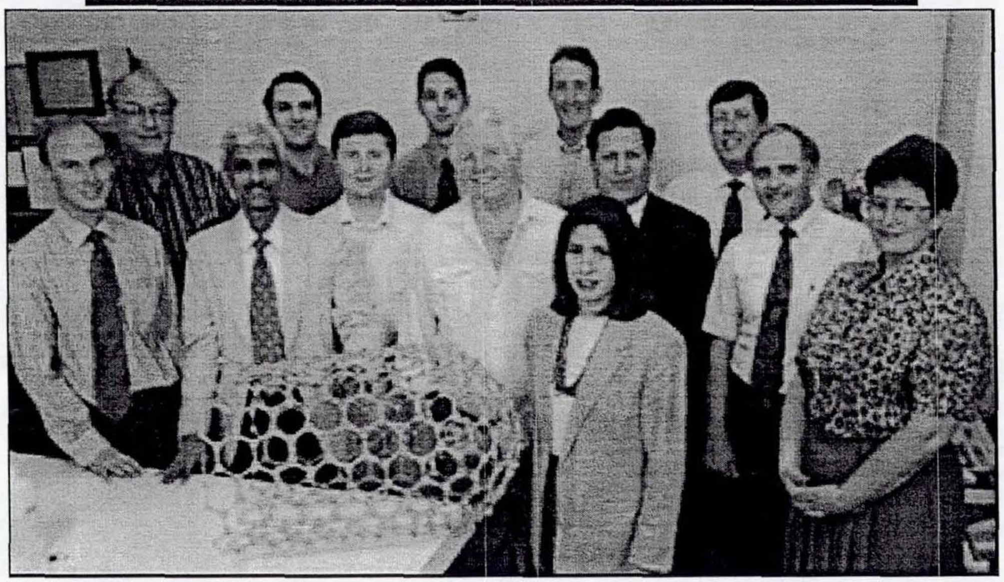
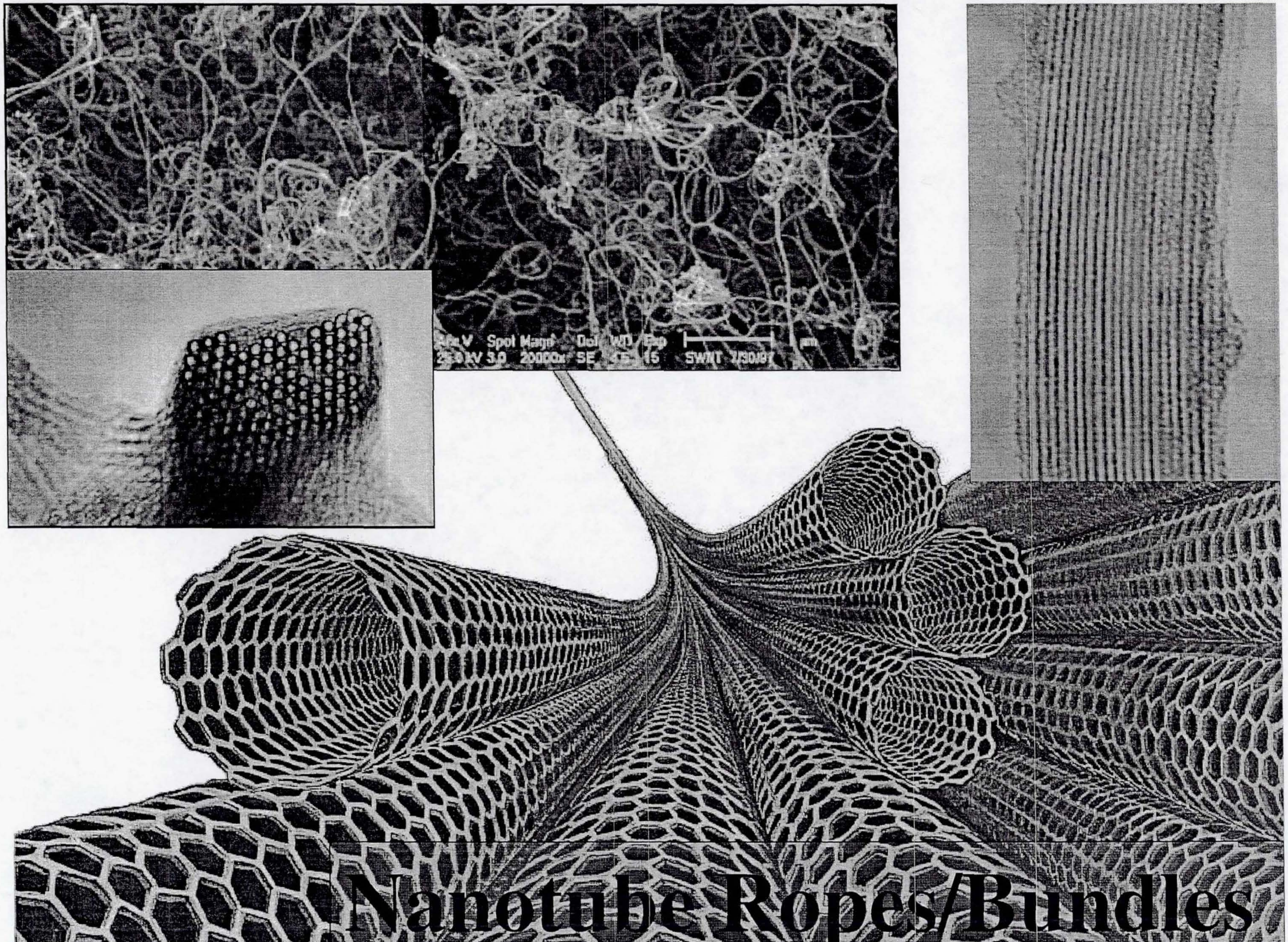


Team Members

- Dr. Leonard Yowell, project lead
- Dr. Carl Scott
- Dr. Sivaram Arepalli
- Dr. Pavel Nikolaev
- Dr. Brian Mayeaux
- Dr. Brad Files
- Dr. Erica Sullivan
- William Holmes
- Beatrice Santos
- Dr. Olga Gorelik
- Dr. Rodrigo Devivar

http://mmptdpublic.jsc.nasa.gov/jscnano/




Nanotube Ropes/Bundles

Why Single Wall Carbon Nanotubes?

Mechanical Properties

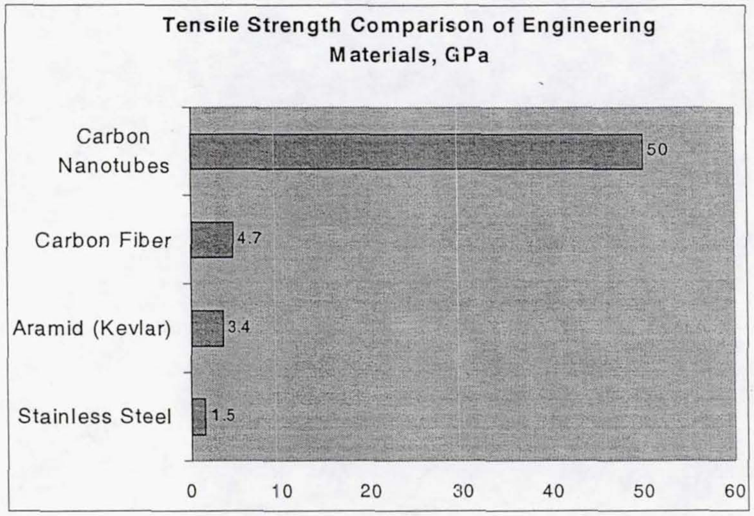
- much stronger/lighter than steel

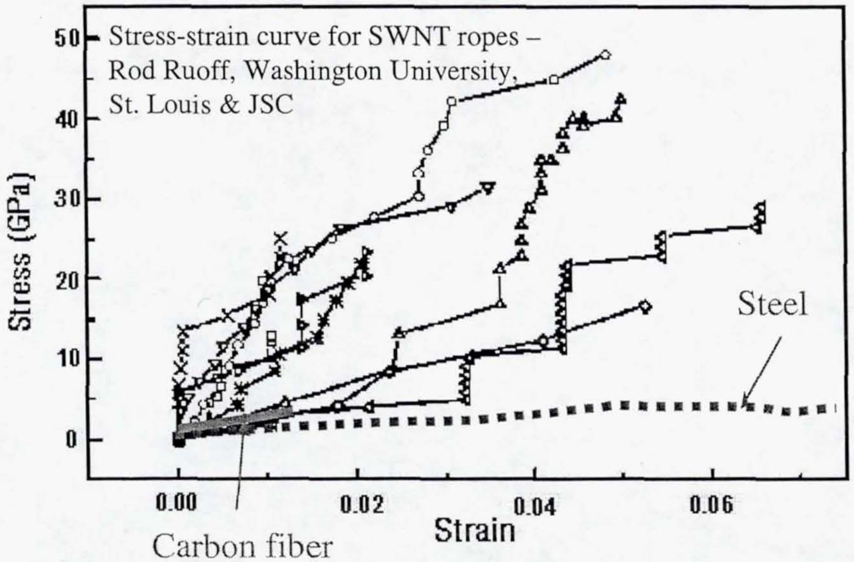
Thermal Properties

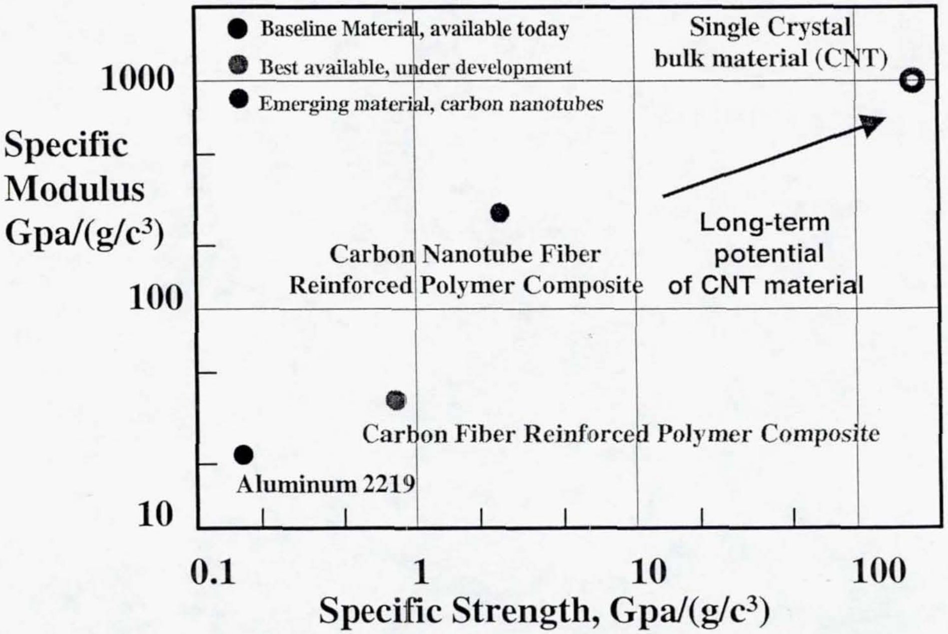
- high longitudinal conductivity (diamond)
- low transverse conductivity (C_{60})

Electrical Properties

- metallic, semiconducting tubes
- high conductivity (copper)



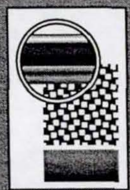




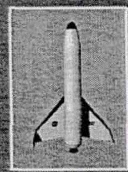
NASA Nanotechnology Roadmap

C A P A B I L I T Y

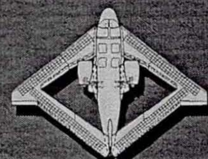
Multi-Functional Materials



High Strength Materials
(>10 GPa)



Reusable Launch Vehicle
(20% less mass, 20% less noise)



Revolutionary Aircraft Concepts
(30% less mass, 20% less emission, 25% increased range)

Autonomous Spacecraft
(40% less mass)

Bio-Inspired Materials and Processes

Adaptive Self-Repairing Space Missions

Increasing levels of system design and integration →

Materials	• Single-walled nanotube fibers	• Nanotube composites	• Integral thermal/shape control	• Smart "skin" materials	• Biomimetic material systems
Electronics/ computing	• Low-Power CNT electronic components	• Molecular computing/data storage	• Fault/radiation tolerant electronics	• Nano electronic "brain" for space Exploration	• Biological computing
Sensors, s/c components	• In-space nanoprobes	• Nano flight system components	• Quantum navigation sensors	• Integrated nanosensor systems	• NEMS flight systems @ 1 μW

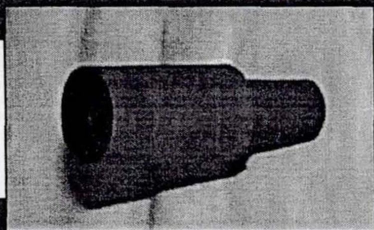
2002 — 2004 — 2006 — 2011 — 2016 ······>

JSC Nanoscale Materials Approach

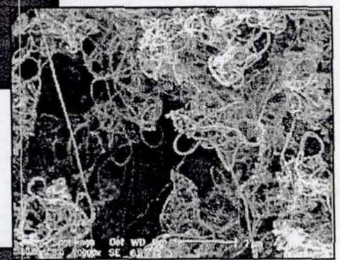
- **Growth and diagnostics**
  - Ensure a reliable source of nanotubes with controlled properties using diagnostics and modeling to understand and improve processes
- **Purification and chemistry**
  - Develop processing methods for nanotubes to enhance structural, thermal, electrical, and chemical properties
- **Characterization**
  - Develop and employ characterization techniques to examine nanotubes and nanoscale materials
- **Applications**
  - Conduct initial studies or sponsor development of applications of nanoscale materials
- **Collaboration**
  - Establish a scientific network of academic, industry, and government partners to leverage resources and disseminate knowledge

JSC Nanotube Materials Approach

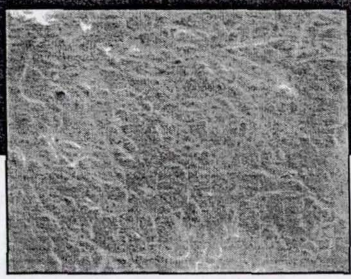
1 Make targets for laser process from graphite powder and metal nitrates



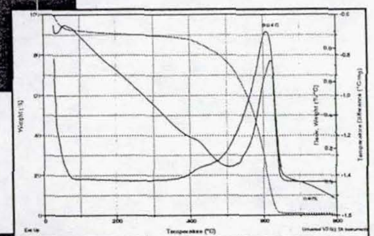
2 Produce single-wall nanotubes using laser process



3 Nanotube purification

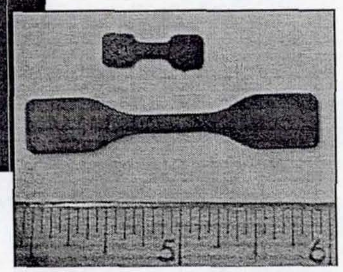


4 Nanotube Characterization for purity, length, diameter



5 Specimen fabrication (composites, etc.)

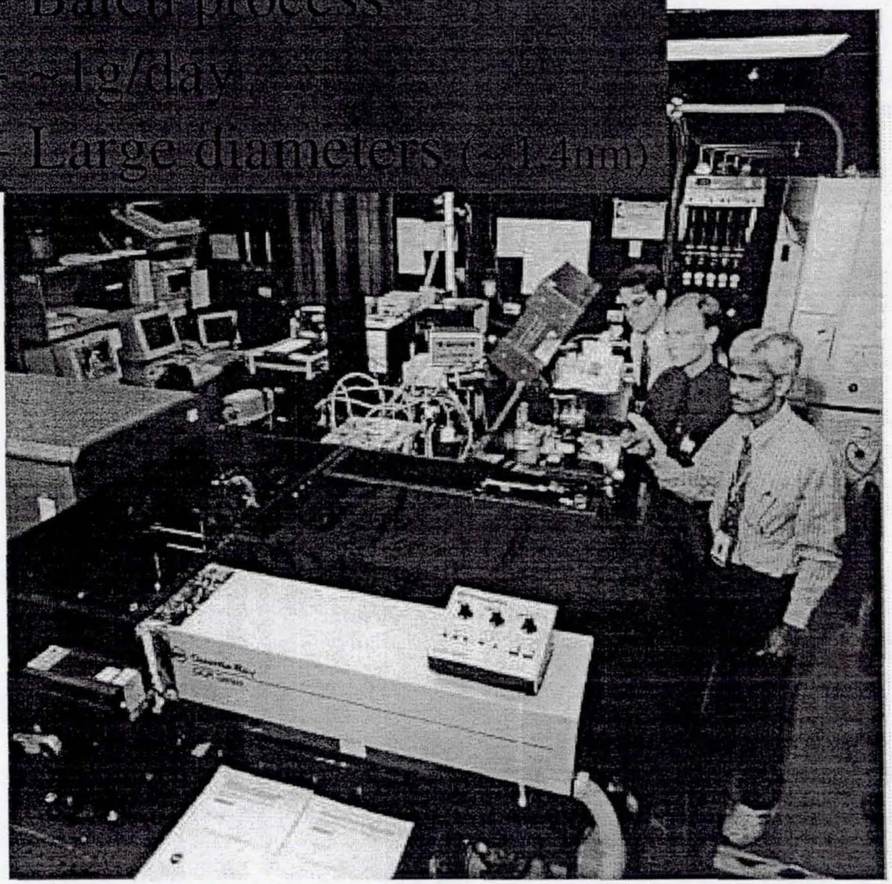
6 Testing and analysis

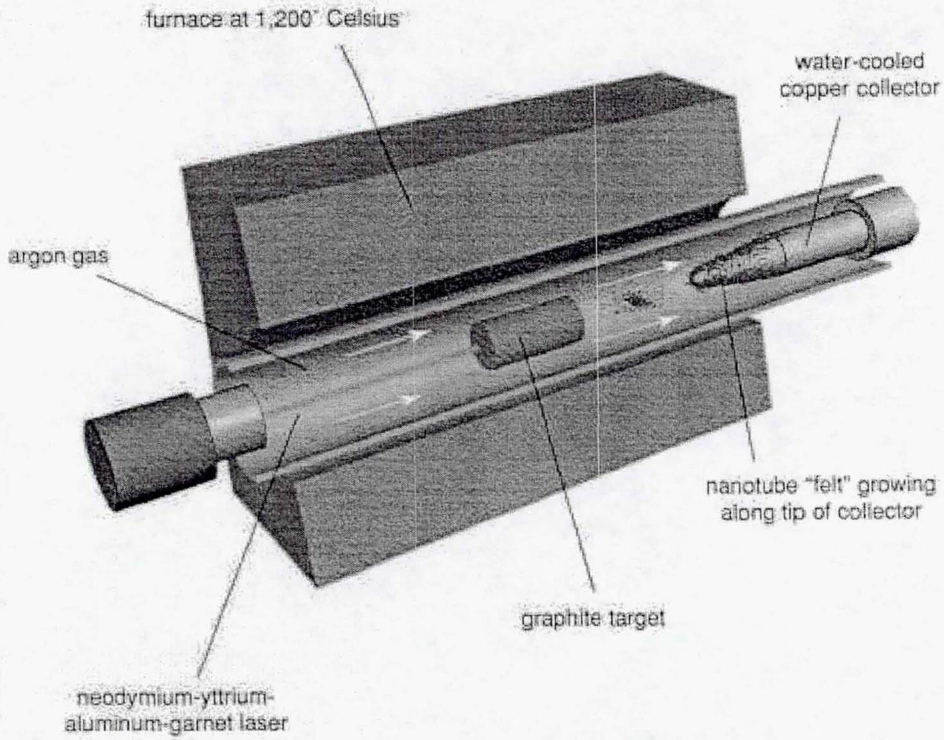


Pulsed Laser Vaporization – "Laser" Process

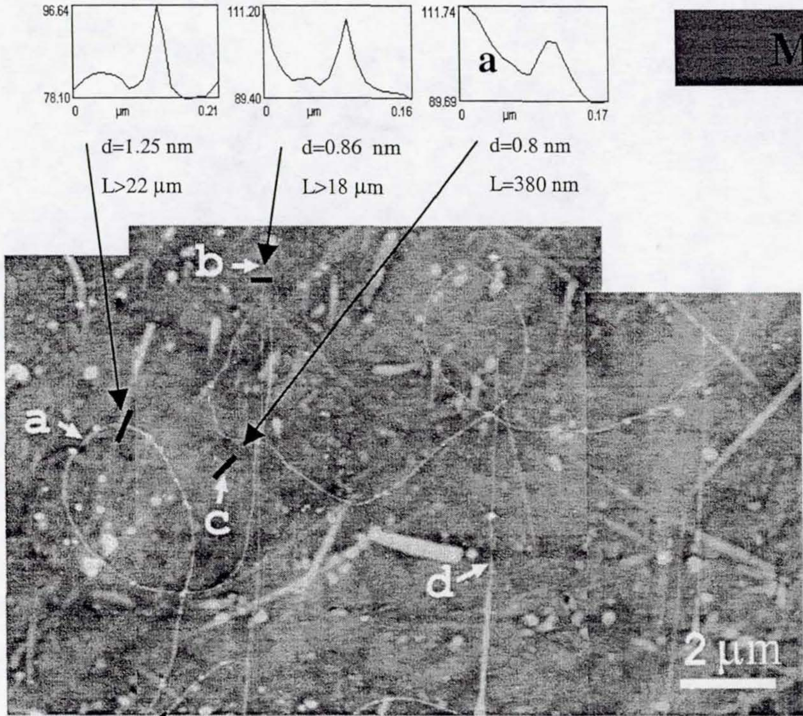
$$\textbf{Graphite} \xrightarrow[\substack{\textbf{4000-5000 K} \\ \textbf{argon}}]{\textbf{Co, Ni Catalysts}} \textbf{fullerenes + } \underline{\textbf{SWNT}} \textbf{ + impurities}$$

[redacted]



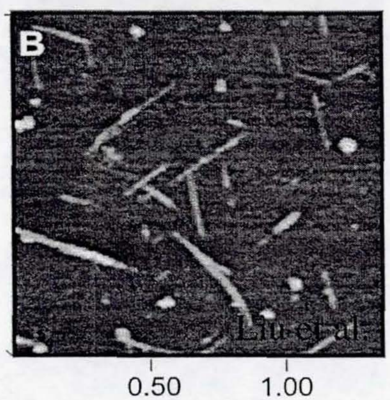


Growth and Diagnostics



as-produced

processed



Measurements of nanotube lengths as produced

- Nanotube **length** is extremely **important** for stress transfer in composite materials.
- Impossible to determine lengths of individual nanotubes from conventional TEM, SEM or AFM images because they bundle
- Processing (purification, sonication) seems to cut tubes
- Measured tensile strength (Ruoff) indicates long tubes
- Individual tubes longer than ~10 µm are required for strong ropes (Yakobson)

Our observation:

- We see very long (≥20µm) individual tubes and thin bundles

NASA Growth Mechanism Workshop

Sivaram Arepalli, Pavel Nikolaev, William Holmes and Bradley S. Files, *Applied Physics Letters,* Vol. 78, March 12, 2001, pp. 1610-12 (2001).

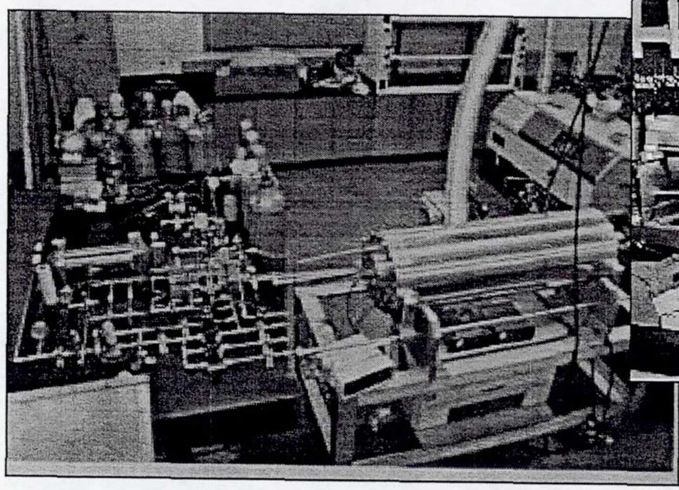
NASA
Success
Stories

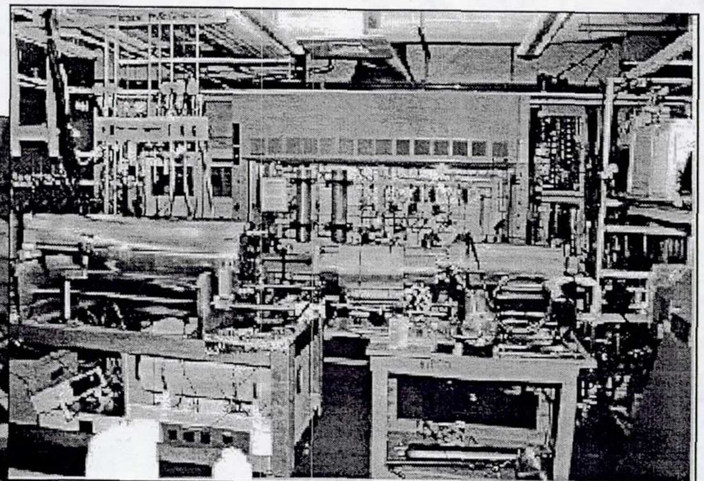
High Pressure CO (HiPCO) Process

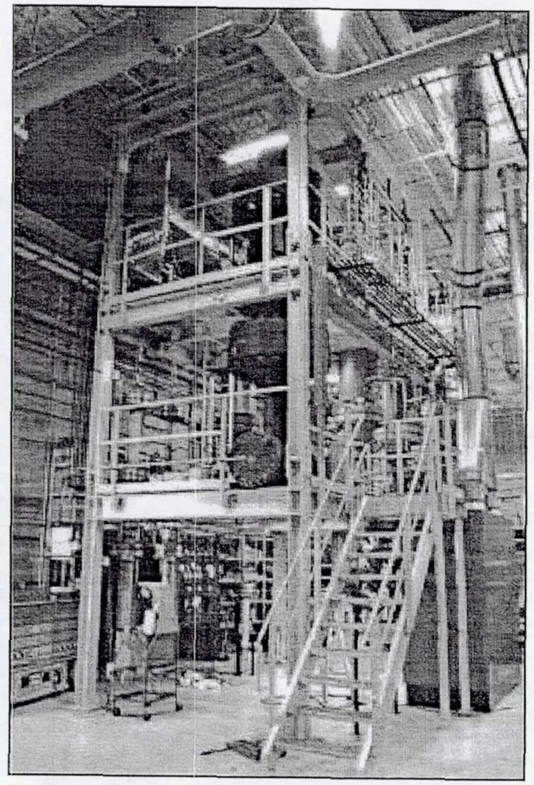
$$CO + CO \xrightarrow[\substack{900\text{-}1200\ C \\ 10\text{-}40\ atm}]{\text{Fe, Ni Catalysts}} CO_2 + \underline{\text{SWNT}} + \text{impurities}$$

- Continuous process
- 10-100's g/day
- Small diameters (0.7nm)
- Company spin-off (CNI)

Rice Univ. → Carbon Nanotechnologies, Inc.
& NASA

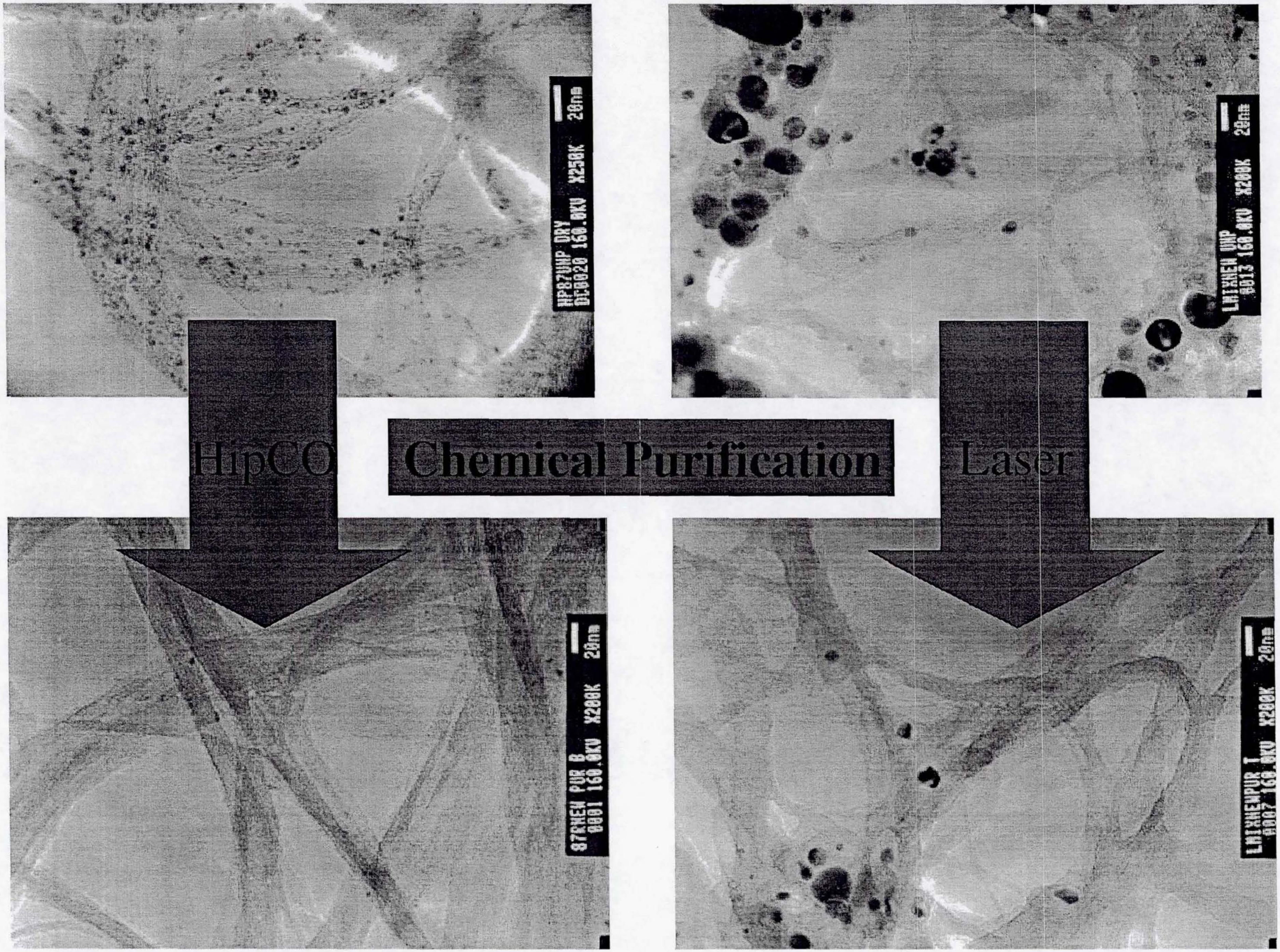






Improved Production Capability

- **Growth and Production**
  - Ensure a reliable source of nanotubes with controlled properties using diagnostics and modeling to understand and improve processes
- Laser Ablation Simulations and Diagnostics
  - Summer Faculty Fellow Program
  - In-situ measurements of process parameters
  - Computational Fluid Dynamics Simulations
    - Collaboration with Dr. Robert Greendyke at UT-Tyler
- Arc Process Diagnostics and Simulations
  - Collaboration with Dr. Samir Farhat at University of Paris 13


HipCO
Chemical Purification
Laser

Purification/Chemistry and Characterization

Purification techniques for HiPCO and Laser produced nanotubes

JSC

1. Boiling in H_2O (100C, 24 hrs) ► 2. Reflux in CH_3COOH ► 3. Reflux in 2M HCl ► 4. Reflux in conc. HCl ► 5. Reflux in HNO_3 at 100C

Rice

1. Soft baking (225C, 24 hrs in wet air) ► 2. Stirring in conc. HCl at room T for 26.5 hrs ► 3. Repeated water wash until pH=7 ► 6. Reflux in HNO_3 at 100C

- Use **standard characterization protocol** to evaluate purified nanotube material and assess…
  - **PURITY**
  - **HOMOGENEITY**
  - **THERMAL STABILITY**
  - **DISPERSABILITY**

Joint NASA / NIST Workshop – May 27-29, 2003

→ ***Techniques – TGA, SEM/TEM (+EDS), Raman, UV/Vis***

Characterization

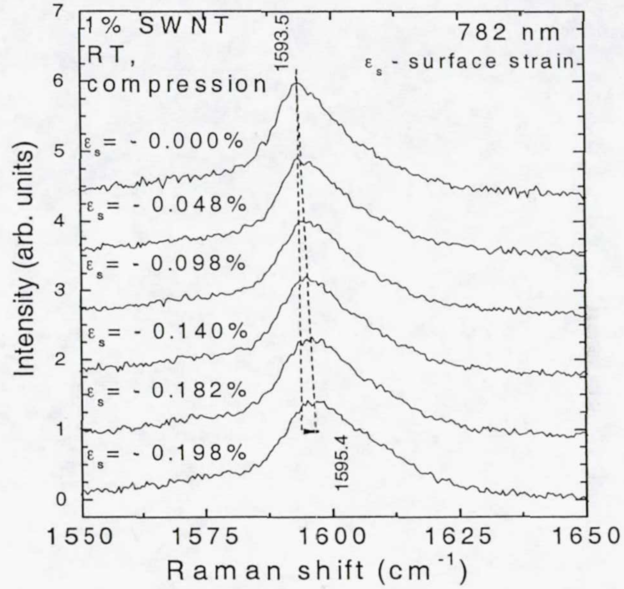
Load Transfer in Nanotube Composites

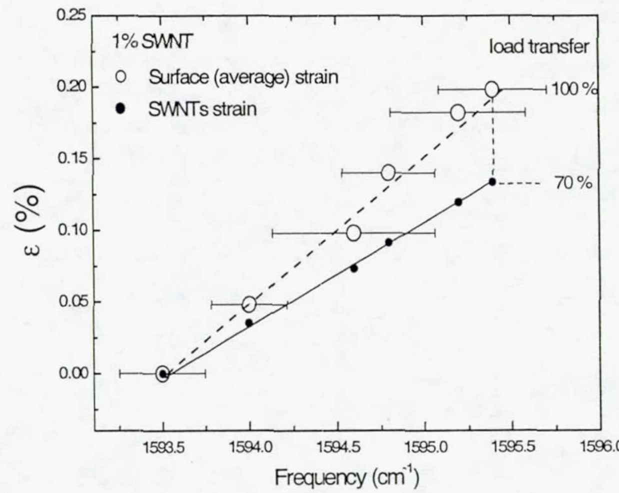
- **<u>New Tool</u>** - Raman spectroscopy in combination with standard mechanical tests (four point bend) is very useful for testing SWNTs composites.

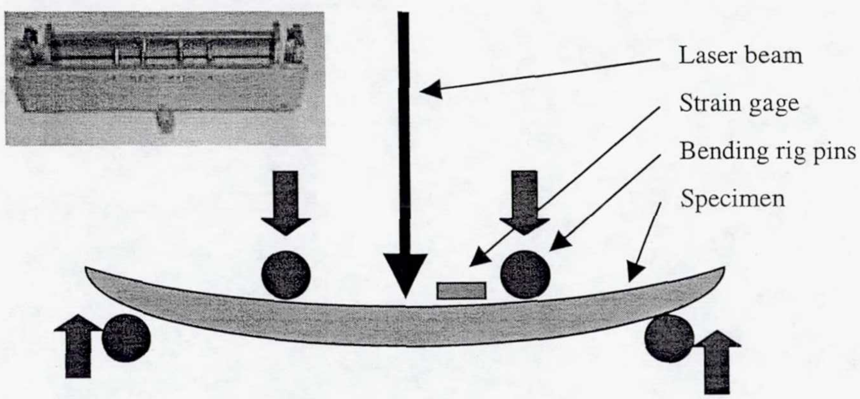
- Frequency of the tangential mode shifts with applied external compression stress.

- Allows determination of elastic properties of SWNTs/ropes embedded in composite - load transfer.

- **<u>70% Load Transfer</u>** (1%SWNT in epoxy)





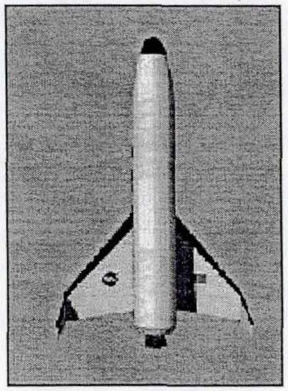


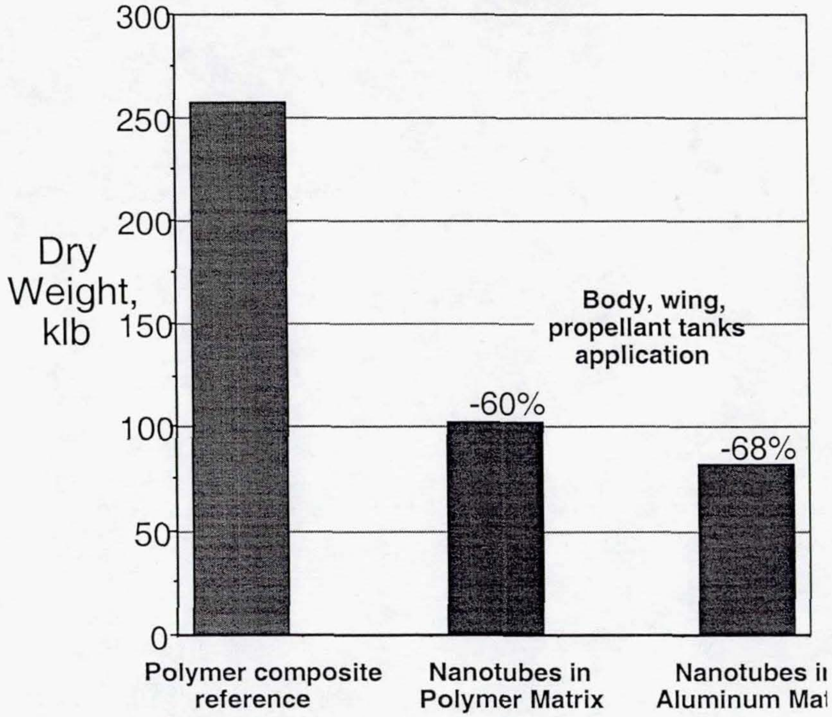
Nanoscale Materials and Processes Applications for Human Spaceflight

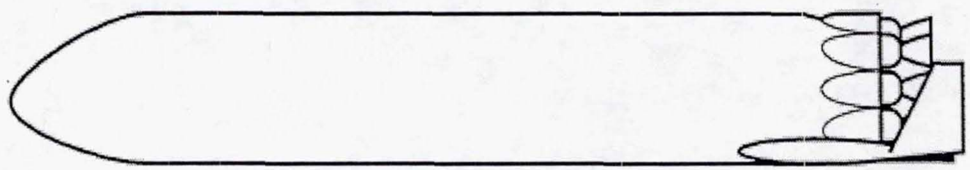
SUPPORT	APPLICATION	PARTNERS	TRL 1	2	3	4	5
SBIR Phase II	**Ultracapacitors**	EP, Glenn	X	X	X	X	
Rice (NCC 977)	**Electrostatic Discharge Materials with Nanotubes**	Rice, LaRC	X	X	X		
Code R	**Proton Exchange Membrane – PEM - Fuel Cells**	EP, Glenn, GB Tech	X	X			
CDDF – ES	**Nanotube-Based Structural Composites**	Rice, UH, LaRC	X	X			
Code R	**RCRS - Regenerable CO_2 Removal System**	EC, GB Tech, Ames	X				
CDDF – ES	**Ceramic Nanofibers for Thermal Protection Materials**	ES3, Ames, Glenn, USAF	X				
SBIR Phase I CDDF - ES	**High Thermal Conductivity Fabric for Spacesuits**	EC, Rice, ORNL	X				
CDDF – NX	**Radiation Resistance/Protection**	NX, Rice, PV, LaRC, Ames	X				
None	**Active Thermal Control Systems for Space**	EC	X				
CDDF – ES	**Nanoshells for Thermal Control Coatings**	ES3, Nanospectra, Goddard	X				

Structural Composites

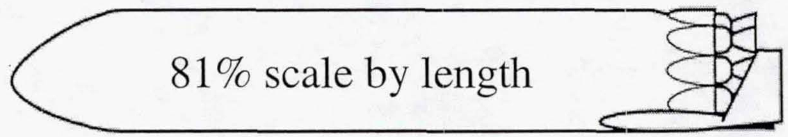
Nanotube Impact on Vehicle Scale



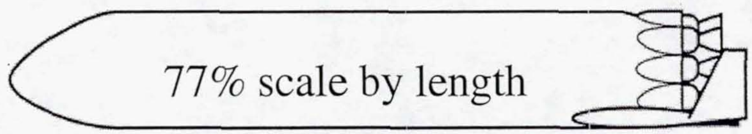




Baseline polymer composite structures and tanks



Nanotubes in polymer matrix
Replace body, wing structures and propellant tanks

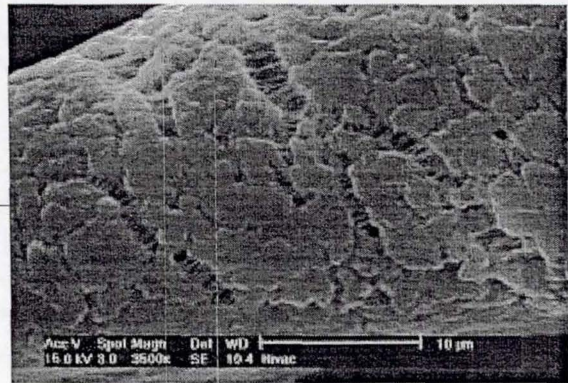


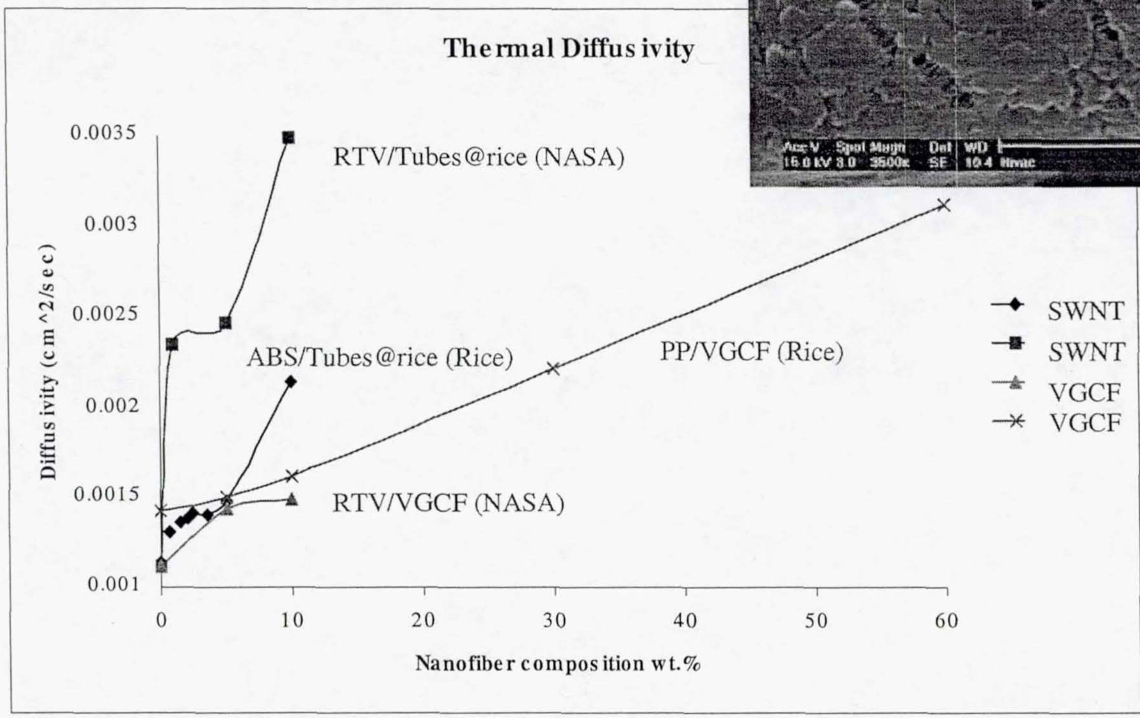
Nanotubes in aluminum matrix
Replace body, wing structures and propellant tanks

High Thermal Conductivity Fabric for Spacesuits

-Nylon Spandex/SWNT fabric improves crew member's thermal comfort

- Increased heat transfer rate from astronaut to sublimator

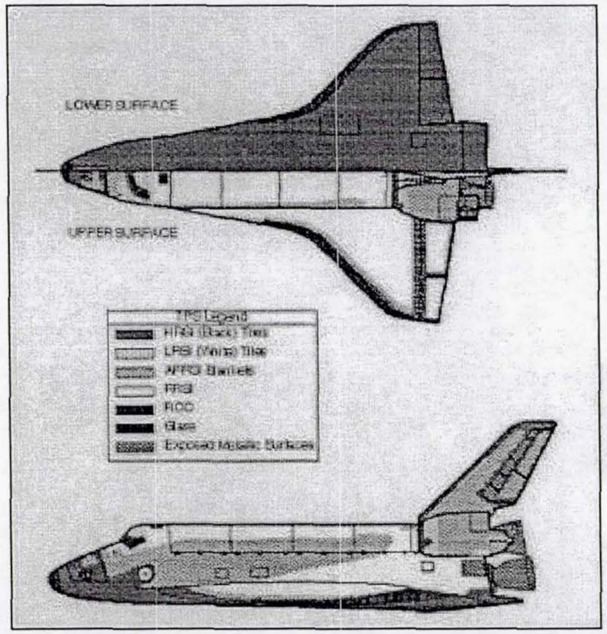


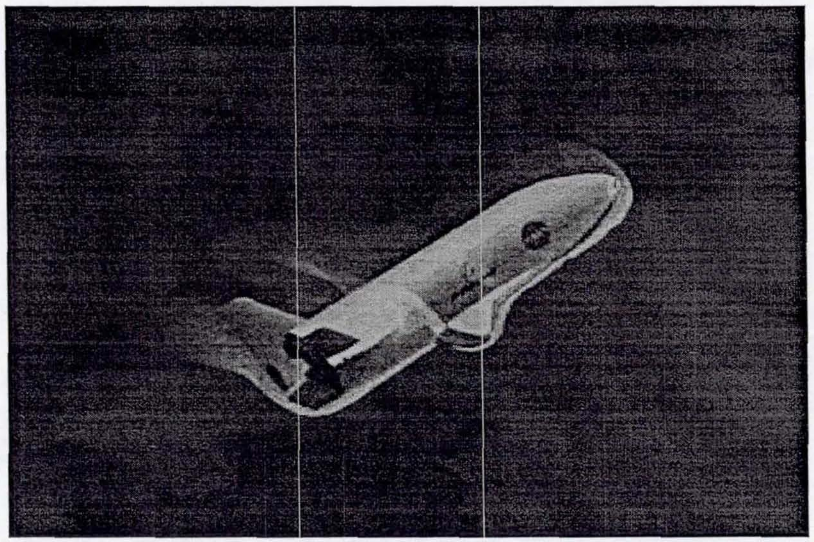


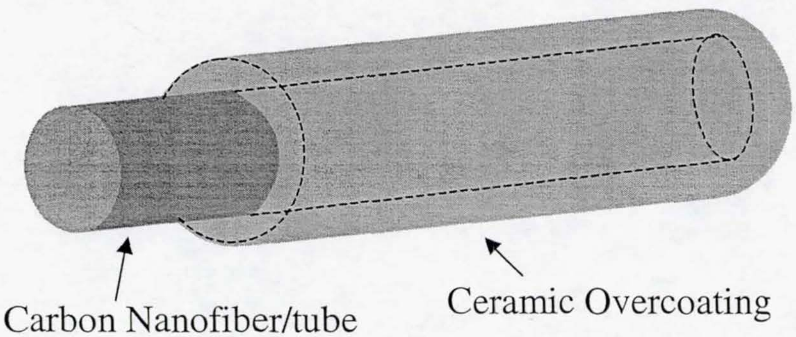
- SWNT thermal properties are extremely anisotropic; heat x-fer is high along length
- SWNT conductivity is comparable to that of diamond (2150 W/m-K)

Thermal Protection System (TPS) Materials

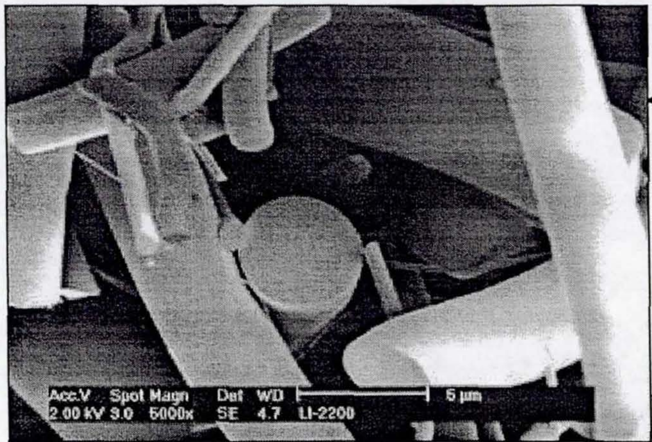
- Next Generation Tiles
  - Optimization of thermal properties at low, intermediate, and high temperatures allows TPS weight to be minimized, and improves vehicle performance.
- Ceramic Nanofibers
  - VGCF/SWNT templating via sol-gel processing







Ceramic Nanofibers for Thermal Protection Materials

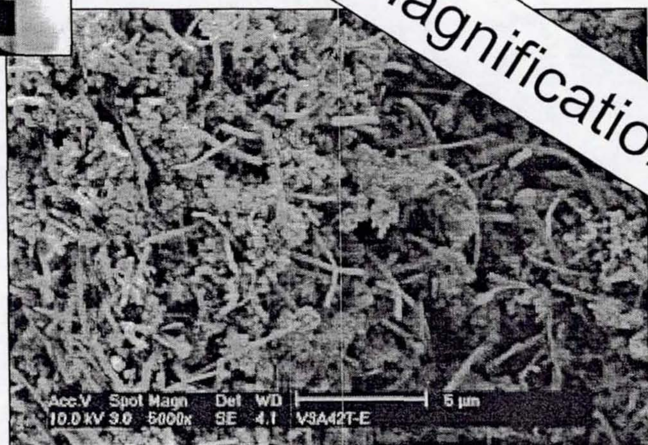


Current LI-2200 Shuttle Tile
Solid Fibers
1-5µm (1000-5000nm)

Same Magnification - 5,000X

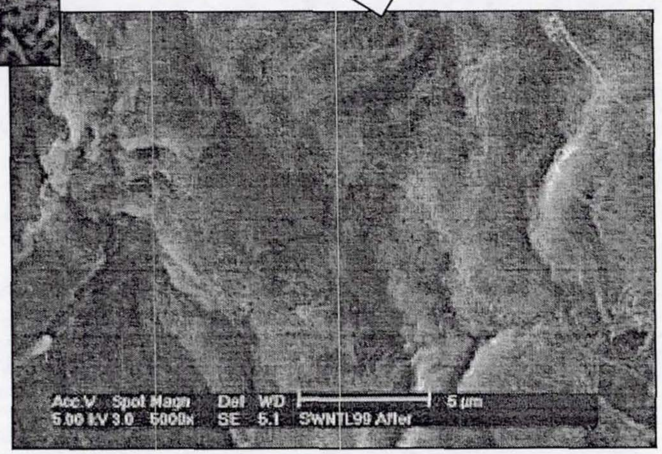
Proposed

Hollow Fibers
0.1-0.3 µm (100-300nm)
Based on Carbon Nanofibers

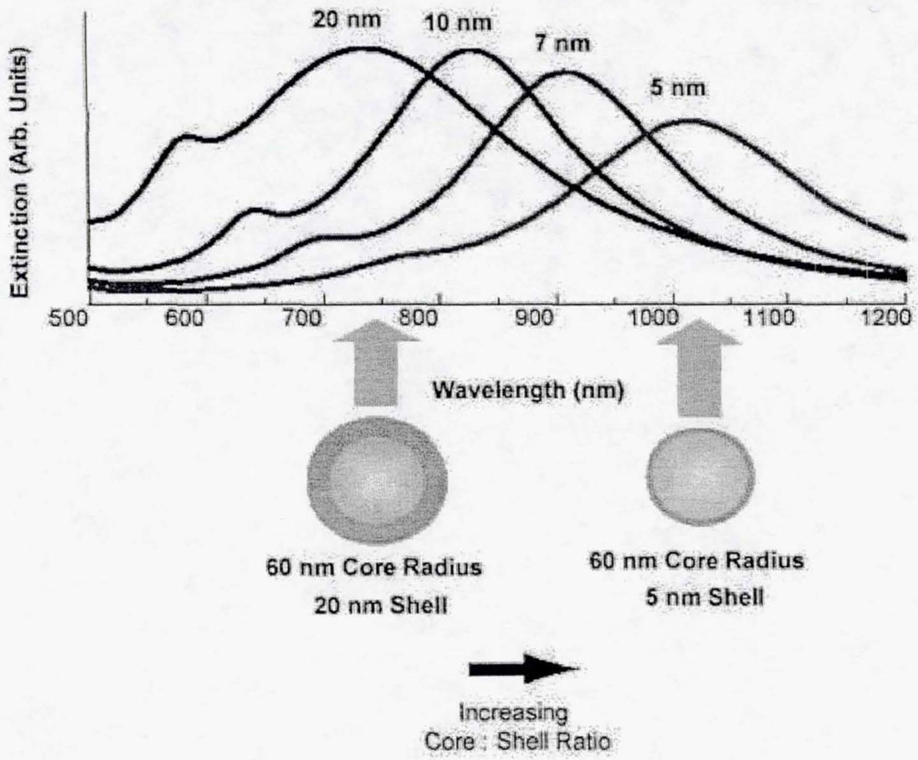


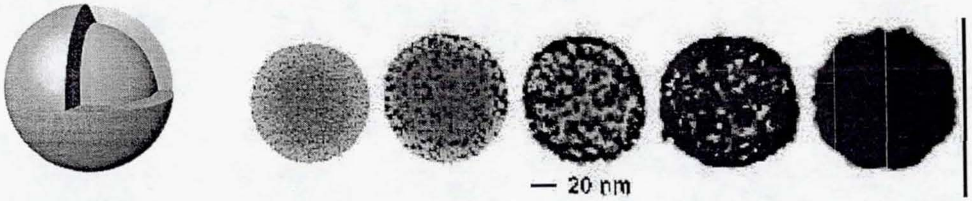
Proposed

Hollow Fibers
0.01-0.05 µm (10-50nm)
Based on Carbon Nanotube Ropes



Nanoshells for Thermal Control Coatings





Courtesy of NanoSpectra

- Nanoshells offer possibility of *designing* thermal control coatings
- Thermo-optical properties manipulated by nanoshell geometry
  - ratio of silica core to shell thickness
  - independent of overall organization of nanoshells
- Interested in nanoshell design with low solar absorbtivity and high emittance

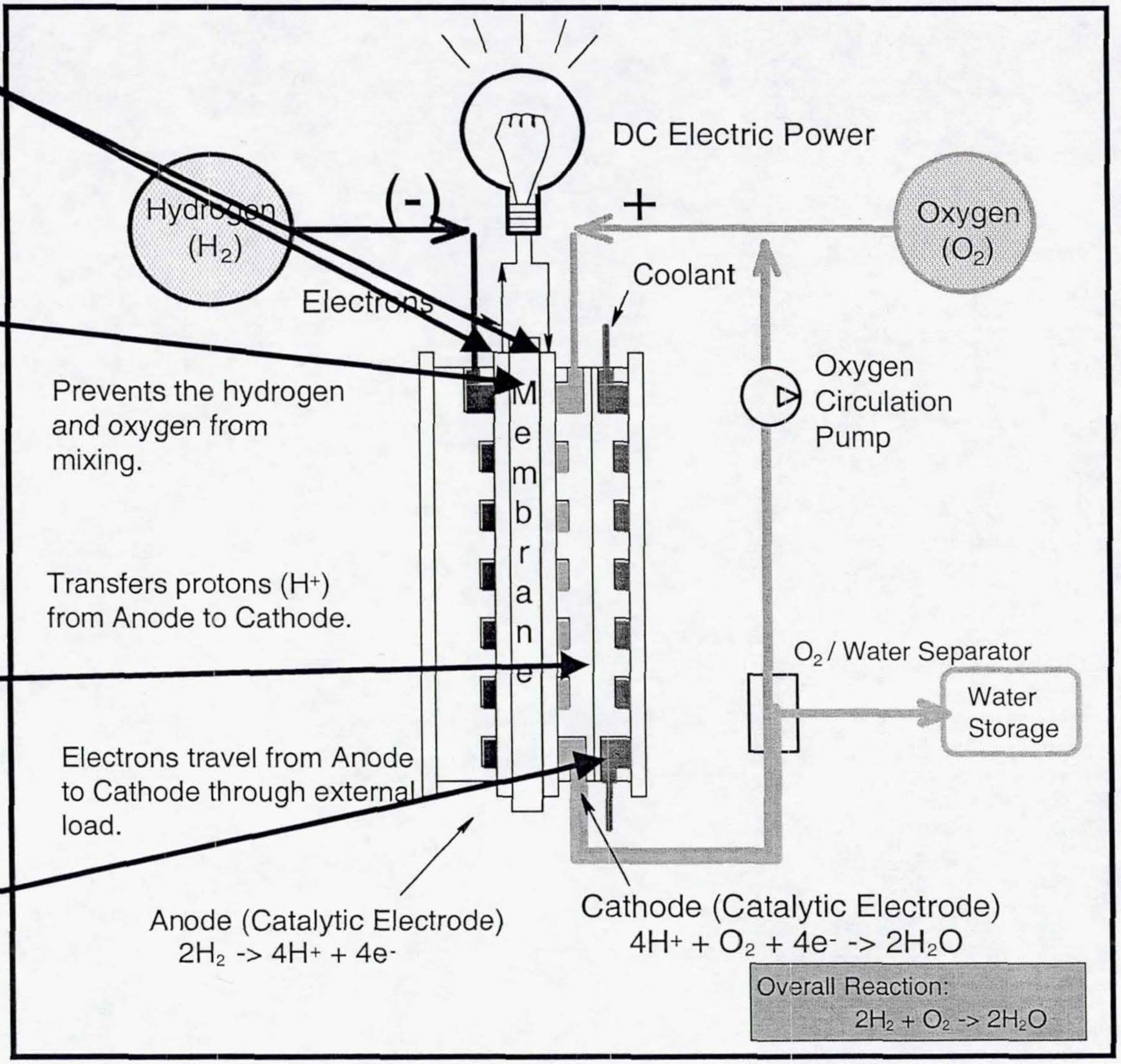
Proton Exchange Membrane (PEM) Fuel Cell

Electrodes
Catalyst Support Layer

Proton Exchange Membrane

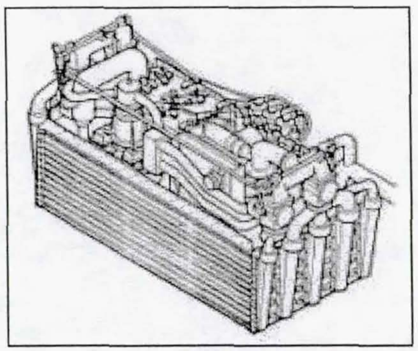
Thermal Management Materials (High k)

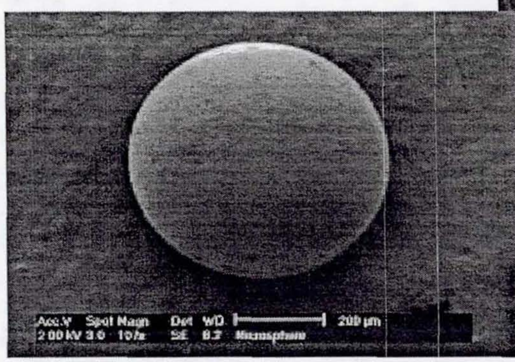
Water Management (wicking)



“CO_2 Scrubber”
RCRS –Regenerable CO_2 Removal System

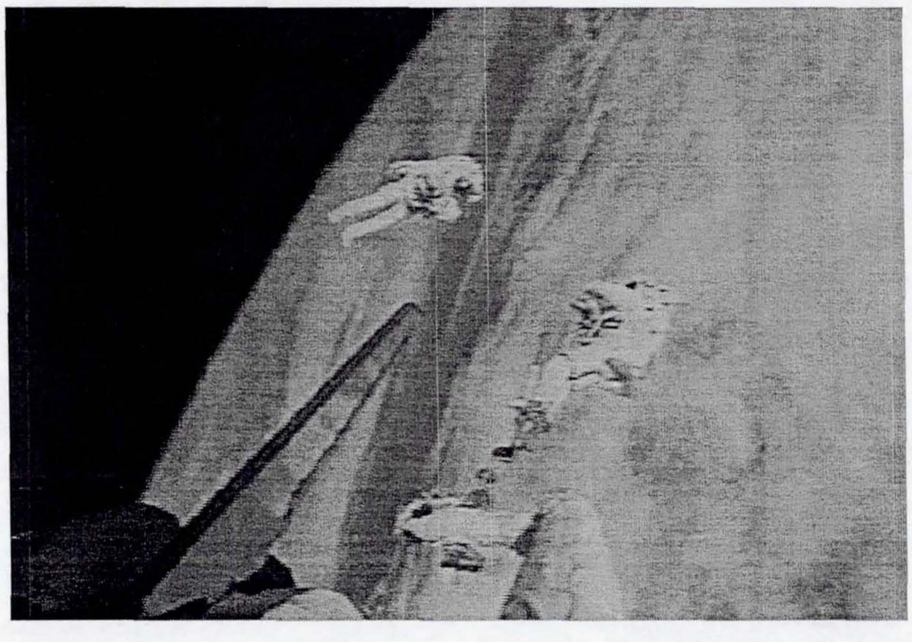
- High surface area beads coated with amine-based chemical adsorbant
- When system is opened to space, material gets cold and not enough CO_2 is removed
- When CO_2 is adsorbed, material heats up, thereby limiting the amount of adsorption
- Need for new material: high surface area, improved thermal conductivity, ability to be coated with amine system
- Proposal currently in to the SLI program for funding for a NASA-led activity, as part of a larger proposal on RCRS
  - Carbon Foam Subscale Bed
  - Nanotube Array Bed (MWNT)
  - Carbon Whisker Bed
  - Amine Sheet Bed





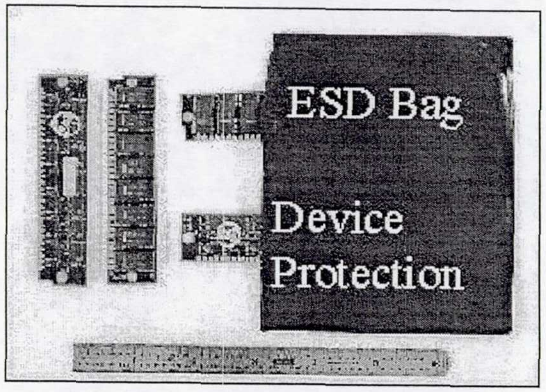
Ultracapacitors

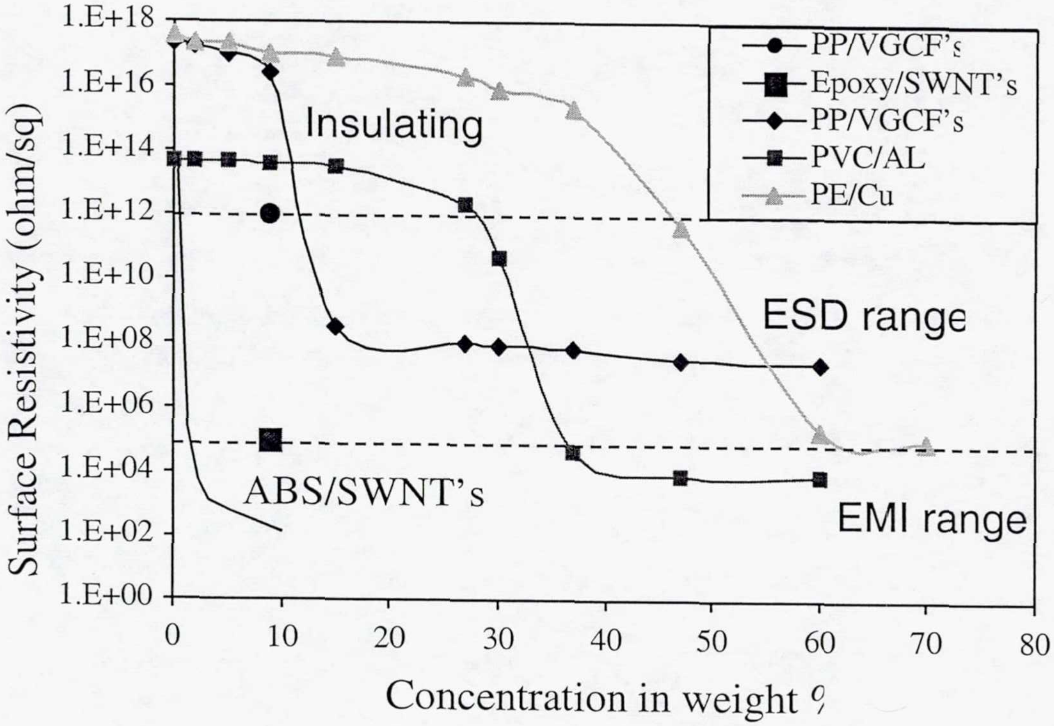
- **Application**
  - **Use nanotubes as electrodes for energy storage, probably to be used in a hybrid system with batteries**
- **Current Collaborators**
  - **SBIR – ReyTech Corp., Inorganic Specialists**

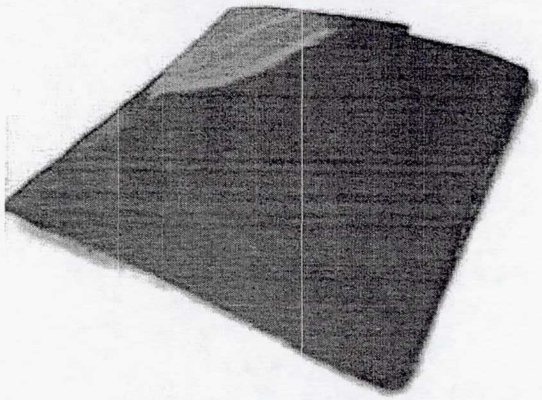


Electrostatic Discharge Materials with Nanotubes

- Applications
  - ESD packaging for humidity extremes
  - Light-weight conductive avionics racks and mounts
  - Oxygen and flame resistant ESD packaging



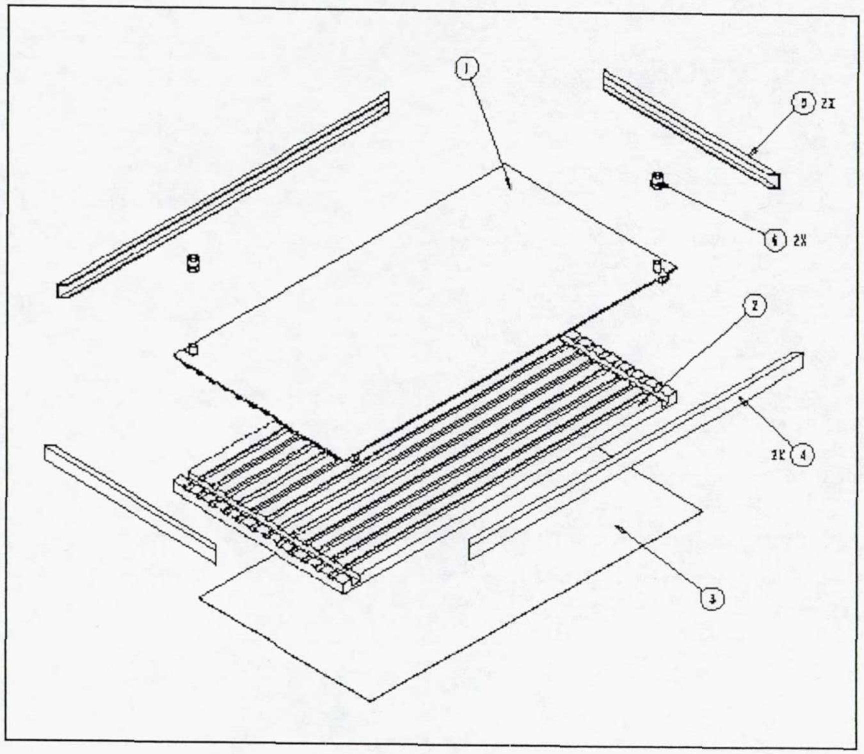




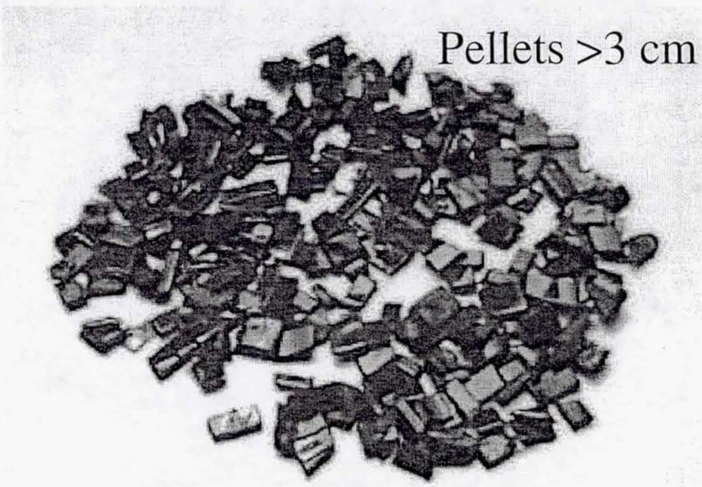
E.V. Barrera et al., Rice University

Active Thermal Control Systems for Space

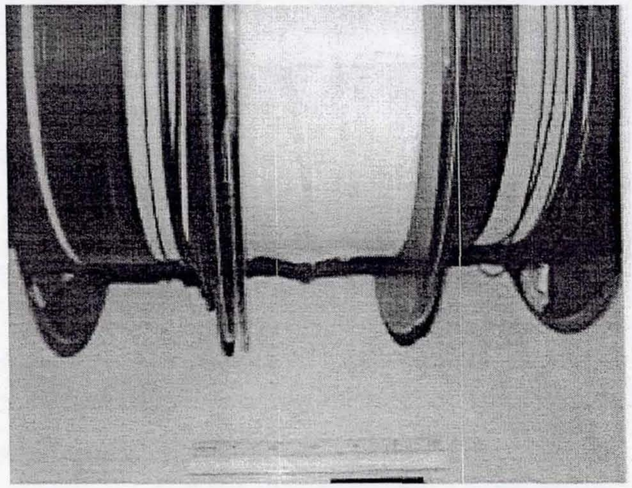
- Four Basic Subsystems
  - **<u>Heat Acquisition</u>**
    - Advanced Cold-Plate Design
      - Carbon Fiber Composite (ThermalGraph Panels @ k=800W/m*K)
    - Carbon Fiber Velvet (Energy Sciences Lab.)
      - Thermal interface
  - **<u>Heat Transport</u>**
    - Heat transport fluids (BP Amoco, Mainstream Eng.)
      - Low freezing point
      - Non-toxic
      - High C_p (PPG)
  - Heat Rejection
  - Control and Monitoring



In-Space Manufacturing

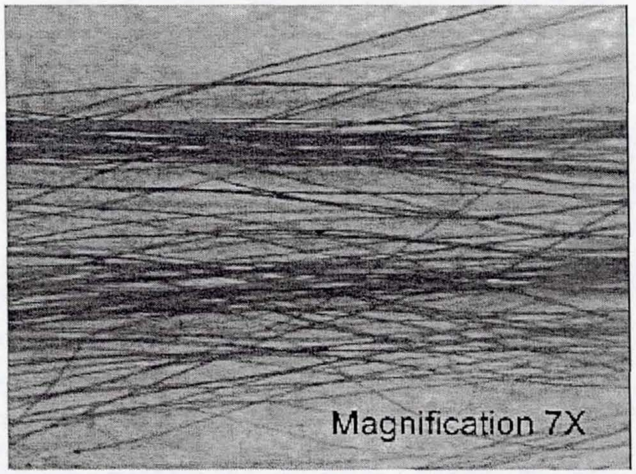


Mixing aggregate
and Masterbatching

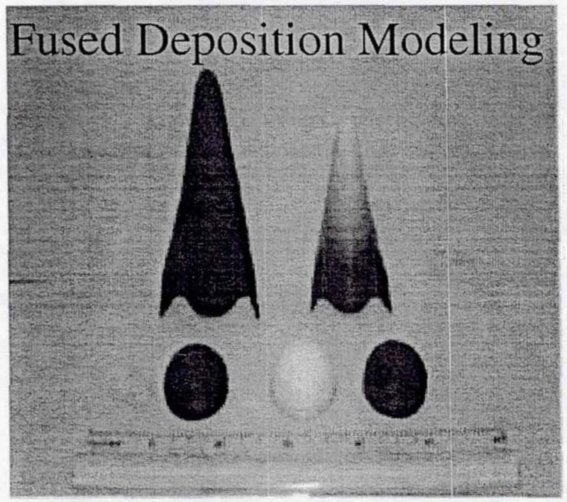


Wire ~2 mm dia. Feedstock

Fibers 25-100 μm dia.



FDM Parts



E.V. Barrera et al., Rice University

Other Applications for Discussion

- EVA Lights
- Cold Cathodes
- Carbon-carbon
- Gas sensors
- Thermally conductive adhesives, greases
- Water purification
- Antennas

Government Collaborations

NASA Glenn Research Center
• Functionalization, purification, high temp. mat'ls (Meador, Gray)

NASA Ames Research Center
• Nanotubes (JSC) / modeling of HiPco (Meyyappan, Srivastava)

NASA Langley Research Center
• <u>**Code R $**</u> – Production/purification (JSC) for use in SWNT composites (Siochi, Sutter)

NASA Marshall Space Flt Center
• Nanotubes, MMCs (Gill, Hudson)

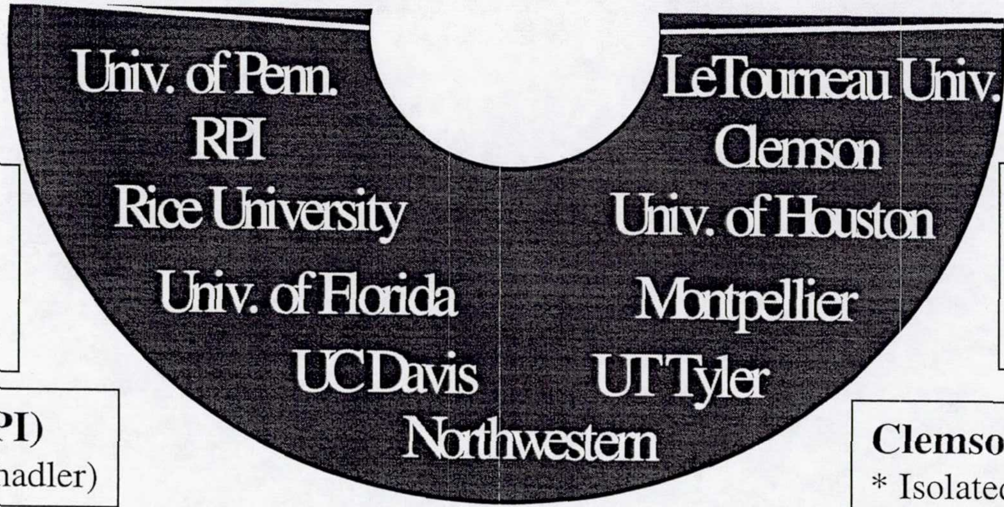
Air Force Research Lab.
• Composites, characterization, purification (Maruyama)

Naval Research Lab.
• Composites (Imam)

Nat'l Renewable Energy Lab
• Purification (Heben, Dillon)

Oak Ridge Nat'l Lab.
• Thermal characterization (Wang, Dinwiddie)

University Collaborations



Univ. of Pennsylvania
- **<u>CDDF</u>** - Thermal Mgmt. Mat'ls (Fischer)
- Composites (Luzzi, Winey)

Rensselaer (RPI)
- Composites (Schadler)

Rice University
- **<u>Cooperative Agreement</u>** – Advanced Nanotechnology Mat'ls and Applications Yr. 5/5 (Smalley, Tour, Barrera, Margrave)
- Computational Mat'ls Sci. (Yakobson)
- Nanoshells (Halas)

University of Florida
- Isolated SWNTs (Rinzler)

Univ. of Calif. - Davis
- Nanocrystalline Ceramics (Mukherjee)

Northwestern
- Mechanics/composites (Brinson)
- Nanotubes (Ruoff)

LeTourneau Univ.
- **<u>Summer Faculty Fellow</u>** Nanotube growth process (DeBoer)

Clemson University

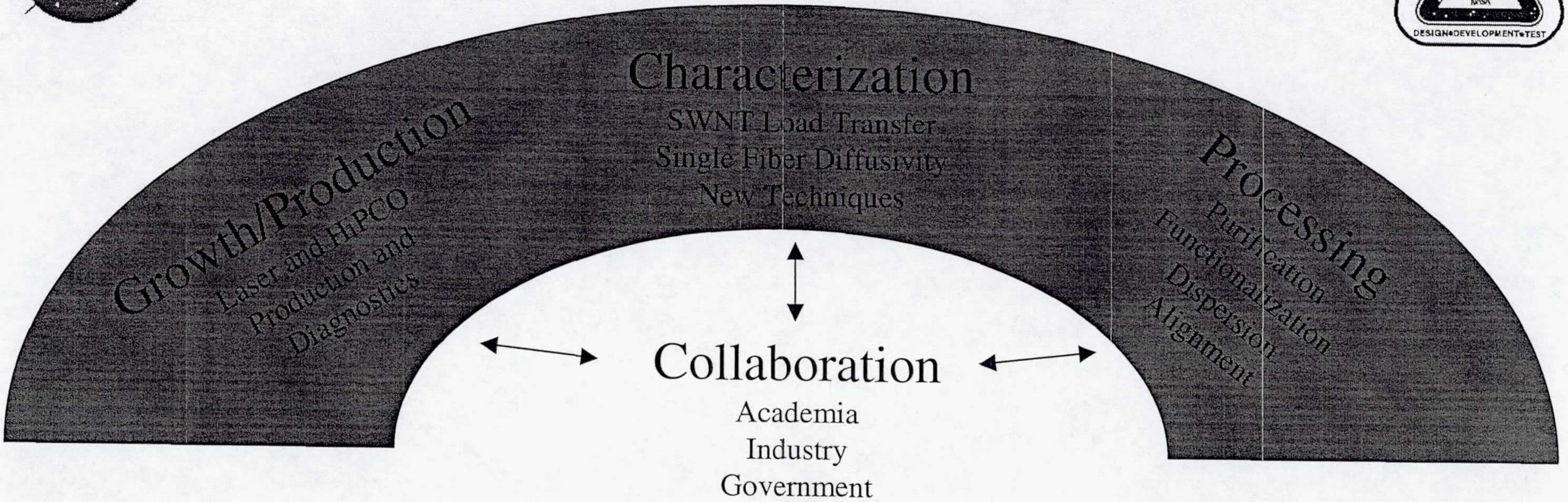
* Isolated SWNTS - STM (Carroll)

University of Houston
- **<u>ISSO</u>**, year 3 of 3 – Raman Characterization (Iliev, Hadjiev)
- **<u>GSRP</u>**, year 2 – Polymer chem., dispersion, composites (Mitchell, Krishnamoorti)

Univ. of Montpellier
- Arc process (Bernier)

Univ. of Texas - Tyler
- **<u>Summer Faculty Fellow</u>** - CFD of Laser process (Greendyke)

Nanoscale Materials and Processes



Applications for Human Spaceflight

SUPPORT	APPLICATION	PARTNERS	TRL 1	TRL 2	TRL 3	TRL 4	TRL 5
SBIR Phase II	**Ultracapacitors**	EP, Glenn	X	X	X	X	
Rice (NCC 977)	**Electrostatic Discharge Materials with Nanotubes**	Rice, LaRC	X	X	X		
None	**Proton Exchange Membrane – PEM - Fuel Cells**	EP, Glenn	X	X			
CDDF – ES	**Nanotube-Based Structural Composites**	Rice, UH, LaRC	X	X			
None	**RCRS - Regenerable CO_2 Removal System**	EC, Ames	X				
CDDF – ES	**Ceramic Nanofibers for Thermal Protection Materials**	ES3, Ames, Glenn, USAF	X				
SBIR Phase I CDDF - ES	**High Thermal Conductivity Fabric for Spacesuits**	EC, Rice, ORNL	X				
CDDF – NX	**Radiation Resistance/Protection**	NX, Rice, PV, LaRC, Ames	X				
None	**Active Thermal Control Systems for Space**	EC	X				
CDDF – ES	**Nanoshells for Thermal Control Coatings**	ES3, Nanospectra, Goddard	X				

Education
Museum of Natural Science

Nano-Bio
JSC Life Sciences

Composite Materials

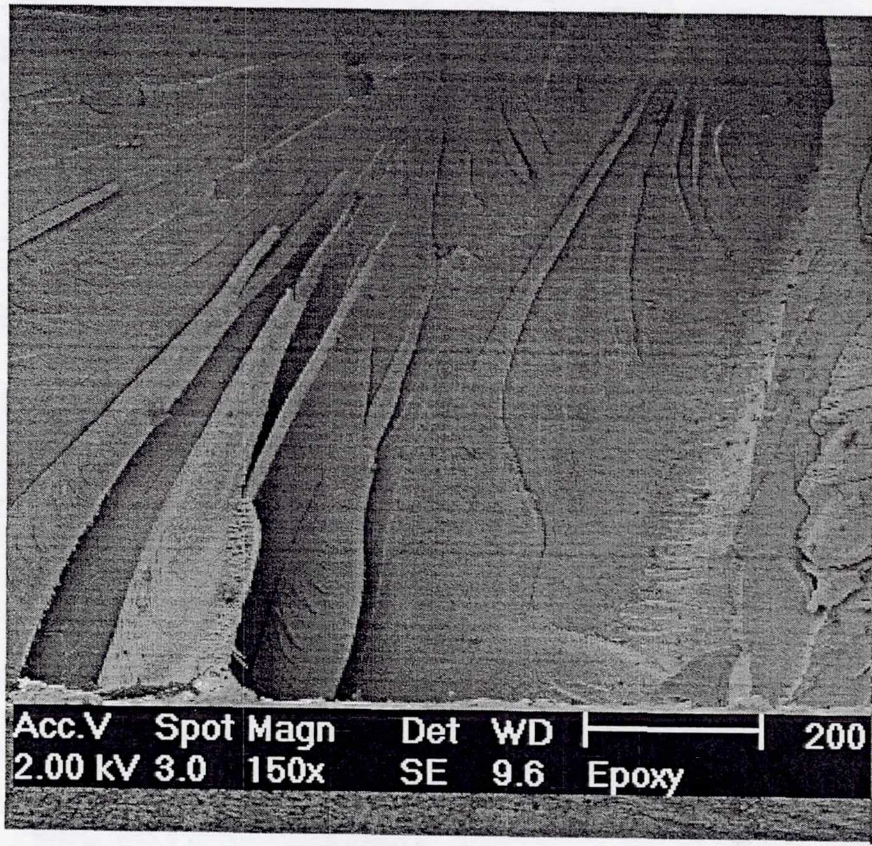
I have issues…

- Dispersion
- Interface
- Morphology
- Orientation
- Processing

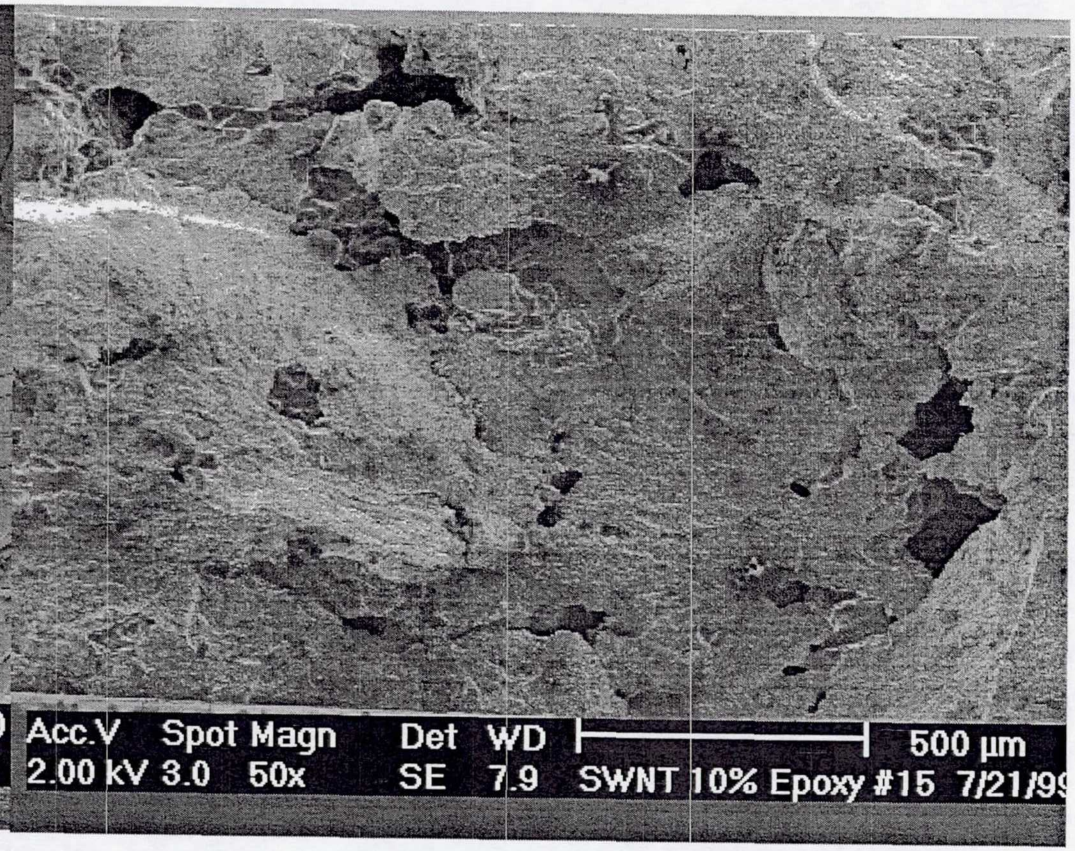
Interfaces

- If you compare a 1 nm fiber to a 1 micron fiber, you have a million times as many fibers for the same volume fraction,
- Interfaces are of interest in all composite materials
- In these nanocomposites the percentage of interfacial area is greatly multiplied
- Maybe all regions are interface
- Nanotube composites are very brittle

- Samples with nanotubes found to have more brittle characteristics than control samples.



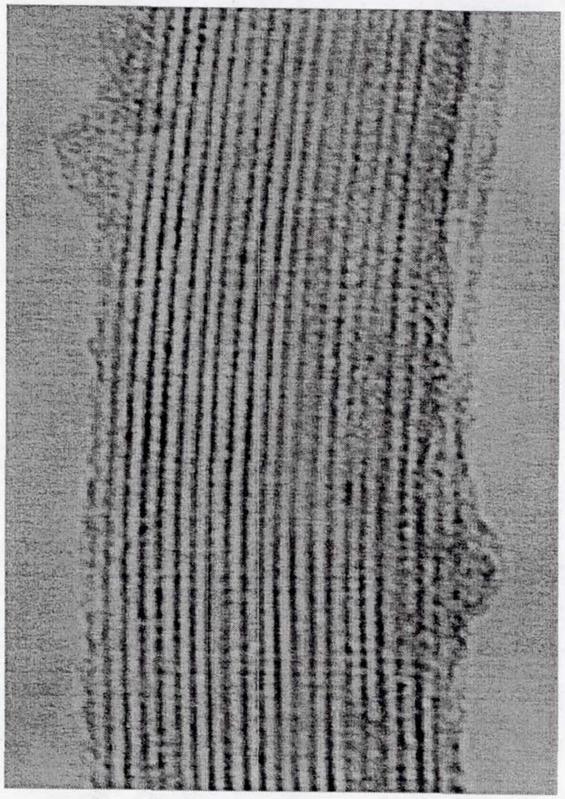
Control Sample



10% Nanotubes

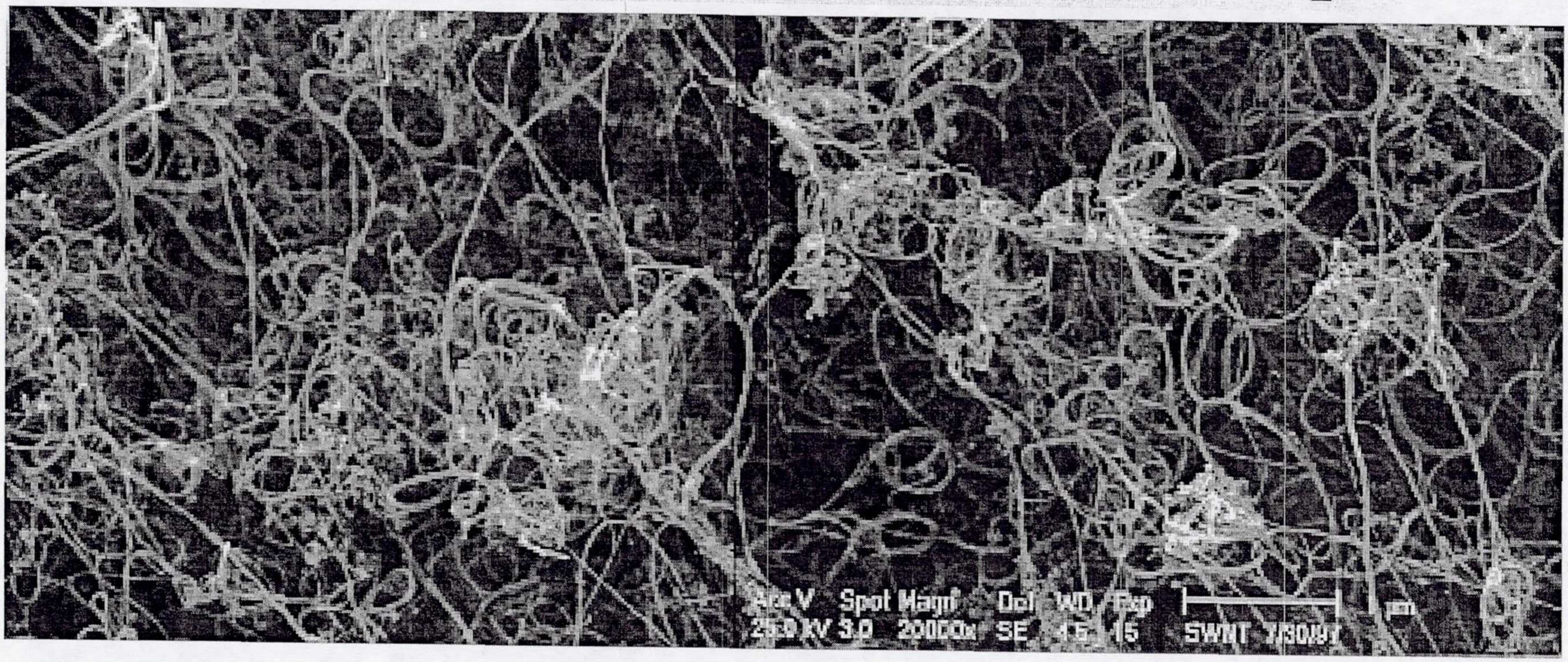
Dispersion

TEM image of a bundle of single wall nanotubes

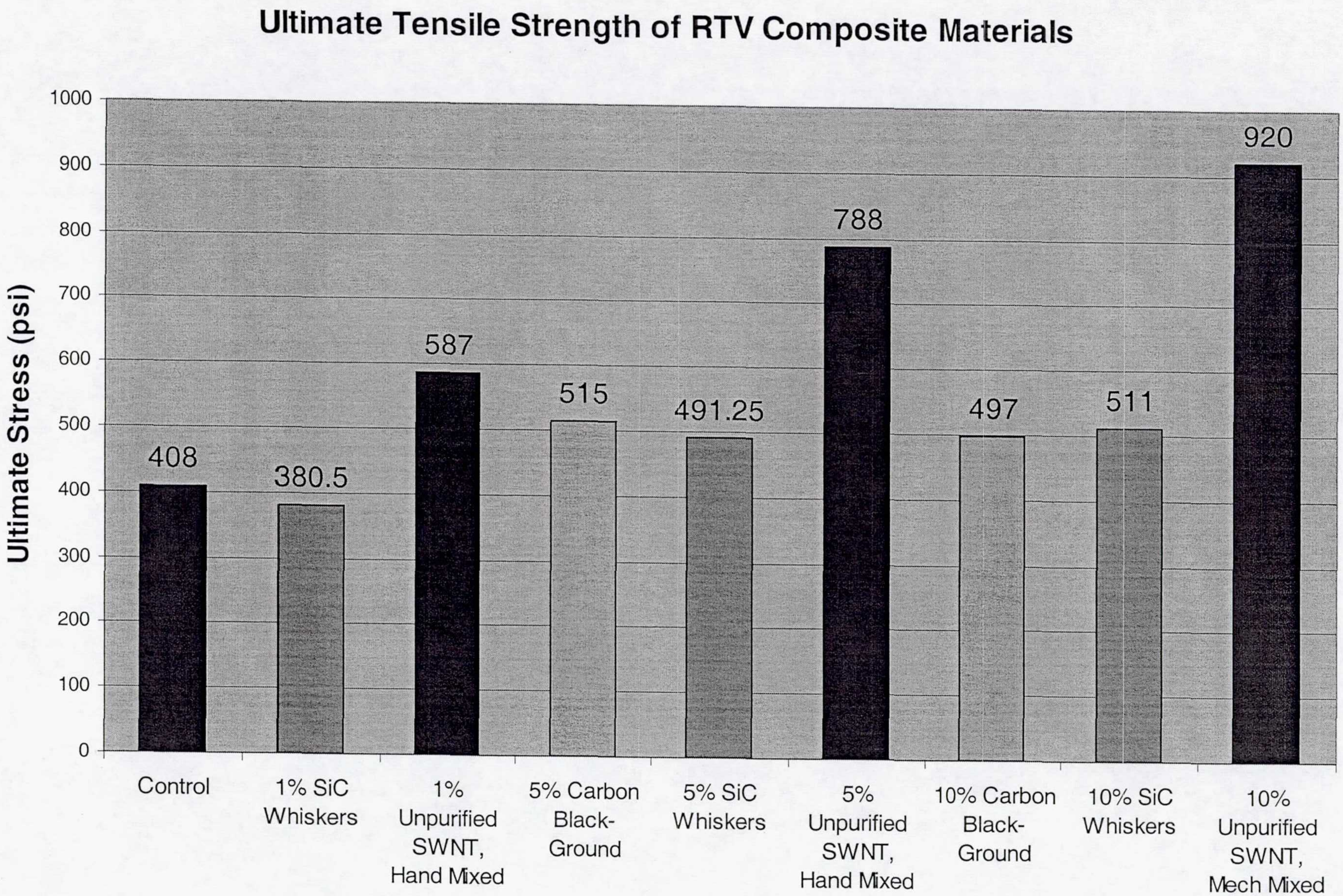


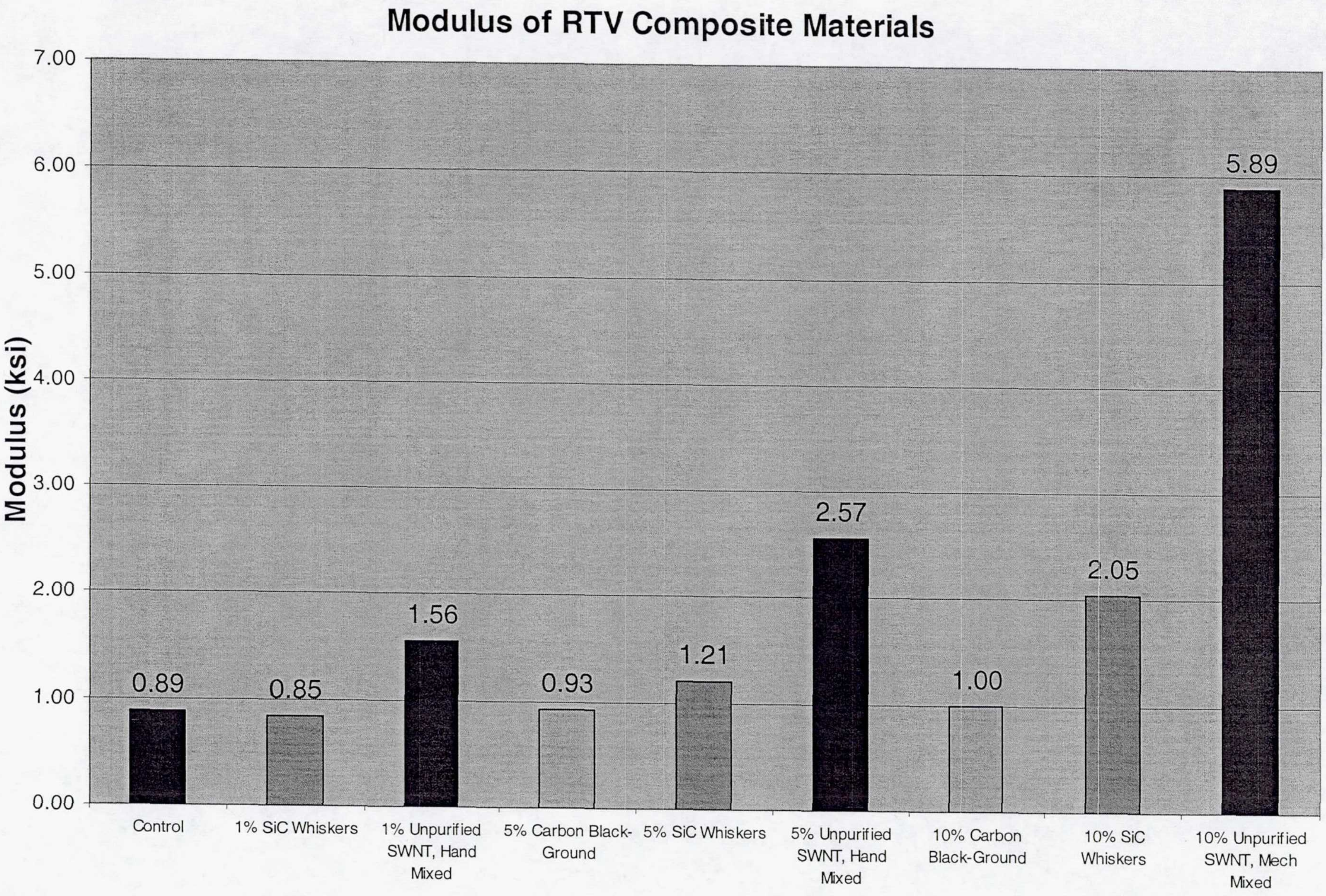
The carbon on the walls does not appear to be nanotubes.
Is there also other carbon inside? What is the purity?

Morphology:
SEM of As-Produced Nanotube Ropes

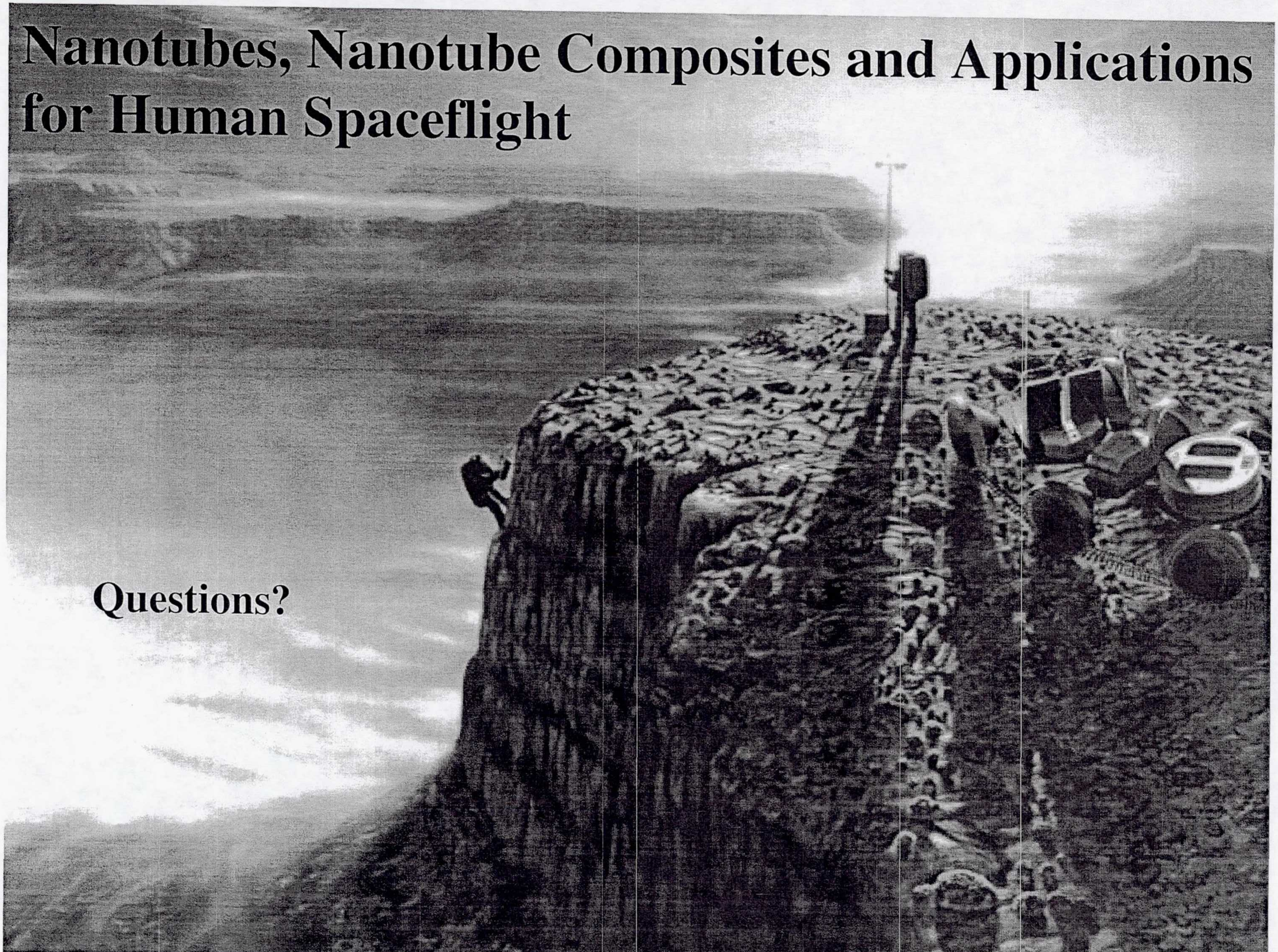


How can you put this "Angel Hair" into a composite and expect to get strengthening?


Ultimate Tensile Strength of RTV Composite Materials
Ultimate Stress (psi)
1000
900
800
700
600
500
400
300
200
100
0
408
380.5
587
515
491.25
788
497
511
920
Control
1% SiC Whiskers
1% Unpurified SWNT, Hand Mixed
5% Carbon Black-Ground
5% SiC Whiskers
5% Unpurified SWNT, Hand Mixed
10% Carbon Black-Ground
10% SiC Whiskers
10% Unpurified SWNT, Mech Mixed


Modulus of RTV Composite Materials
Modulus (ksi)
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.89
0.85
1.56
0.93
1.21
2.57
1.00
2.05
5.89
Control
1% SiC Whiskers
1% Unpurified SWNT, Hand Mixed
5% Carbon Black-Ground
5% SiC Whiskers
5% Unpurified SWNT, Hand Mixed
10% Carbon Black-Ground
10% SiC Whiskers
10% Unpurified SWNT, Mech Mixed

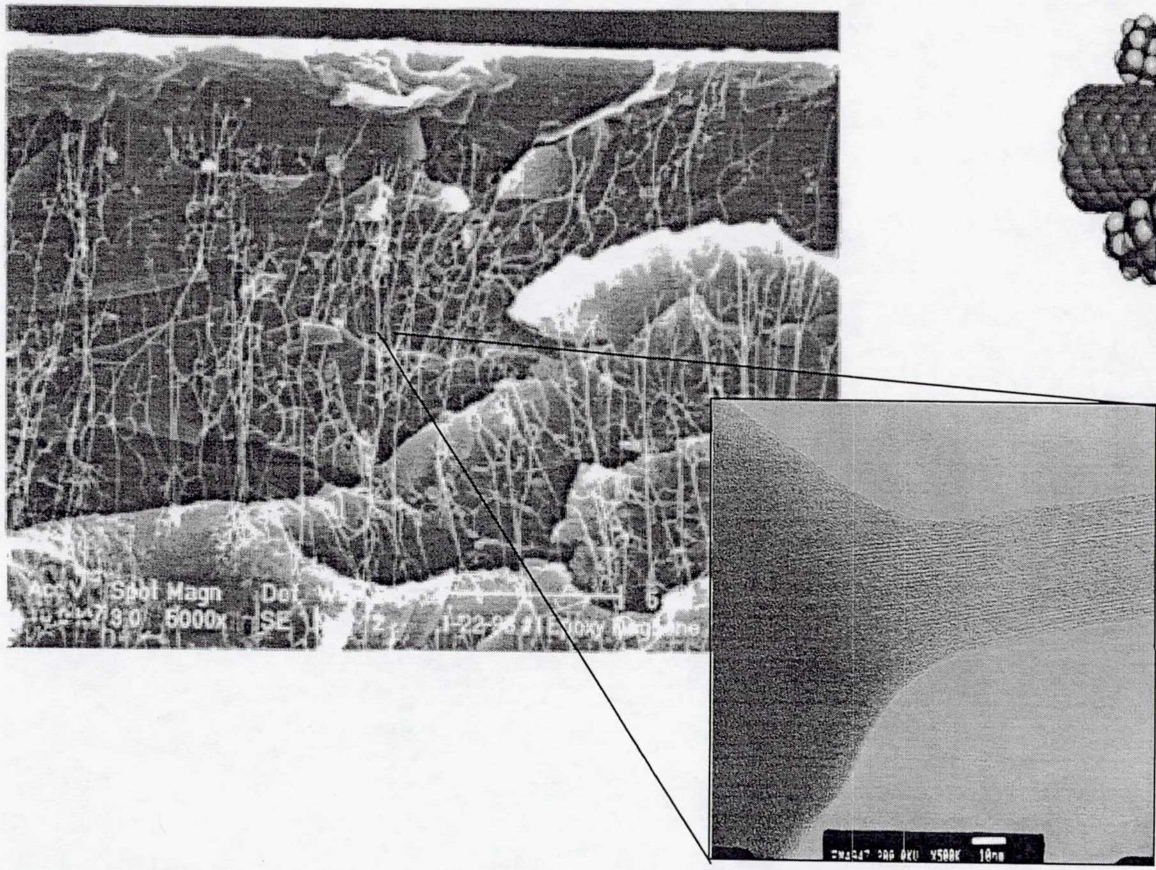
Nanotubes, Nanotube Composites and Applications for Human Spaceflight

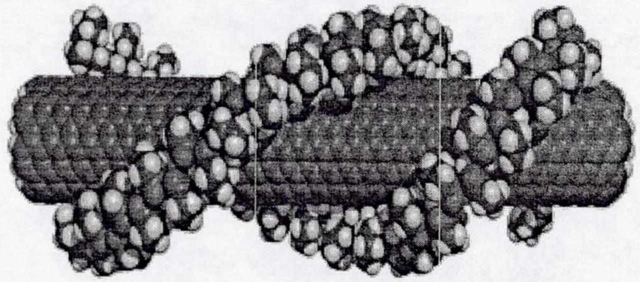


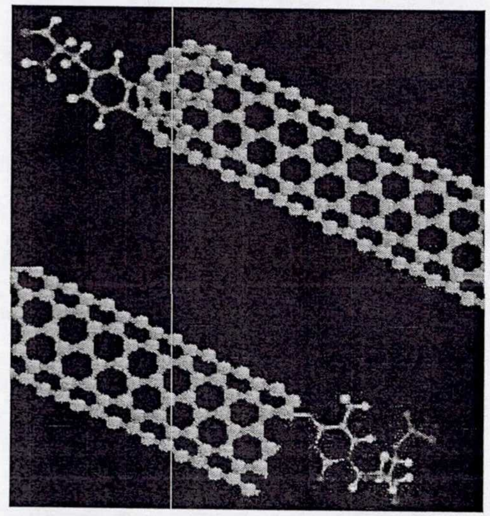
Single Wall Carbon Nanotube Composites

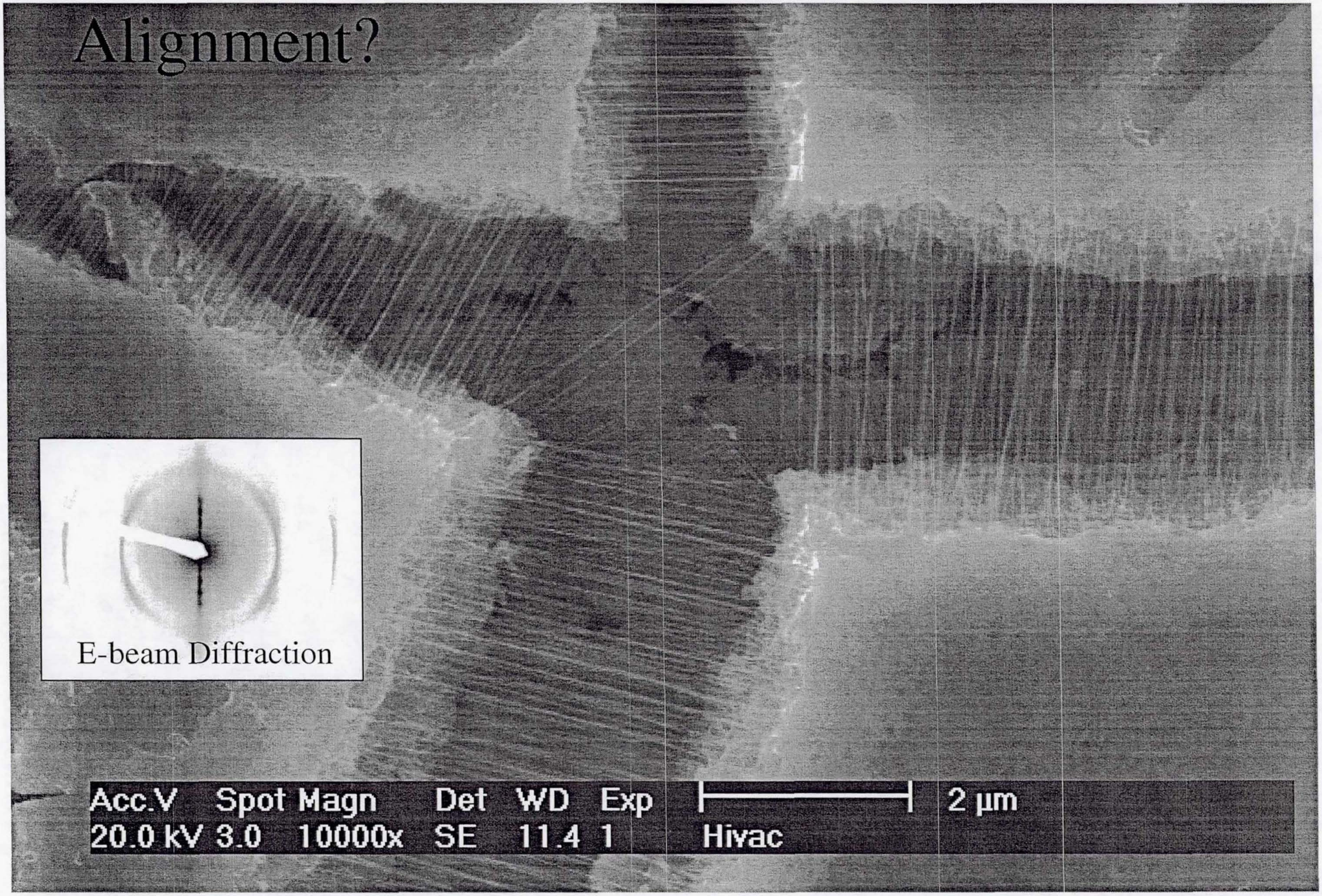
- Polymer/SWNT processing
- Bonding (functionalization)

•Dispersion of SWNTs/Bundles
•Alignment









SWNTs in Sol-Gel Zirconia