Literally Big Nano: Nano-Engineered Composites for Aerospace and Infrastructure Applications

NECST

nano-engineered composite aerospace
structures consortium

University of Tokyo, GMSI GCoE Seminar
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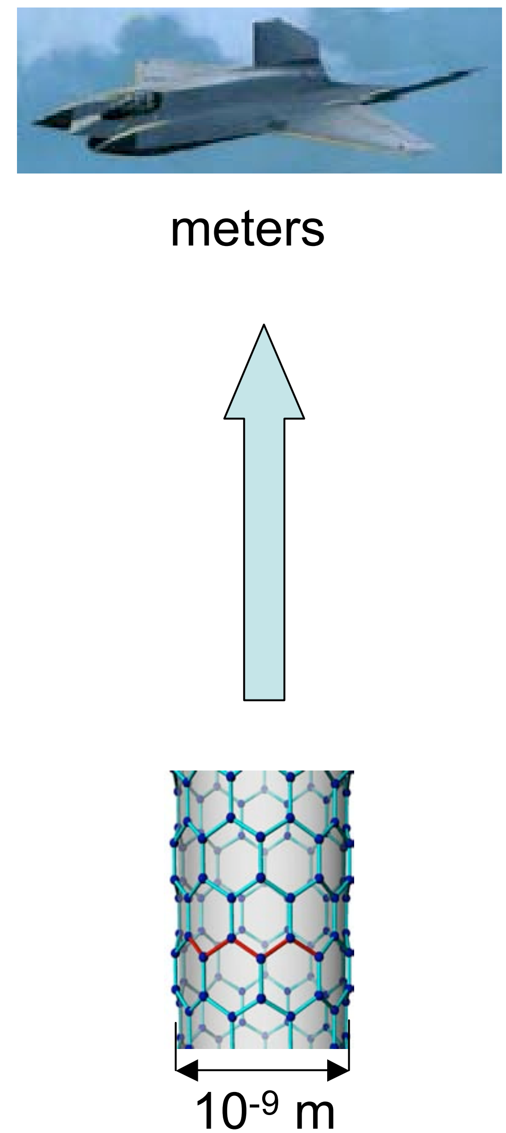
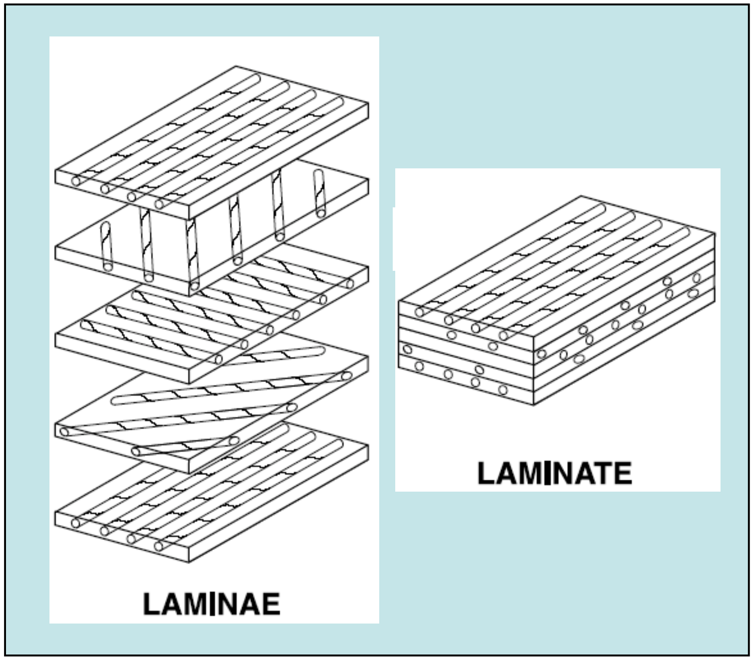
Overview: “Of Nanotubes and Airplanes”

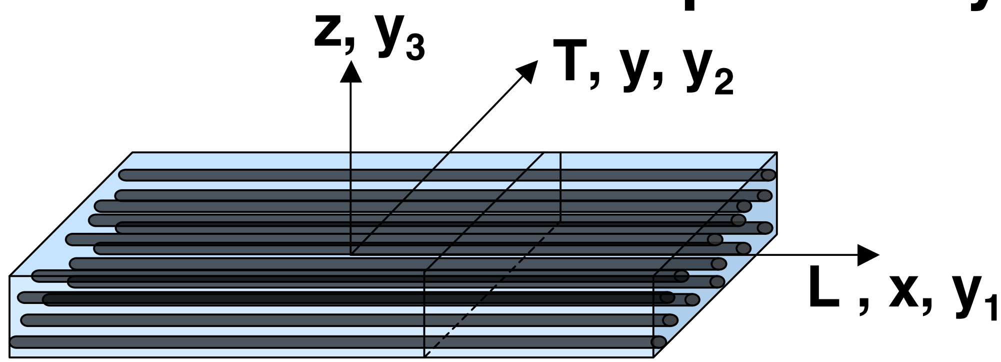
- Opportunities and challenges in advanced composites, and the role of nanotechnology
- Polymer composites and nanocomposites using aligned carbon nanotubes
  - **Nano-engineered** (fiber-based) advanced composites for aerospace applications
  - Controlled-morphology **polymer nanocomposites**
- Supporting work and extensions



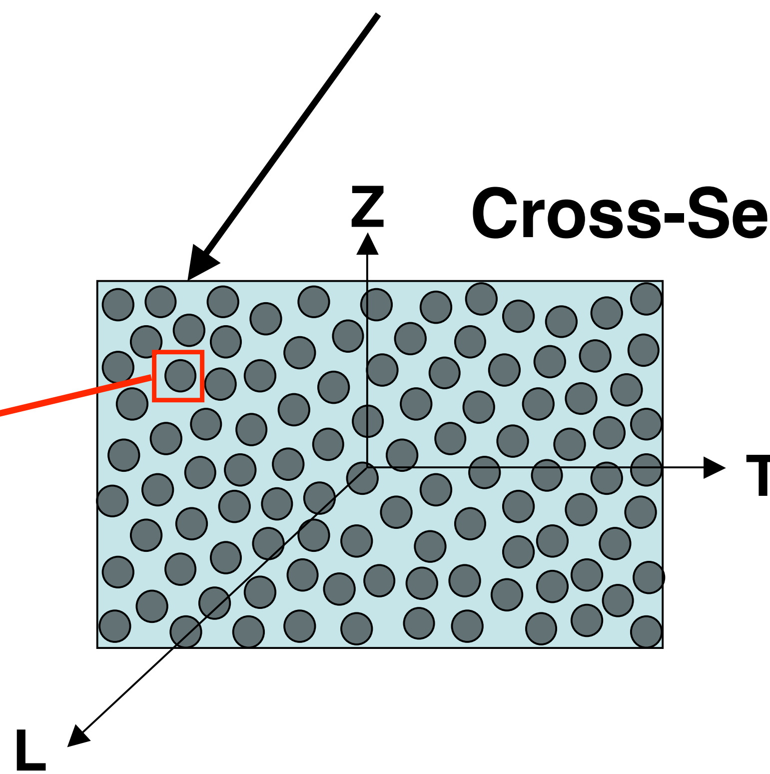
Existing (Laminated) Advanced Composites

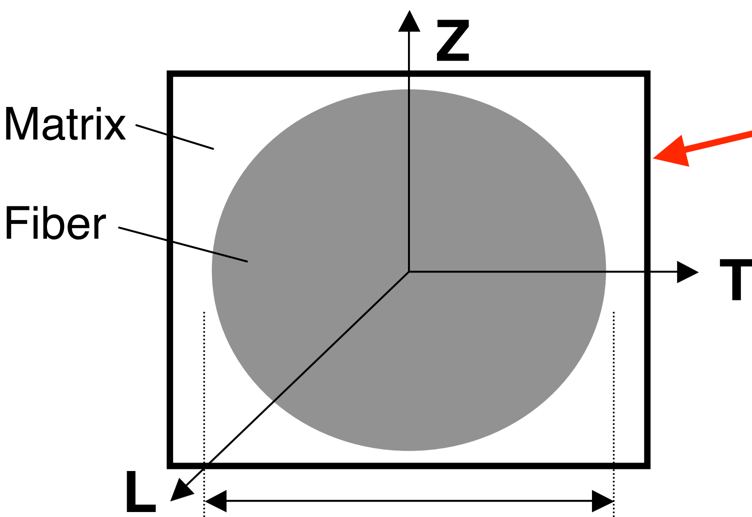


Unidirectional Composite Ply



Cross-Section





~ 7 μm
(carbon/epoxy)

Advanced Composites and Carbon Nanotubes (CNTs)

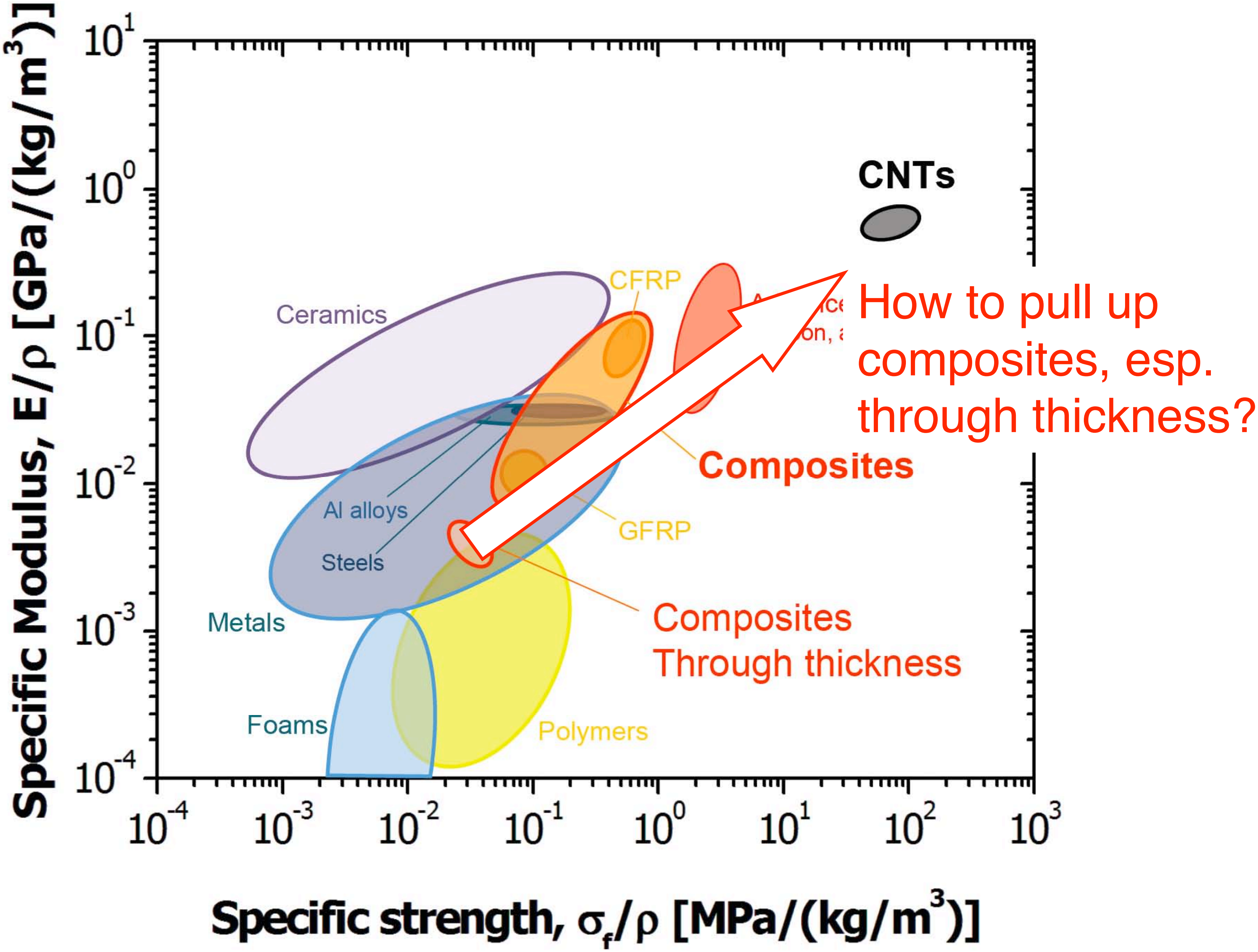


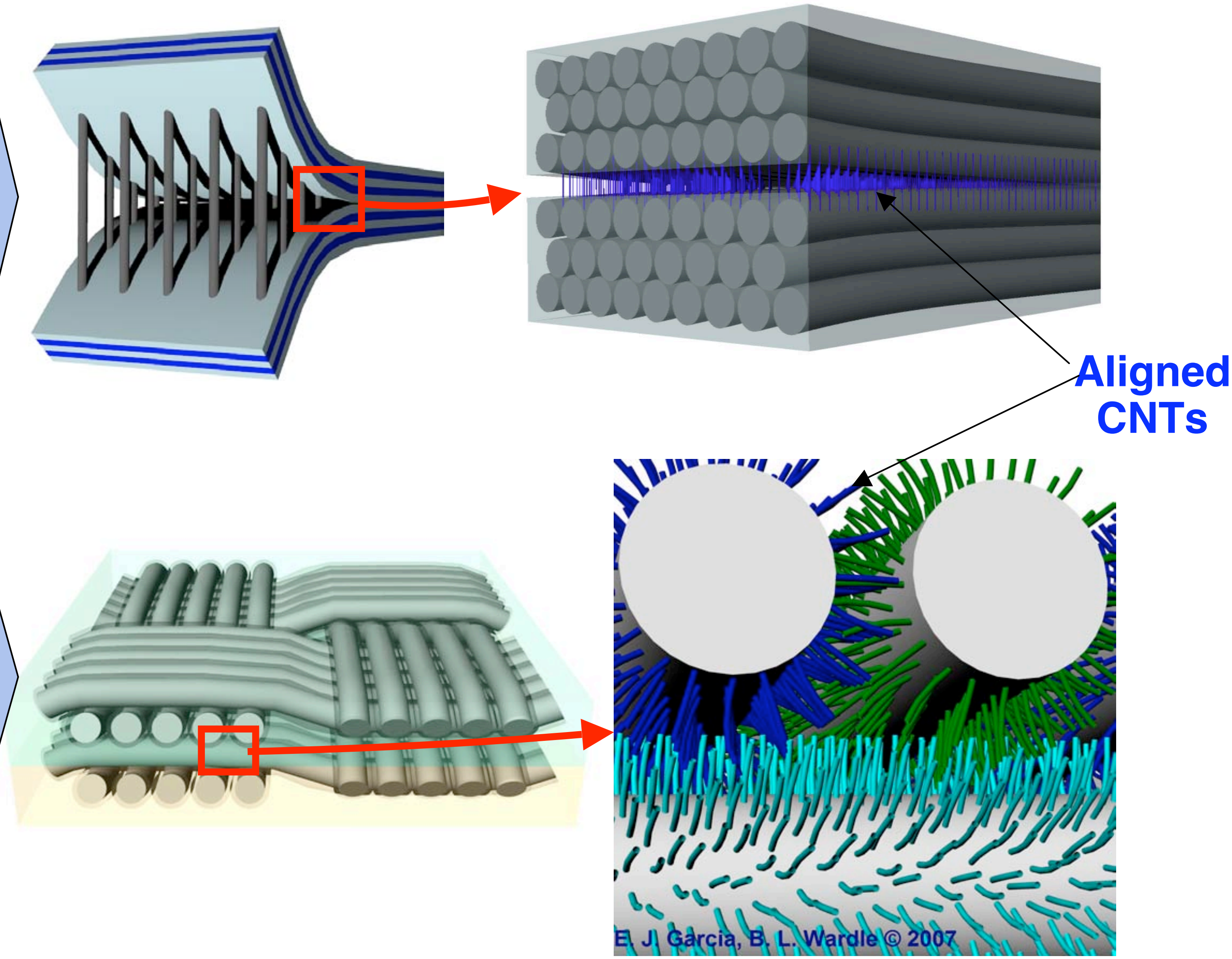
Chart after M.F. Ashby

Nano-Engineered (Hybrid) Composites

Use aligned CNTs to reinforce and tailor existing advanced composites

1. "Nanostitching"

2. "Fuzzy Fiber" Reinforced Plastic (FFRP)

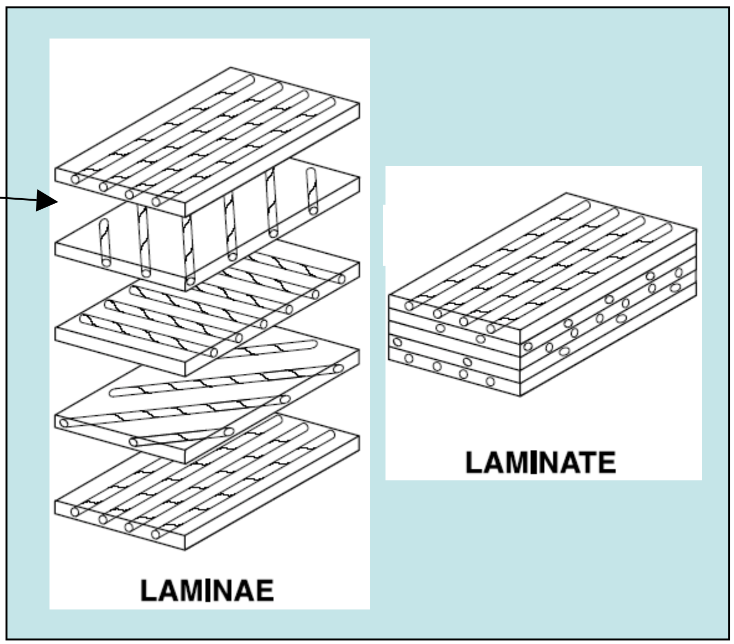


Garcia, Wardle, et al., *Comp. Sci. Tech.* and *Composites A.*, 2008.

Composite Opportunities for 3D Nanoscale Enhancement and Tailoring

- Fix weak interfaces in composites
  - Delamination (cracking between plies)
  - Toughness at interface ~100-1000X less than in-plane direction
- Conductivity enhancement: electrostatic discharge, EMI shielding, lightning-strike protection, thermal enhancement
- Other key properties such as laminate bearing strength, etc.

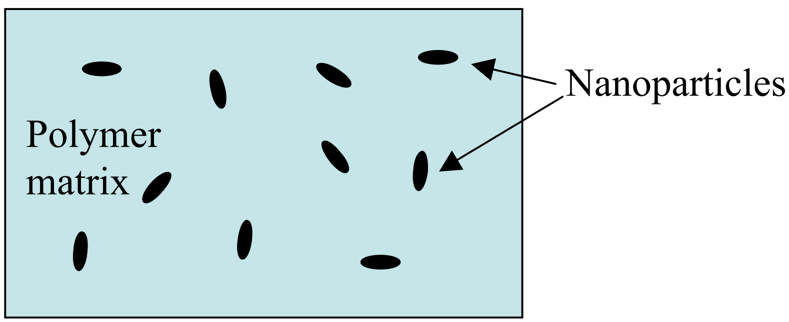
Plies held together by polymer



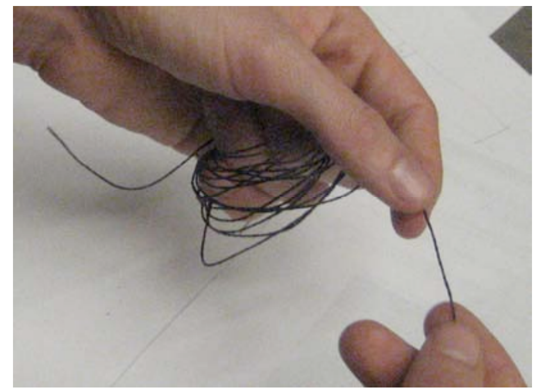
787 image courtesy of Boeing

Nanocomposites, Yarns, and Nano-Engineered Composites

<u>Nanocomposites:</u> Modify matrix (typically polymer) by addition of nanoparticles, including CNTs



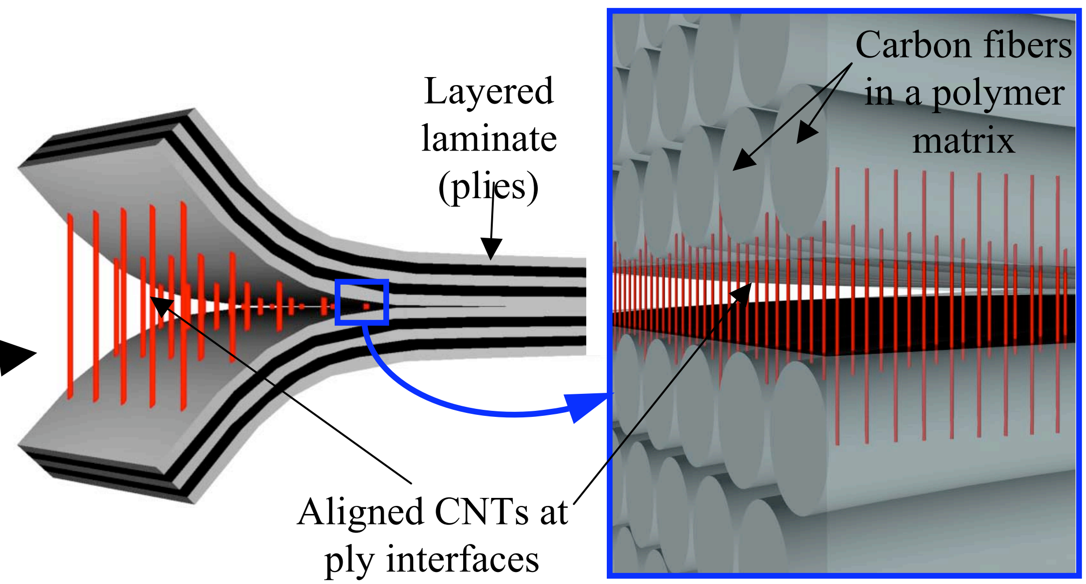
<u>CNT Yarns, Sheets, Hybrid Fibers:</u> Replace (carbon) fiber with discontinuous-CNT forms



<u>Nano-engineered Composites</u>

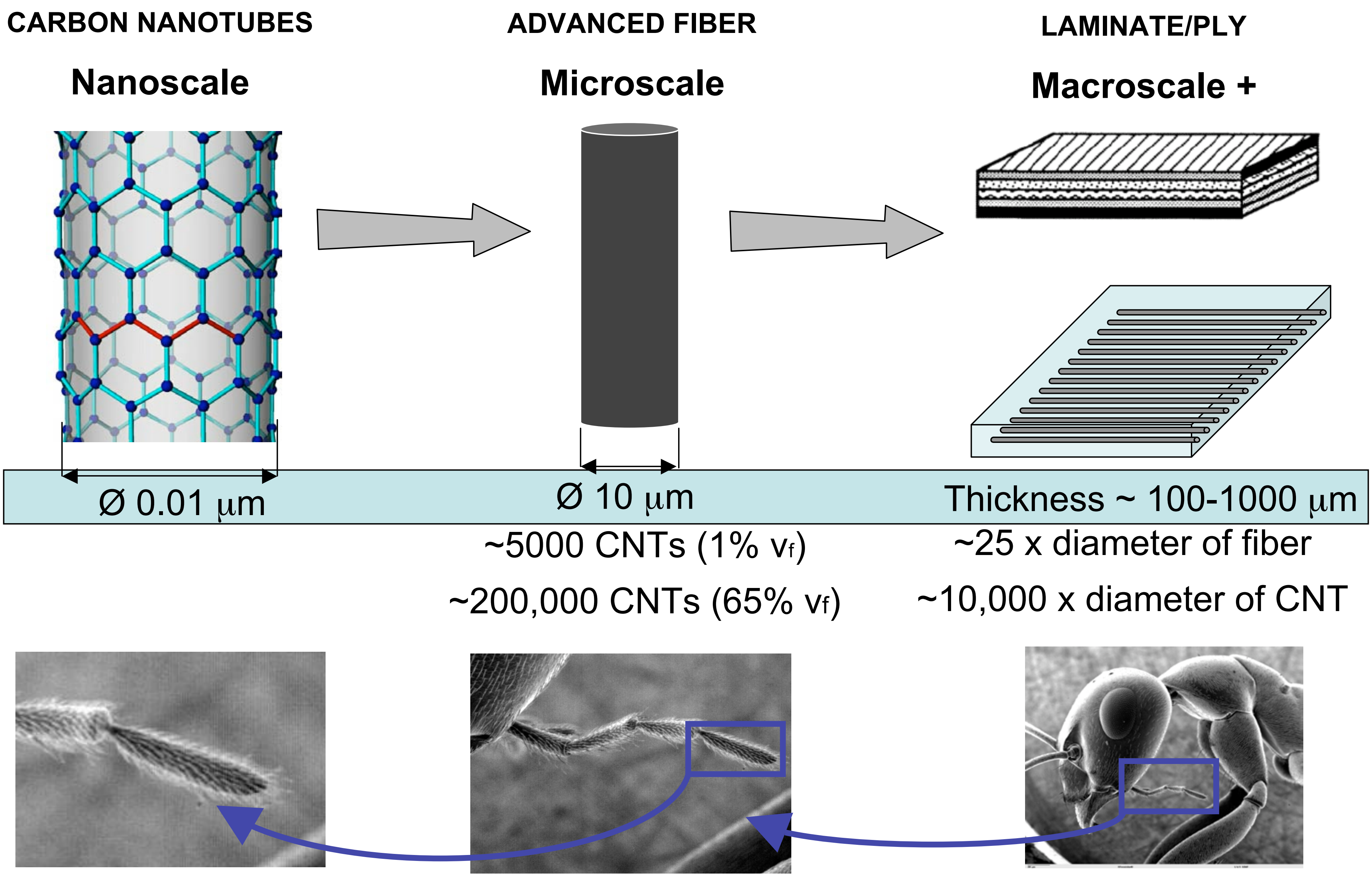
– Hybrid composites using aligned CNTs to reinforce and tailor existing composites

– E.g., “stitch” across ply interlaminar regions



Illustrations not to scale

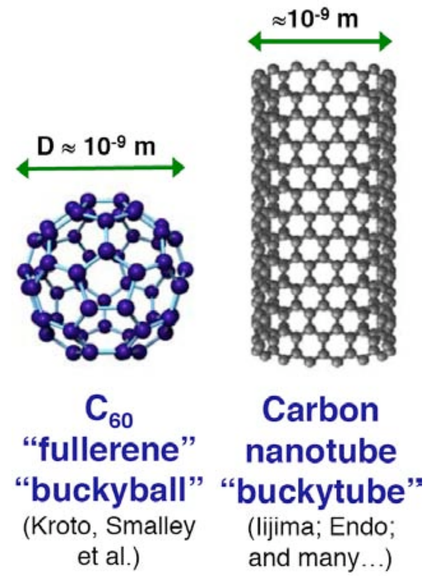
Scale Challenge for Hybrid Composites

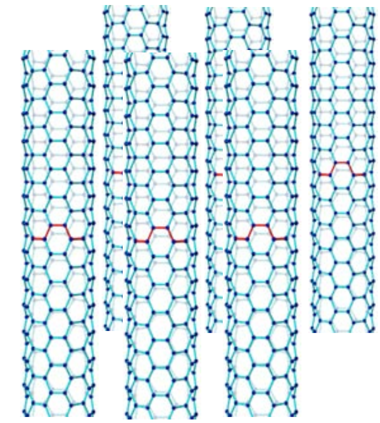


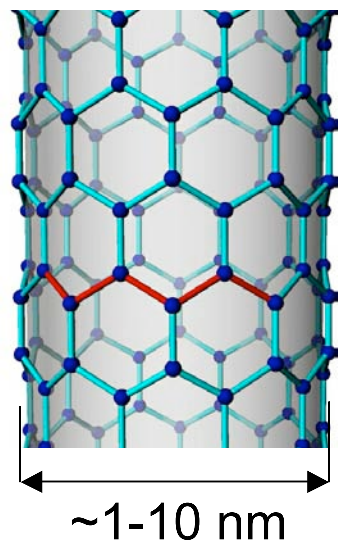
A Very Little (Femto?) on Carbon Nanotubes (CNTs)

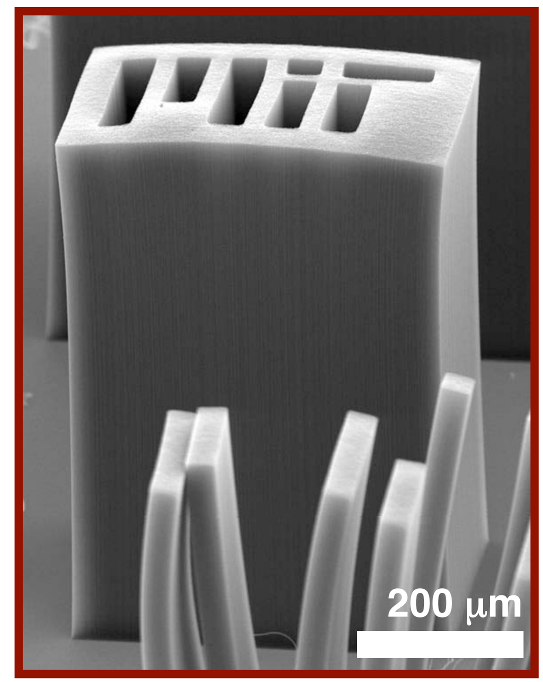
- Rolled graphene sheet (Iijima 1991, Endo), "Buckytubes"

- CNTs are not the same and differences are IMPORTANT
  - Single vs. multi-walled
  - Size (diameter and especially length)
  - Purity, or converse, defects
  - Chirality (rolling angle)…
- CNTs are "grown" from catalyst "seeds", sometimes into "forests" using a variety of processes: differences are IMPORTANT
- Intense research worldwide, esp. microelectronics applications (CNTs can be ballistic conductors)



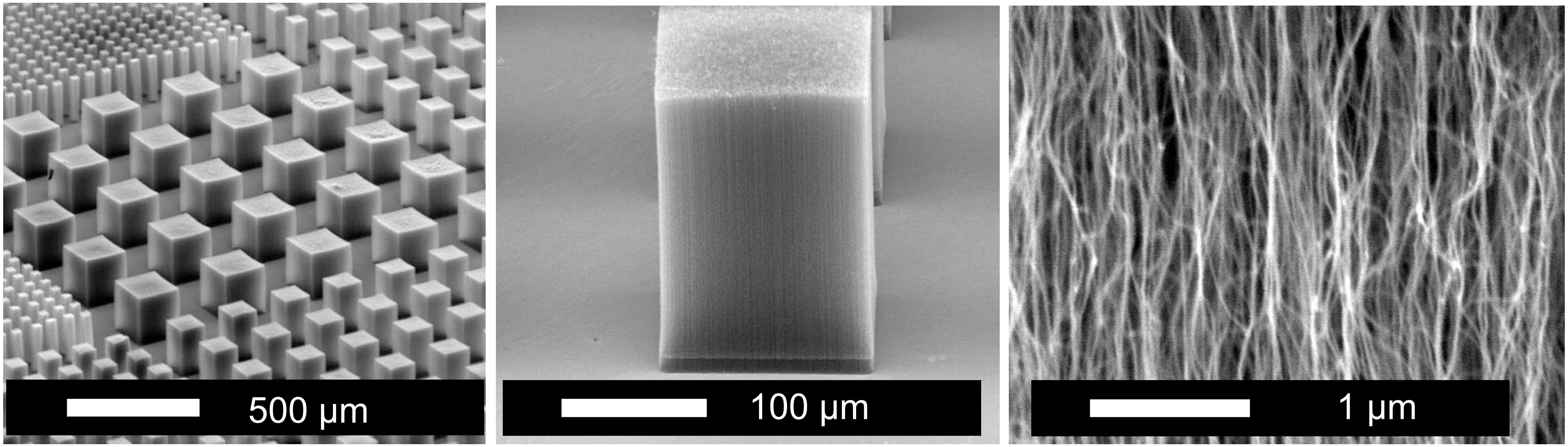




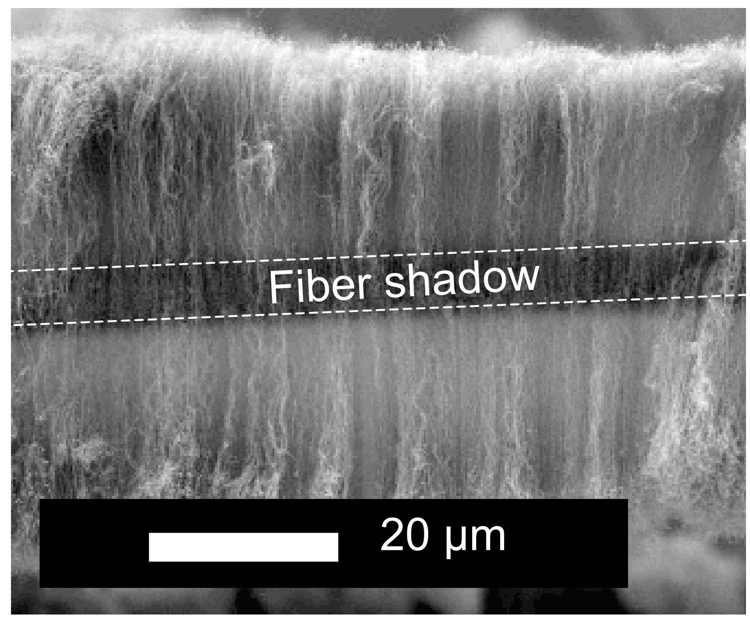


Images: Hart & Garcia

Growth of Aligned CNTs for Composites

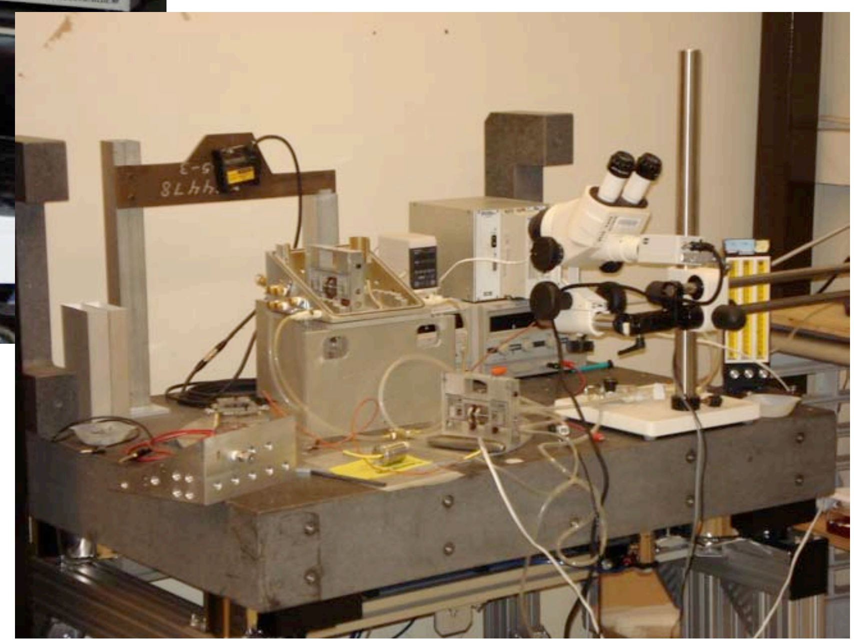


- Atmospheric pressure chemical vapor deposition process
- Self-aligned morphology, 10^{10}-10^{11}/cm^2
- Long forests (up to 5 mm) of continuous CNTs
- 7-10 nm outer diameter, 2-3 walls
- Rapid growth; > 2 microns/second



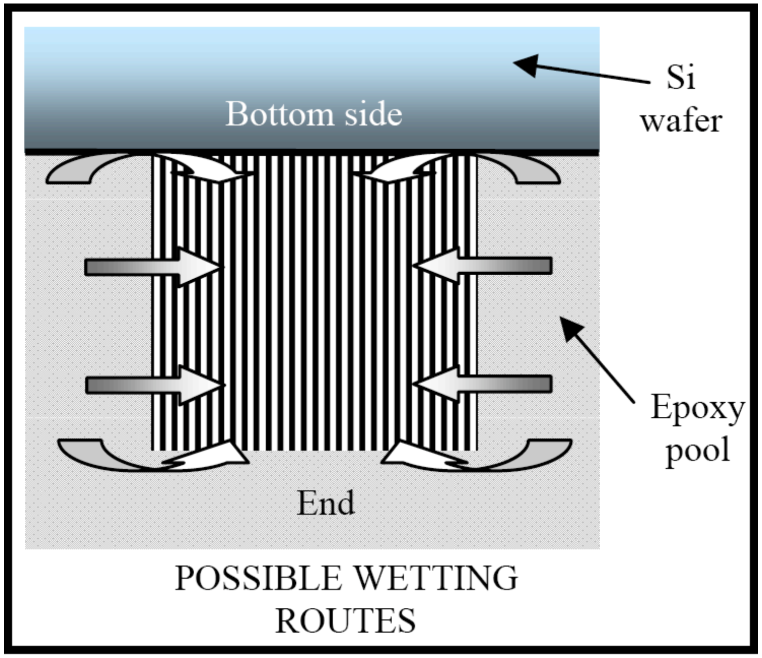
Garcia, Hart, Wardle, *AIAA J.*, 2008 (AIAA SDM 2006).

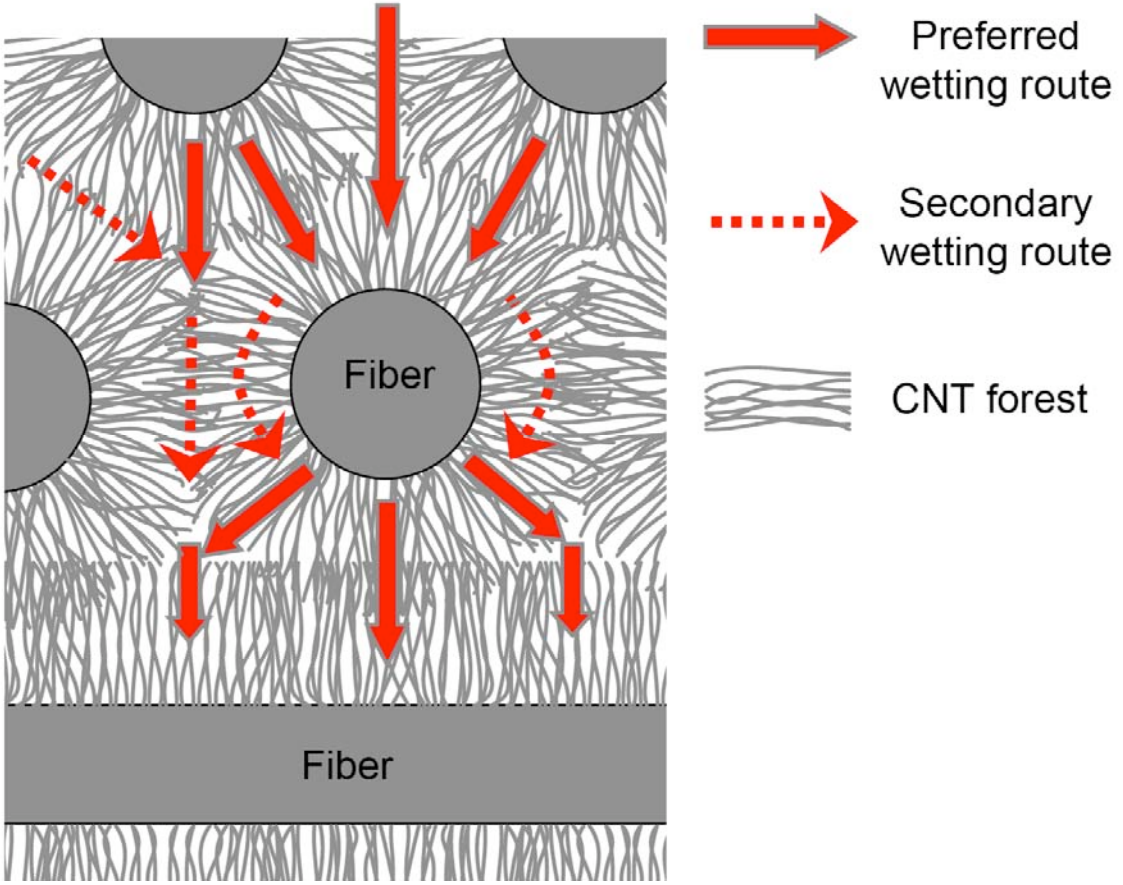
The Wardle Group CNT Farm



EHS Note: Bello, Wardle, et al., *J. Nanoparticle Research,* Jan. 2009; Bello et al., *Carbon*, 2008. Bello, Wardle et al., ICCM 2009.

Processing Nano-engineered Composites Enabled Via Capillarity-induced Wetting of *Aligned* CNTs



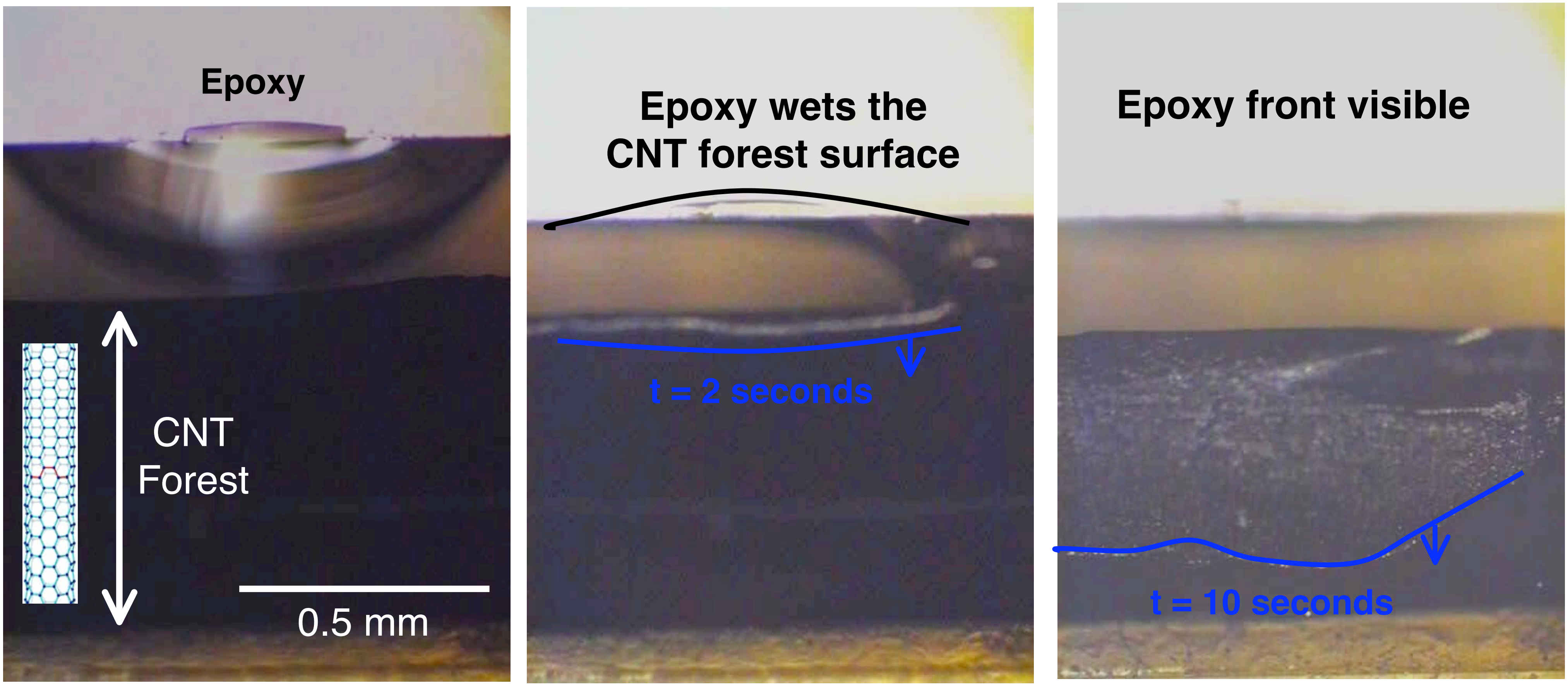


- Identification of wetting route
  - Highly preferred along CNT axis
  - Secondary wetting perpendicular to CNTs

Wardle et al, *Adv. Mat.,* 2008.
Garcia, Wardle et al., *Nanotechnology* 2007.

Garcia, Wardle et al., *Comp. Sci. & Tech.*, 2008.

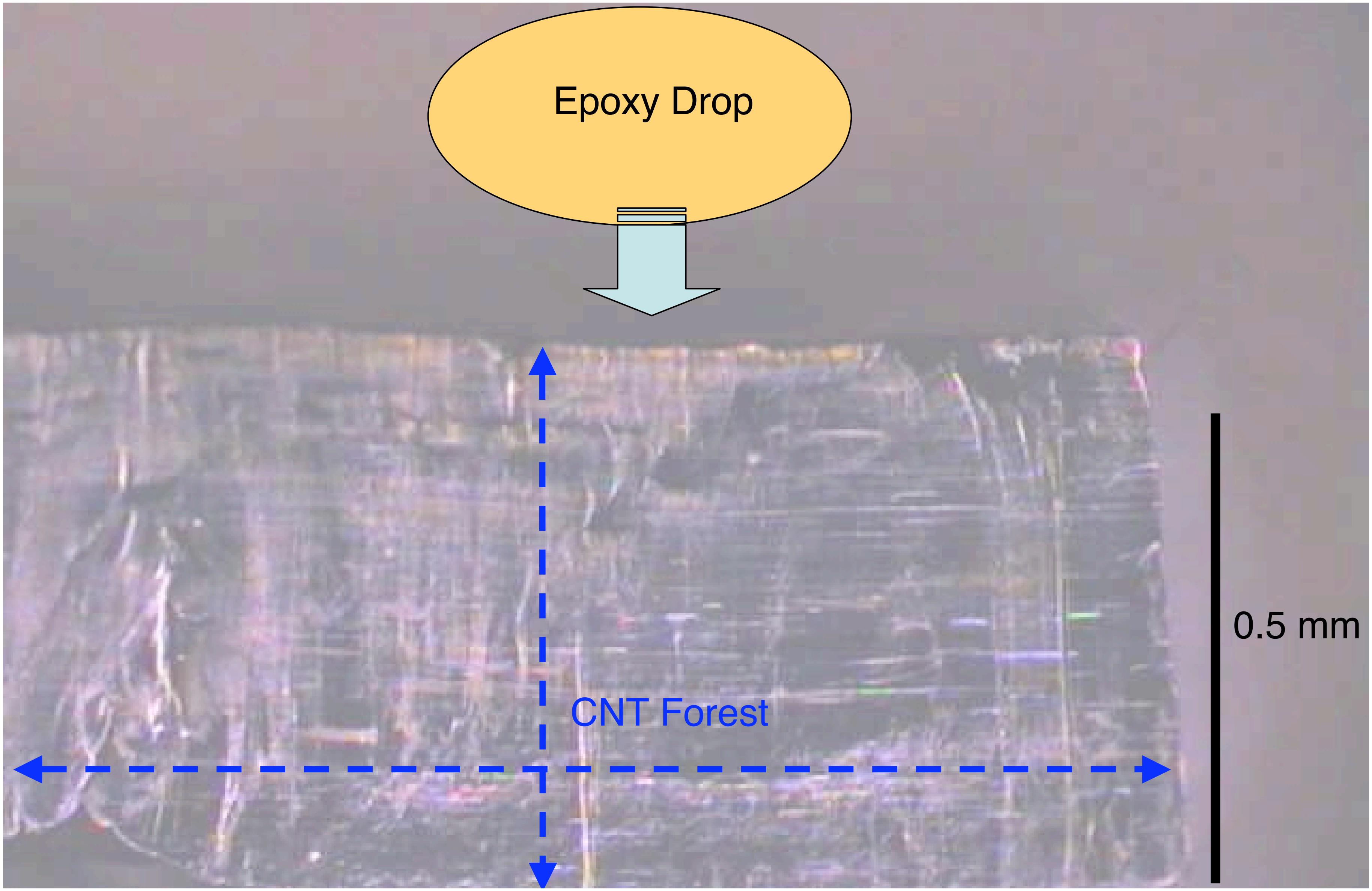
Example of Epoxy Wetting CNTs: Flow-front Visualization

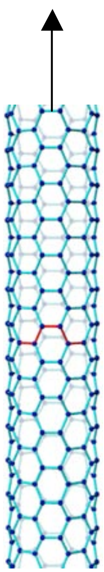


- Volume Fraction of CNT = 1%
- Length of CNT = 0.65 mm
- CNT-CNT spacing = 80 nm
- Wetting time = 13 seconds
- Infiltration Rate = 0.05 mm/s

Cebeci, (Wardle), et al., *SAMPE Fall Conf.*, 2008.

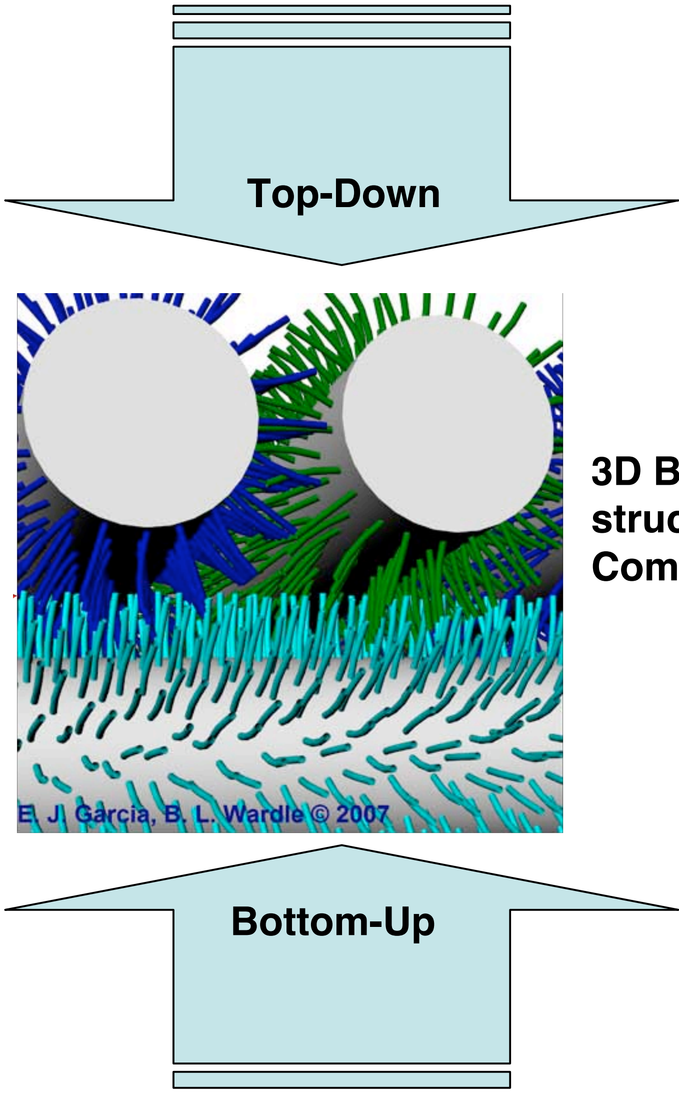
Video of Epoxy (RTM6) Wetting an Aligned CNT Forest





Cebeci, (Wardle), et al., *SAMPE Fall Conf.*, 2008.

Long-range Nanostructured Order Via Combined Top-down and Bottom-up Processing



3D Bulk Nano-structured Composite

Woven advanced fibers
~60% of volume

+

Aligned CNTs grown on fiber substrate
~1% of volume

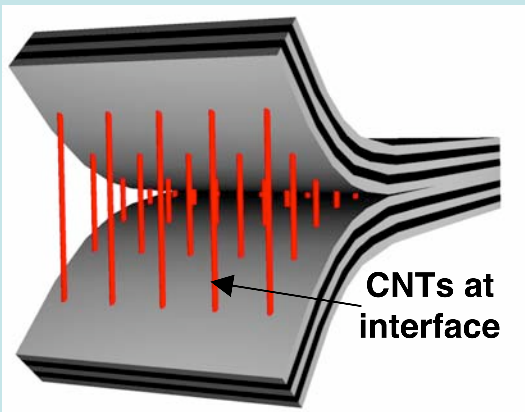
+

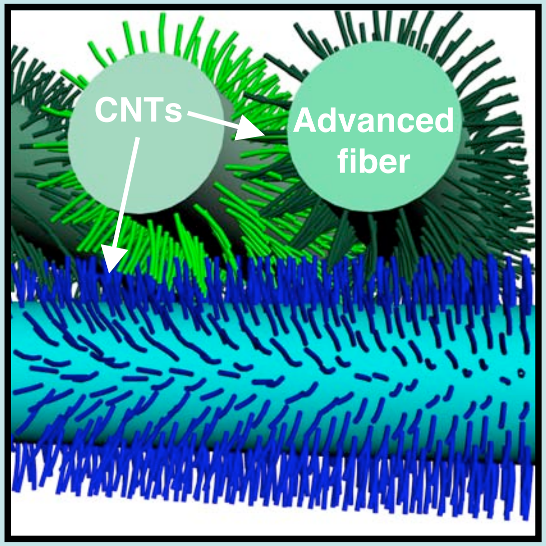
Existing advanced polymers
~40% of volume

Garcia, Wardle et al., *Comp. Sci. & Tech.*, 2008.

Wardle Group Nano-Engineered Composites Research

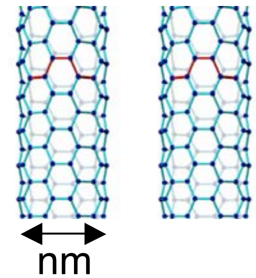
(1) Nano-engineered Composites





'Nanostitched' and 'fuzzy' fiber laminates

(3) Materials engineering



meters

Next-generation advanced composites

(2) Structural design

(4) Processing/fabrication

Research areas:

(1) *Nano-engineered composite mechanics* of plies, laminates and substructures

(2) *Structural design* (bonded and bolted joints, impact resistance and tolerance, etc.)

(3) *Materials engineering* of nanocomposites (interface topics: CNT-CNT, CNT-polymer, CNT-fiber)

(4) *Processing/fab* (CNT alignment, dispersion, integration with existing composite manufacturing)

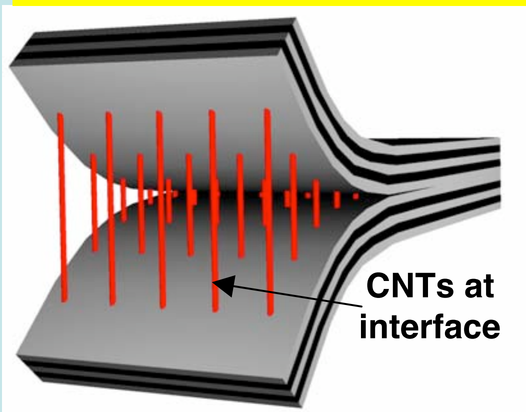
B. L. Wardle, wardle@mit.edu, Dec '09-16

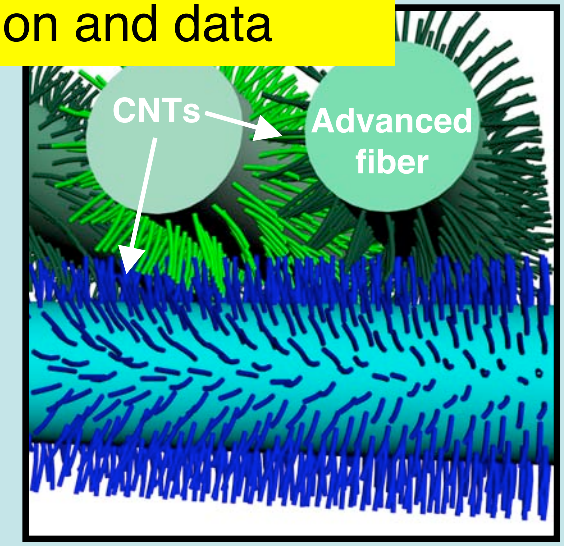
Recent Contributions

3. Nanocomposite mechanics
4. New CNT growth catalyst (discovery)

(1) Nano-engineered Composites

1. Key modeling result
2. Laminate fabrication and data





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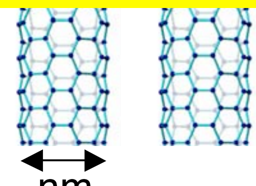

meters

Next-generation advanced composites

(2) Structural design

5. Moving towards continuous manufacturing

(4) Processing/fabrication

6. Something different

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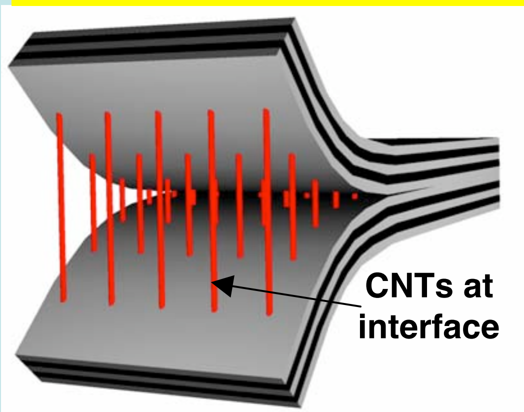

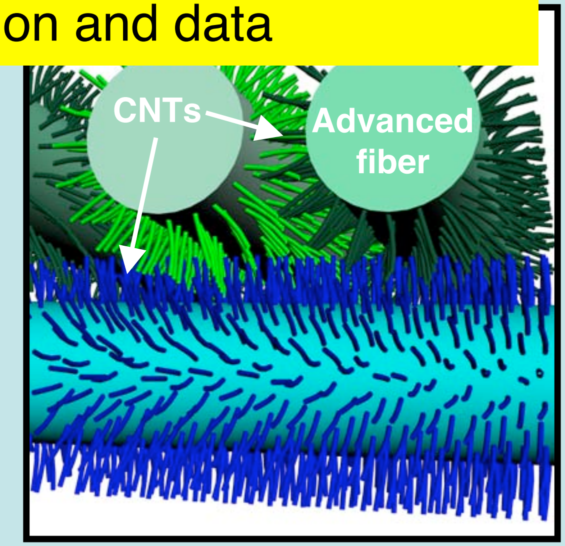

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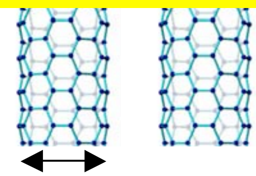

meters

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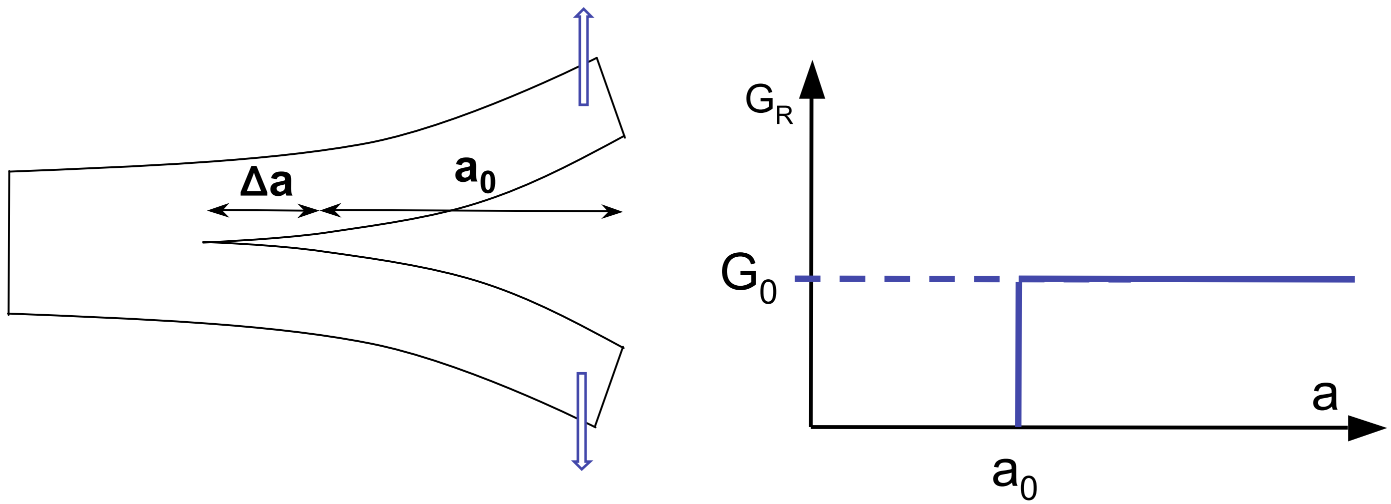
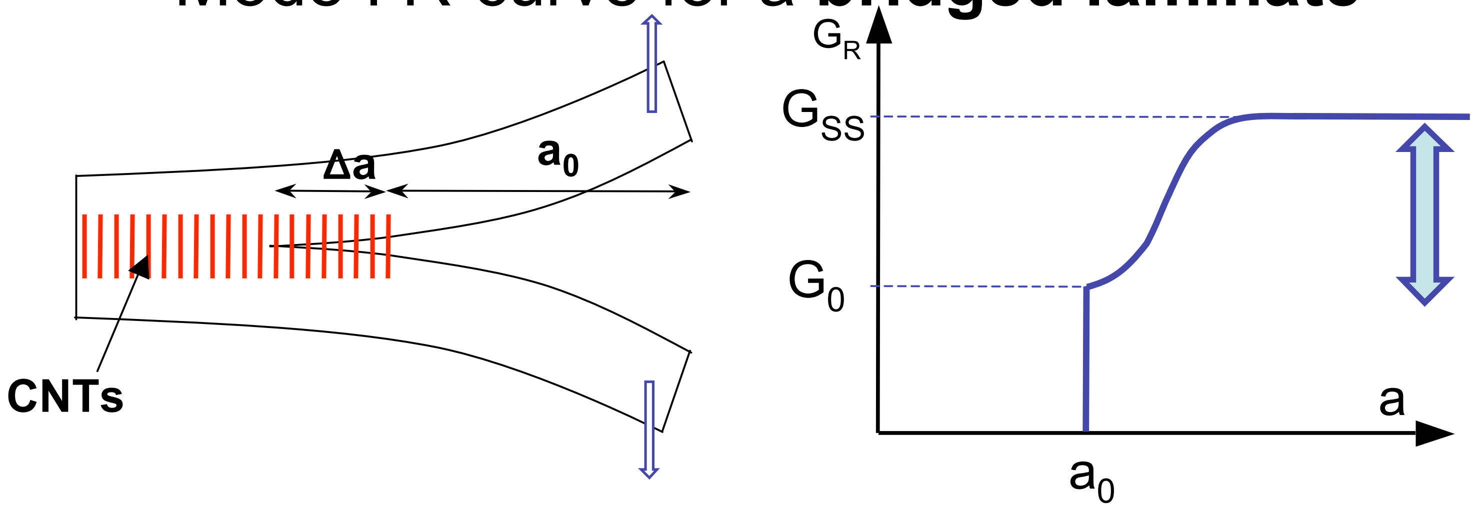
Toughening Mechanism of CNT/Fiber Bridging

- Mode I R-curve for a **non-bridged laminate**



- Mode I R-curve for a **bridged laminate**



G_{SS}/G_0 ratio
obtained as a function of the parameters of the problem

Steady-state Solution for Mode I Toughening

- Using the expression for the closing traction in the J-integral result for toughening:

$$G_R(\Delta a) = G_0 + 2\int_0^{\widetilde{u}(\Delta a)} p(x)\,du$$

$$p(x) = \frac{v_{CNT}\tau_c L_{CNT}}{r} - \frac{2v_{CNT}\tau_c}{r}u(x)$$

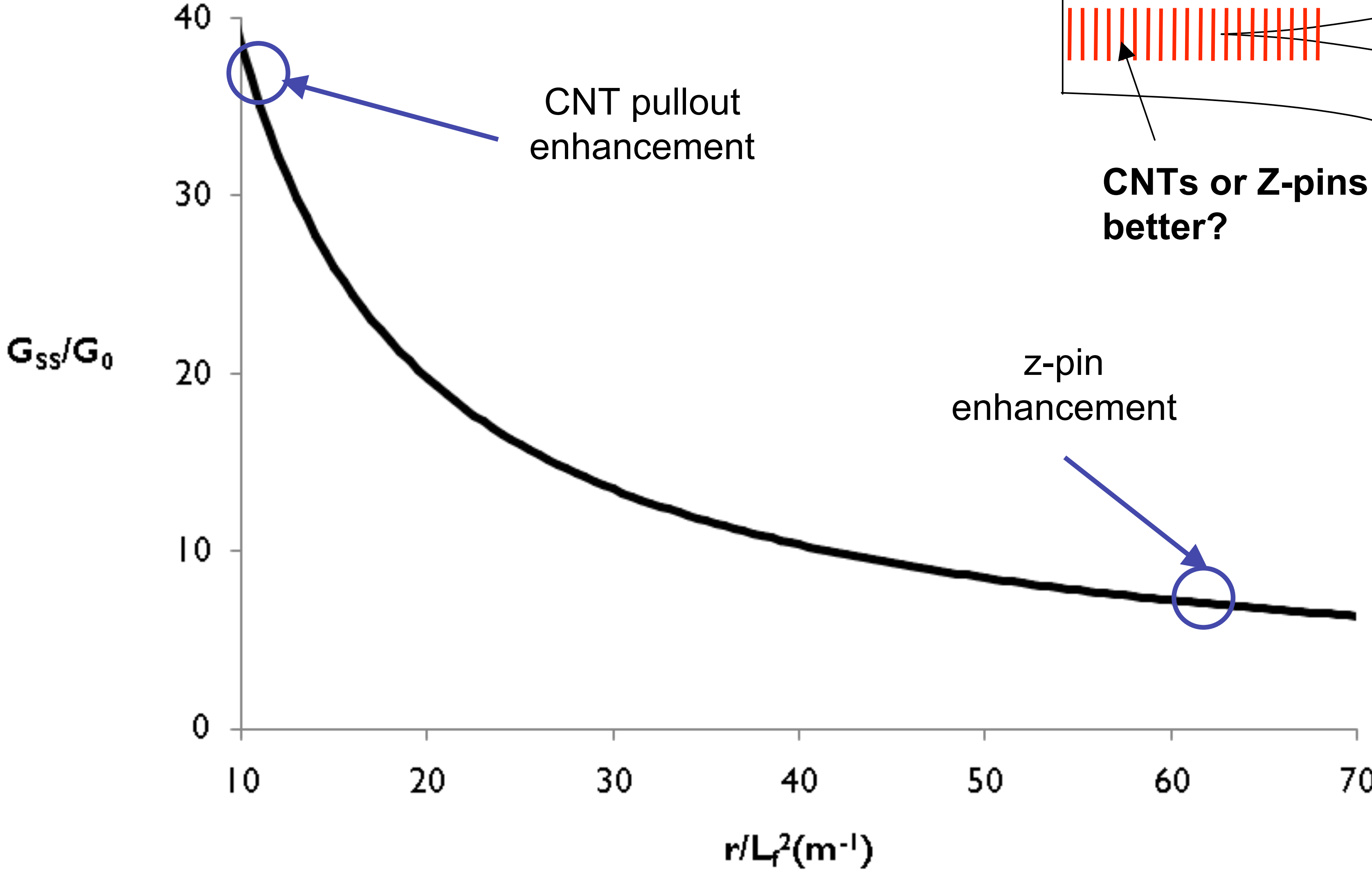
Yields:

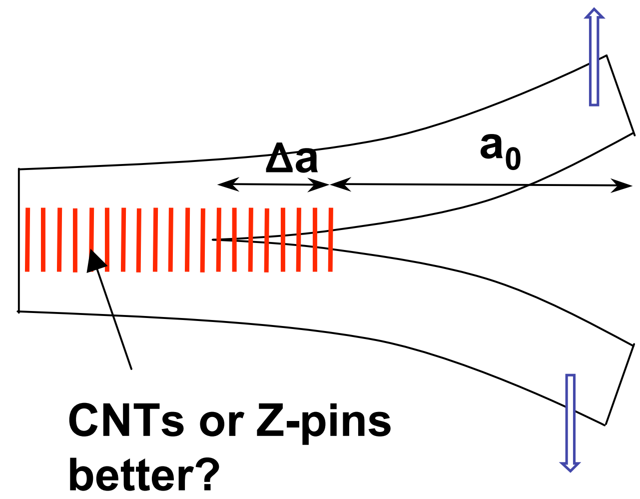
$$\frac{G_{ss}}{G_0} = 1 + \frac{1}{2}\left(\frac{L_{CNT}}{r}\right)\frac{v_{CNT}\tau_c L_{CNT}}{G_0}$$

- G_{ss}/G_0 is a function of the **fiber aspect ratio** and **pullout energy**

Blanco, (Wardle) *et al., J. Composite Materials,* April 2009.

Effect of Scale of Reinforcement: CNTs vs. 'Z-pins'





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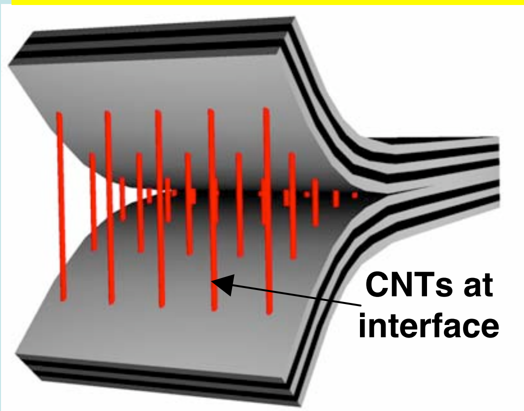
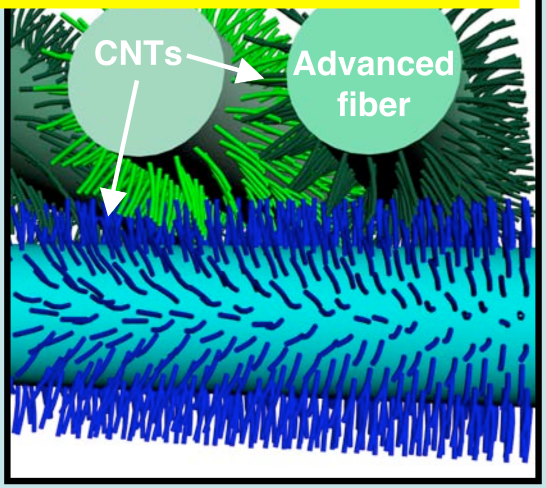
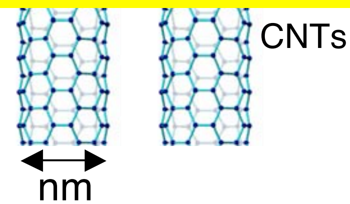




'Nanostitched' and 'fuzzy' fiber laminates



meters

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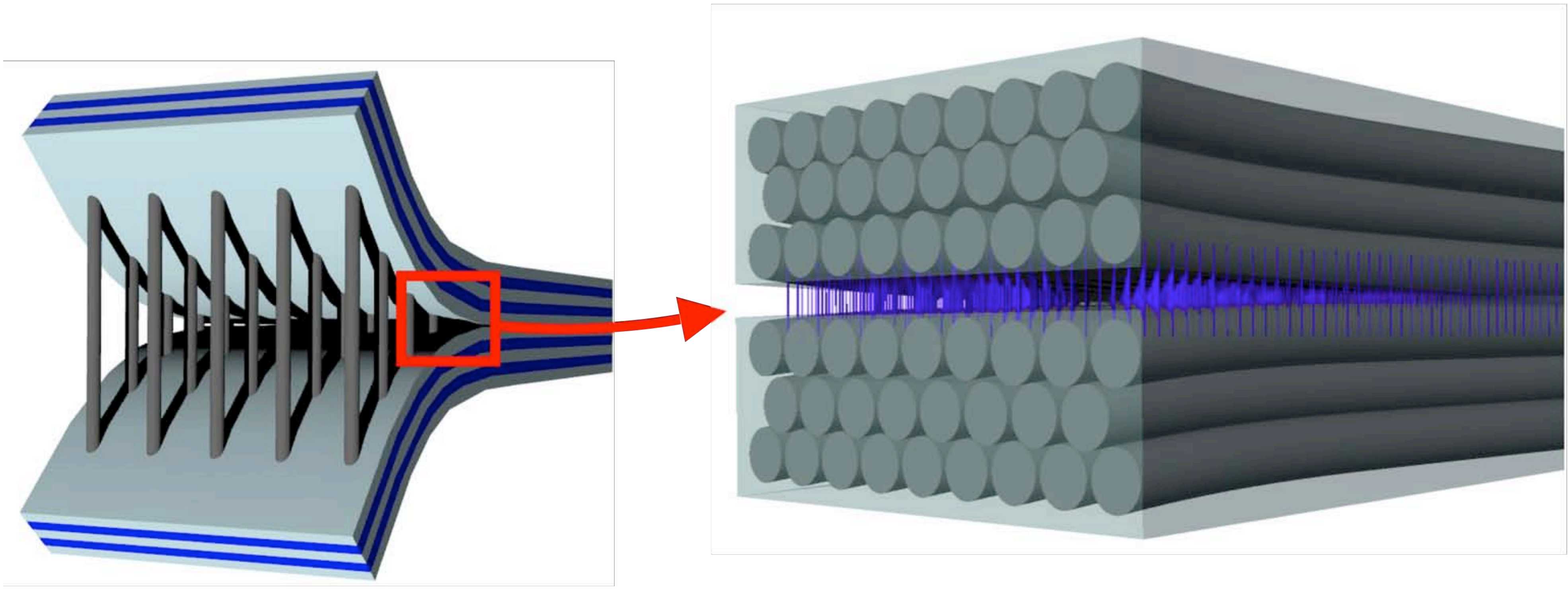
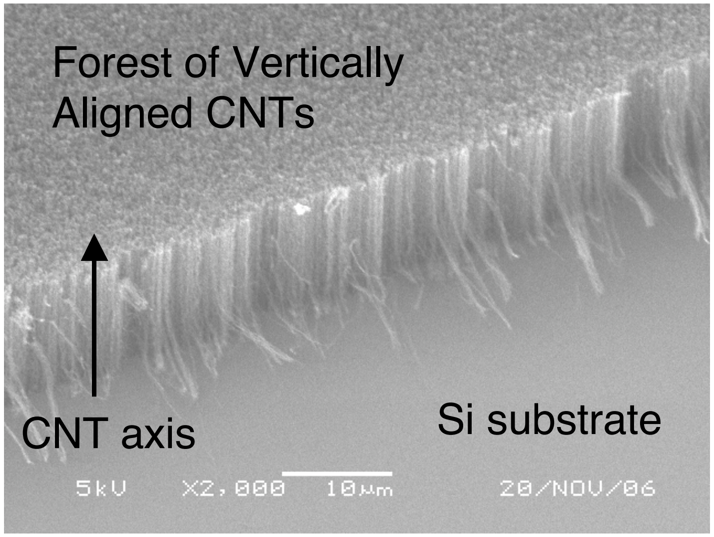
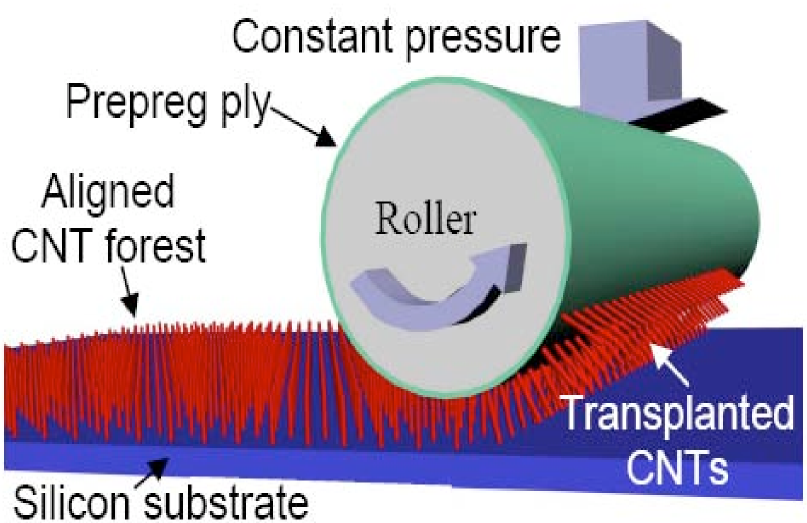
1st Architecture: ‘Nanostitches’ = Aligned CNTs at Ply Interfaces

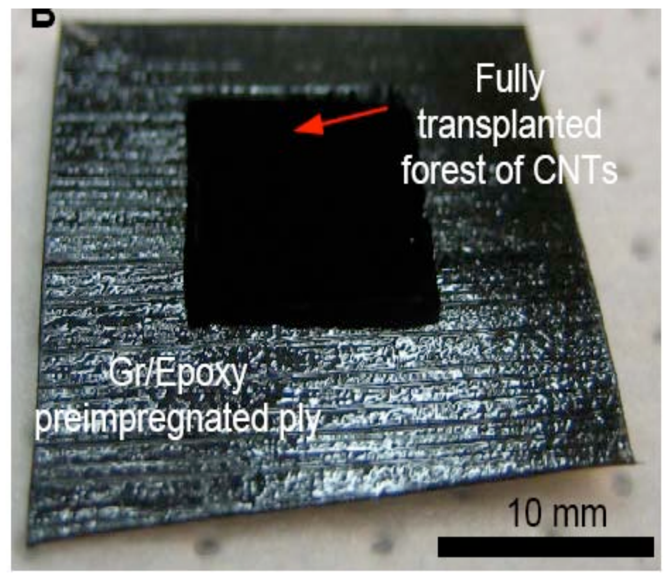


Nanostitching: Aligned CNT Transfer to Aerospace Graphite/Epoxy Composite Prepreg



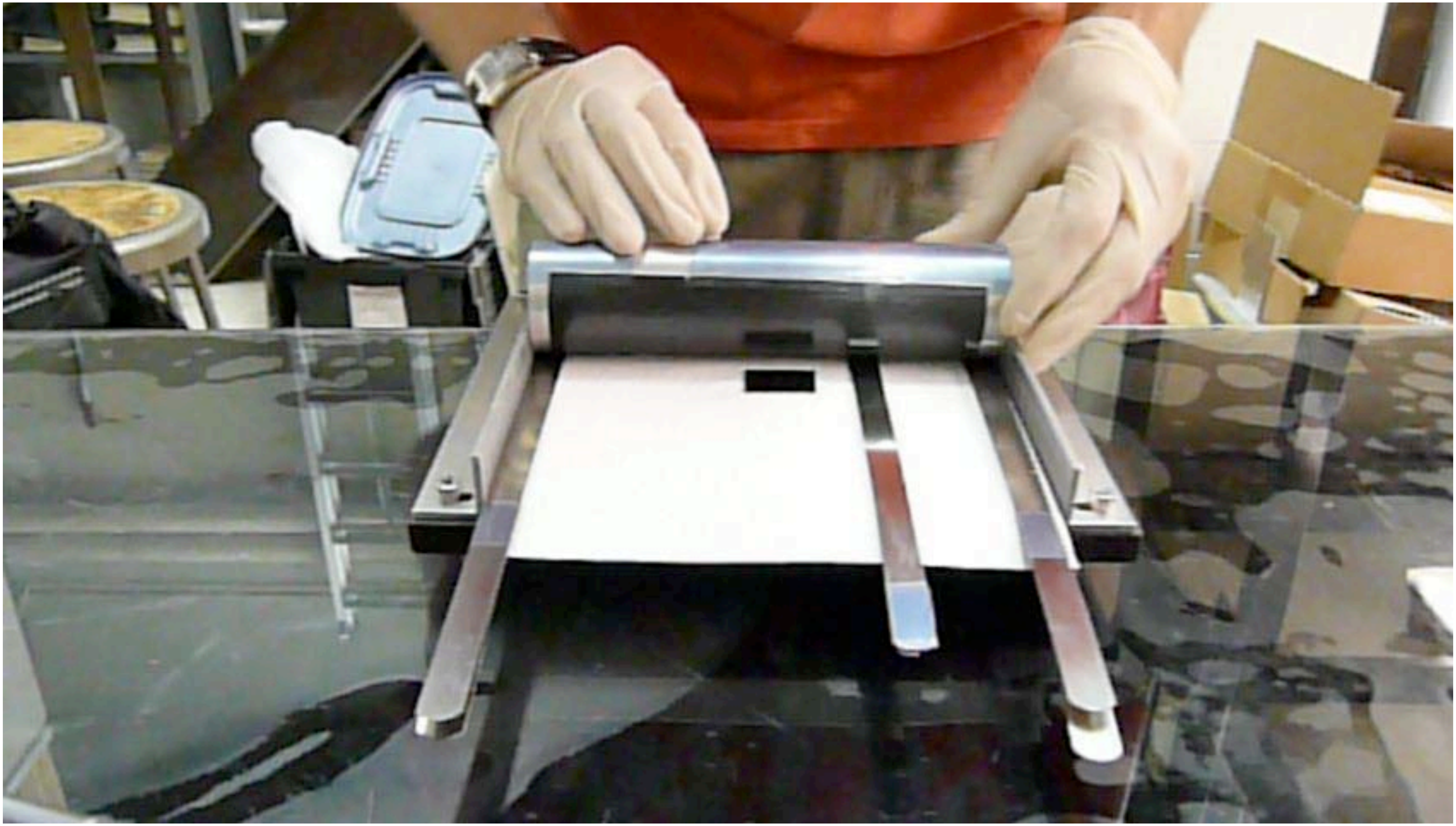
1. Grow aligned CNTs on high-temp. substrate
2. Transplant CNTs to composite at low-temp.
3. Process the composite



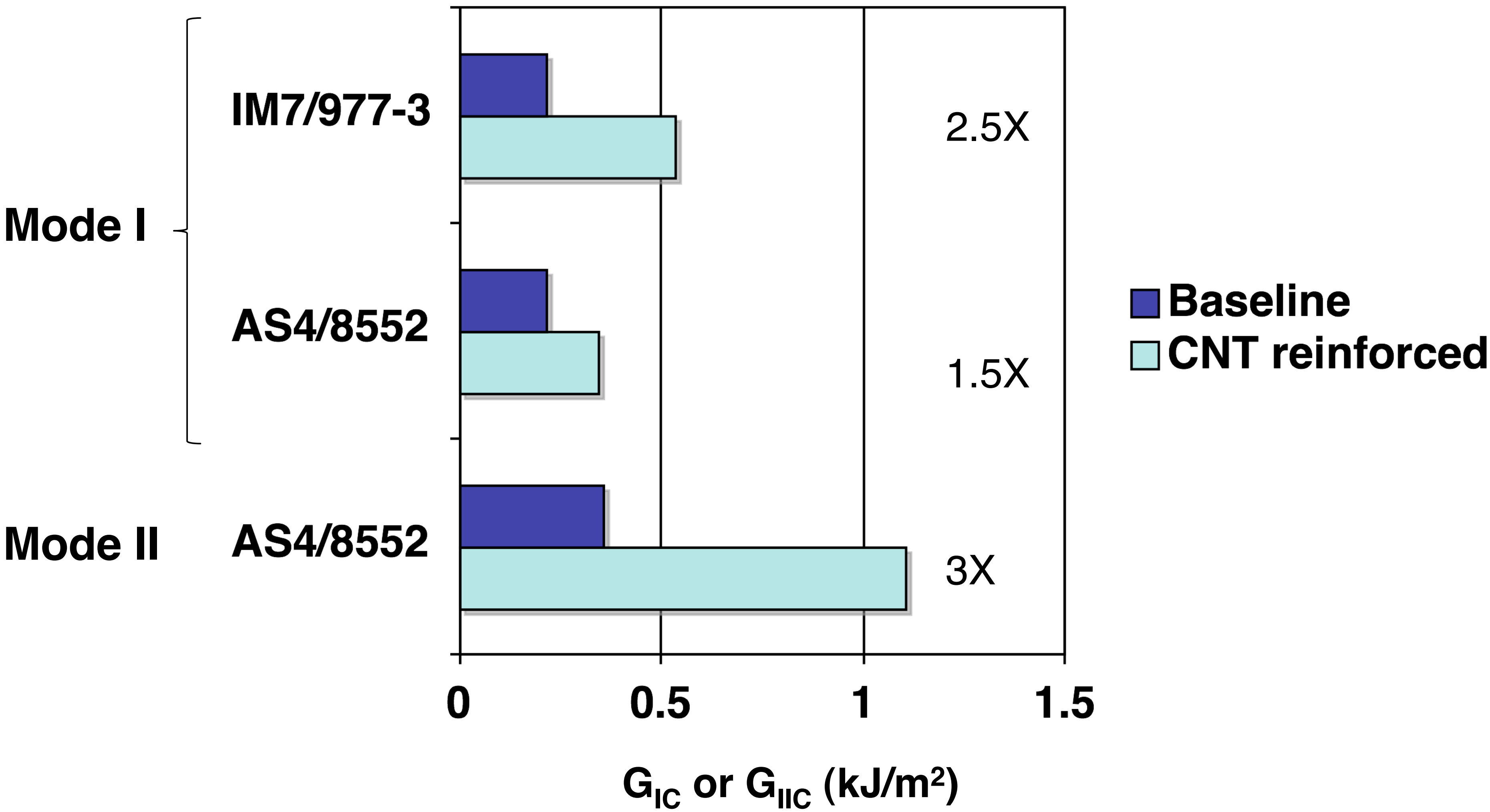


Garcia, Wardle, et al., *Composites A.*, 2008.

Video of Nanostitch Transfer to Prepreg

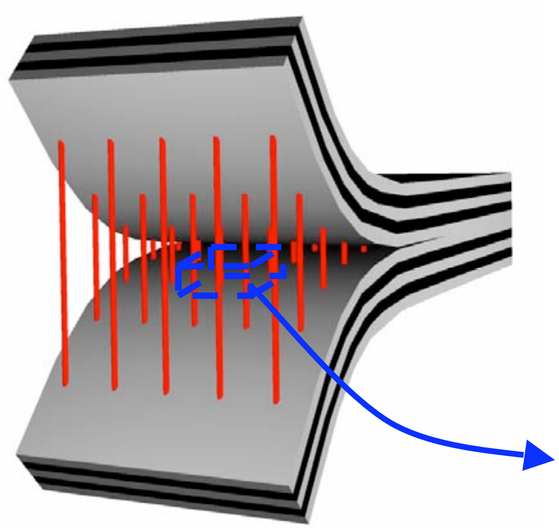


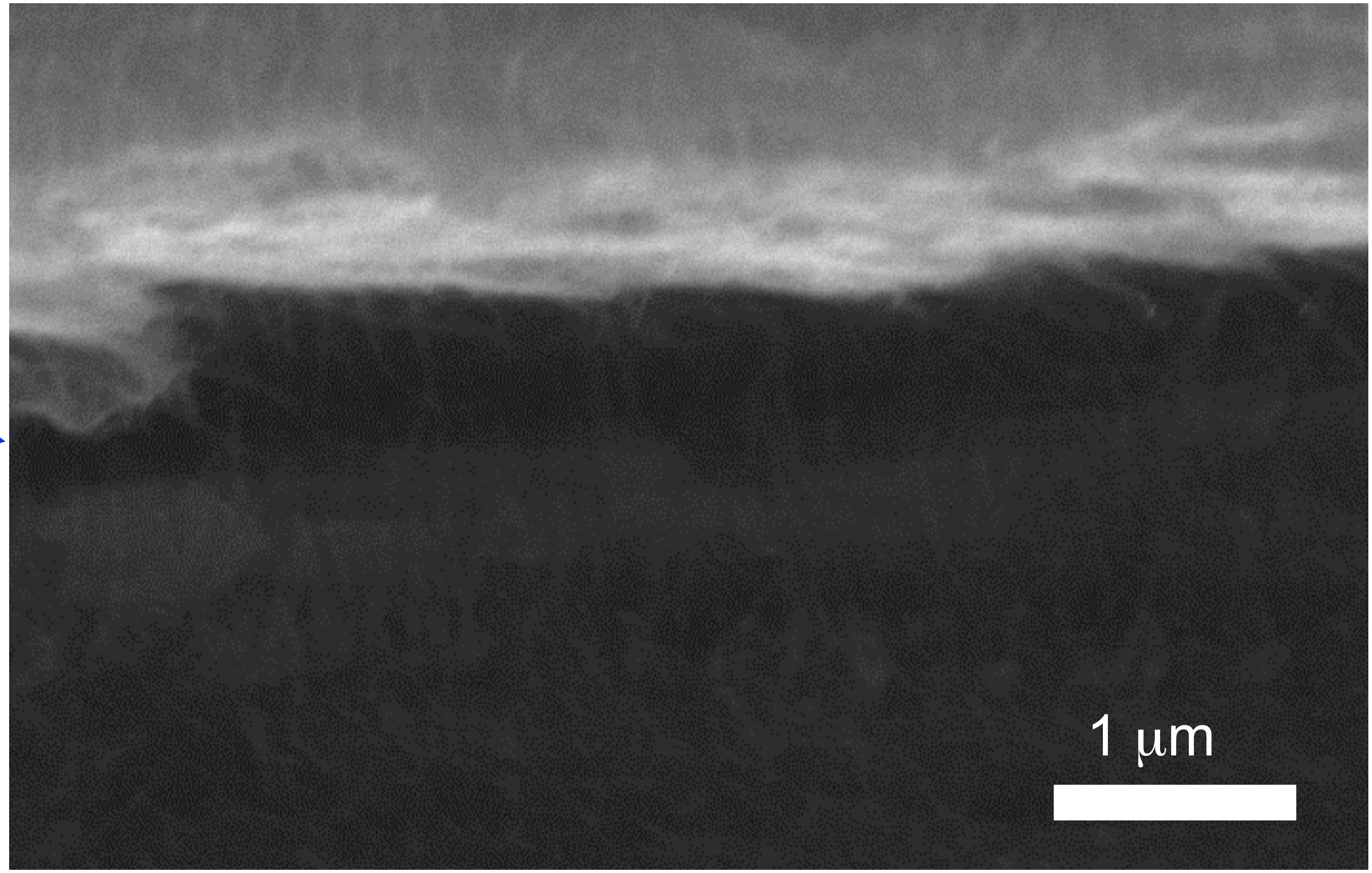
Summary Fracture Data on Two Prepreg Systems Reinforced with Aligned CNTs



Garcia, Wardle, et al., *Composites Part A*, 2008.

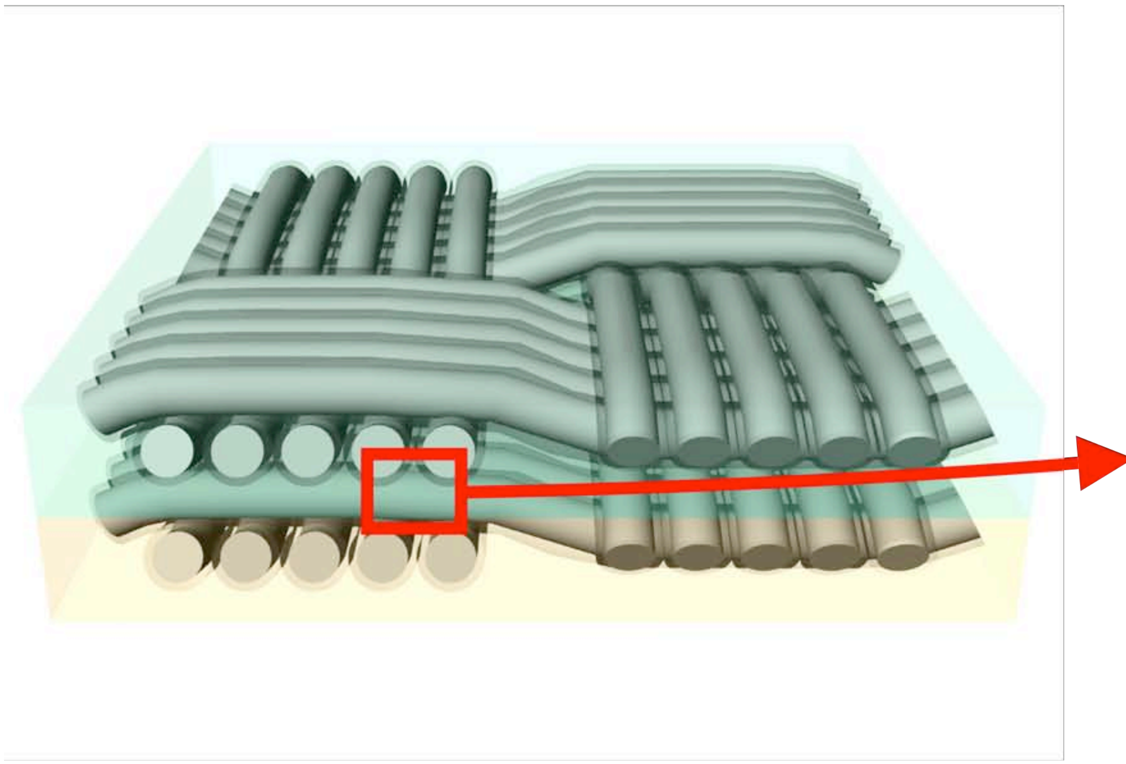
Observation of Mode I CNT Pullout Consistent with Bridging Modeling

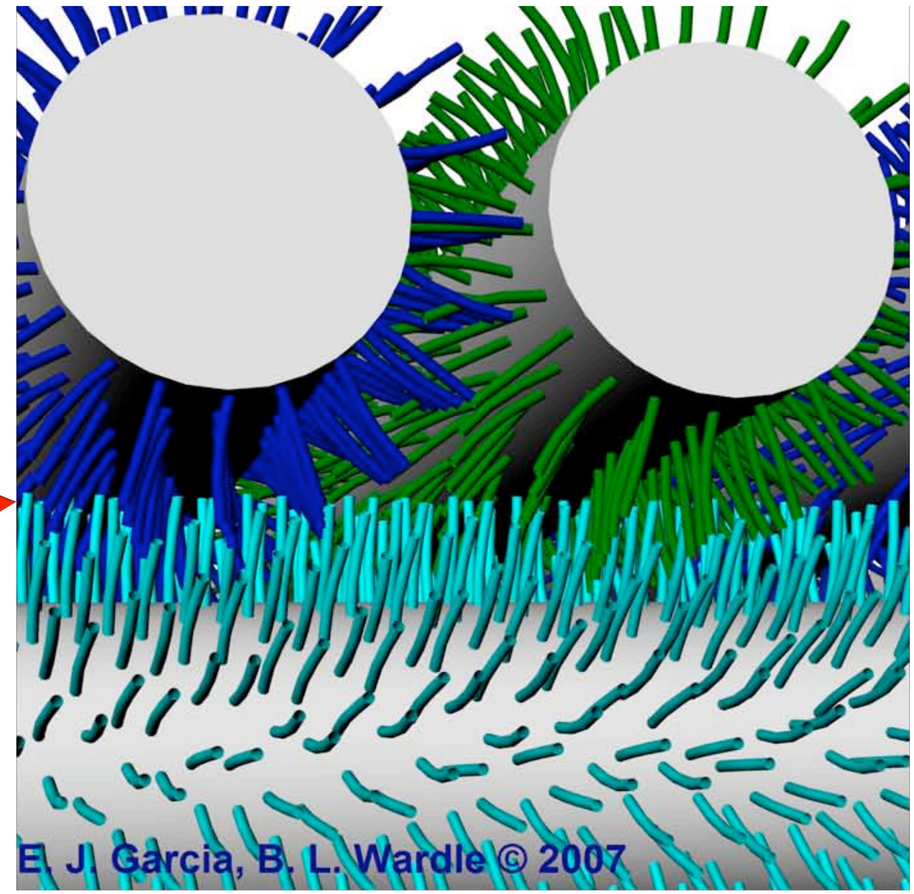




Garcia, Wardle, et al., *Composites Part A*, 2008.

2nd Architecture: Fuzzy Fiber Reinforced Plastics (FFRPs) = Aligned CNTs Everywhere

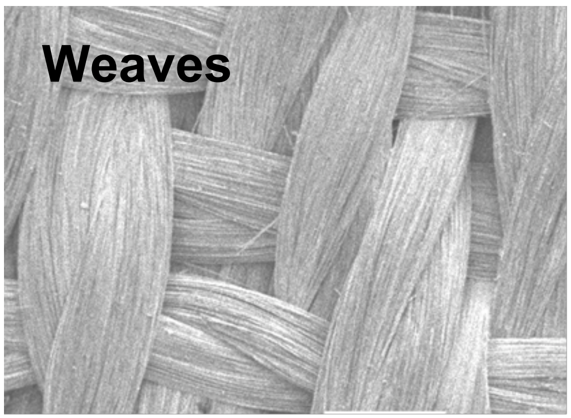


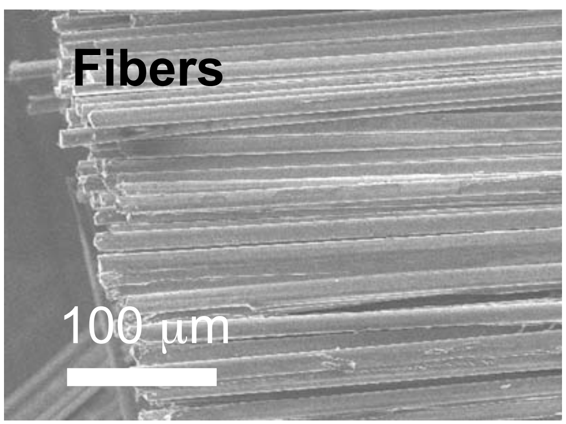


Garcia, (Wardle), et al., *AIAA J.,* 2008 (AIAA SDM 2006). *Composites Science & Technology*, 2008.

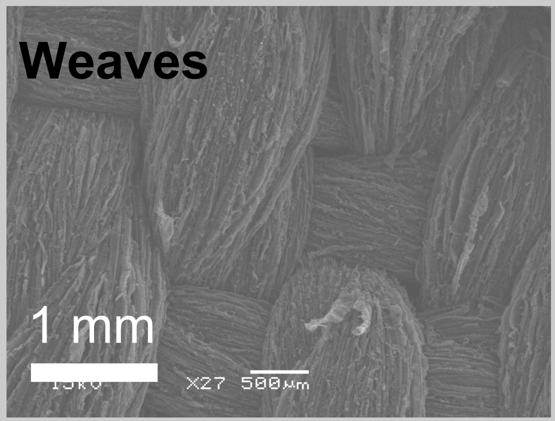
Aligned CNT Growth on Alumina Cloth for Composites

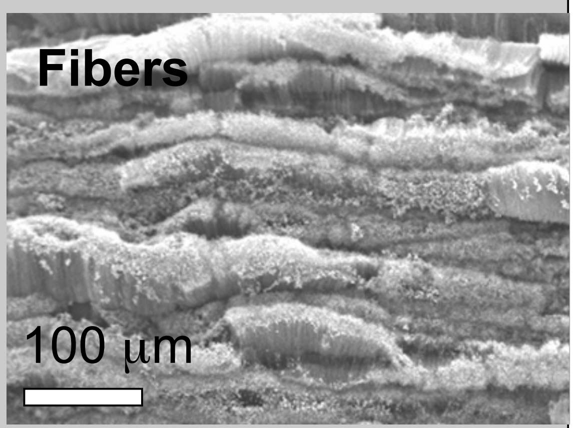
Bare Alumina Cloth





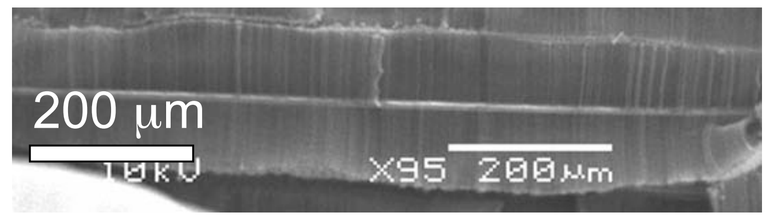
Cloth with CNTs

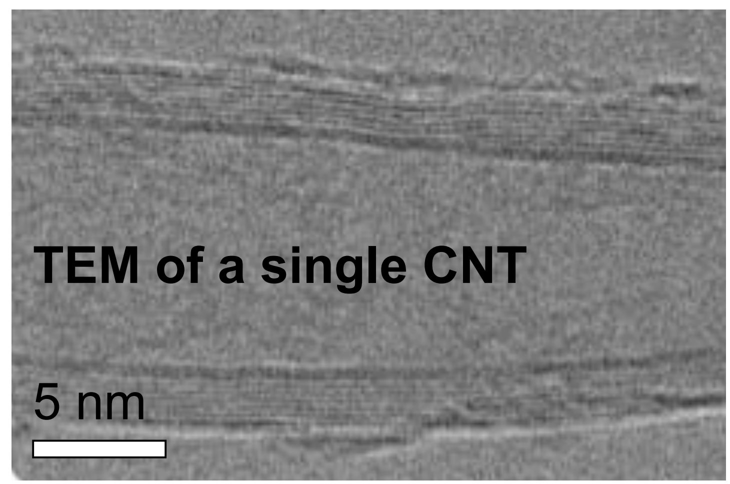




- Short (~20μm), uniform, and dense CNTs

Single fiber with aligned CNTs

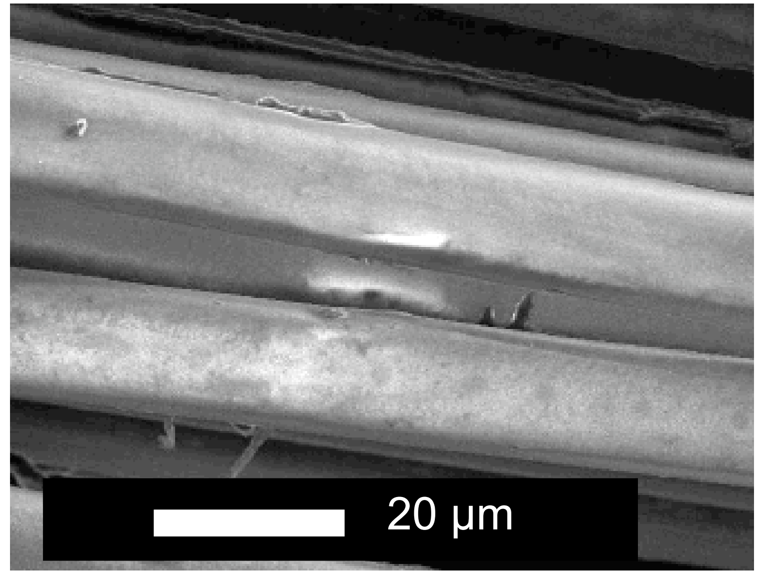




Garcia, Hart, Wardle, *AIAA J.,* 2008 (AIAA SDM 2006).
Yamamoto et al., *Carbon*, 2009.

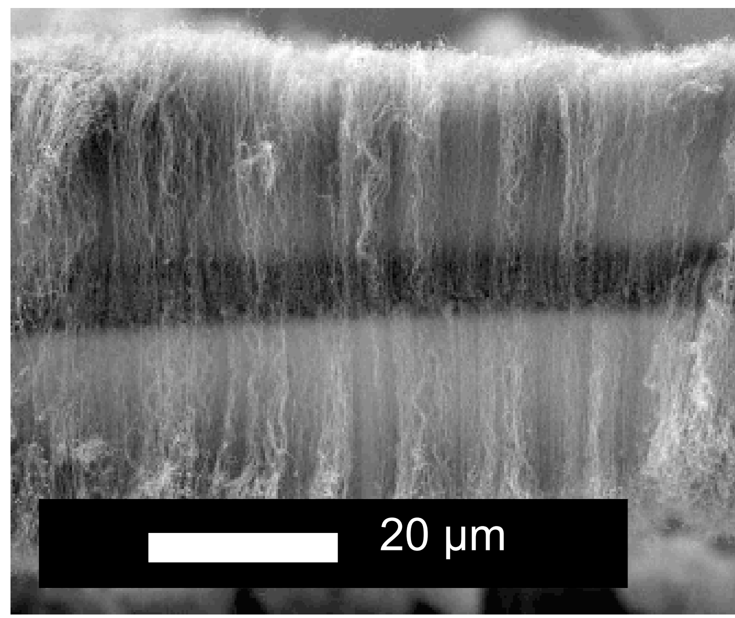
Intralaminar Reinforcement - Growth of CNTs on Alumina Fiber Cloth and Hose

Before Growth



After Growth

≈125 mm

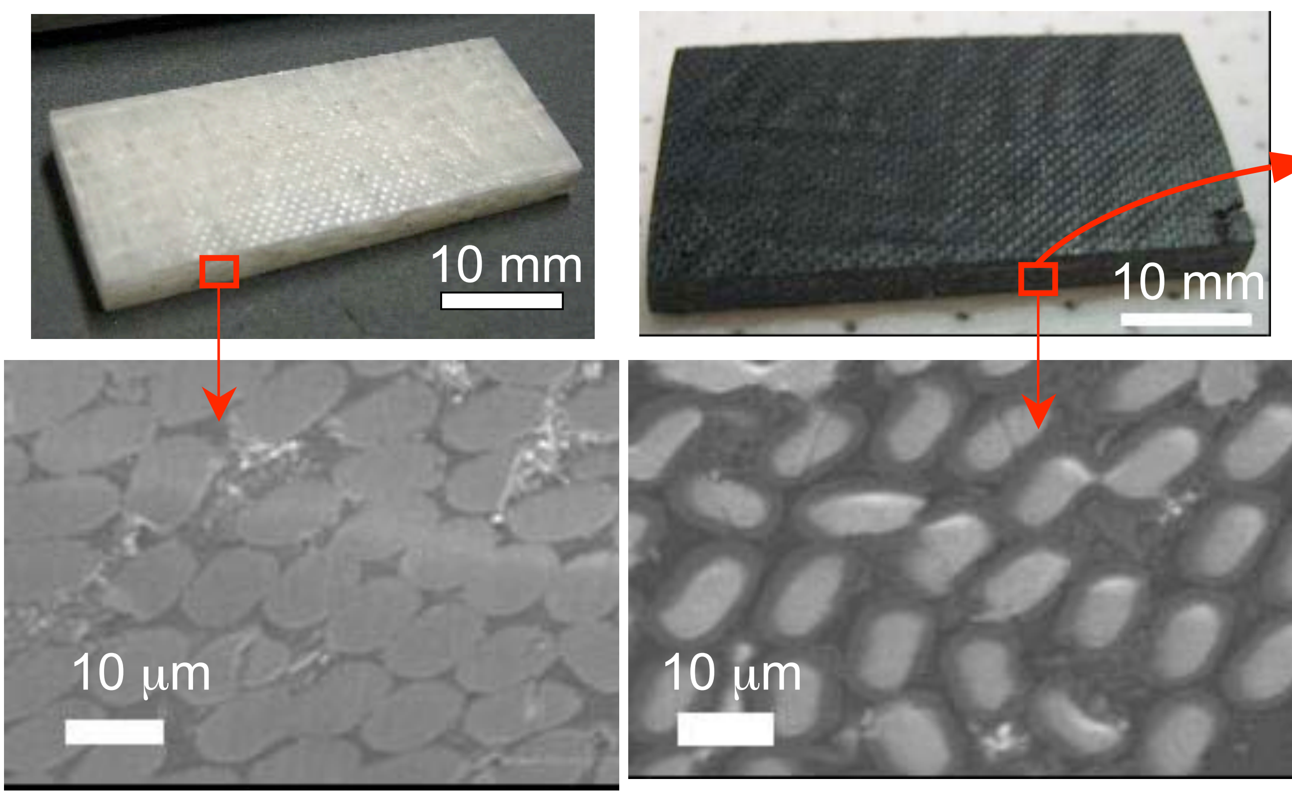


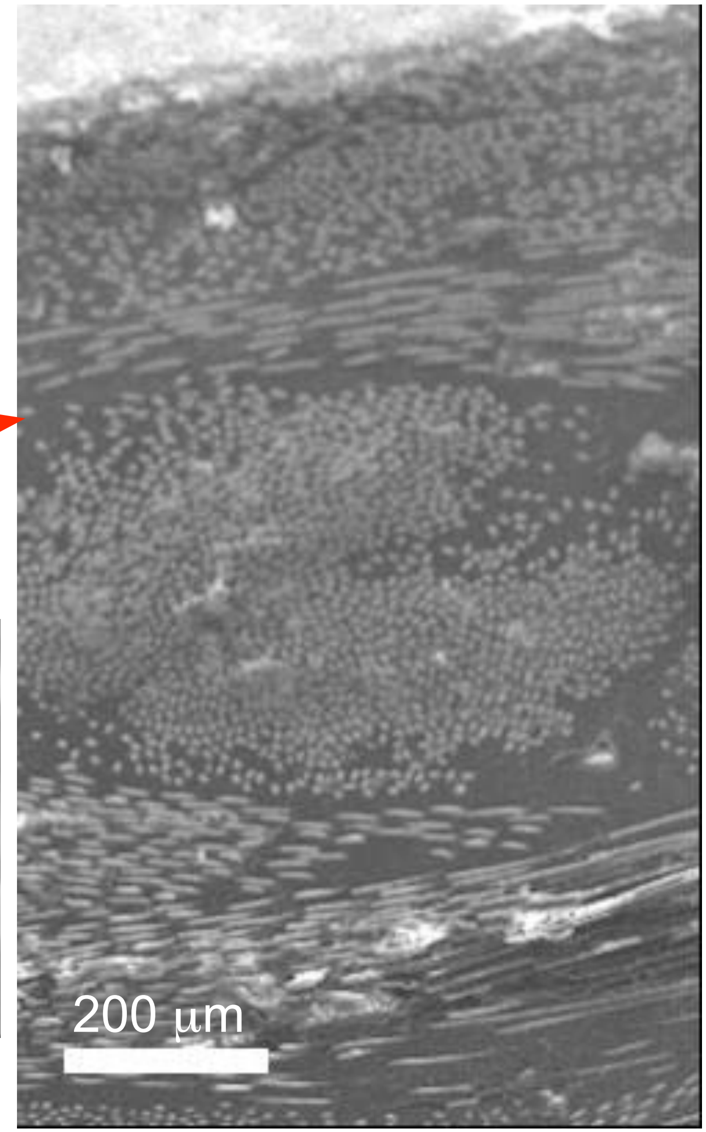
Garcia et al., AIAA SDM, April 2006, Yamamoto et al., ICCM-16, July 2007, Yamamoto et al., *Carbon*, 2009.

‘Fuzzy Fiber’ Composites Realized

- No voids observed @ 10 micron resolution

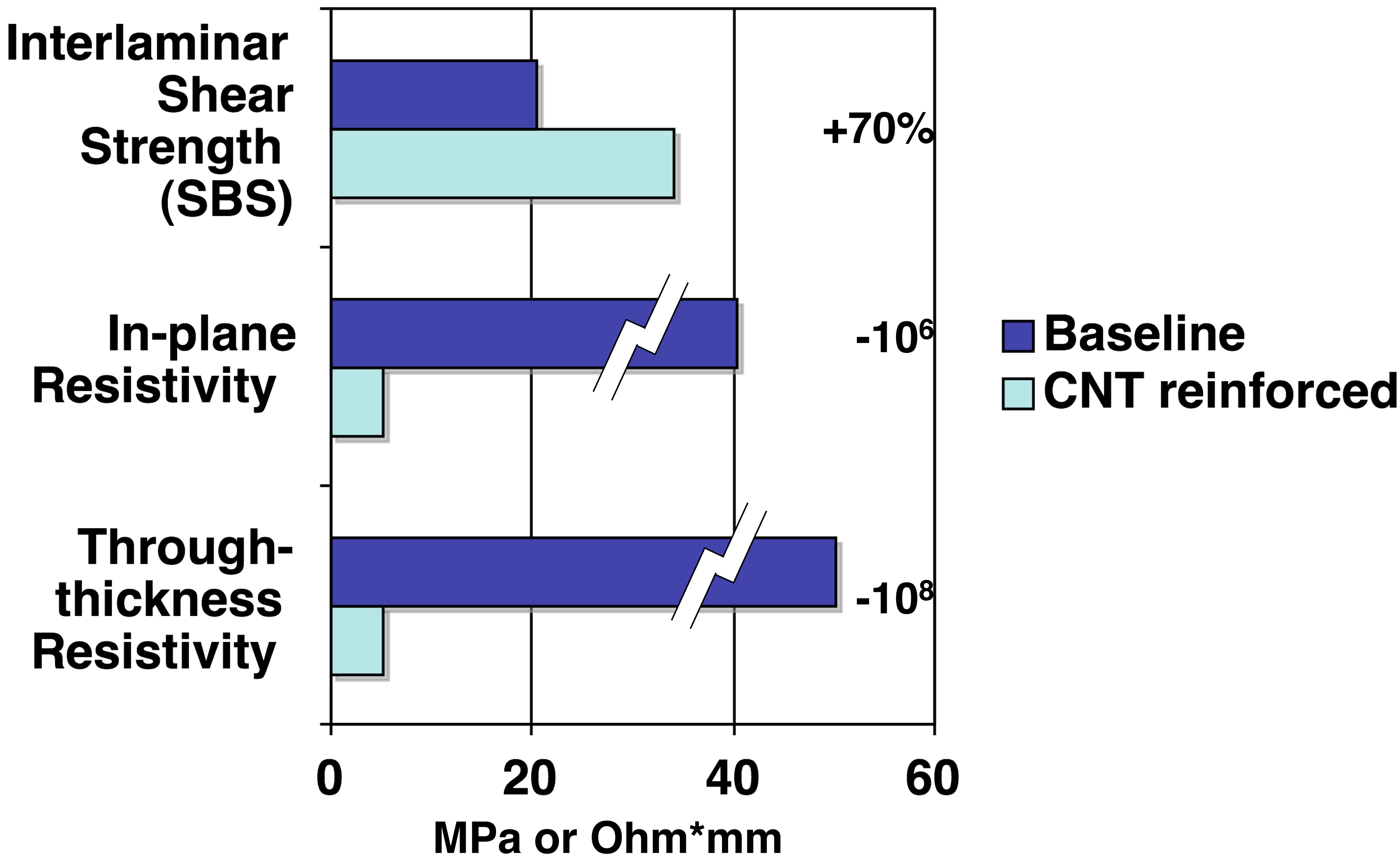
Without CNTs **With CNTs**





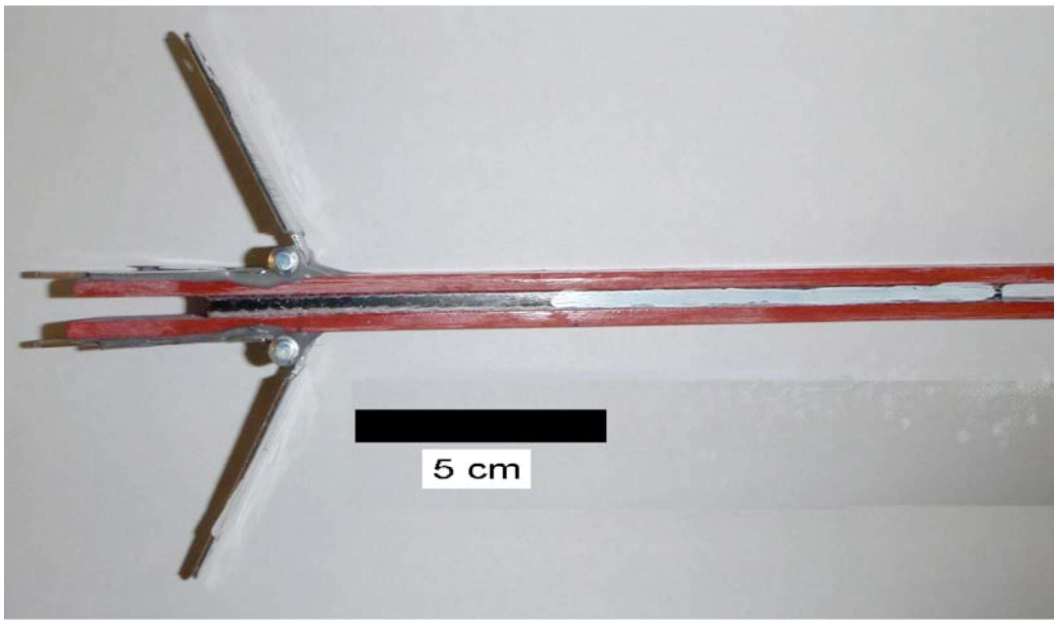
Garcia, Wardle, et al., *Comp. Sci. & Tech.*, 2008.

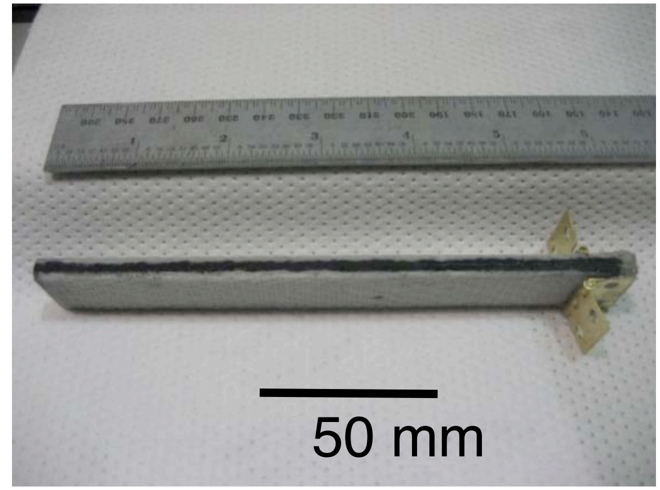
Summary Laminate-level Data for ‘Fuzzy Fiber’ Composites

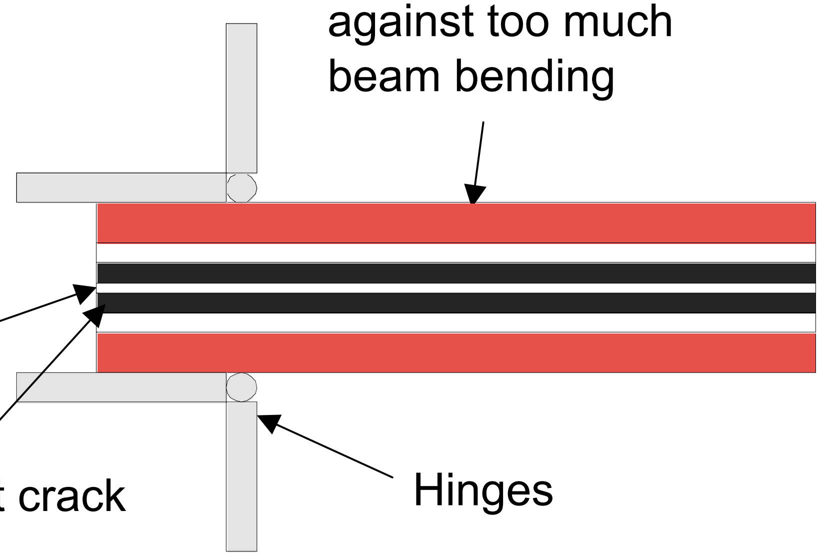


Garcia, Wardle, et al., *Comp. Sci. & Tech.*, 2008.
Yamamoto & Wardle, *AIAA SDM Conf.*, 2008. (Best student paper)

Larger-scale Manufacturing Allows Mode I DCB Testing of Fuzzy-Fiber Composites



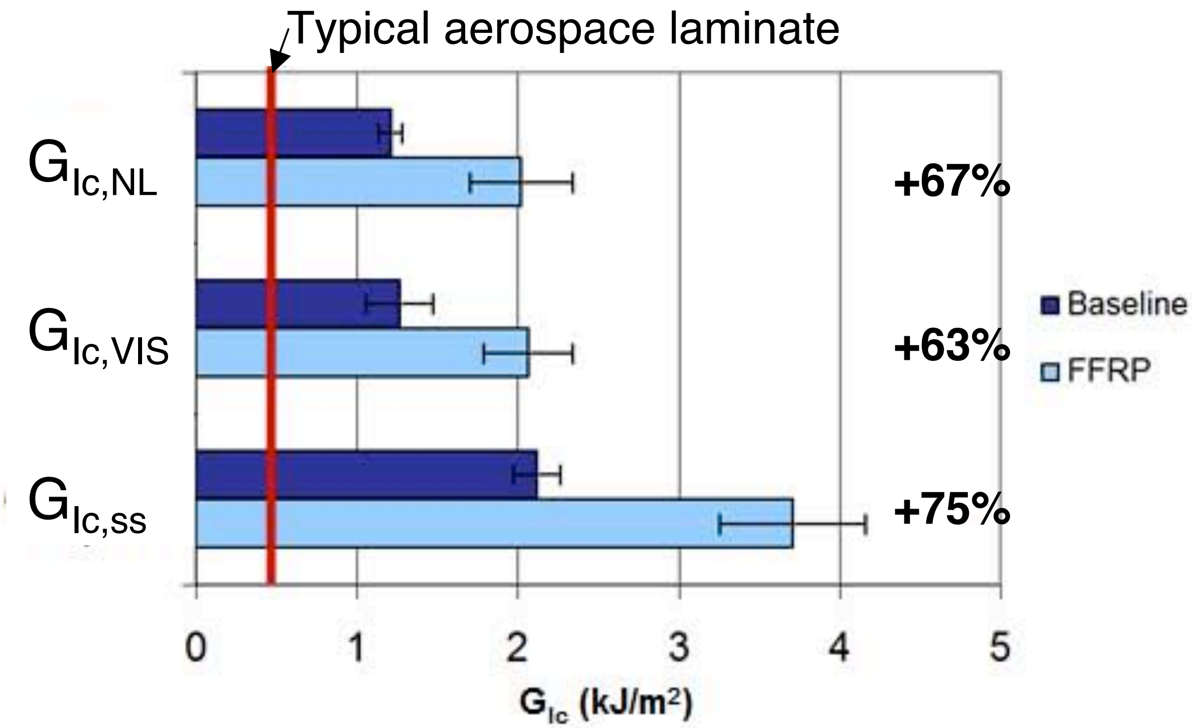


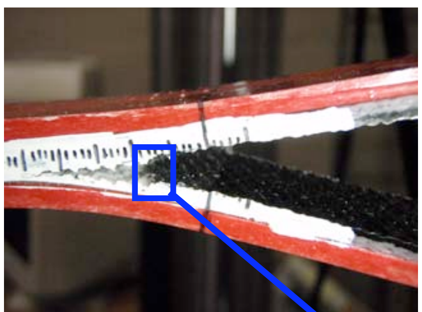


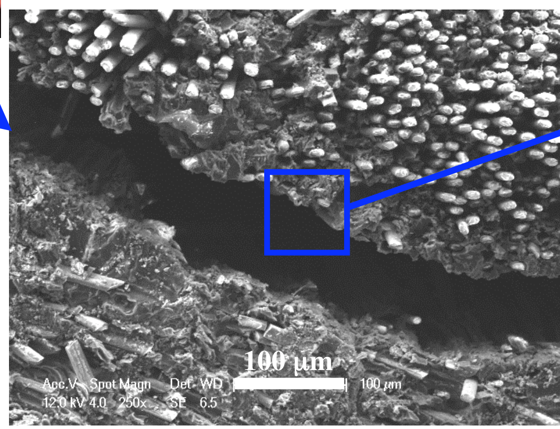
Wicks, (Wardle), et al., *Comp. Sci. & Tech.*, 2010.

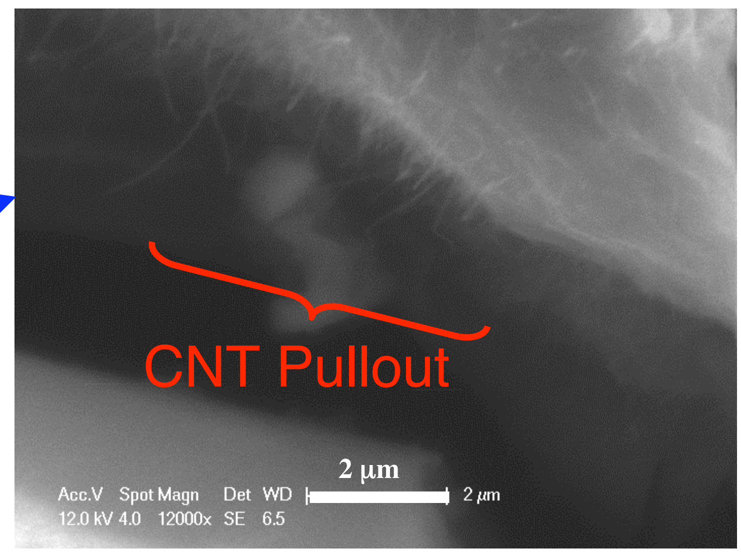
CNTs Toughen a Tough (Woven) System

- Mode I DCB fracture tests show significant toughening
  - Initiation and steady-state
  - Crack bridging by aligned CNTs noted in fracture surfaces



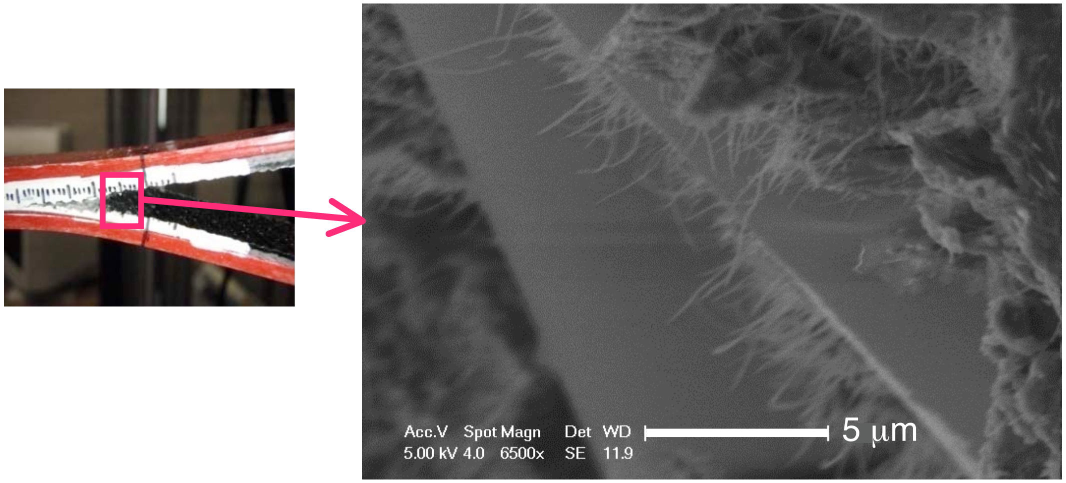






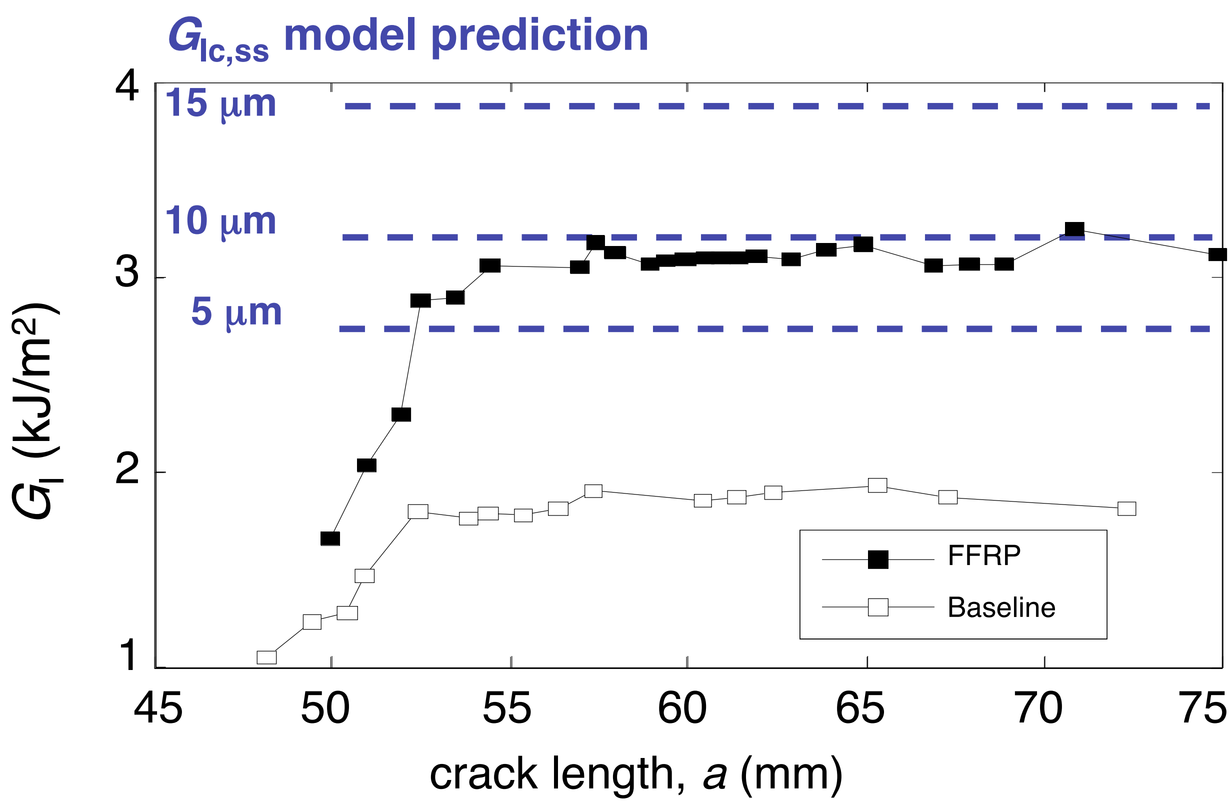
Wicks, (Wardle), et al., *Comp. Sci. & Tech.*, 2010.

Model-Experiment Correlation: Representative R-curves



Experimental values used to populate Mode I toughness model:

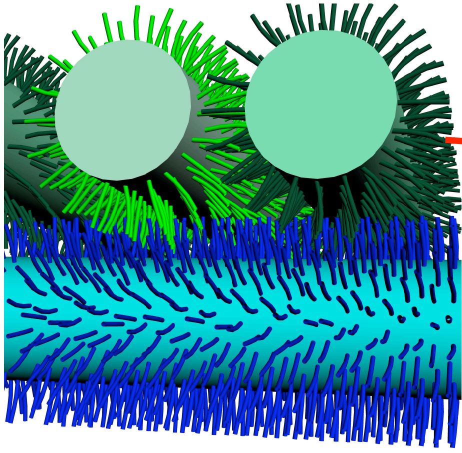
- SEM indicates pulled-out CNTs ~1-3 μm long
- 0.6% V_f, 14 nm diameter CNTs from synthesis/growth



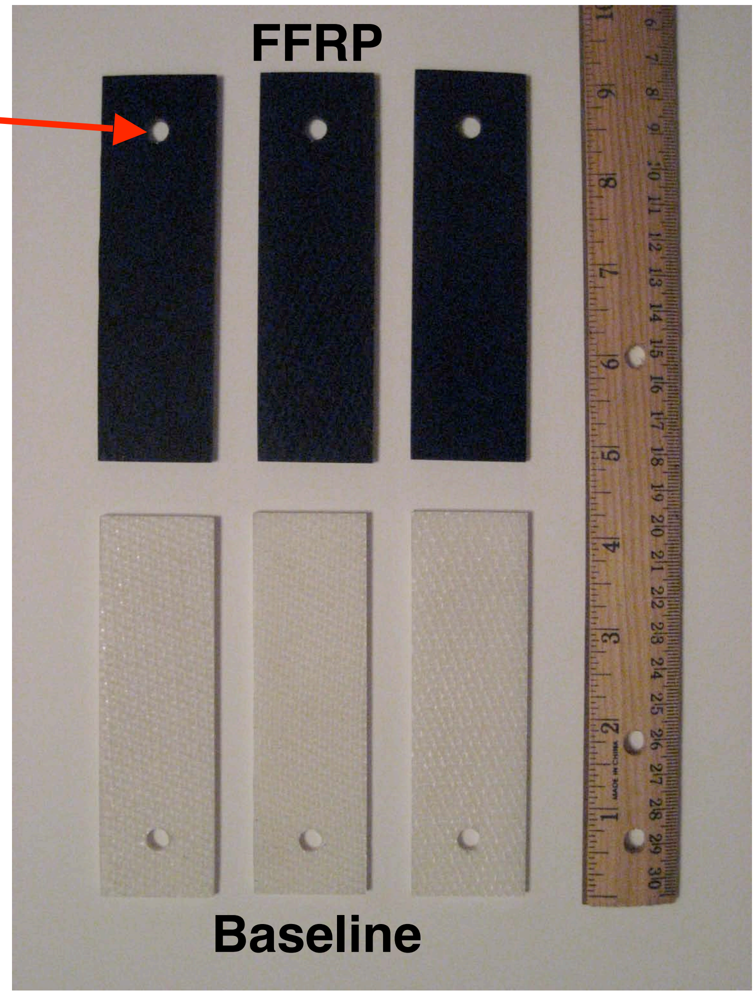
Wicks, (Wardle), et al., *Comp. Sci. & Tech.*, 2010.

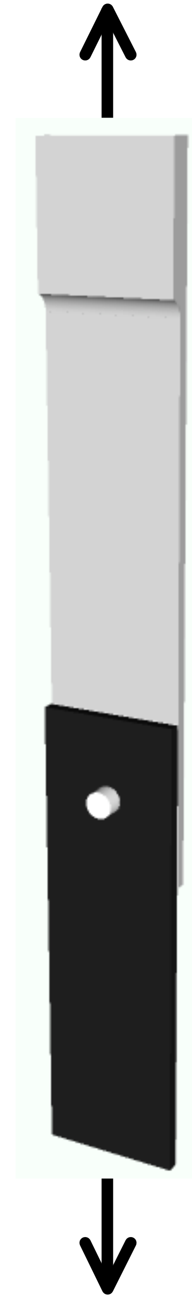
In-plane Strength Assessed via Tension-Bearing Testing

Fuzzy Fibers Contribute
3D-Reinforcement at Hole



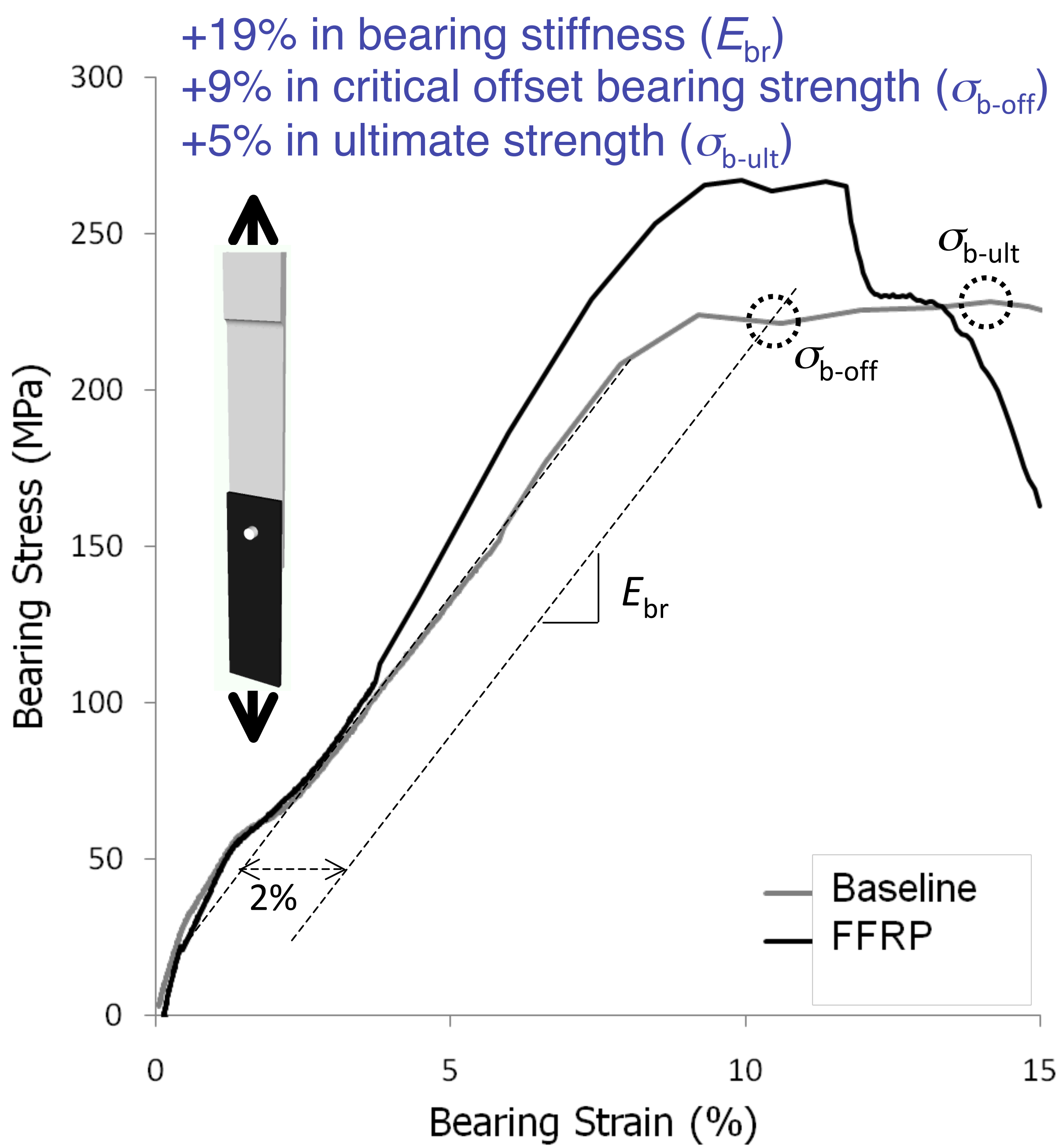
- Assess in-plane strength effects to complement interlaminar fracture
  - 3 samples each
  - ~2% V_f CNTs
  - Post-test characterization via optical and SEM

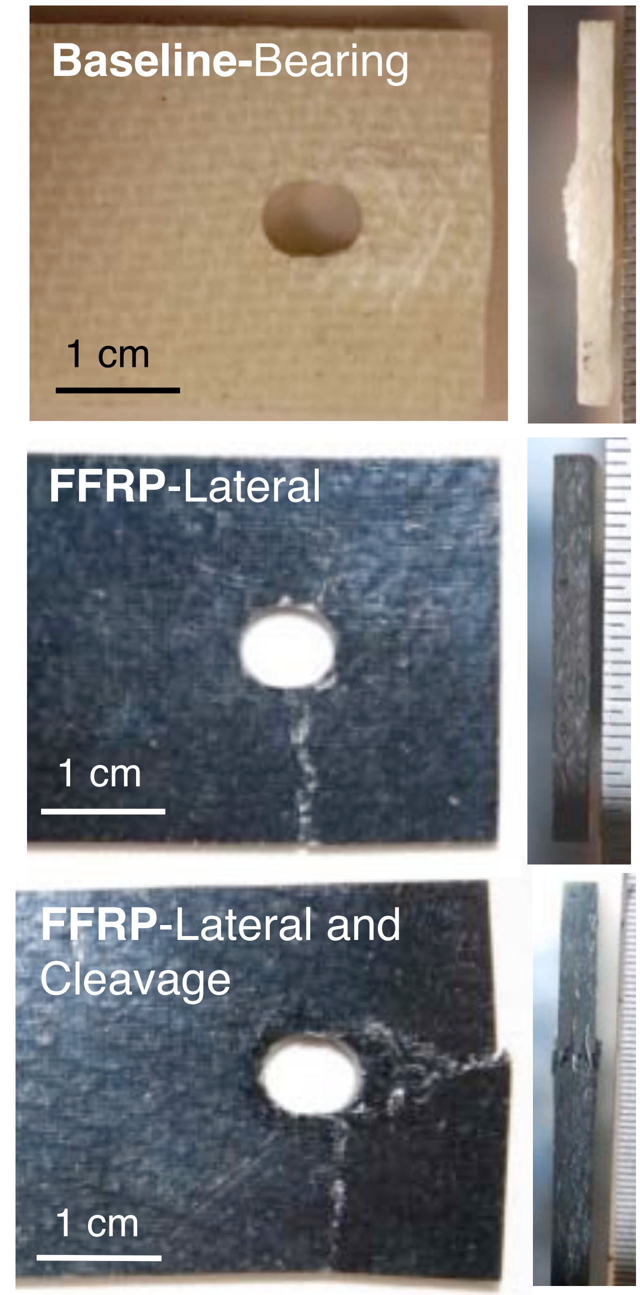




Tests courtesy of Lockheed Martin

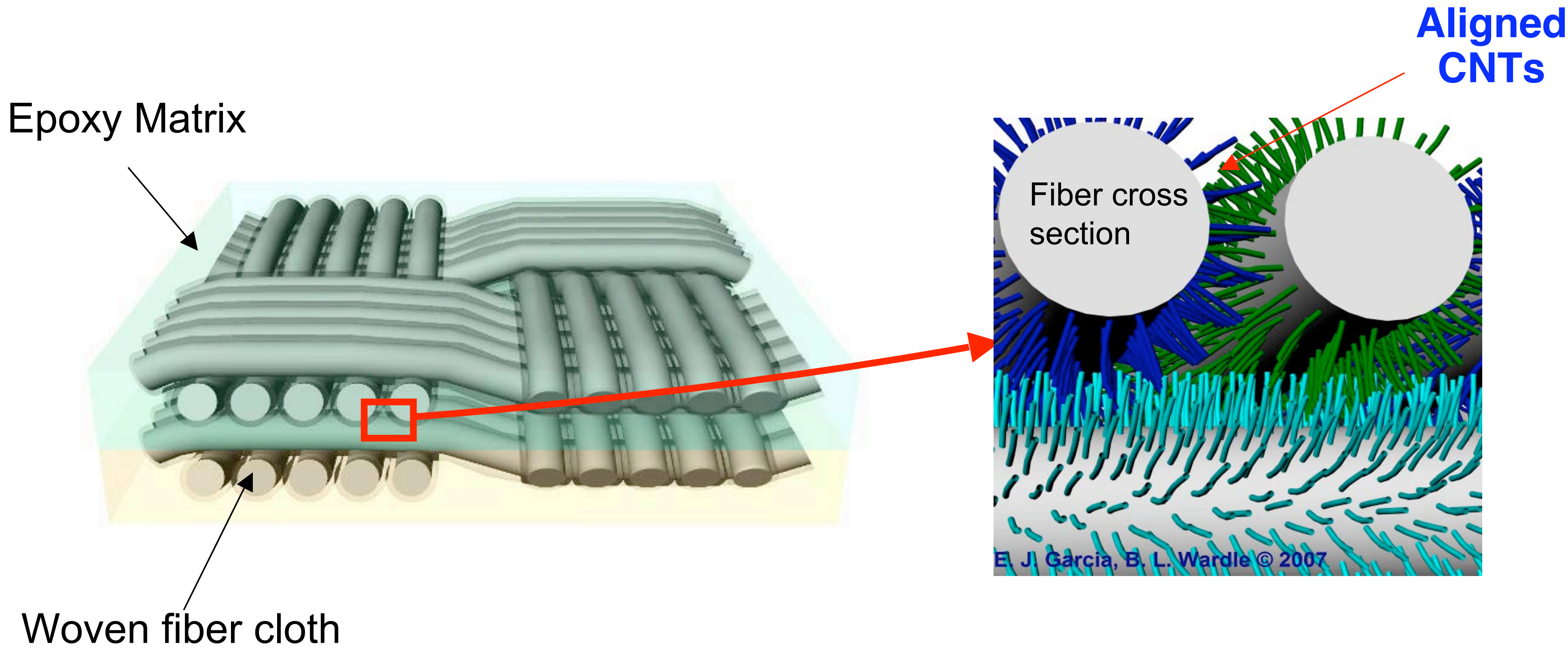
Small Increase in all Values; Clear Failure Mode Change





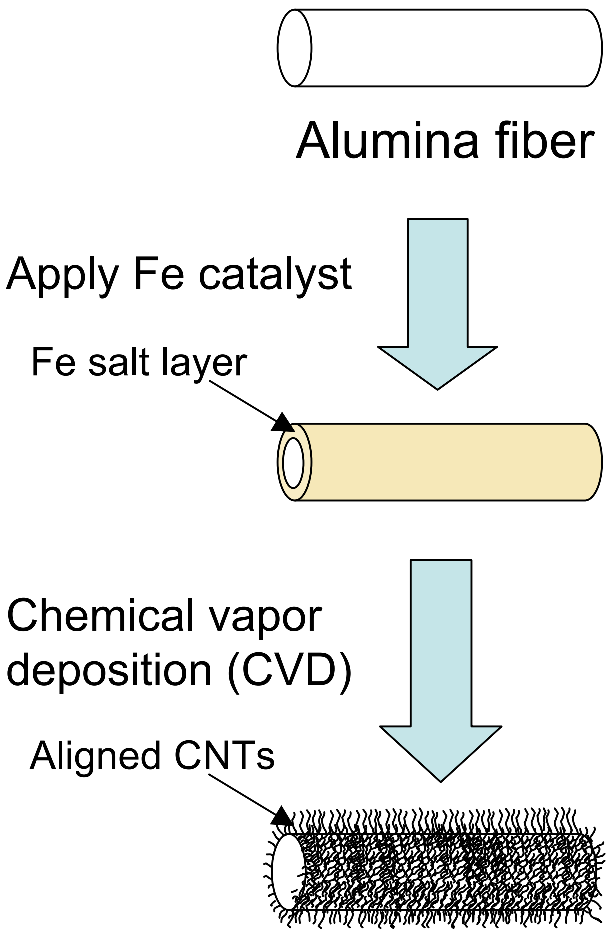
Wicks, (Wardle), et al., *Comp. Sci. & Tech.*, 2010.

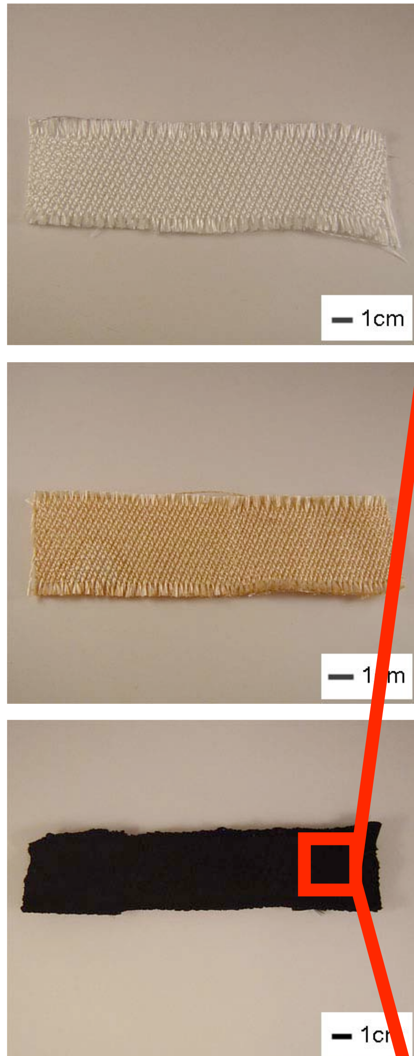
Nano-Engineered Composites

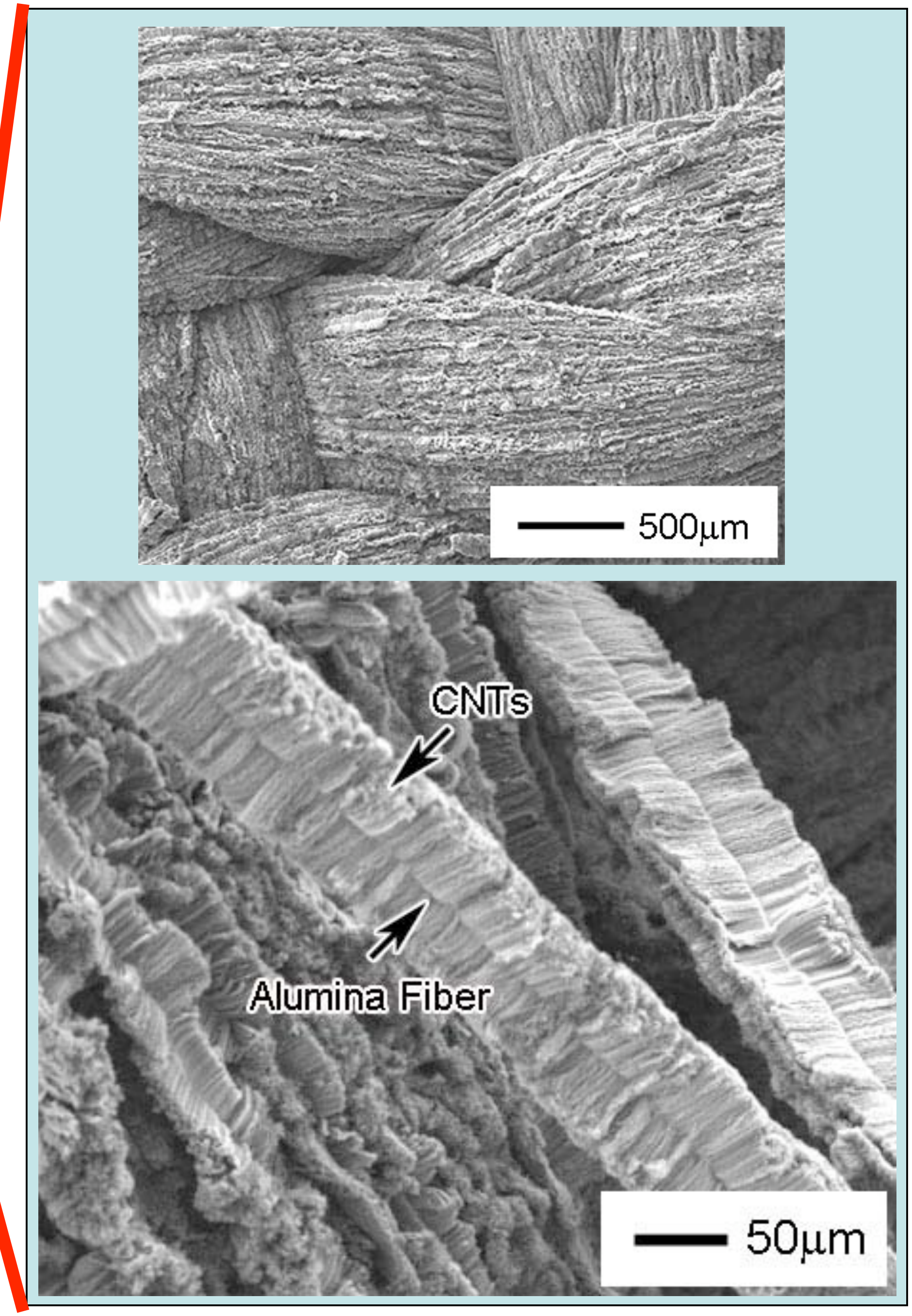


2,000X increase in surface area + **Infusion Process** = **Possible?**

Aligned-CNTs Grown on Cloth for FFRP

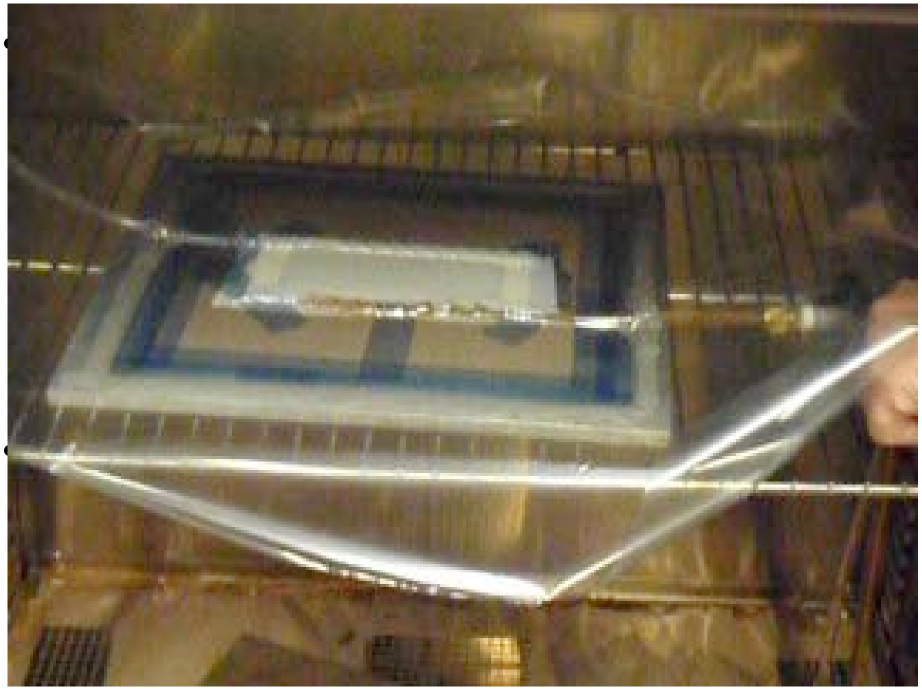


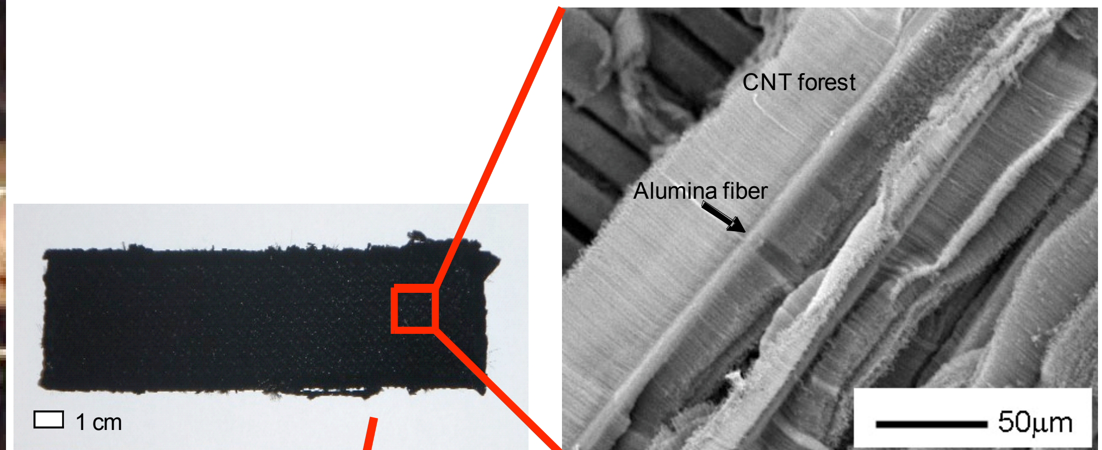


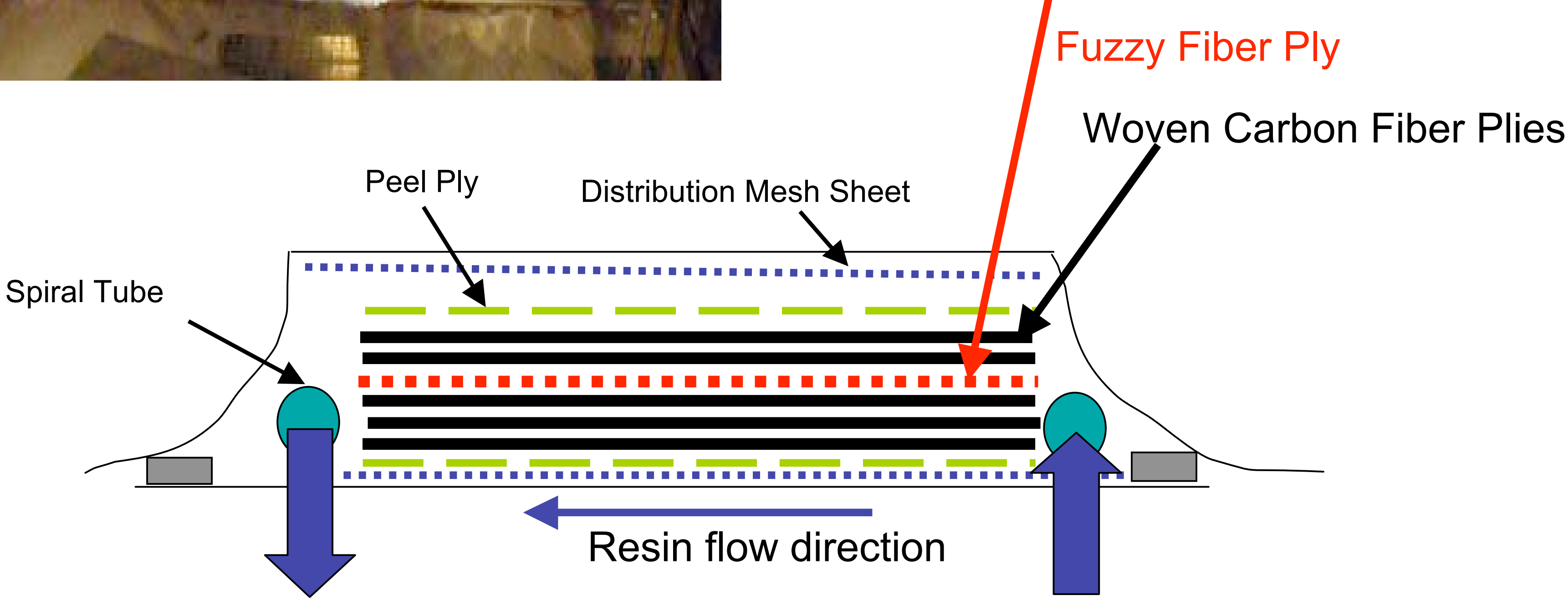


Aligned CNT-Coated alumina fiber, "fuzzy fiber (FF)"

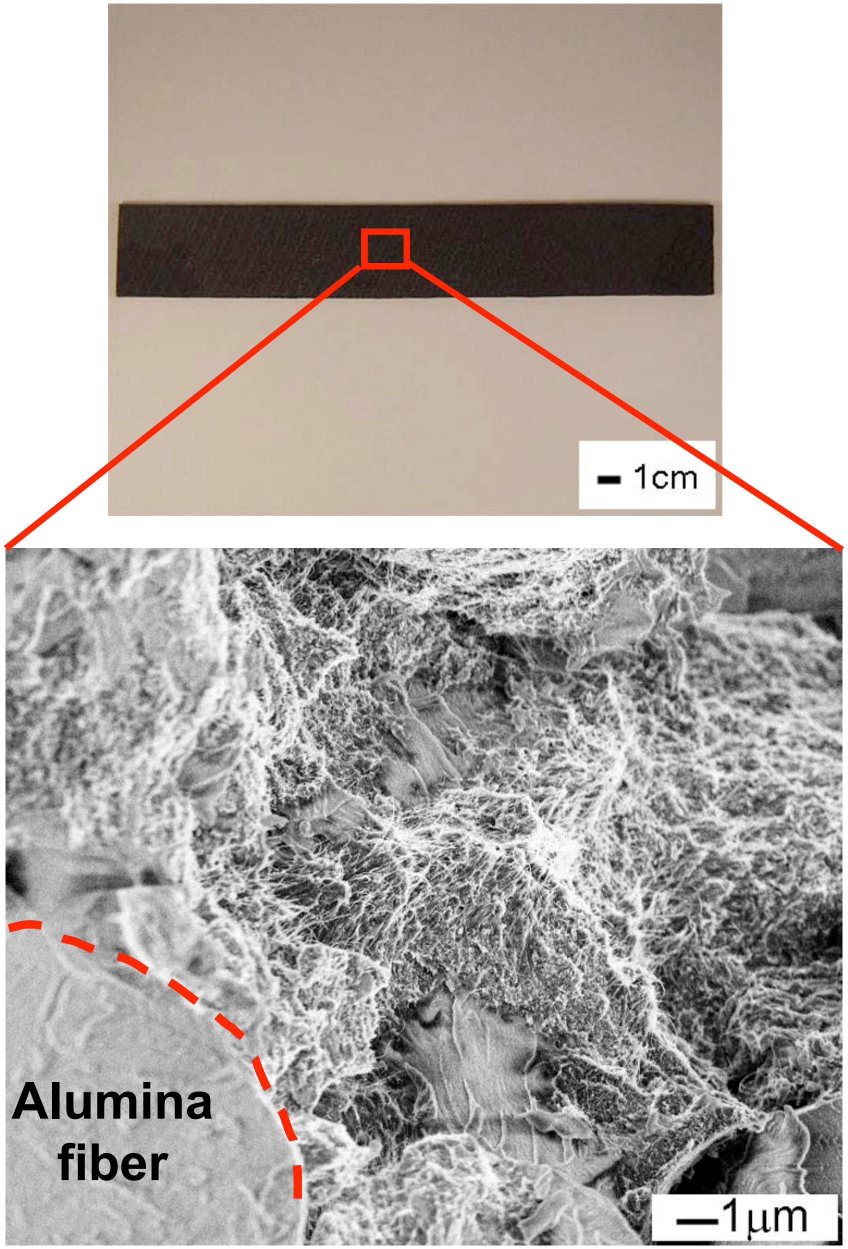
Can FFRP be Infusion-Processed?

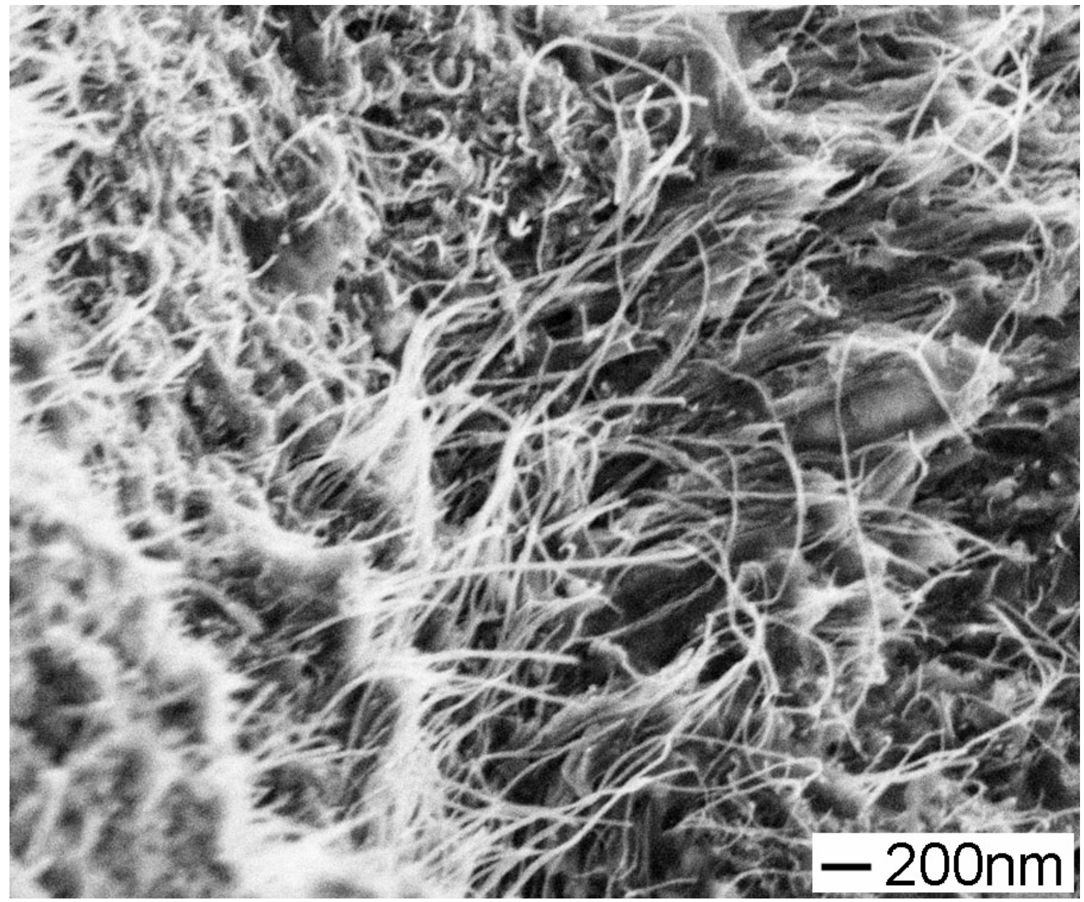






Cryogenic Fracture Surfaces: Microscopy Reveals CNTs Remain on Fibers

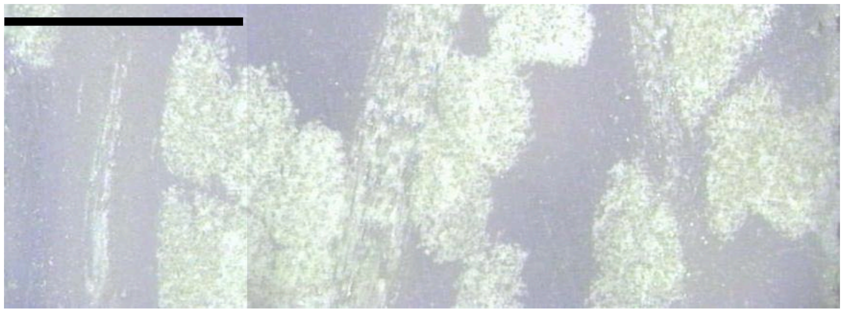




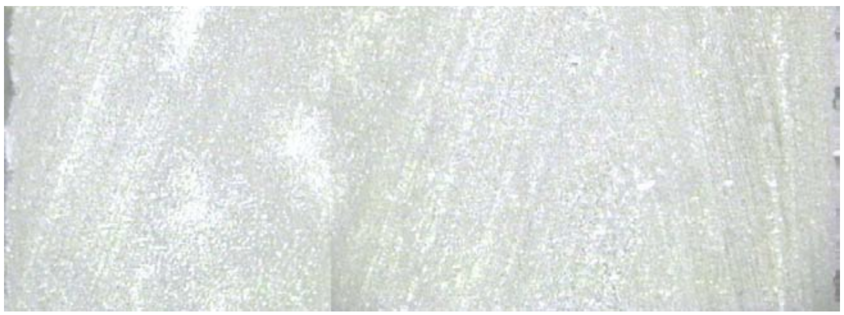
Ishiguro, (Wardle), et al., *ASC Conference,* 2009.

Infusion Yields Improved Void/Volume Fractions

1 mm

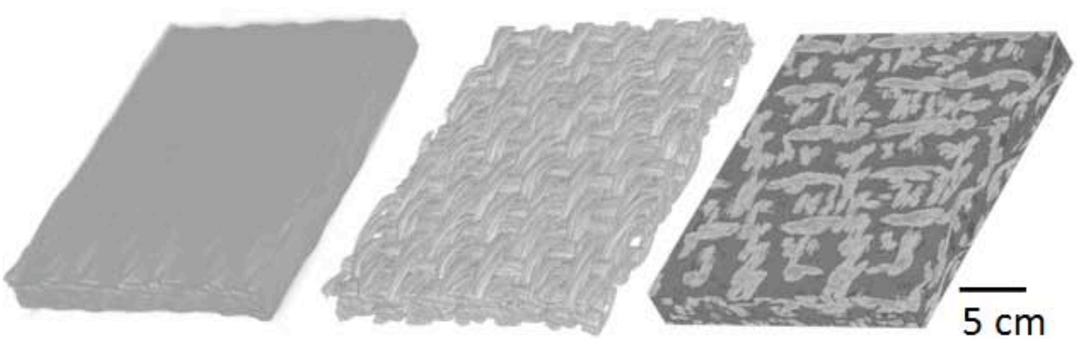


Baseline



FFRP

- Voids are assessed on polished cross sections using optical microscopy
- No meaningful voids, and improvement noted for fuzzy-fiber ply (vs. hand layup)
  - Baseline alumina 0.00 % voids, (hand layup: 0.34%)
  - FFRP 0.09% voids,
    (hand layup: 1.36%)
- Improved fiber volume fraction between FFRP and Baseline samples
  - 7% difference
    (hand layup: 12% difference)
  - Near-term goal is additional process refinements to achieve 0% difference

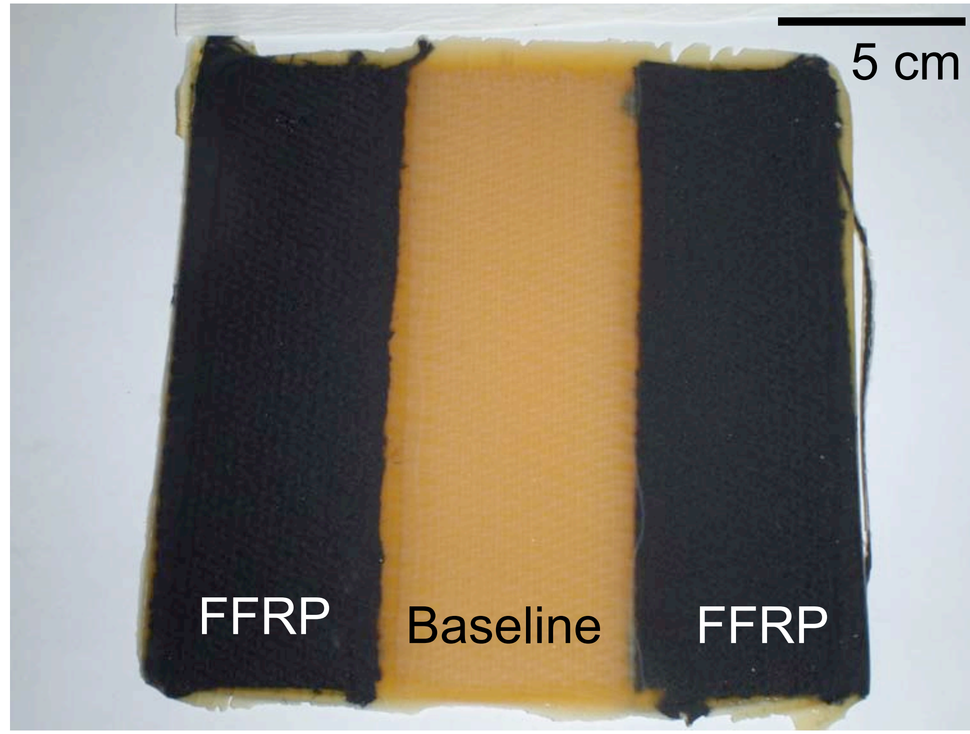


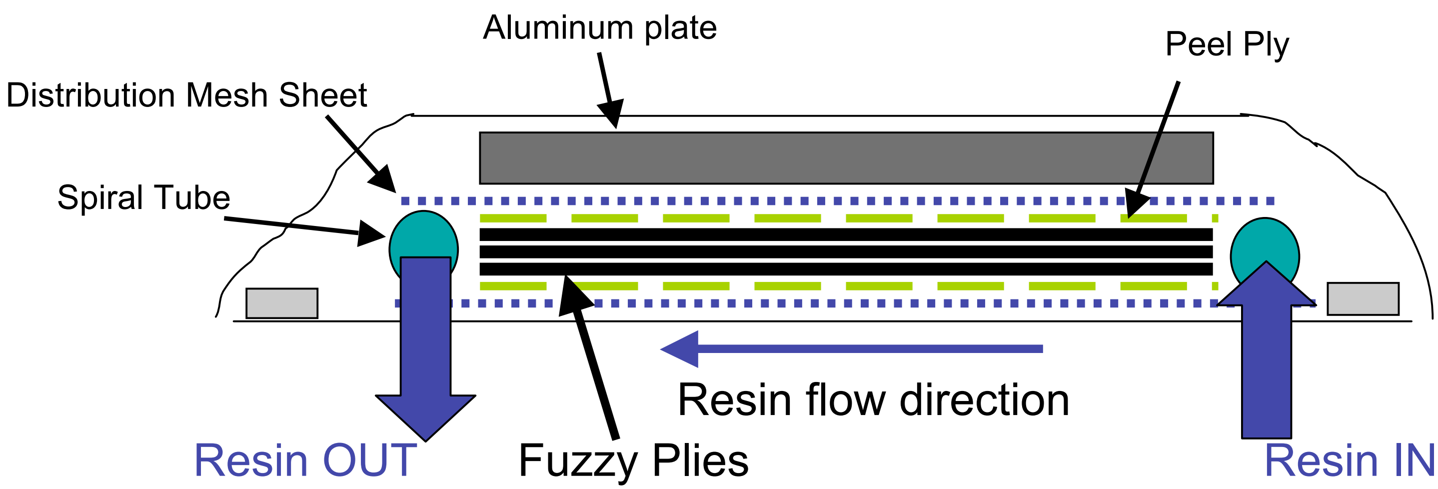
MicroCT analysis being developed for non-destructive void and volume fraction assessment

Ishiguro, (Wardle), et al., *ASC Conference,* 2009.

Infusion Process Refinements: Thickness Control and Uniformity

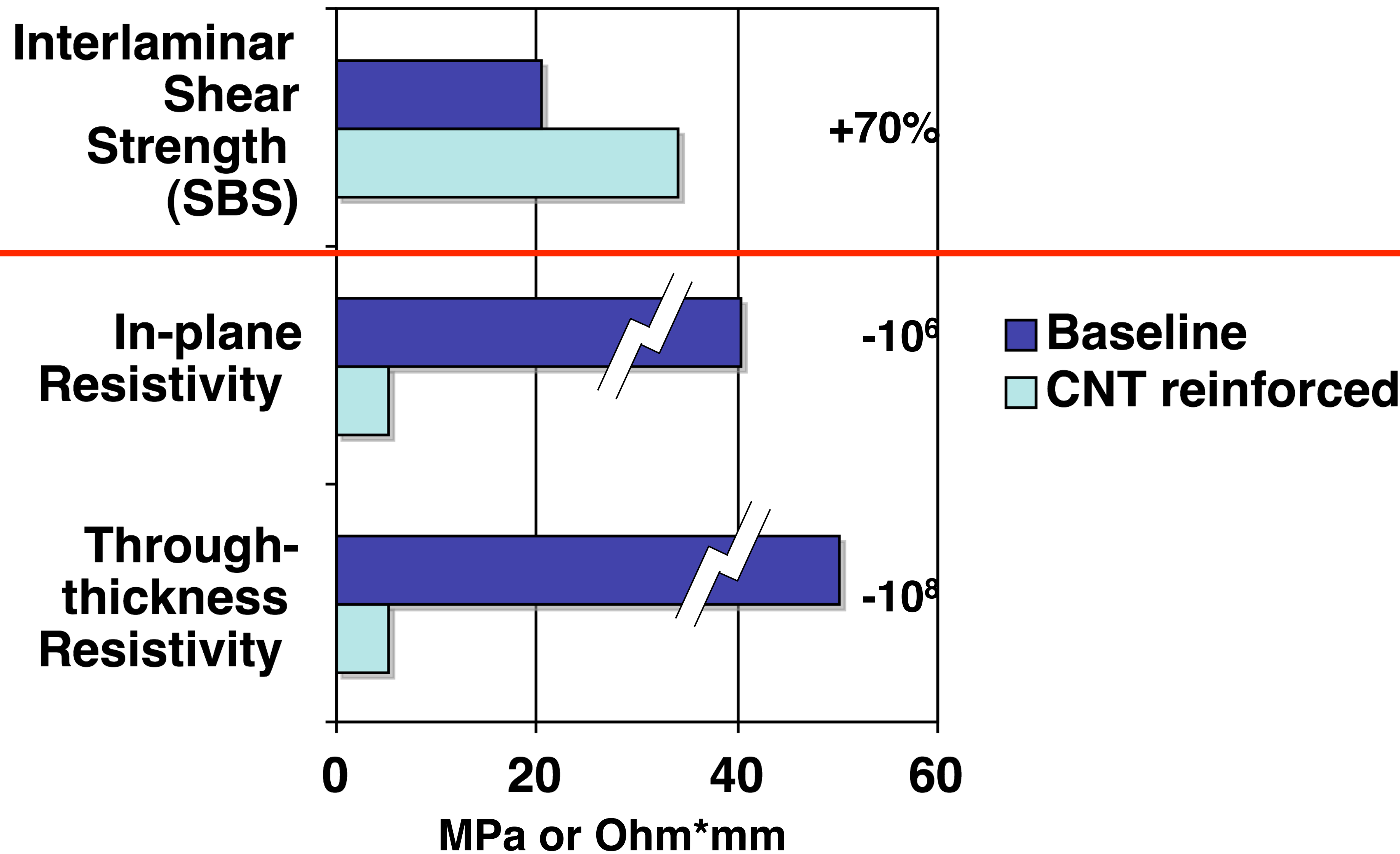
3-Laminate Fabrication





- Vacuum assisted
- Unmodified RTM6 resin (Hexcel)
- Cured at 90 C

Non-mechanical FFRP Attributes Such as Electrical Conductivity Can Enable New Functionality

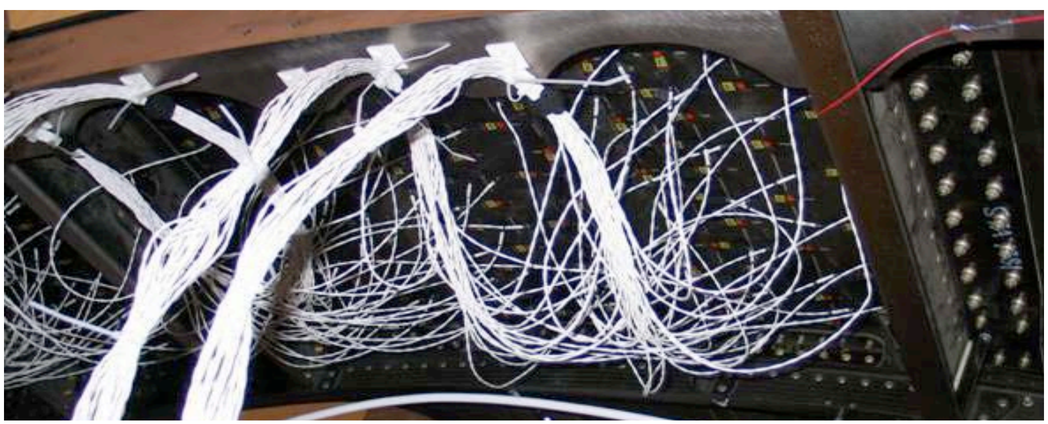


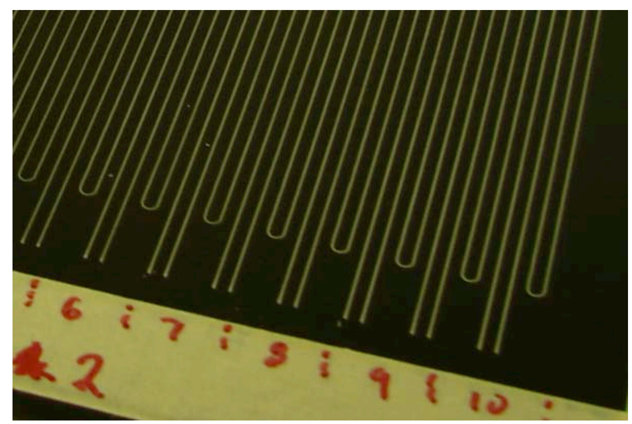
Garcia, Wardle, et al., *Comp. Sci. & Tech.*, 2008.
Yamamoto & Wardle, *AIAA SDM Conf.*, 2008. (Best student paper)

CNT-enabled Non-desctructive Evaluation and Health Monitoring

- SHM improves reliability, safety & readiness at reduced costs
  - Sensors add weight, power consumption & computational bandwidth
  - Cables add weight, complexity, as well as durability & EMI concerns
  - Scaling SHM for large-area coverage has presented challenges

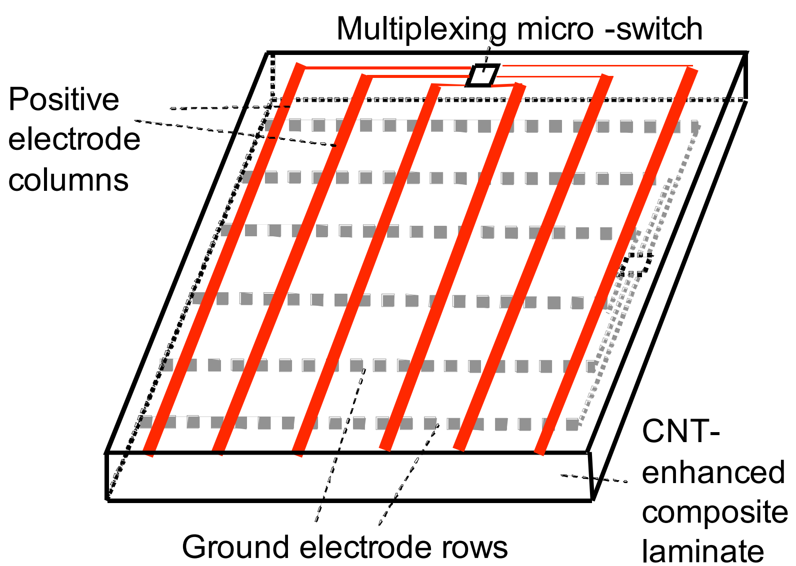
- Proposed CNT-based sensing methodology
  - Sensing elements actually *improve* specific strength/stiffness of structure
  - Conformal direct-write (DW) electrodes lighter & more durable than cable
  - Simple to scale over large structure, maintains good local resolution

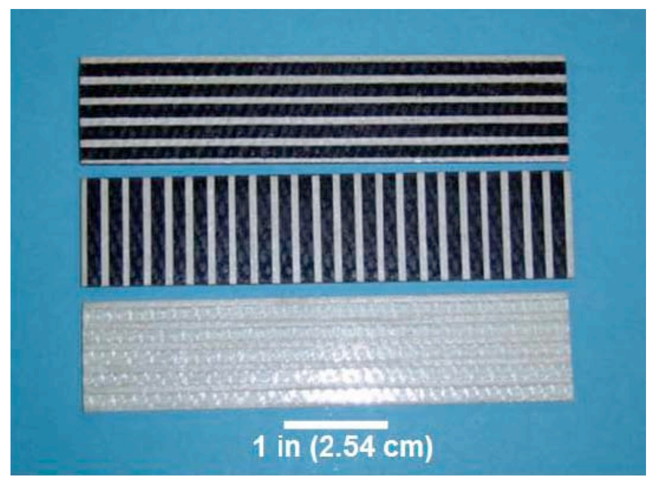




CNT-enabled NDE and SHM

- Aligned CNTs greatly enhance composite laminate properties
  - Mechanically improves toughness and strength
  - Multifunctional capabilities introduced by electrical conductivity & piezoresistivity
- Present research exploits CNTs for *in-situ* damage imaging
  - Direct-write (DW) electrode grids applied similar to LCD technology
  - In-plane & through-thickness resistance measurements collected
  - Surface & sub-surface damage images produced in post-processing



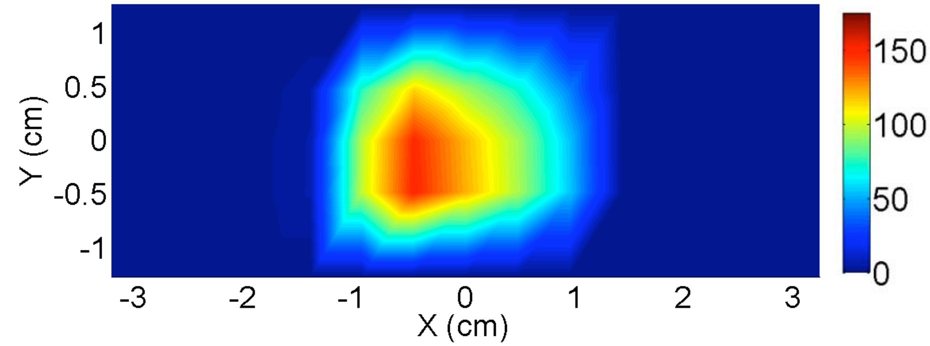


Barber, (Wardle), et al., *SAMPE Fall Technical Conference,* 2009.

Proof-of-concept Results

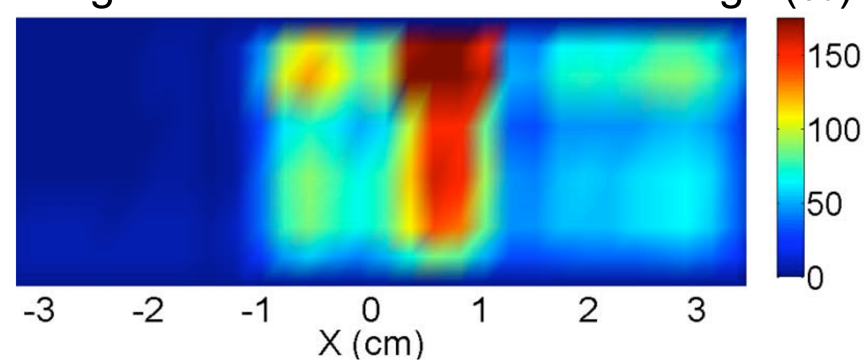
- Baseline specimens (no CNTs) have > 5 MΩ resistance before and after impact, illustrating that there is no suitable conductive path without CNTs
- In-plane resistance between parallel pairs of adjacent traces
  - > 100% change in middle traces, < 10% change for outermost trace pairs
  - Appears to be more sensitive to surface cracking
- Through-thickness resistance at each virtual grid point
  - 56 through-thickness grid points averaged 20 Ω resistance pre-impact
  - > 100% change in middle points, < 10% change for "left" half
  - Resistance offset introduced by cracks across traces on "right" half
  - Appears to be more sensitive to delamination

Front, In-Plane Resistance Change (%)



Back, In-Plane Resistance Change less than 1% (not plotted)

Through-Thickness Resistance Change (%)

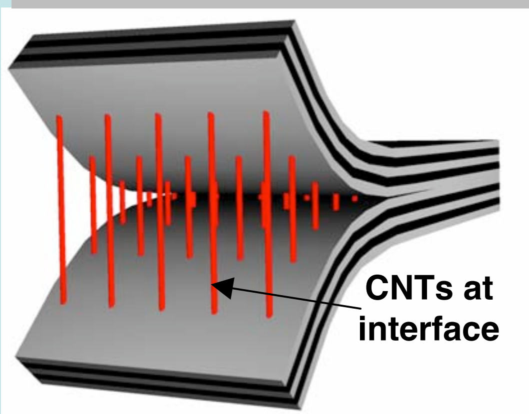


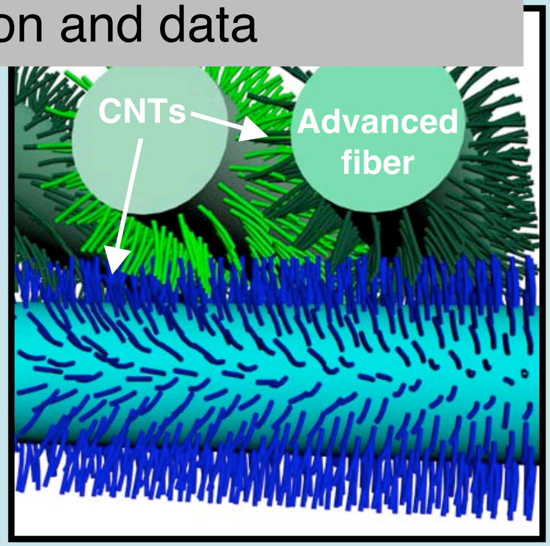
Recent Contributions

3. **Nanocomposite mechanics**
4. New CNT growth catalyst (discovery)

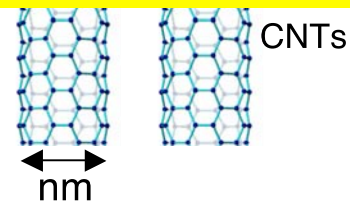
(1) Nano-engineered Composites

1. Key modeling result
2. Laminate fabrication and data





‘Nanostitched’ and ‘fuzzy’ fiber laminates



meters

Next-generation advanced composites

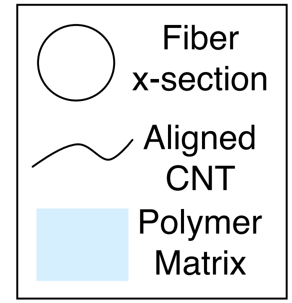
(2) Structural design

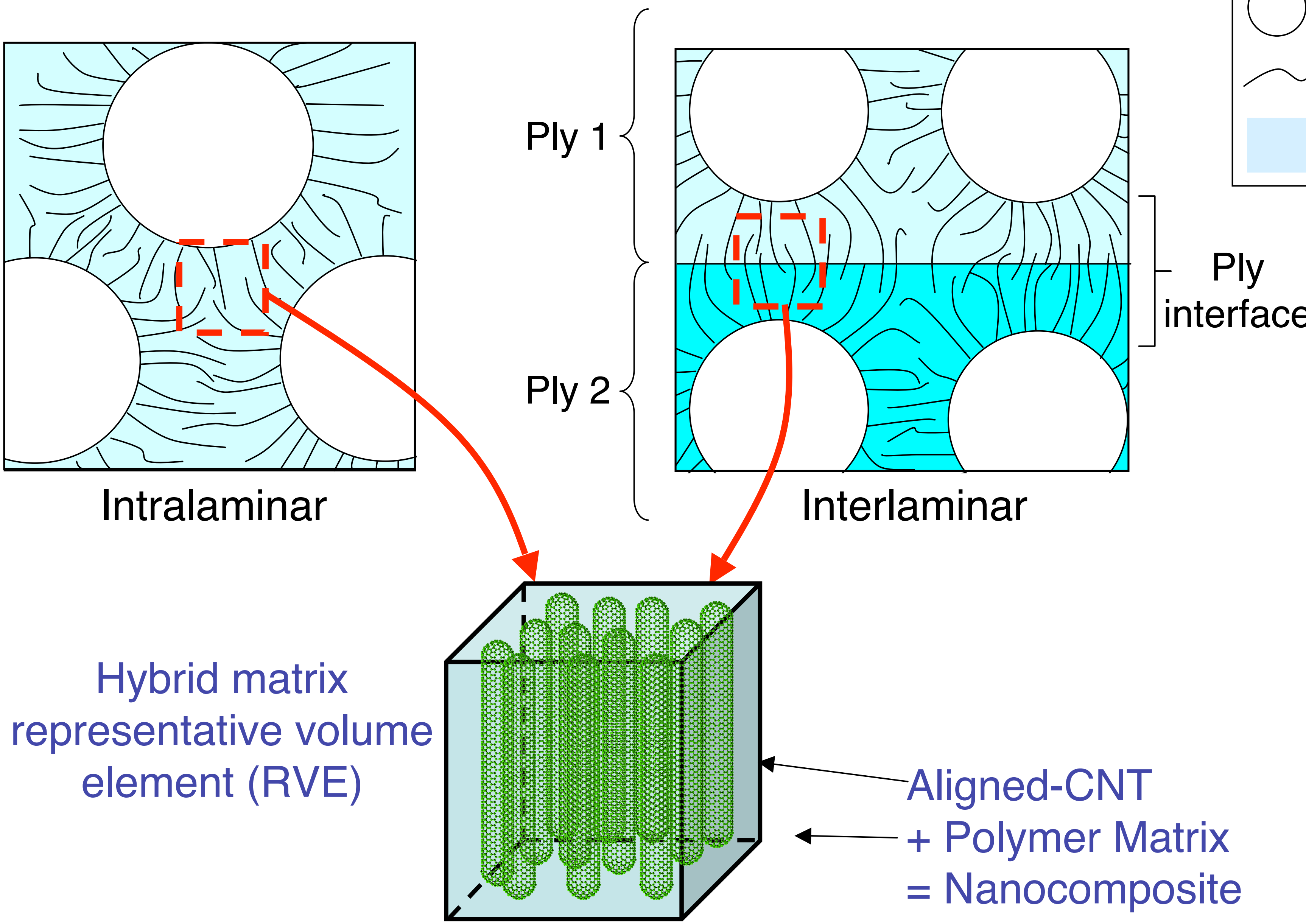
5. Moving towards continuous manufacturing

(4) Processing/fabrication

6. Something different

RVE for Nano-engineered Composites is an Aligned-CNT Polymer Nanocomposite (PNC)

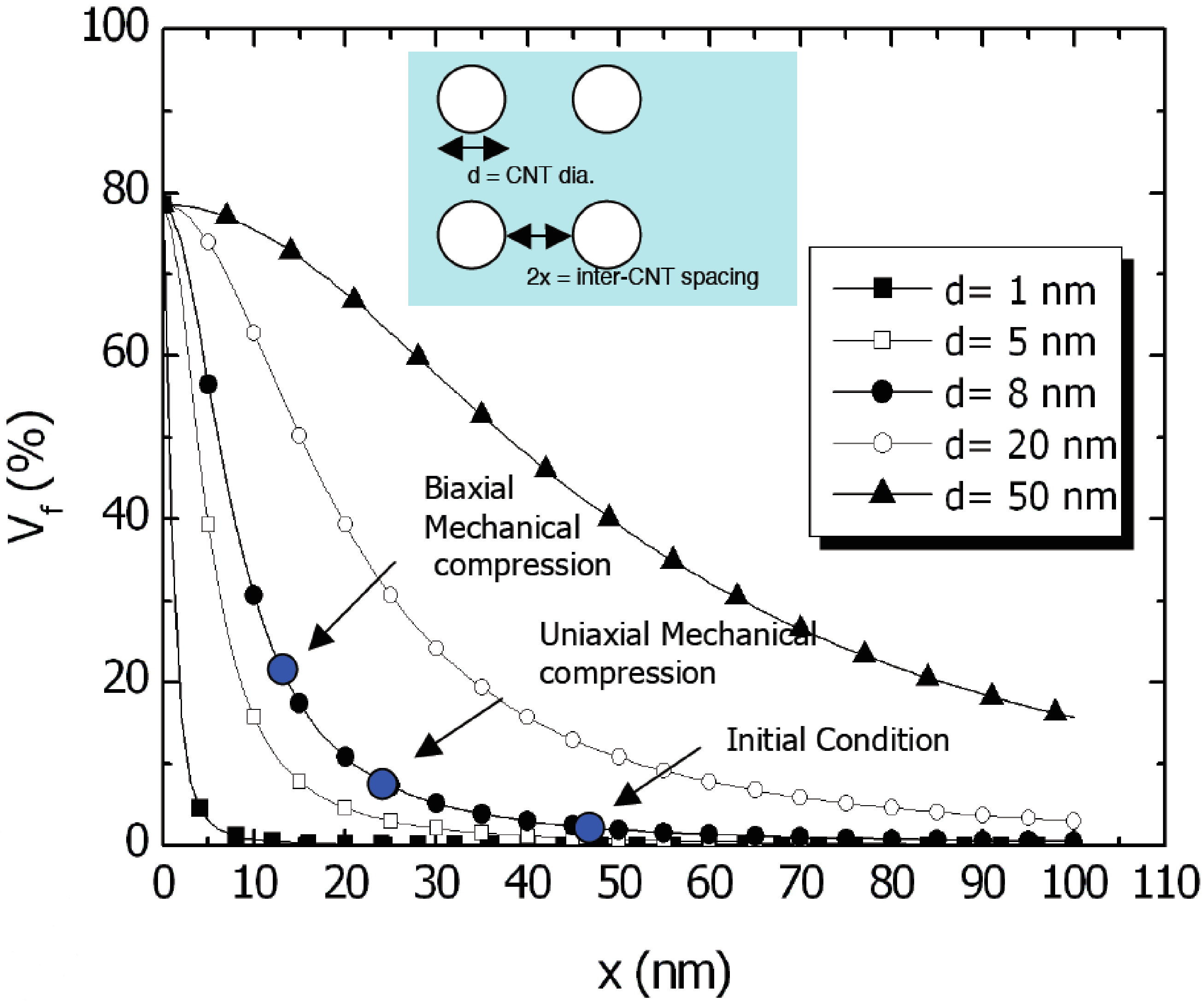




Illustrations not to scale

Wardle et al., *Adv. Materials* 2008; *Nanotechnology* 2007; etc.

Fundamental Property and Transport Studies Using Ideal-Morphology Nanocomposites



- Polymer structure-property changes when CNTs are ~10 nm apart?

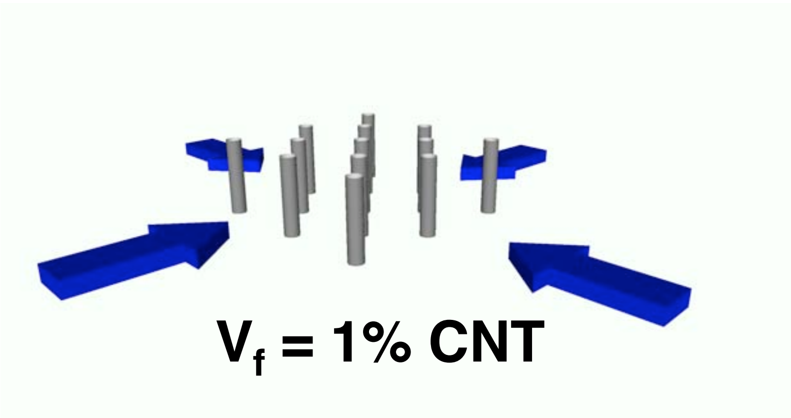
  E.g., CNT spacing is less than polymer characteristic chain lengths…

MD simulation of polyimide & CNTs
[Courtesy G. Odegard, MTU]

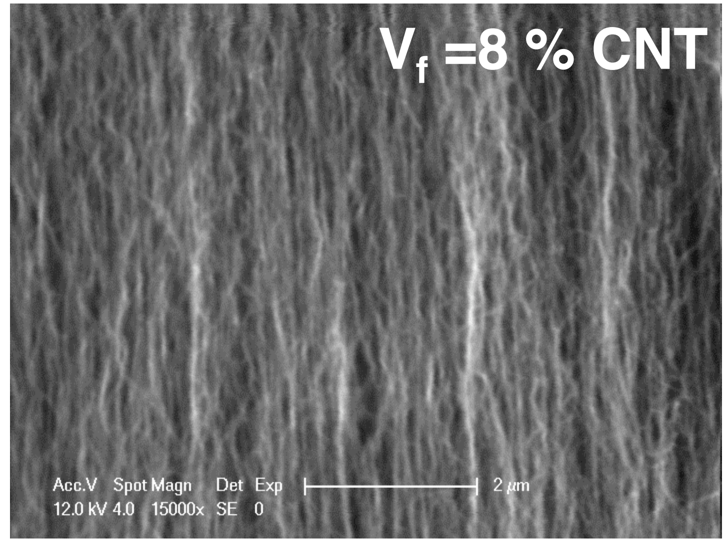
Wardle et al., *Advanced Materials,* 2008.

Platform for Making (near theoretical) High Volume Fraction Nanocomposites

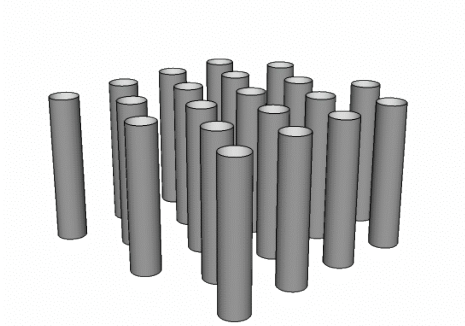
Before mechanical densification



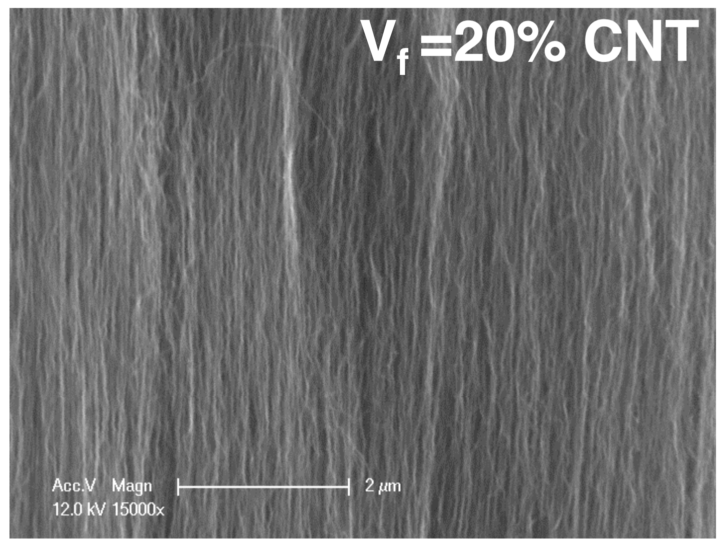
V_f = 1% CNT



After densification

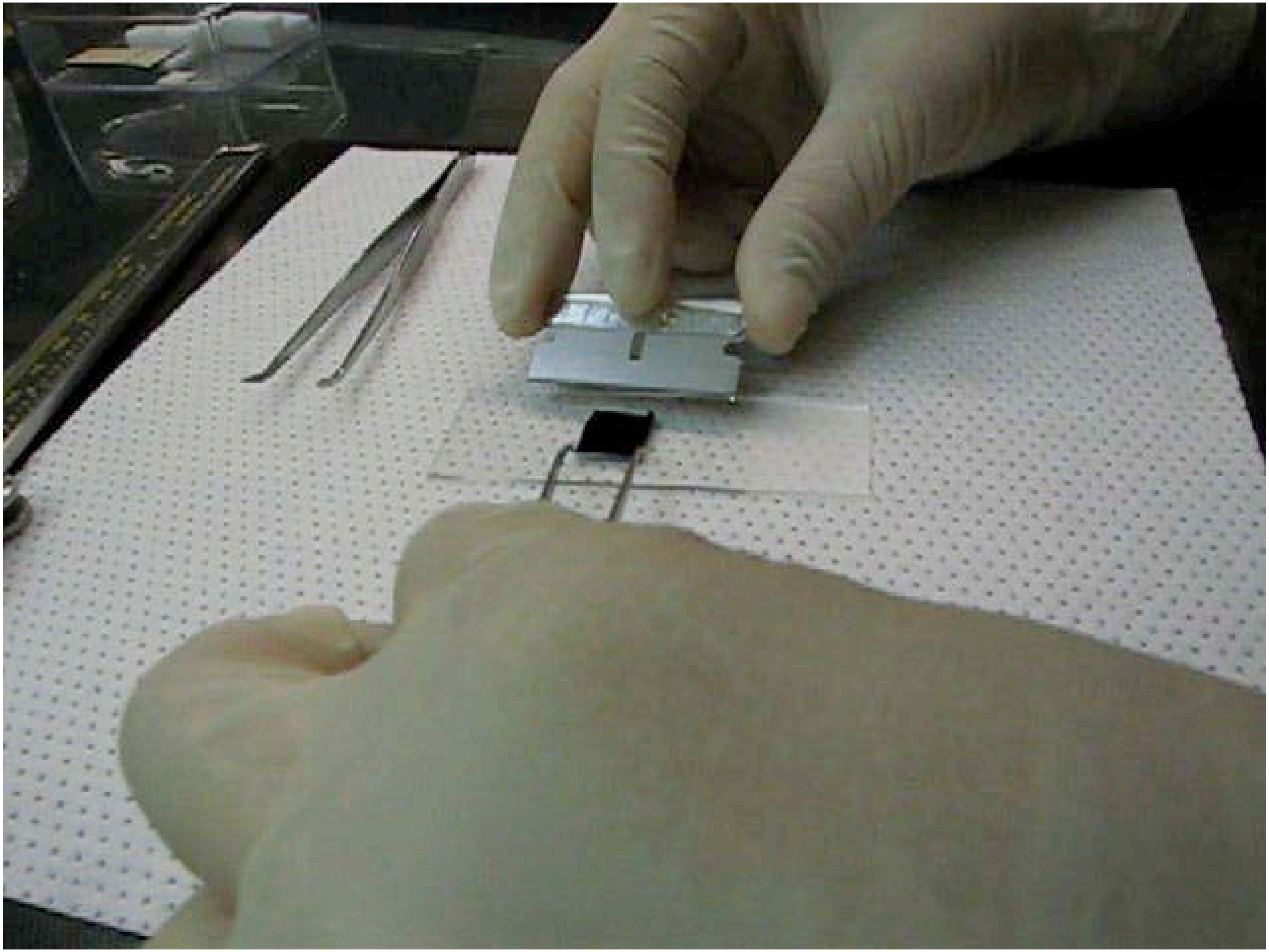


V_f >20% CNT

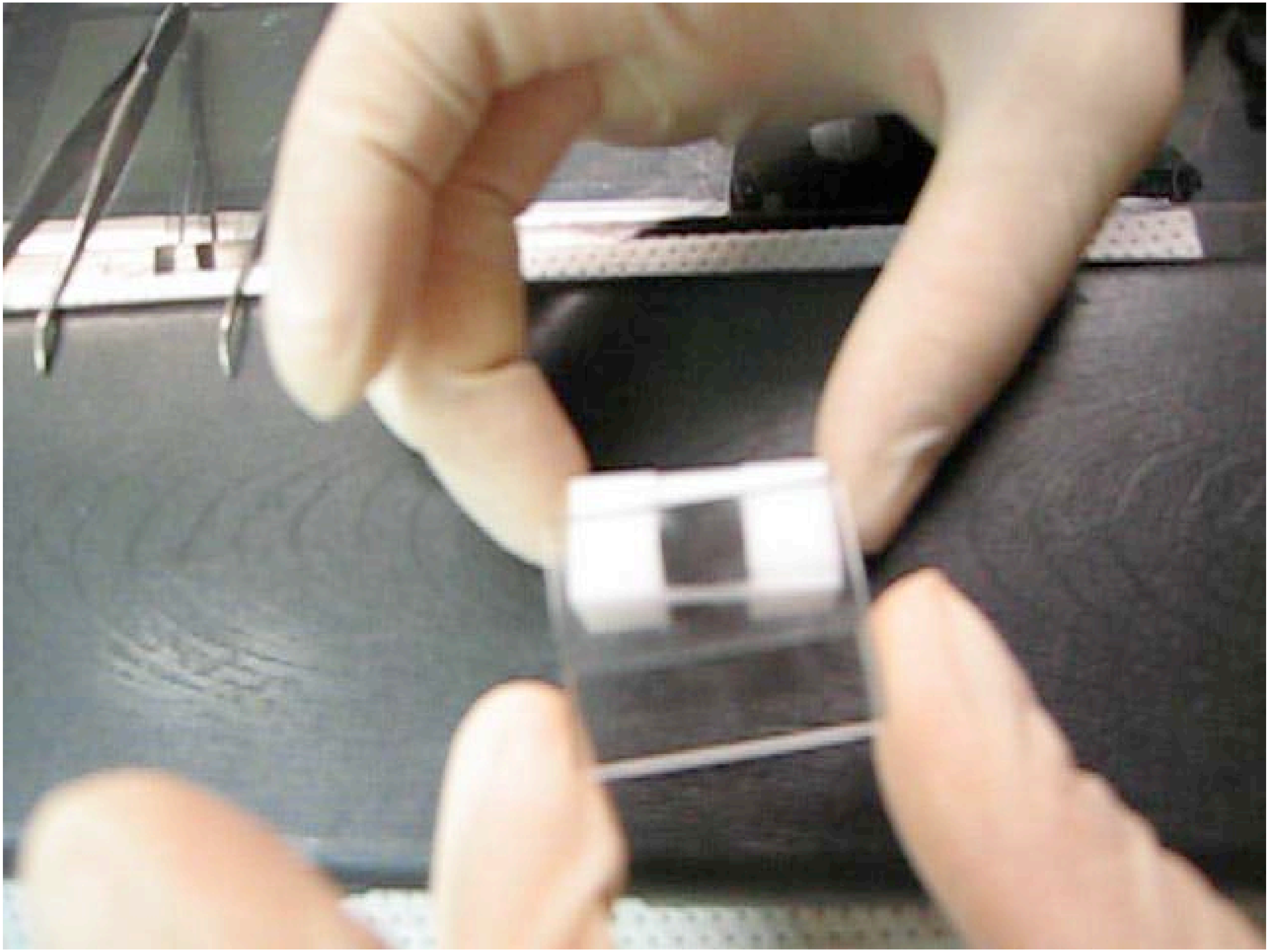


Wardle et al., *Advanced Materials,* 2008.

"EZ" Delamination of Aligned-CNT Forests

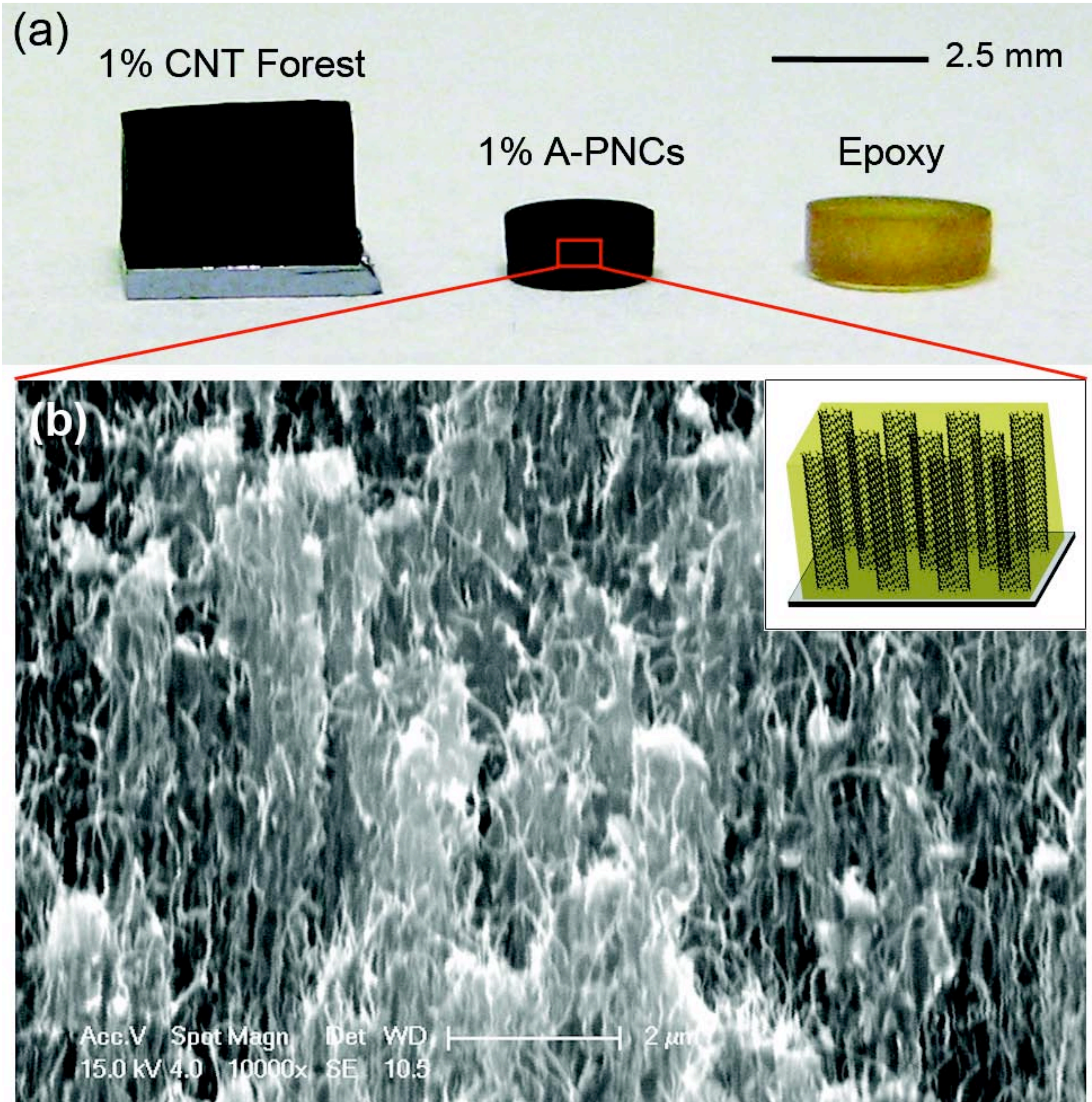


Biaxial CNT Forest Densification Video

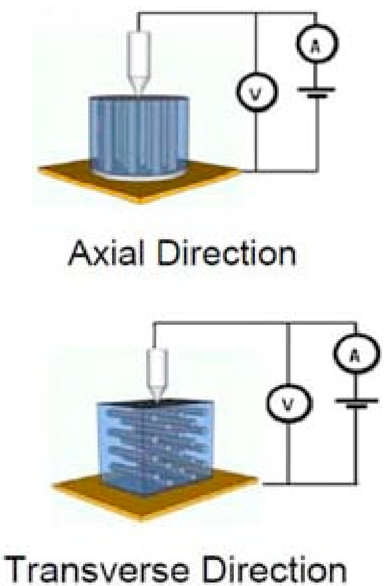


Wardle et al., *Advanced Materials,* 2008.

Variable Volume Fraction Aligned-CNT Polymer Nanocomposites with Controlled Morphology



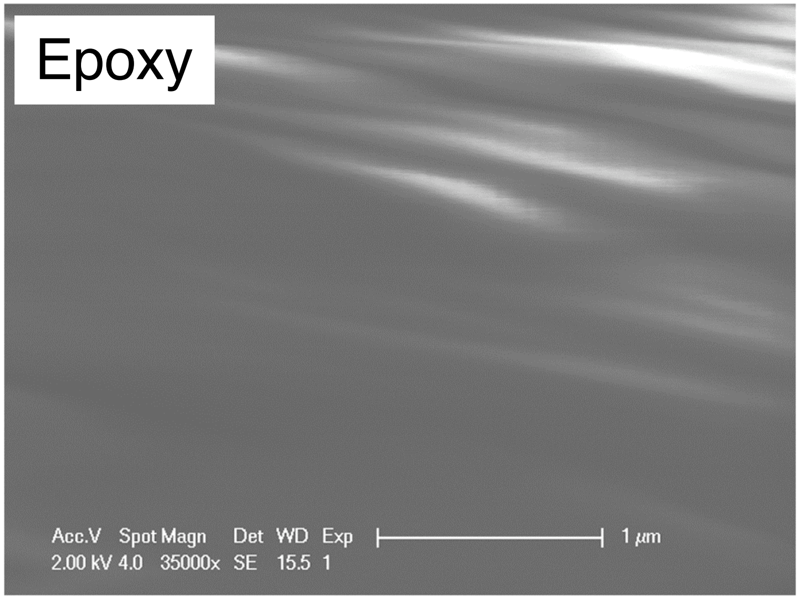
- Vol. fraction varies (CNTs aligned, also random): 1%, 8%, 20% V_f
- Modulus and electrical conductivity characterized

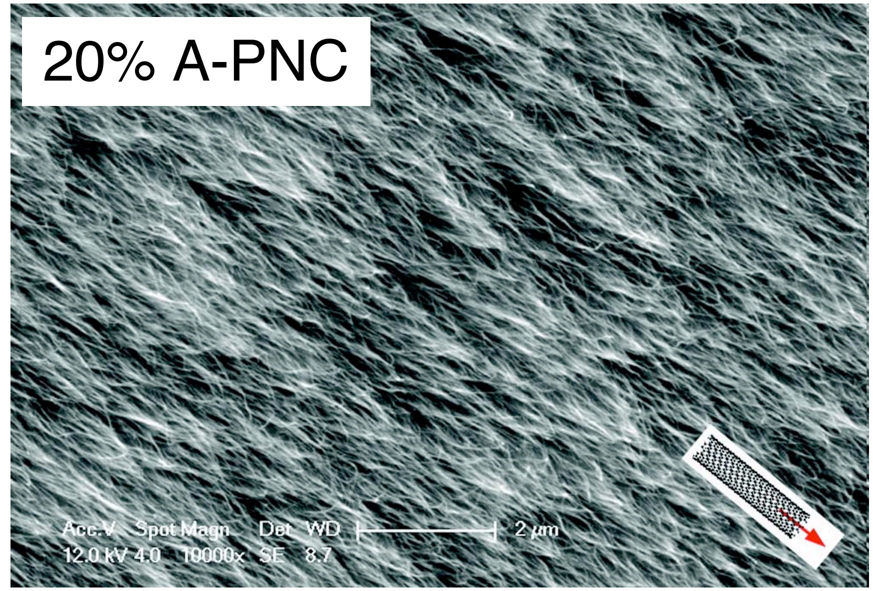


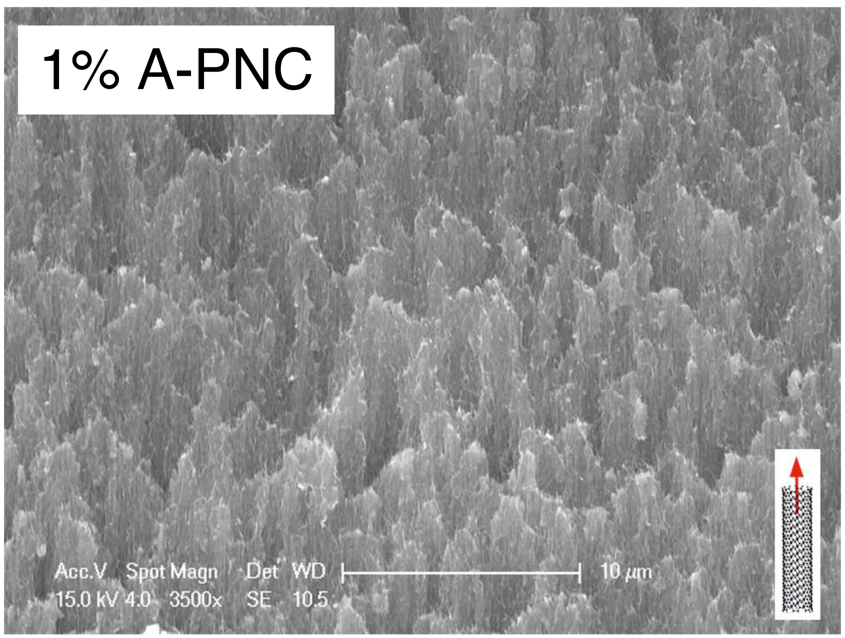
- *Unmodified* RTM6 aerospace-grade epoxy (resin-transfer molding, RTM)

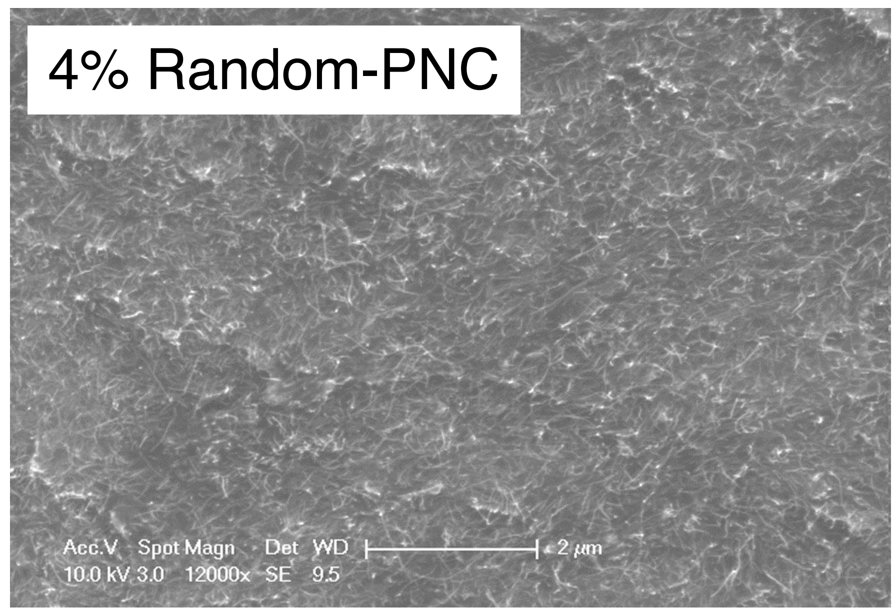
Cebeci, Wardle, et al., *Comp. Sci. Tech.,* 2009.

Aligned-CNT Morphology in Polymer Nanocomposites



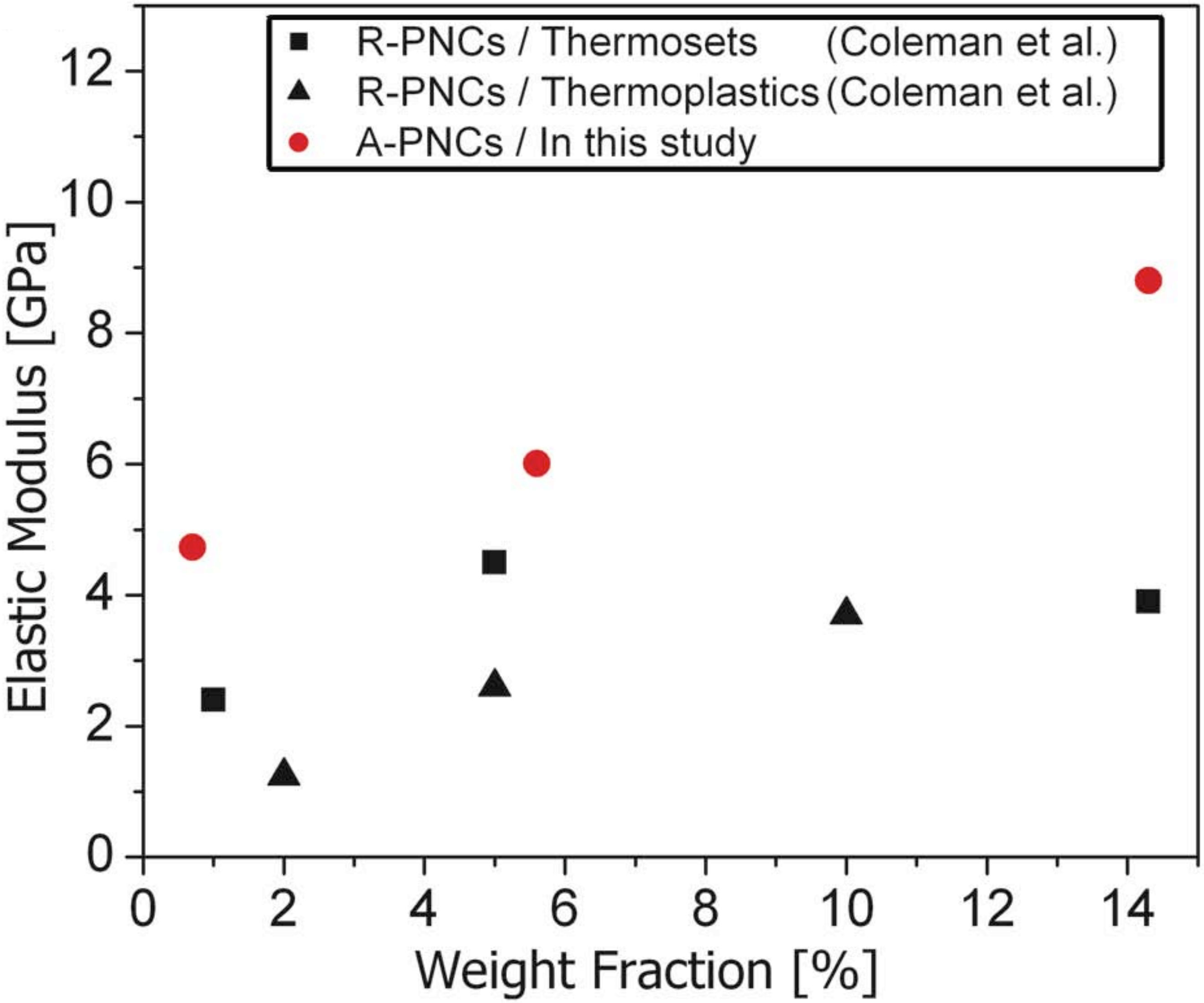






Cebeci, Wardle, et al., *Comp. Sci. Tech.*, 2009.

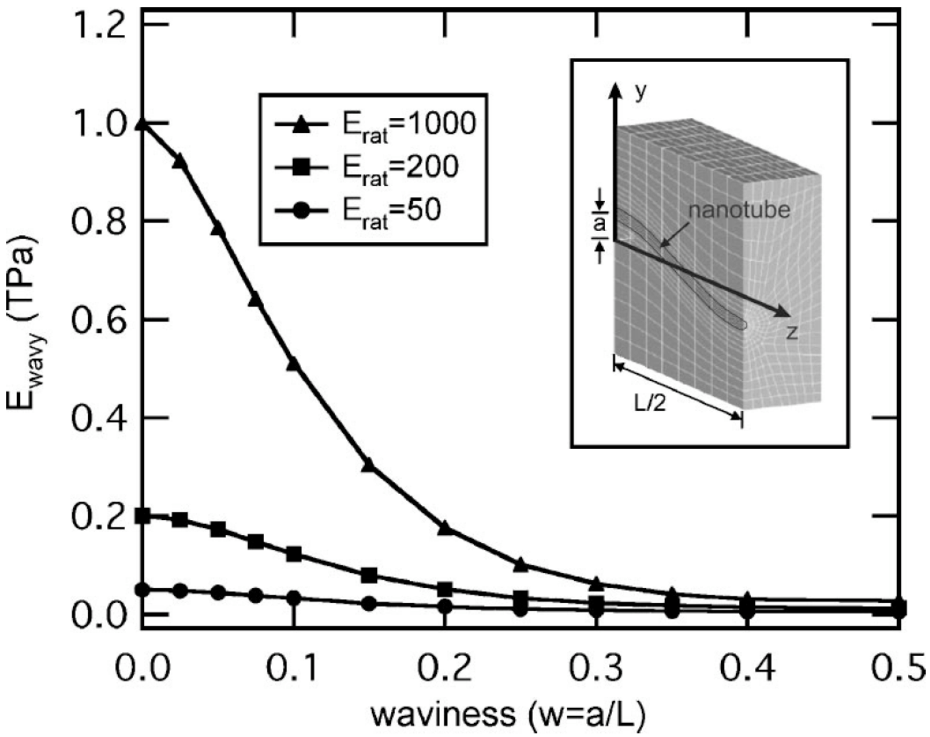
Aligned-CNT PNC Modulus vs. Literature



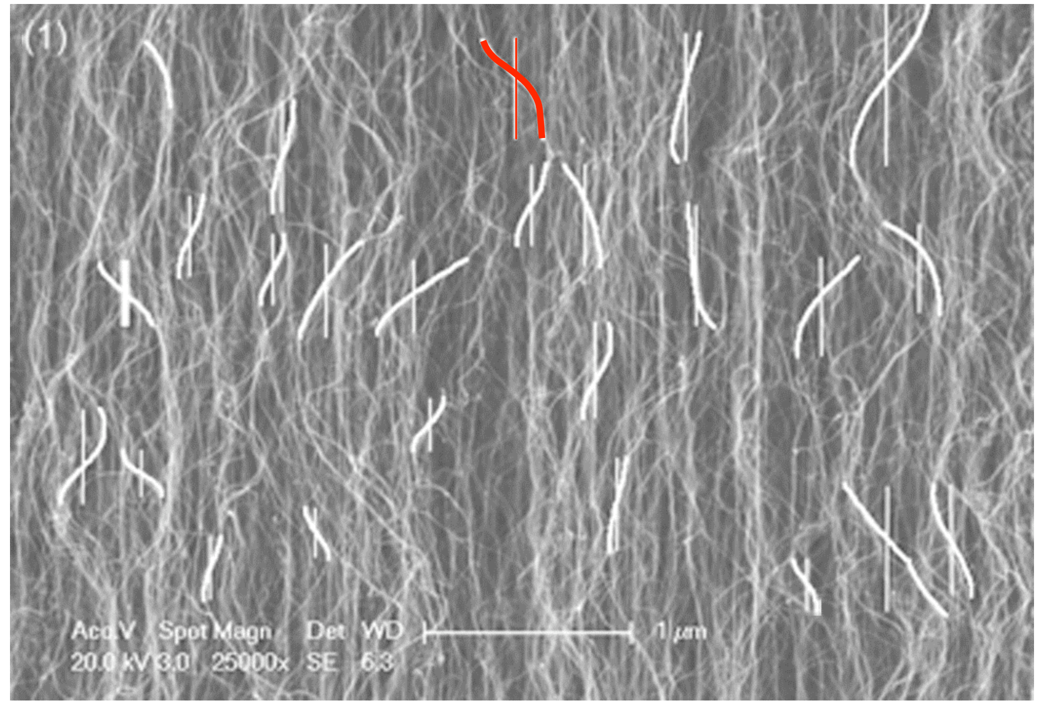
Coleman, J. N., Khan, U., Blau, W. J. & Gun'ko, Y. K. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon* **44**, 1624-1652 (2006).

Cebeci, Wardle, et al., *Comp. Sci. Tech.*, 2009.

Understanding Modulus Using Simple Rule of Mixtures Modified for CNT Waviness



Fisher et al., *APL*, 2002.

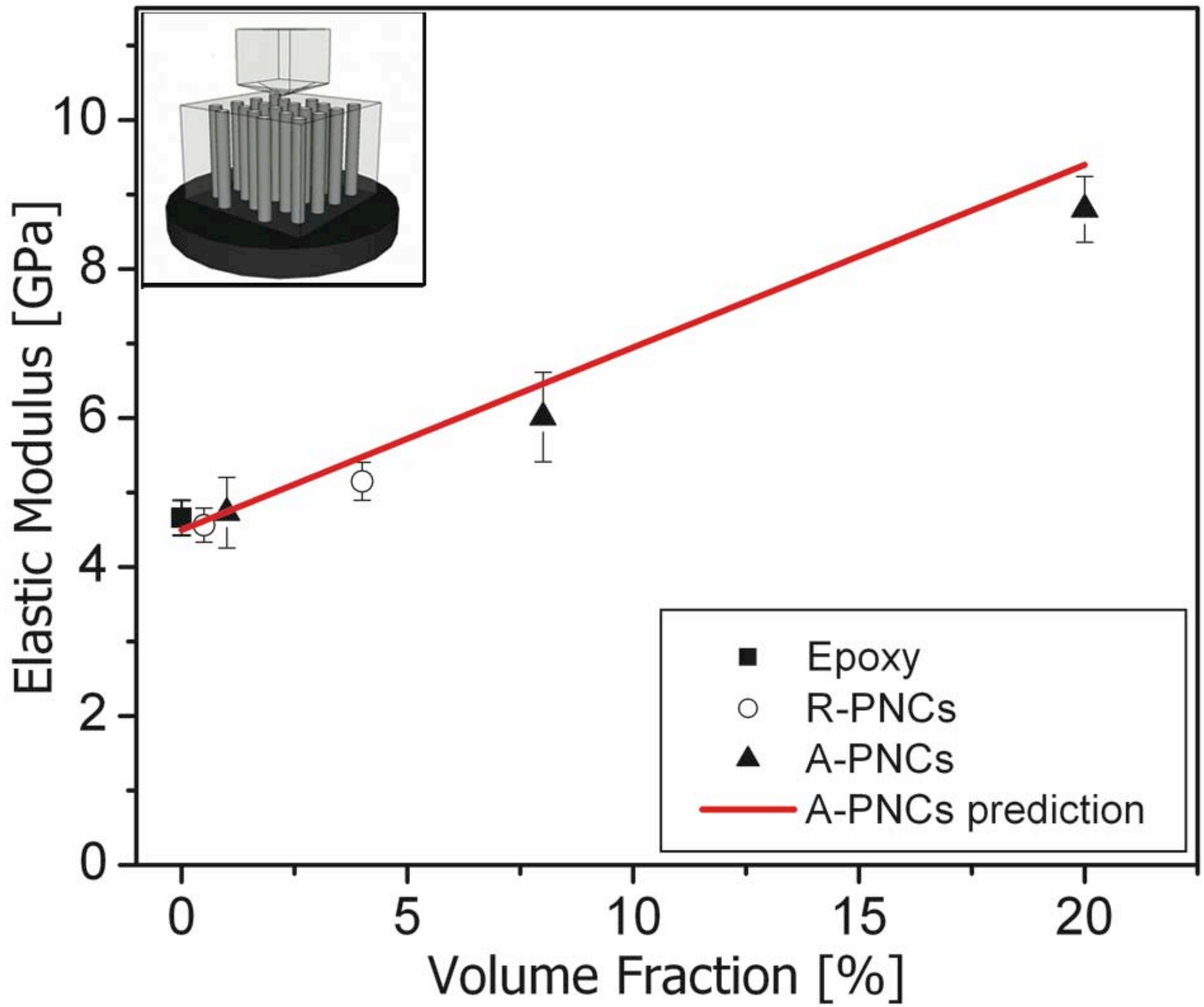


SEM inspection of aligned-CNTs for amplitude-wavelength ratio

Fisher, F. T., Bradshaw, R. D. & Brinson, L. C. Effects of nanotube waviness on the modulus of nanotube-reinforced polymers. *Appl Phys Lett* **80**, 4647-4649 (2002).

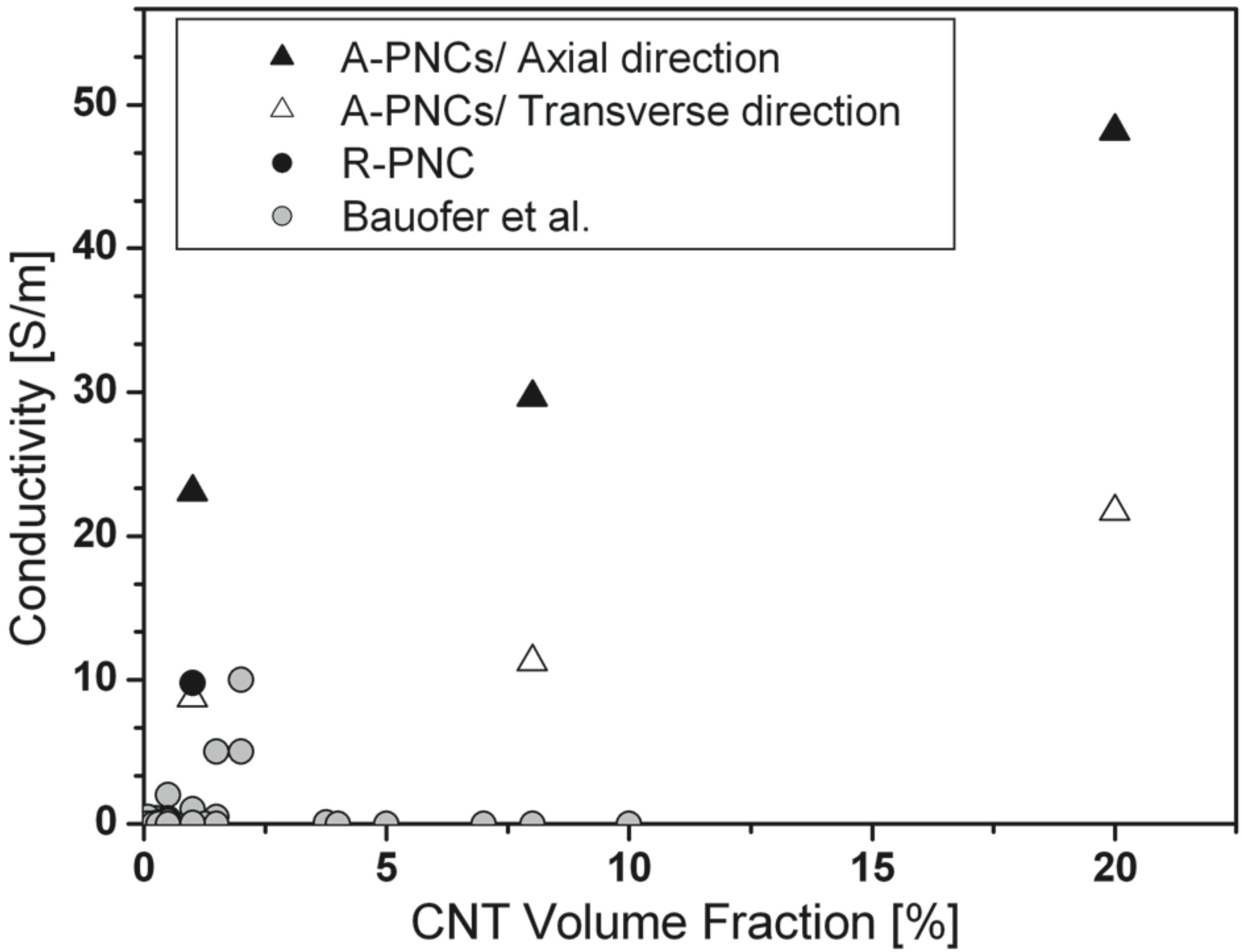
Cebeci, Wardle, et al., *Comp. Sci. Tech.*, 2009.

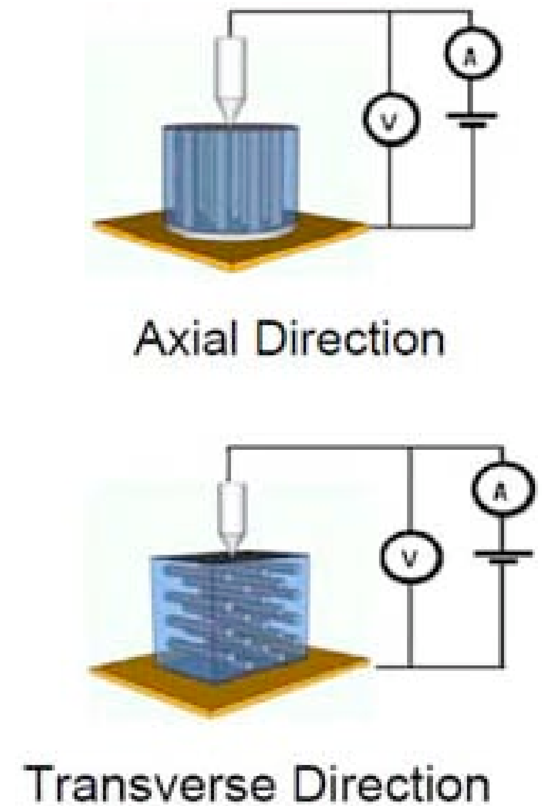
CNT Waviness Seen as Dominant Feature Affecting PNC Modulus



Cebeci, Wardle, et al., *Comp. Sci. Tech.,* 2009.

Direction-dependent Electrical Conductivity Also Shows Effect of Controlled Morphology





Bauhofer, W., Kovacs, J. Z. A review and analysis of electrical percolation in carbon nanotube polymer composites *Compos Sci Technol* **in press** (2009).

Cebeci, Wardle, et al., *Comp. Sci. Tech.*, 2009.

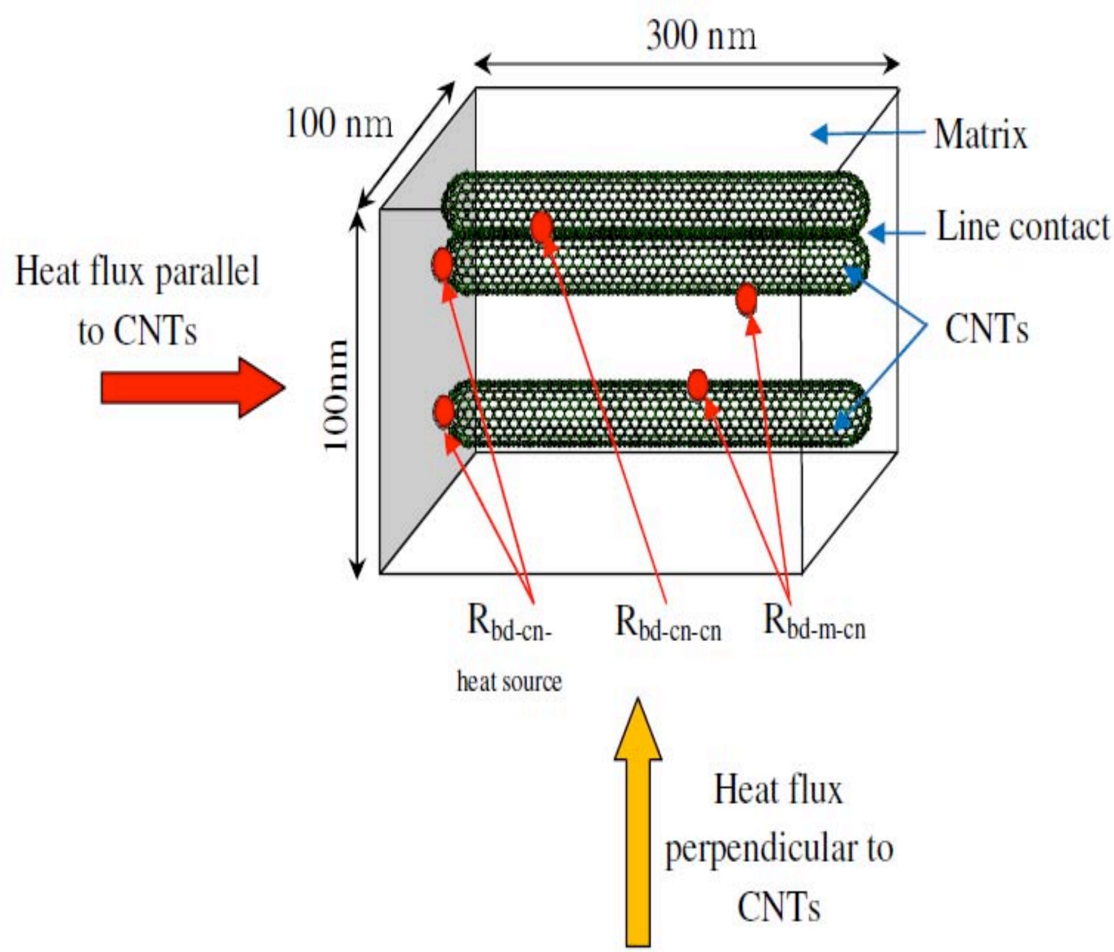
Modeling Thermal Conductivity of CNT Nanocomposites Using Random Walk Algorithm (Off-lattice Monte-Carlo Simulation)

CNT morphology in polymer matrix:

- ✓ Randomly generated in a computational cell (polymeric matrix) with different orientations: (parallel, random and perpendicular to heat flux).
- ✓ With and without inter-CNT contact. Assumes line CNT contact.
- ✓ Spatial CNT agglomeration in matrix.
- ✗ CNT waviness.

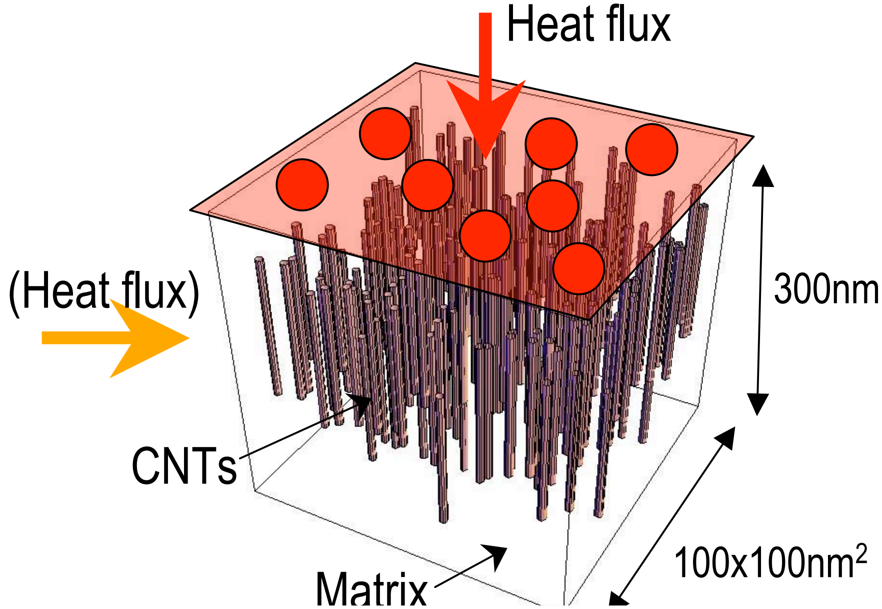
Thermal boundary resistances:

- ✓ CNT-matrix and CNT-CNT TBRs.
- ✗ CNT-heat source TBR.



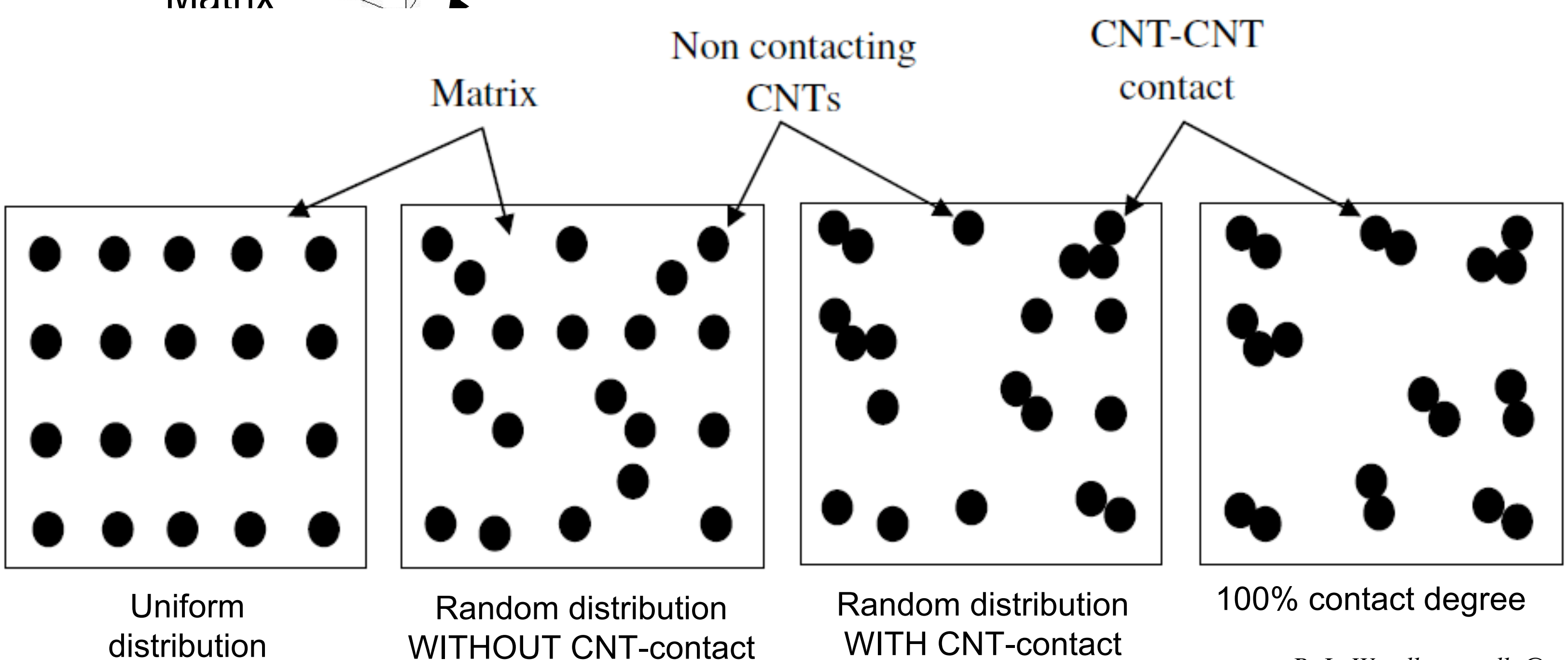
Collaboration with Profs. Maruyama (Univ. of Tokyo) and Papavassiliou (Univ. Oklahoma)

Morphology Effects on Thermal Conductivity of CNT Nanocomposites



Advantages

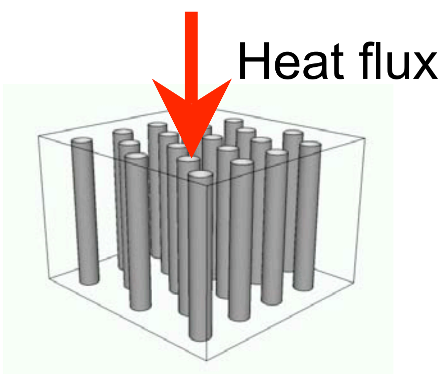
- Faster than MD or finite element method
- TBR explicitly a part of models.
- Allows complex morphologies to be studied

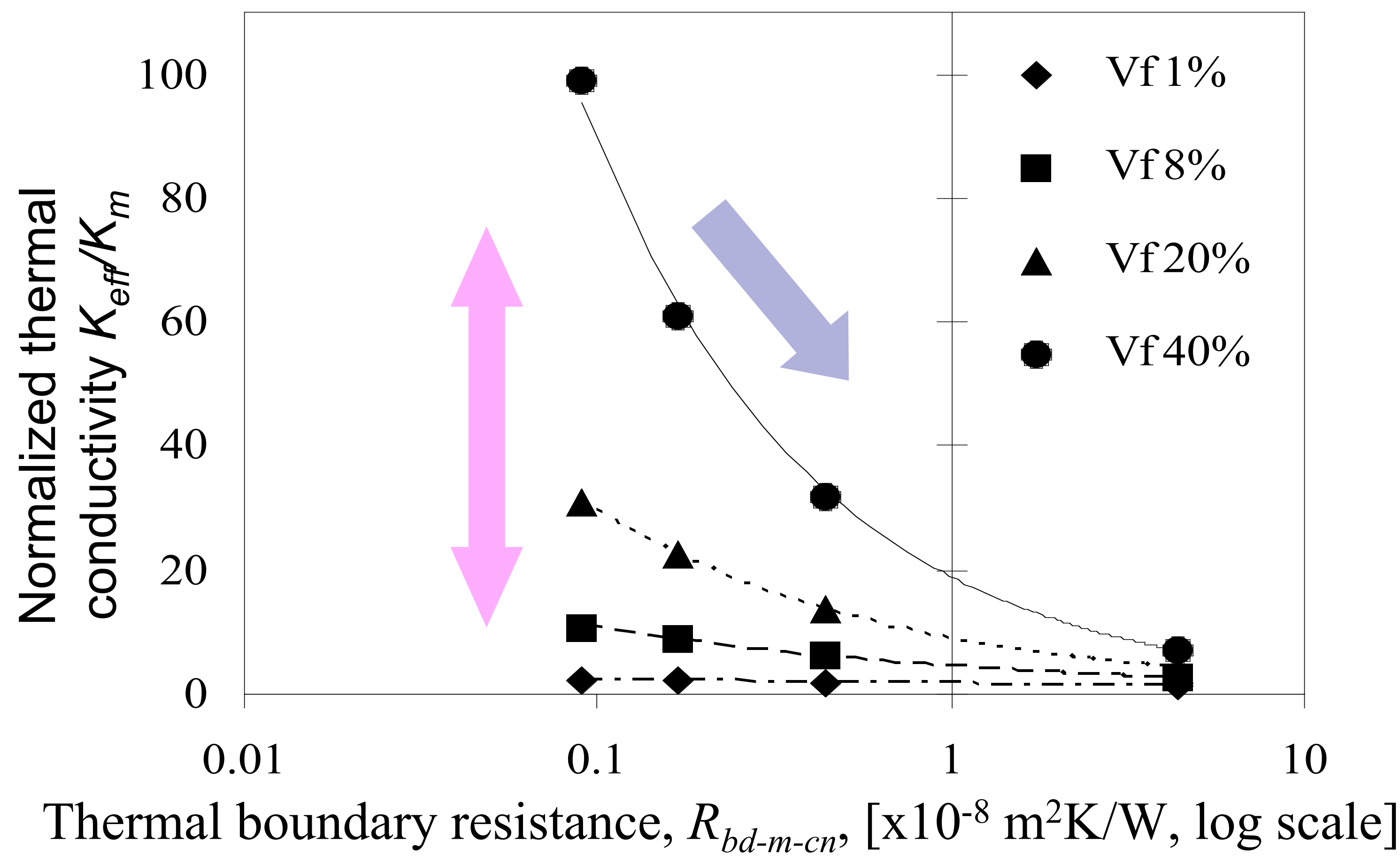


Effect of CNT Volume Fraction

- Increasing R_{bd}: K_{eff} decreases but not smaller than that of pure matrix
- Increasing CNT volume fraction: K_{eff} increases

MWNT-matrix
Along the CNTs

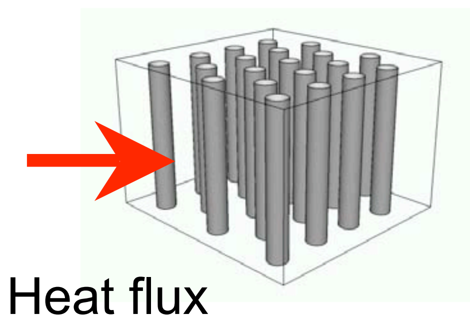


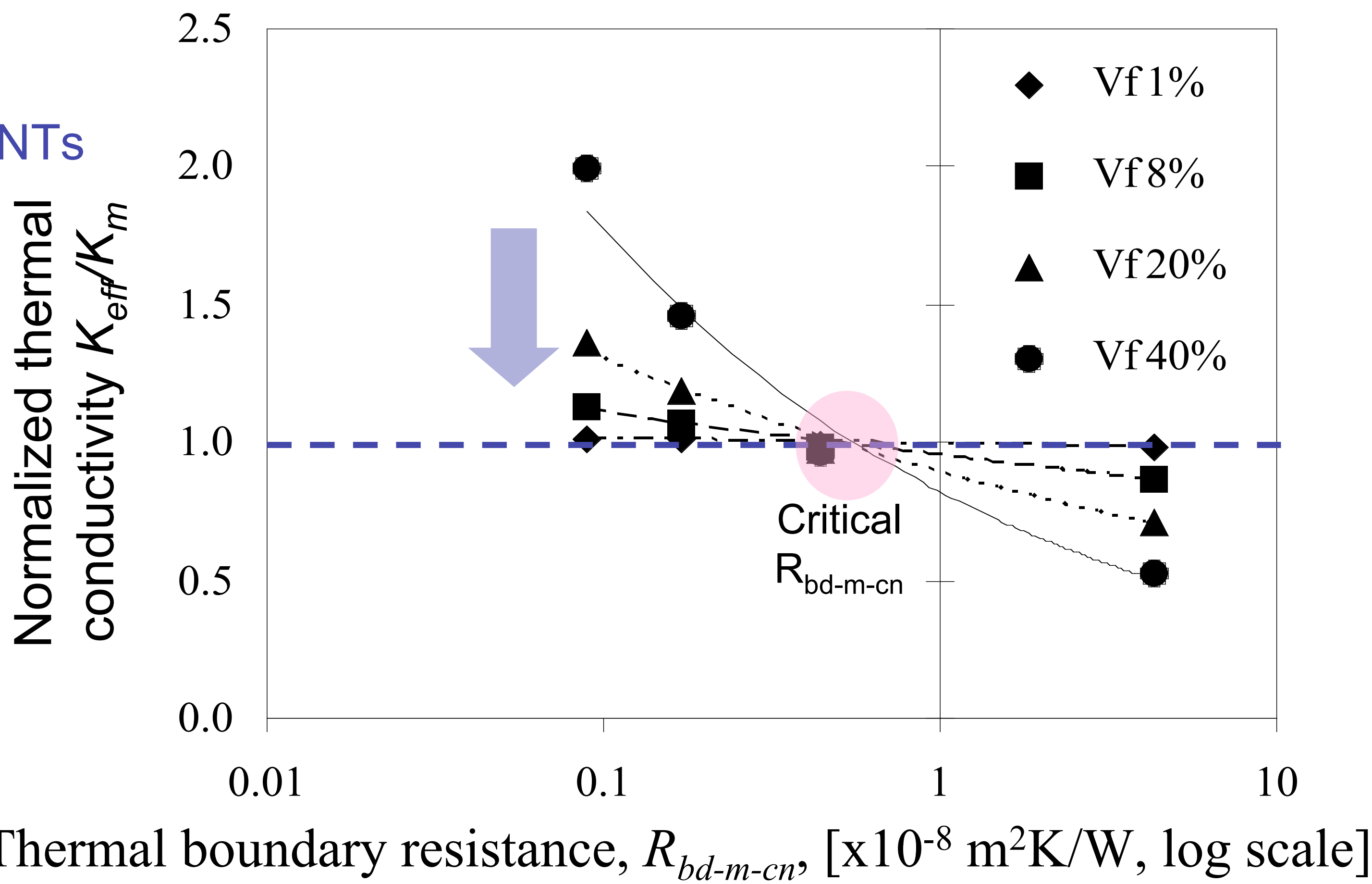


Effect of Heat Conduction Direction

- Increasing $R_{bd-m-cn}$: K_{eff} decreases, and even smaller than that of pure matrix with large CNT volume fraction
- Stronger effects by $R_{bd-m-cn}$ because phonons need to cross more boundaries

MWNT-matrix
Perpendicular to the CNTs





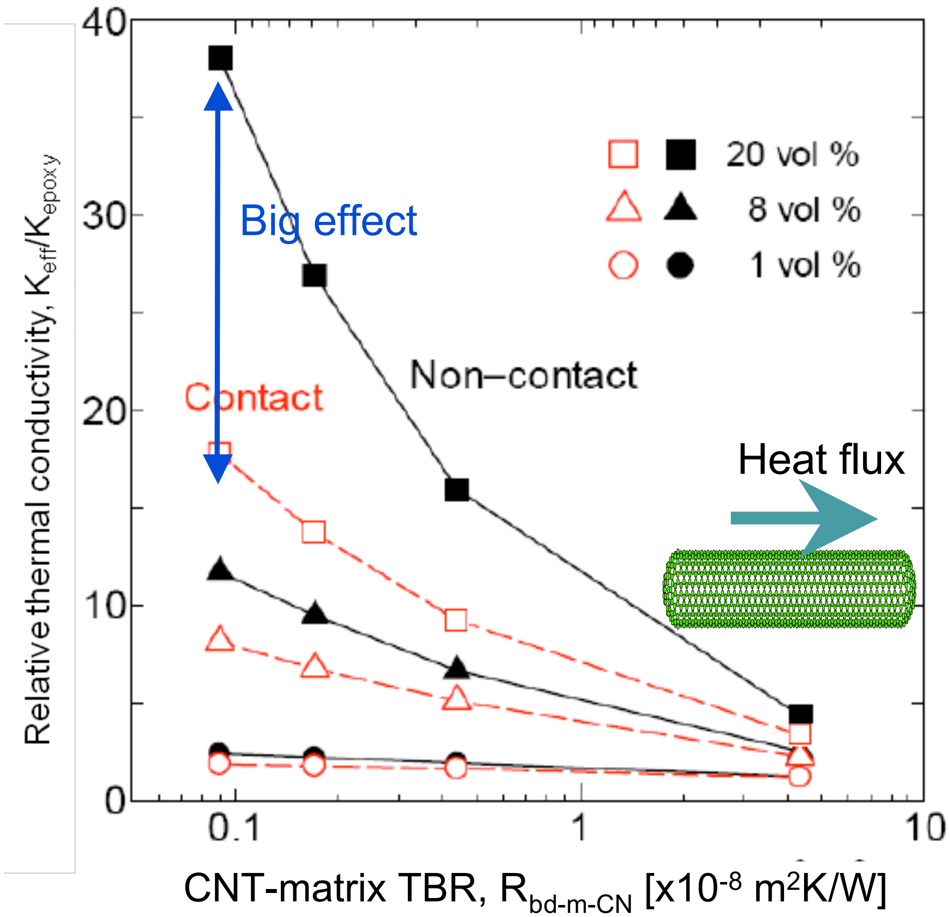
Effects of Inter-CNT Contact

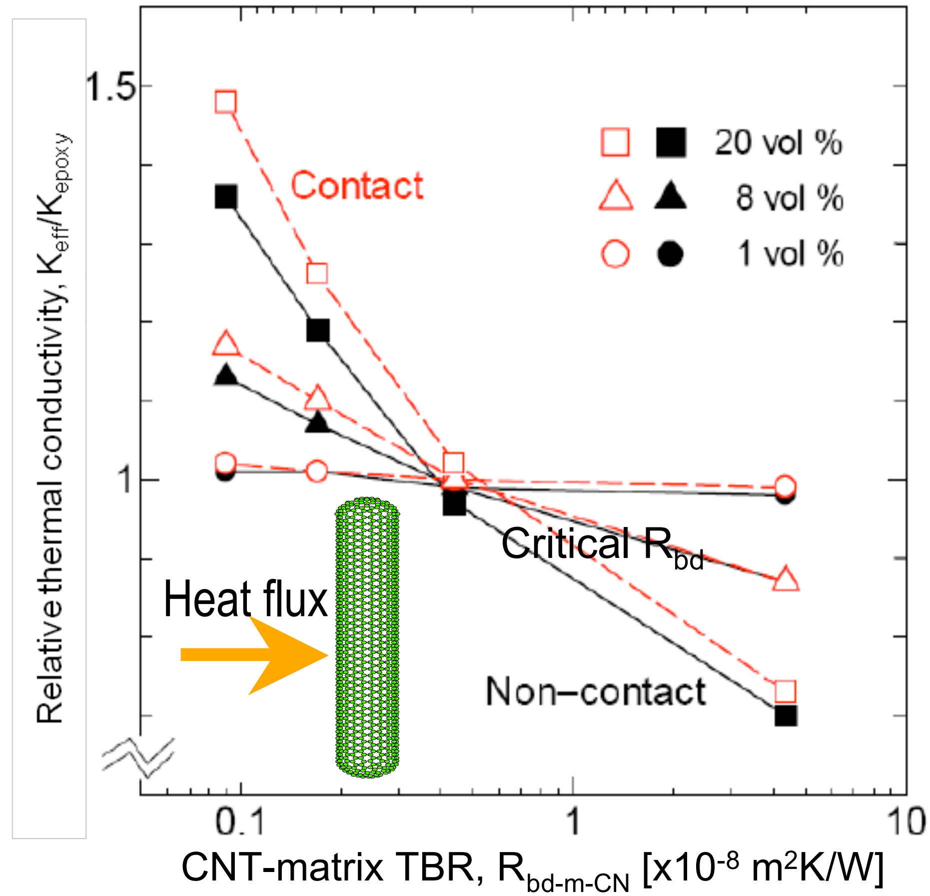
↑ vol% → ↑ K_{eff} & more influenced by R_{bd}
↑ R_{bd} → ↓ K_{eff} & greater than K_{epoxy} (0.2W/mK)

$K_{eff\text{-}contact} < K_{eff\text{-}no\ contact}$

↑ vol% → ↑ K_{eff} & more influenced by R_{bd}
↑ R_{bd} → ↓ K_{eff} & R_{bd} < 0.45x10^{-8} m^2K/W

$K_{eff\text{-}contact} > K_{eff\text{-}no\ contact}$

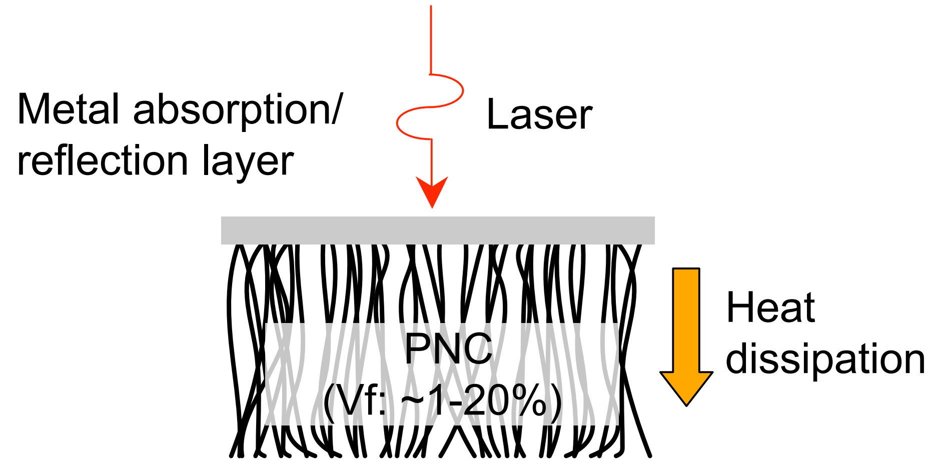




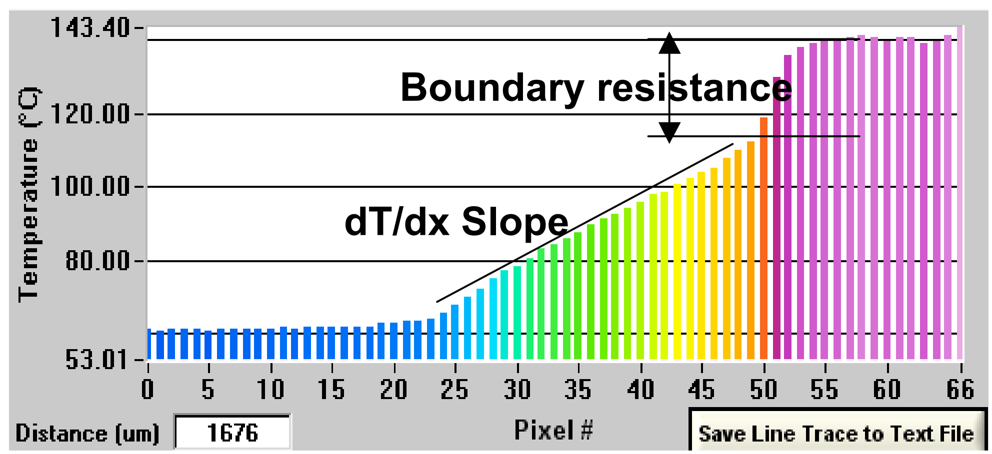
Duong *et al., Nanotechnology* 2009.

Thermal Conductivity Measurements (On-going)

- Picosecond thermoreflectance technique
  - Samples deposited with thin metal heat absorption/laser reflection film (Al 80nm)
  - Heating with laser pulse
  - Surface laser reflectance change measurement (a function of temperature)



- Thermal gradient measurement using a infrared detector
  - Resistive heating (known heat flux) on one side
  - Thermal boundary resistance isolation
  - No interpretation issues
  - Takes advantage of large aligned-CNT and aligned-CNT PNC sample sizes



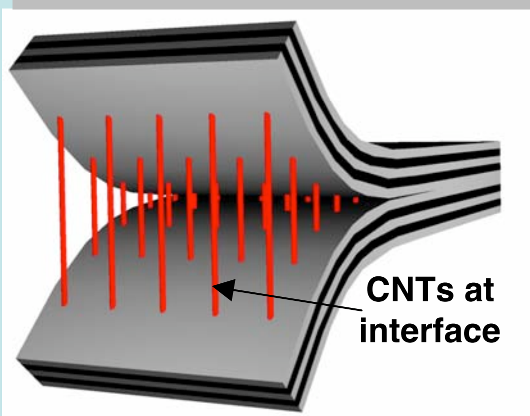
[with Panzer, Marconnet, Goodson at Stanford]

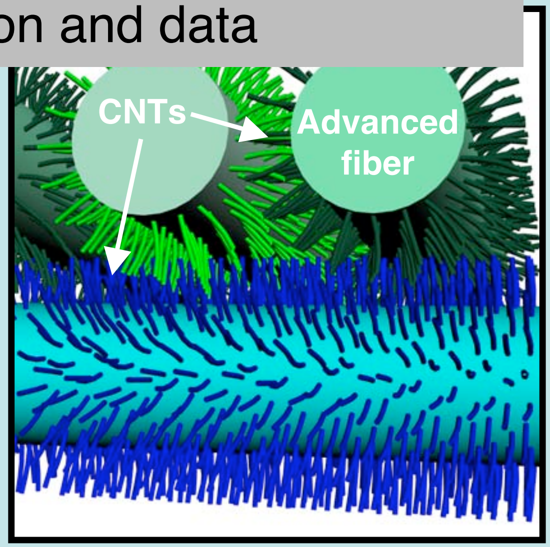
Recent Contributions

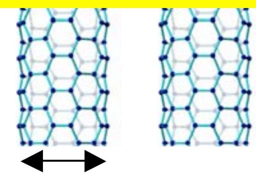
3. Nanocomposite mechanics
4. **New CNT growth catalyst (discovery)**

(1) Nano-engineered Composites

1. Key modeling result
2. Laminate fabrication and data







‘Nanostitched’ and ‘fuzzy’ fiber laminates

meters

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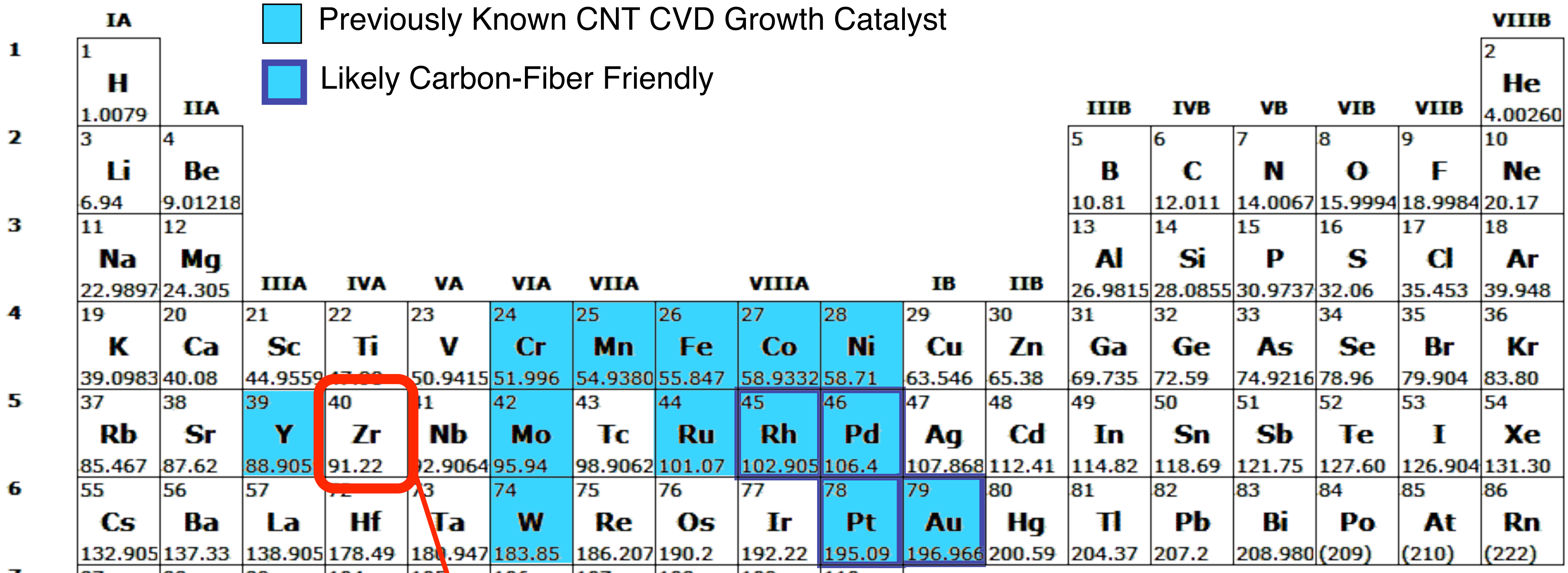
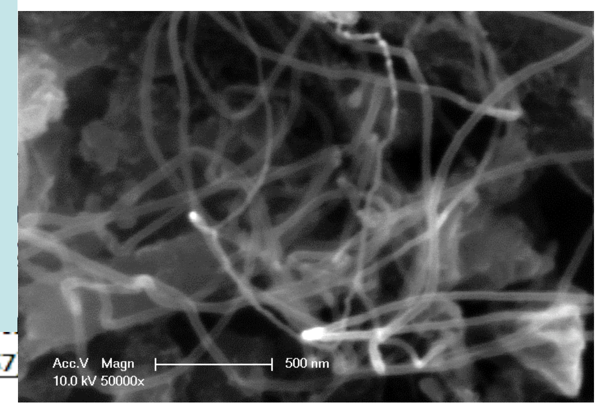
5. Something different

Looking for Carbon Fiber-Friendly CNT Catalysts



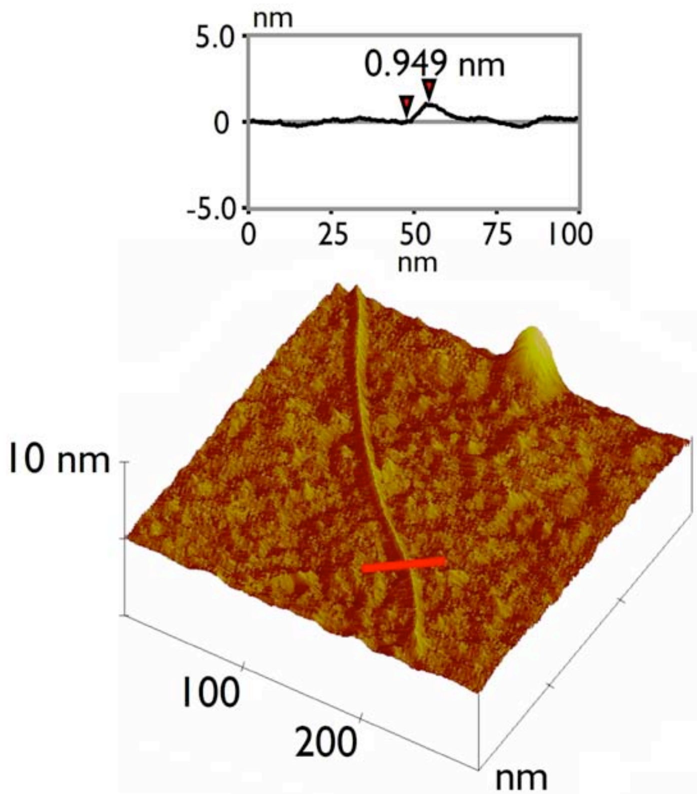
- Zr suspected Carbon-Fiber Friendly
- Not a catalyst, ZrO_2 is
  - New class of catalyst (oxides)?
  - Recently confirmed ZrO_2 is active species via *in situ* X-ray Photoelectron Spectroscopy (XPS) with Hofmann (Cambridge Univ.)



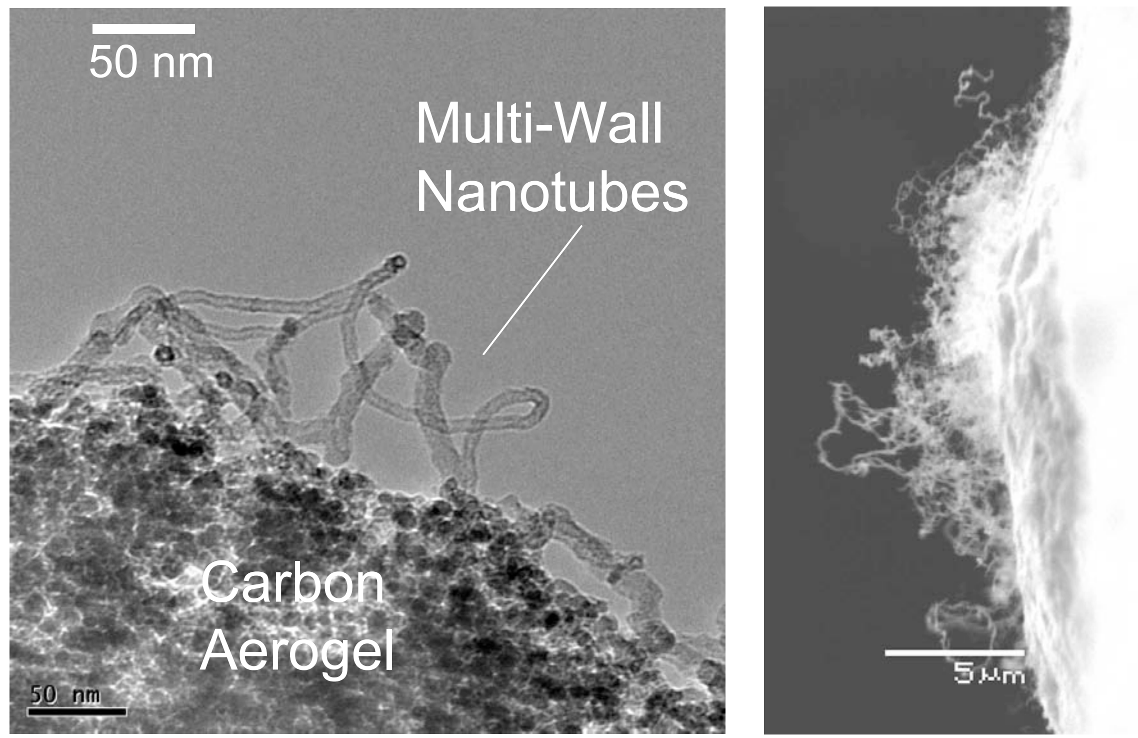
Steiner III, (Wardle) et al., *JACS*, online Aug. 2009.

Zirconia (ZrO_2): A Non-Metallic CNT Catalyst

- ZrO_2 nanoparticles catalyze CNT growth
- Catalyzes MWNTs and SWNTs
- Significant departure from understanding of other catalysts



AFM of Single-Wall Nanotube Catalyzed by ZrO_2

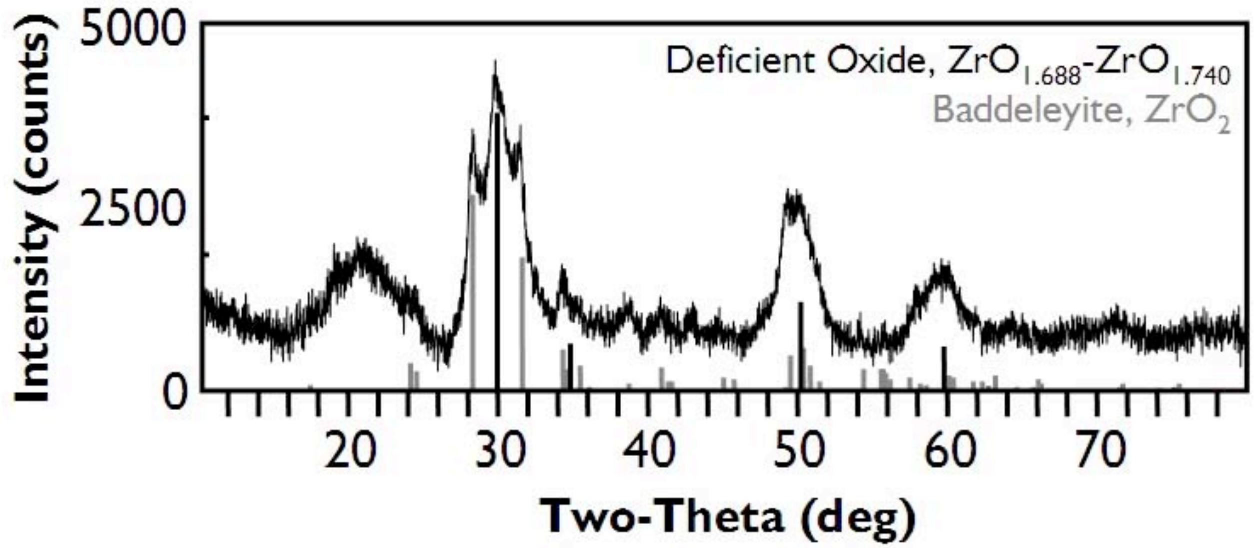


TEM (left) and SEM (right) of Multi-Wall Nanotubes Catalyzed by ZrO_2

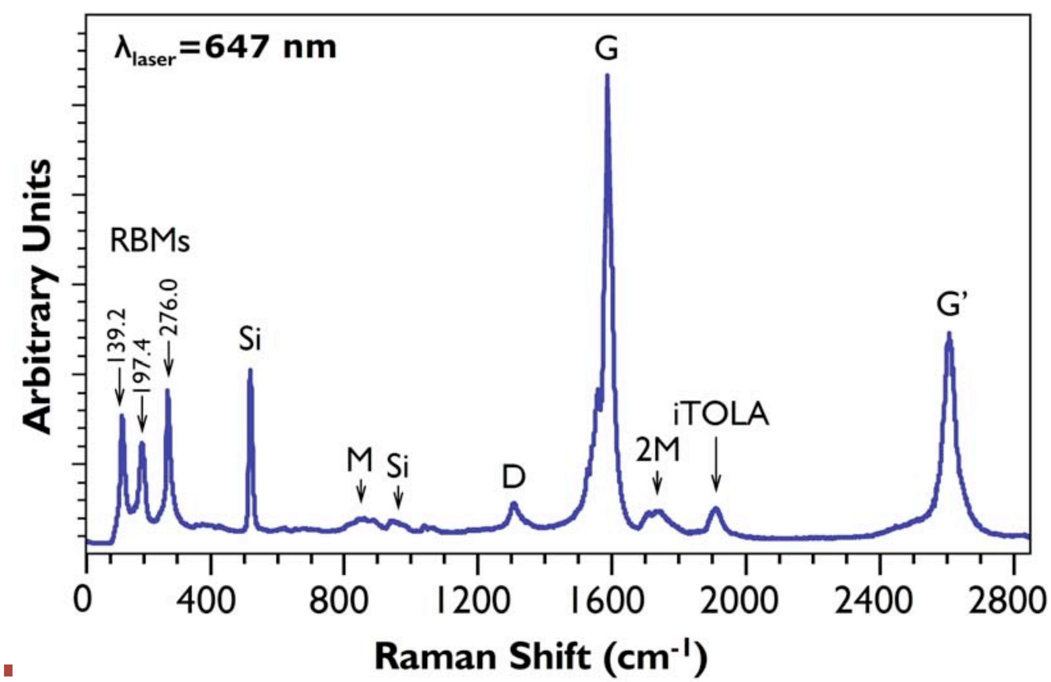
Steiner III, (Wardle) et al., *JACS*, online Aug. 2009.

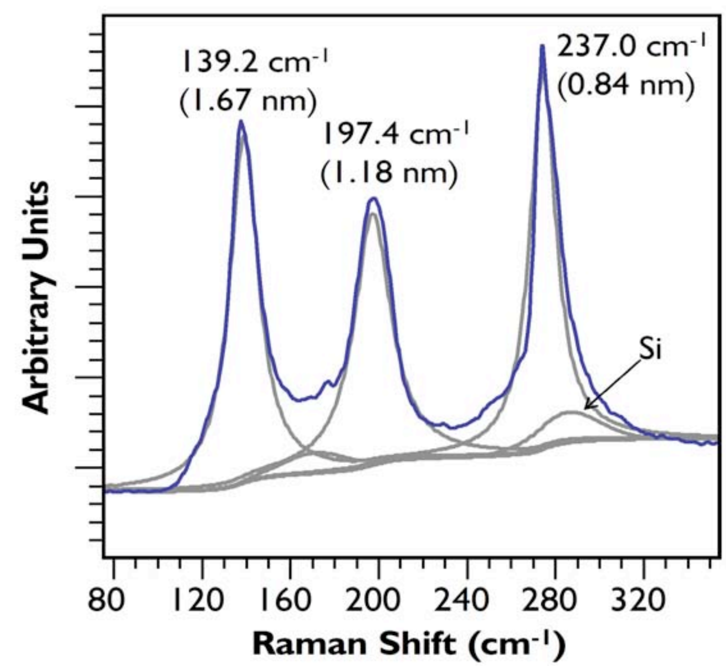
More Evidence of CNTs from Zirconia

Raman Says There's SWNTs

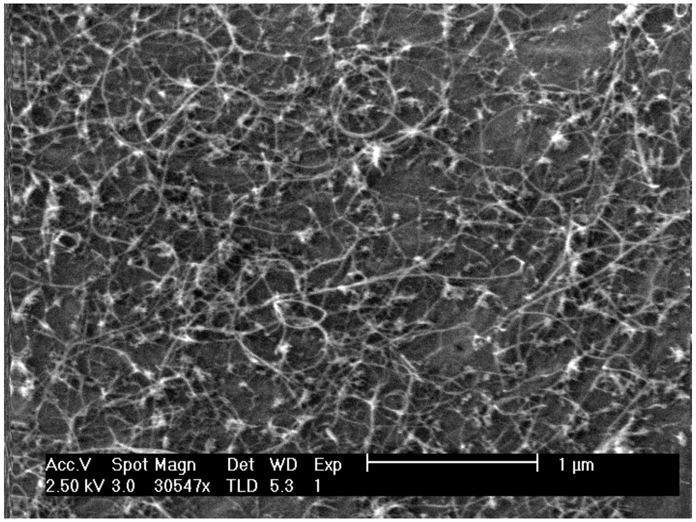


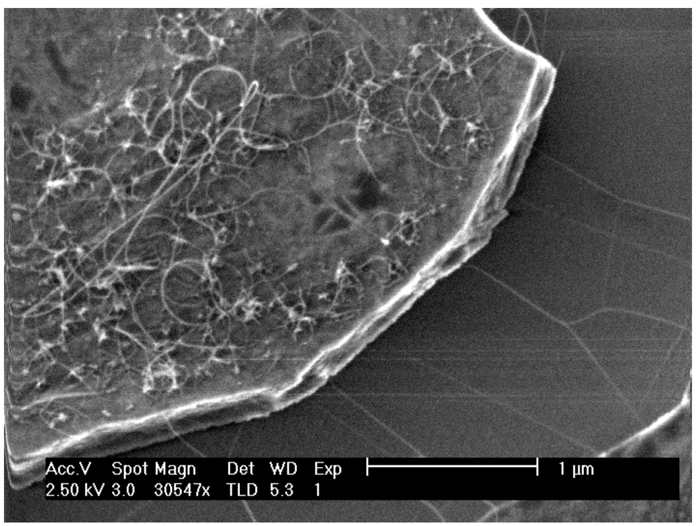
XRD Says There's Zirconia Nanoparticles but no Zr or ZrC!

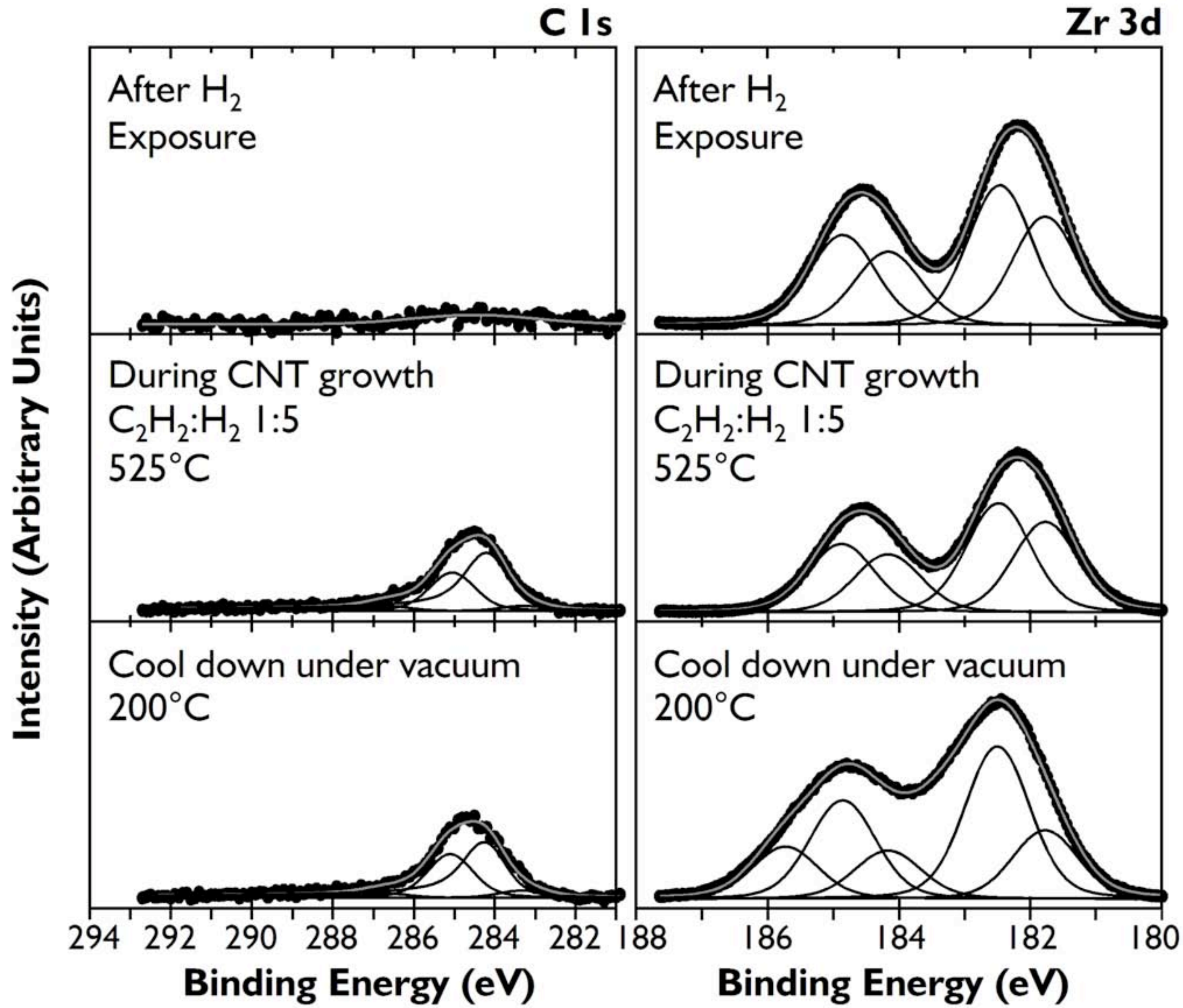




"The Refrigerator Light Problem" Solved: Catalyst is an Oxide *During* CNT Growth





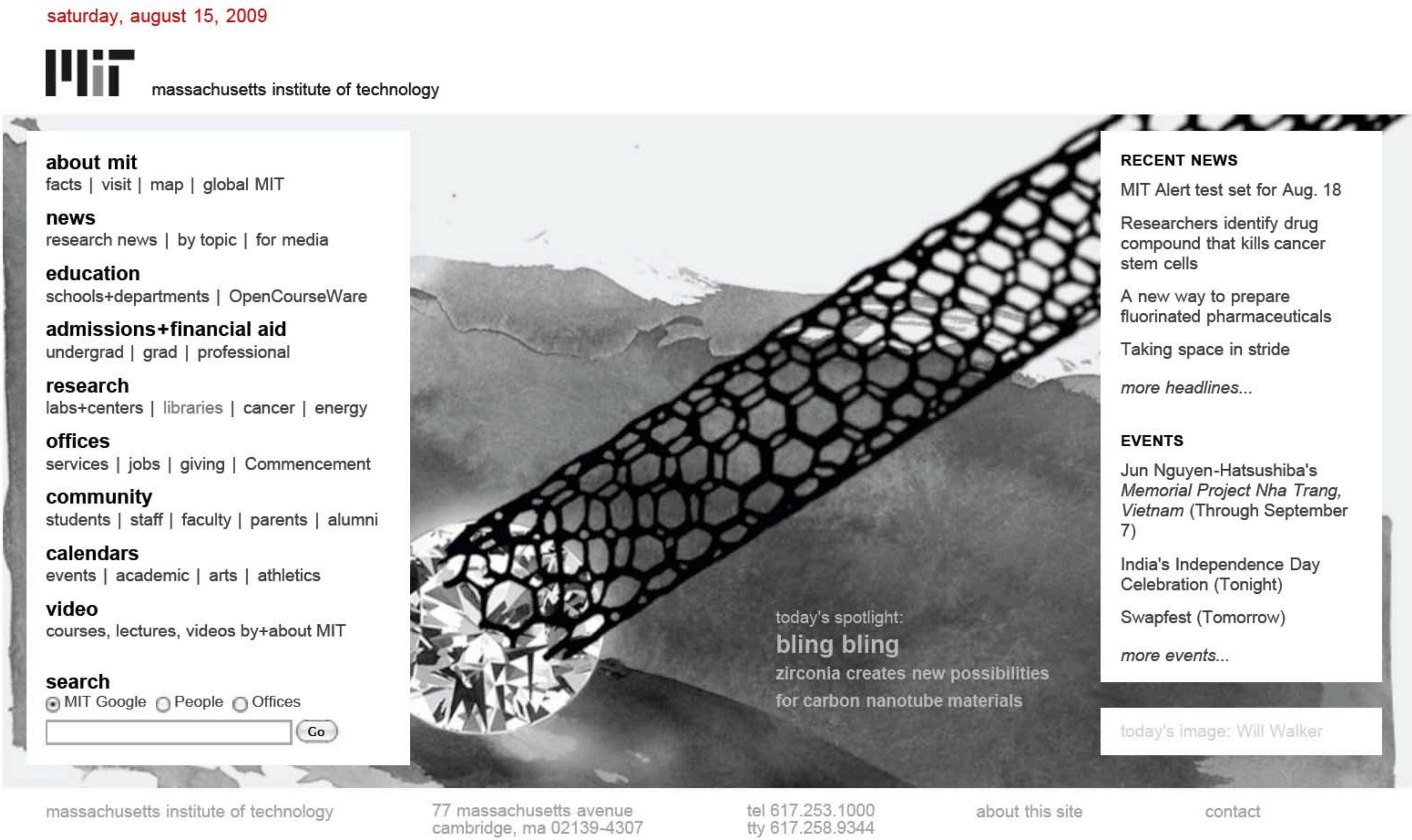


In Situ X-Ray Photoelectron Spectroscopy of Catalyst on Surface

in collaboration with Prof. Stephan Hofmann, Univ. of Cambridge

Steiner III, (Wardle) et al., *JACS*, online Aug. 2009.

Implication-Rich Discovery for CNT Synthesis



Steiner III, (Wardle) et al., *JACS*, online Aug. 2009.

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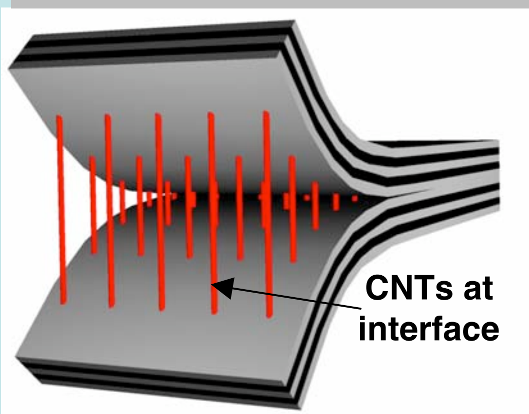

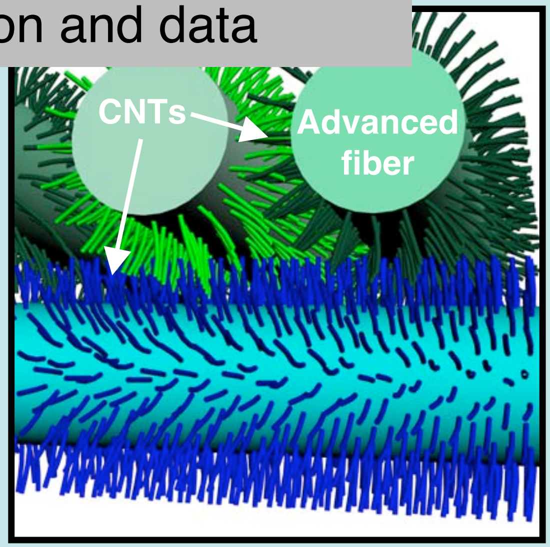

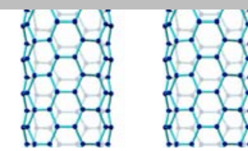

‘Nanostitched’ and ‘fuzzy’ fiber laminates

meters

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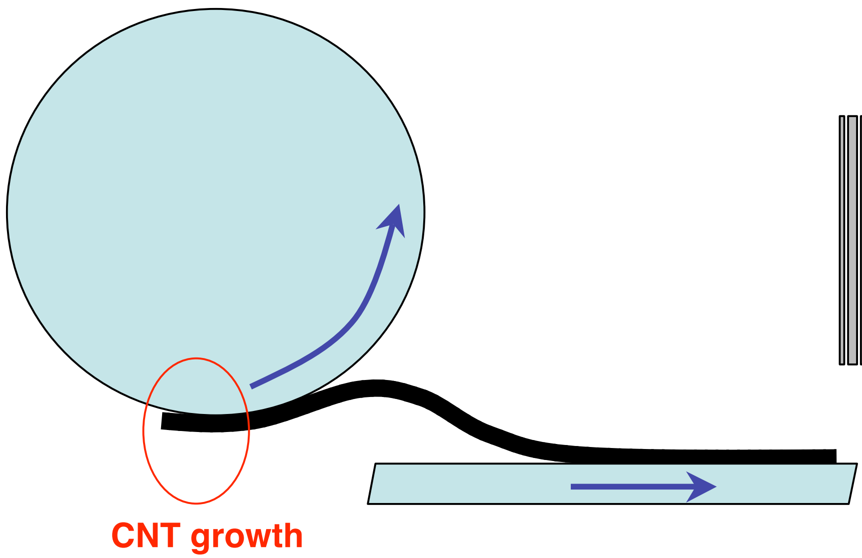
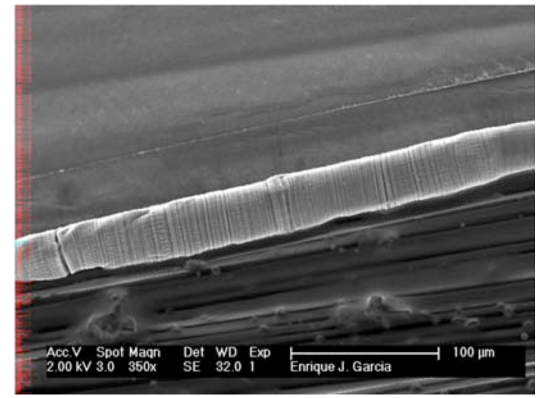
Continuous Manufacturing of Aligned CNTs Requires Moving Growth

- **Aligned CNT films**



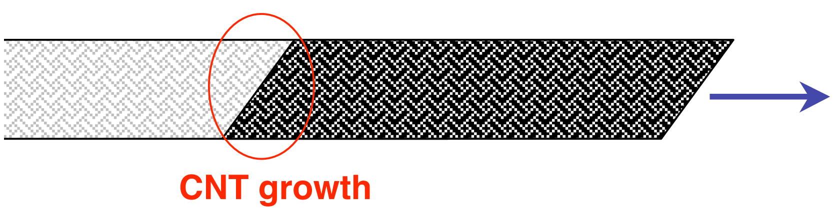
- Prepreg

Aligned CNT film on Gr/Ep prepreg



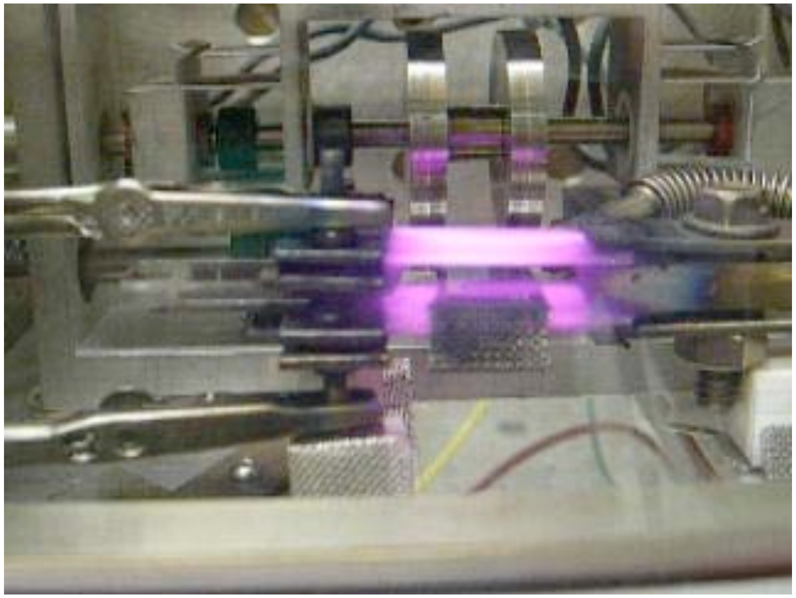
- Infusion (VARTM, RFI, etc.)

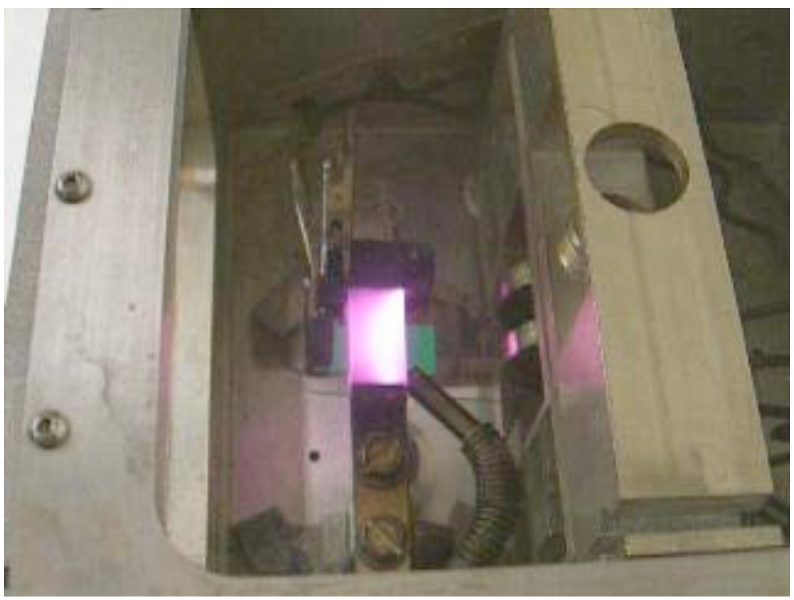
- **Aligned CNTs on fibers**

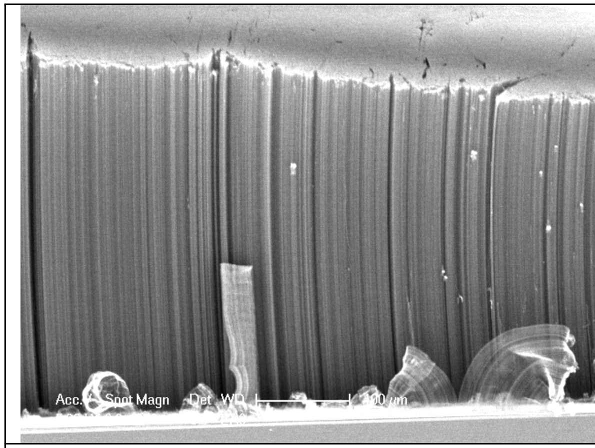


- Infusion
- Prepreg
- Weaving

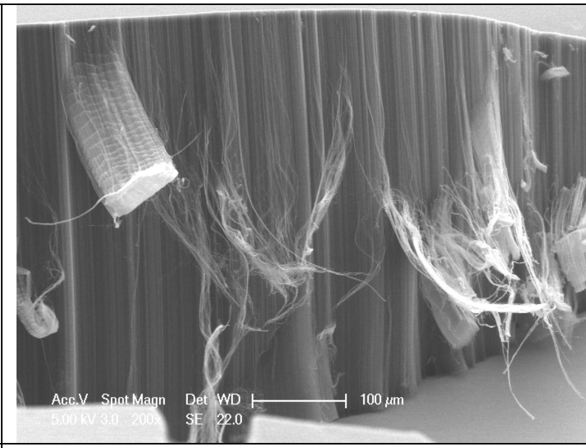
Moving Growth of Aligned CNTs



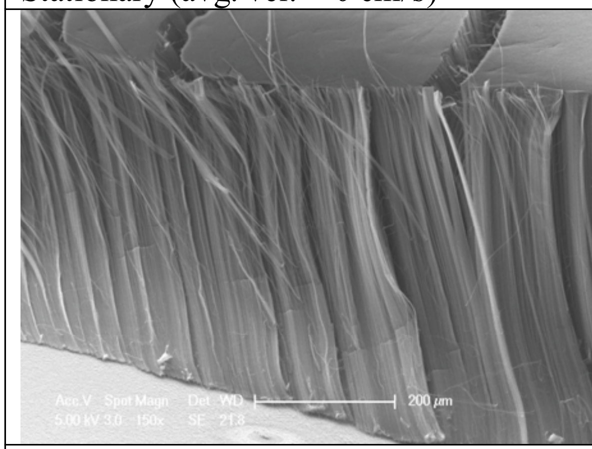




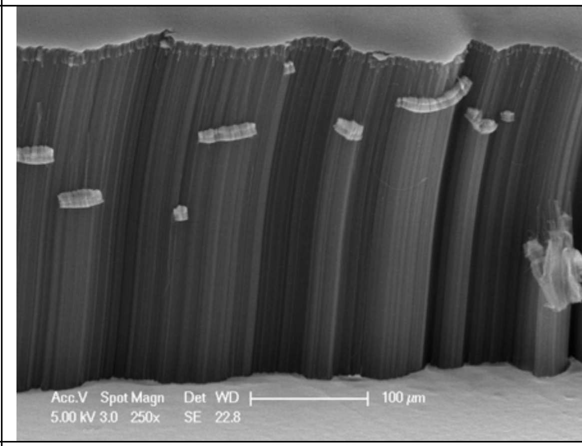
Stationary (avg. vel. = 0 cm/s)



0.1 cm/s



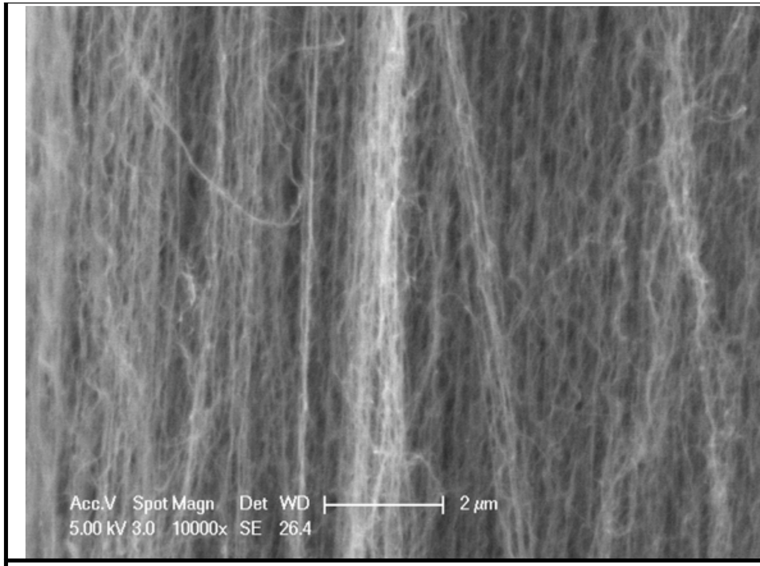
0.5 cm/s



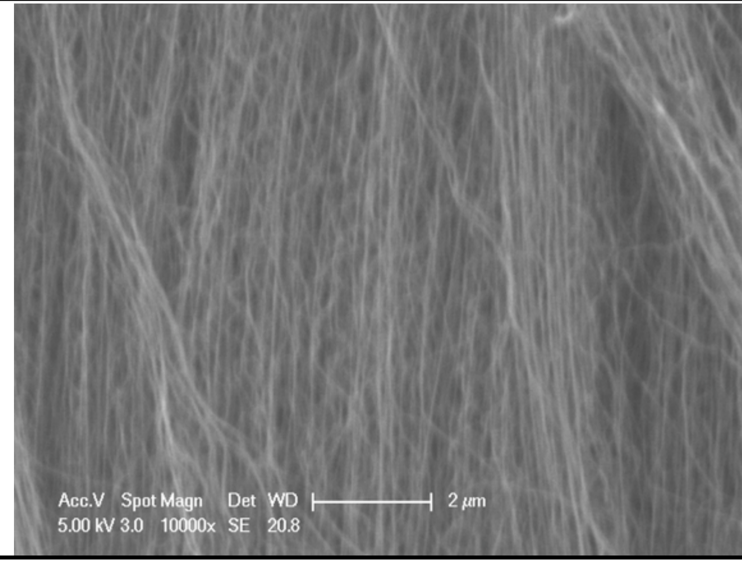
1 cm/s

Guzman deVilloria, (Wardle), et al., *Nanotechnology*, 2009.

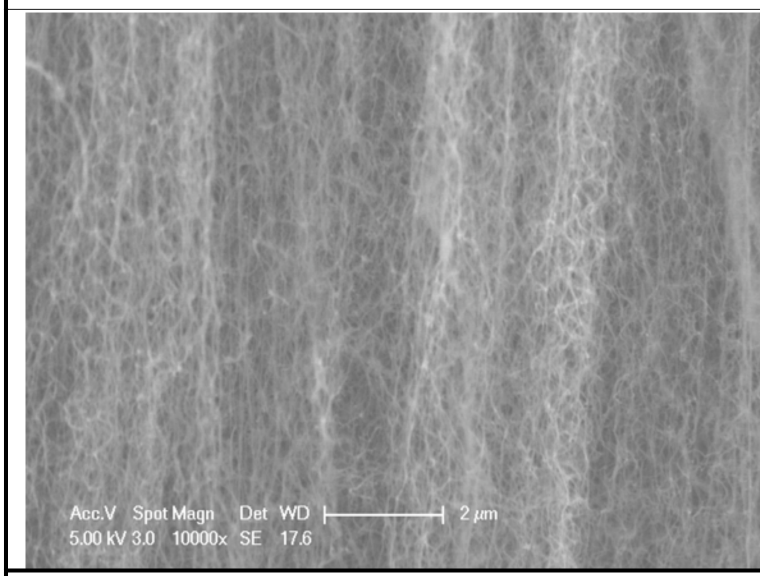
High-Yield Growth at All Substrate Velocities



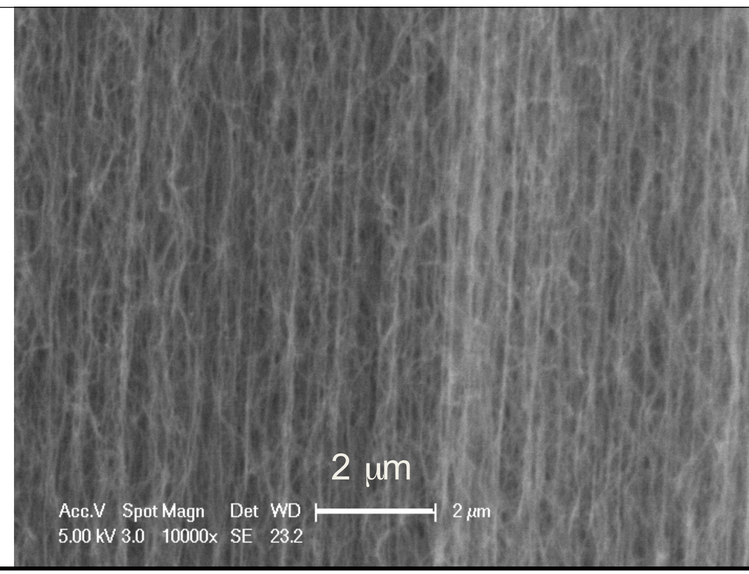
0 mm/s



0.22 mm/s



1. 1 mm/s



2.2 mm/s

Guzman deVilloria, (Wardle), et al., *Nanotechnology*, 2009.

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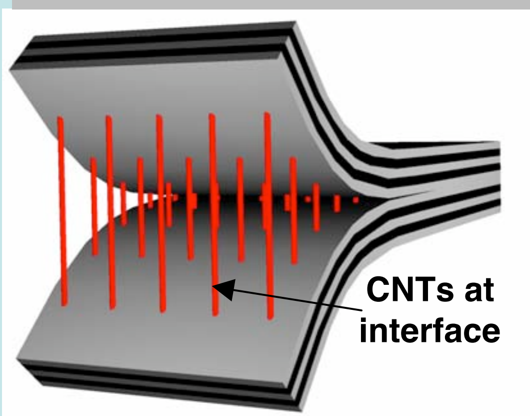

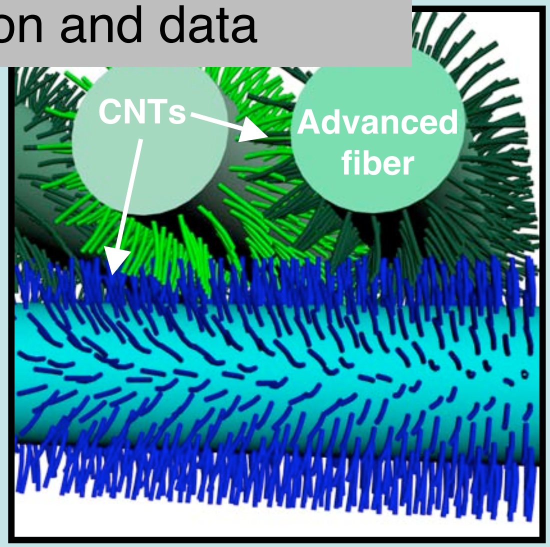

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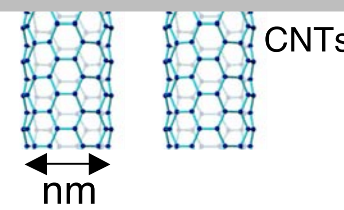

meters

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Revised Dec. 2008

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MIT Aero/Astro

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  - Embraer
  - Lockheed Martin
  - Saab AB
  - Spirit AeroSystems
  - Textron Inc.
  - Composite Systems Technology
  - TohoTenax

NECST
nano-engineered composite aerospace structures consortium

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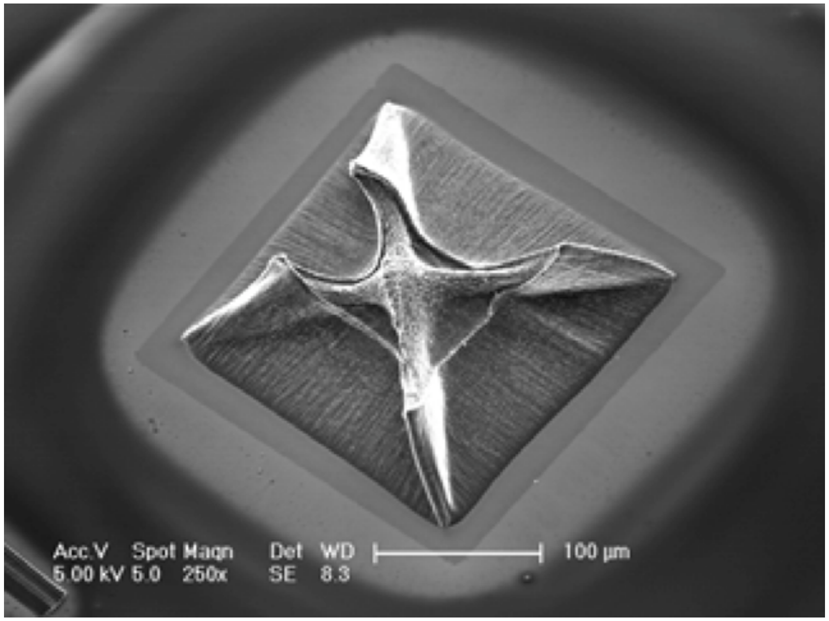
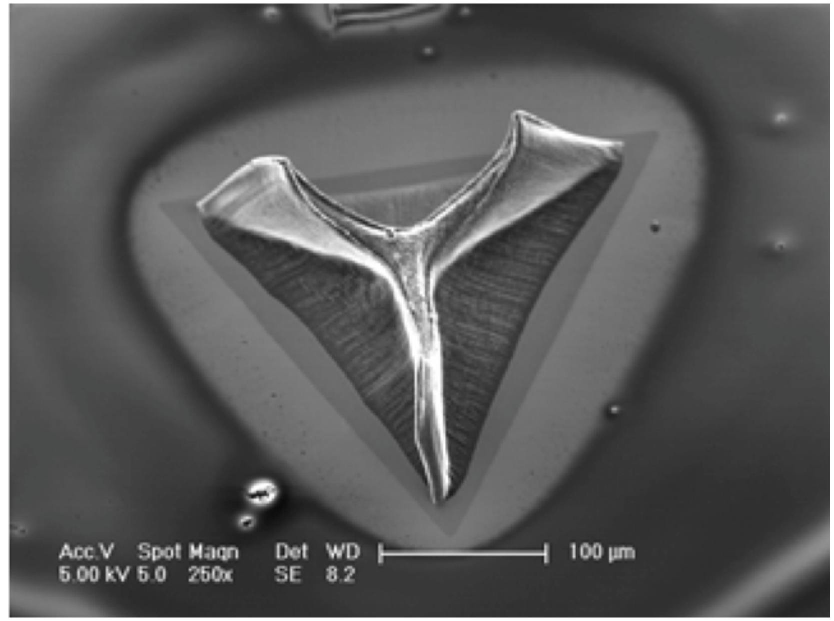
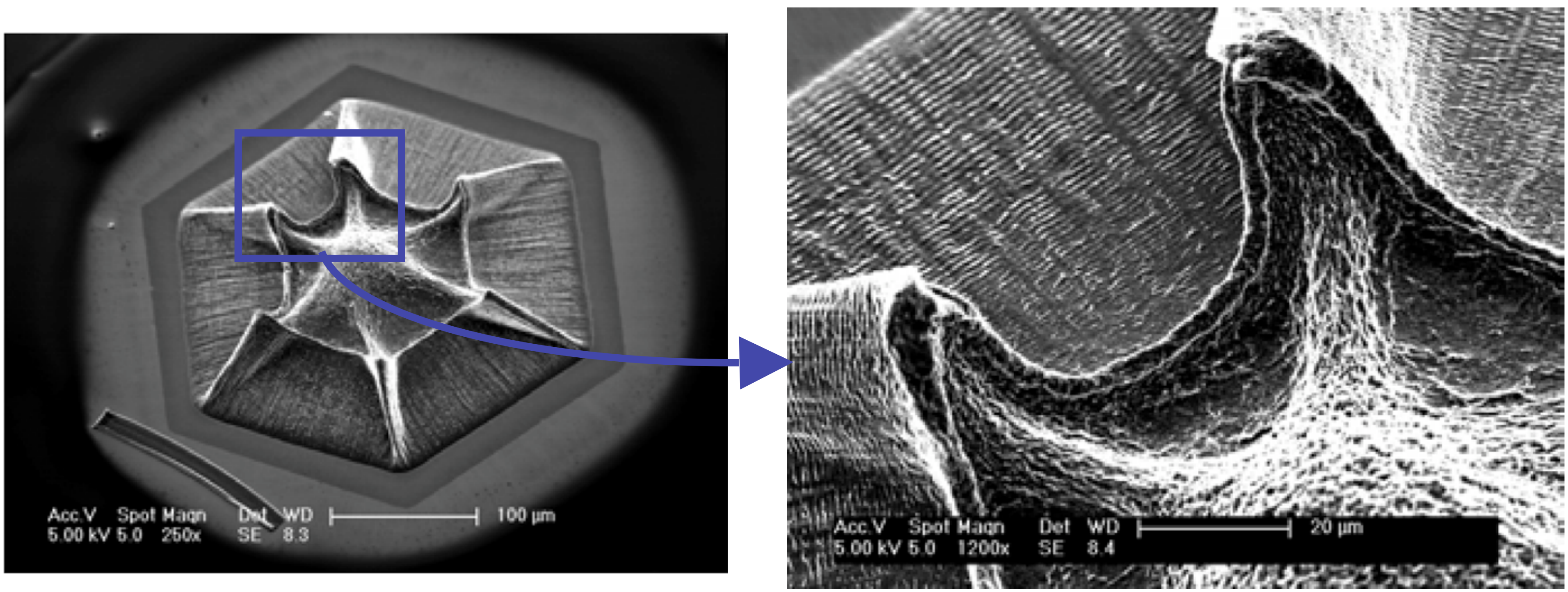
Some aesthetics…

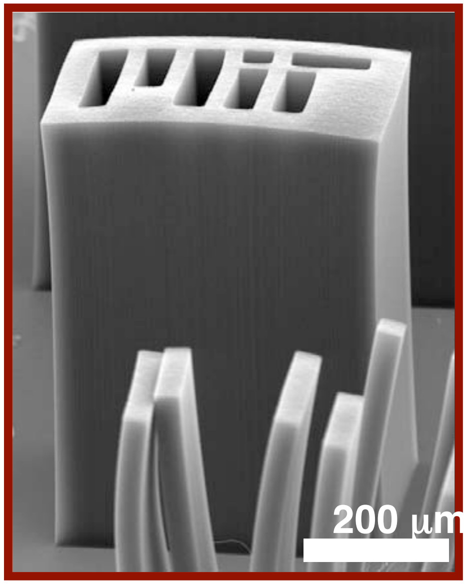






All images: E.J. Garcia

…and some fun.



More at nanobliss.com

Images: A.J. Hart and E.J. Garcia

“something funny happened to the catalyst here (at MI)...”

More at nanobama.com

Images: A.J. Hart

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Thank you.

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