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Experimental and Theoretical Studies of Carbon Nanotube Hierarchical Structures in Multifunctional Hybrid Composites

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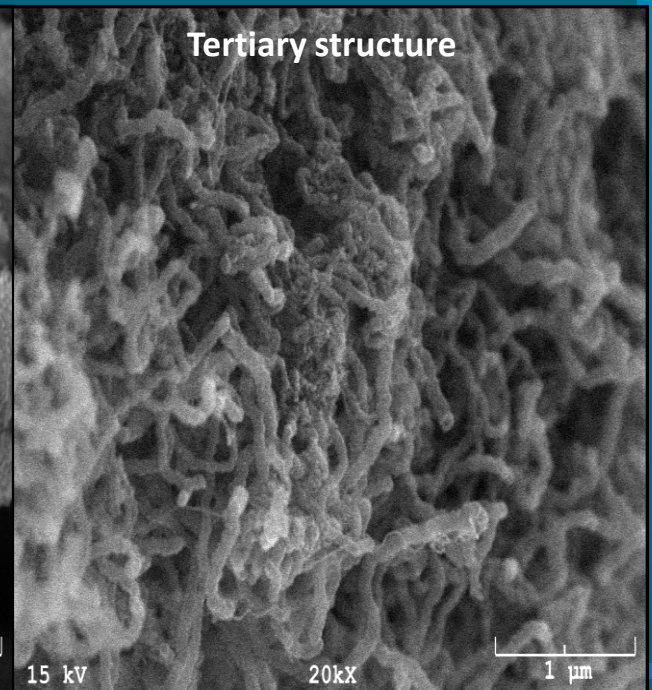
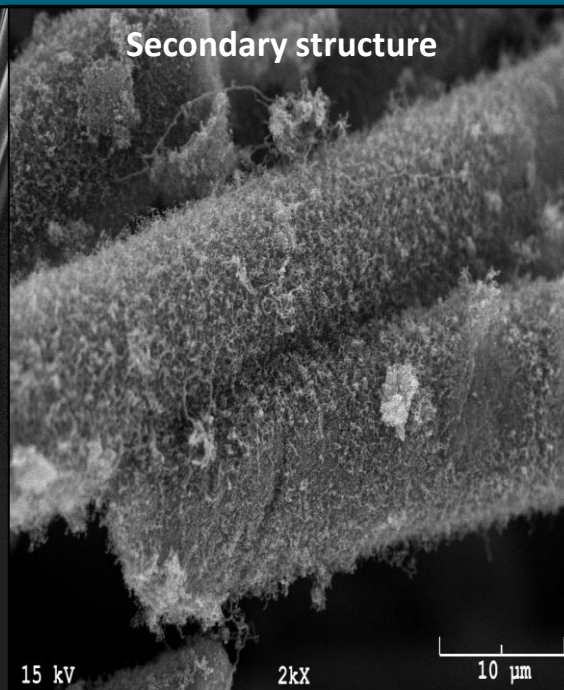
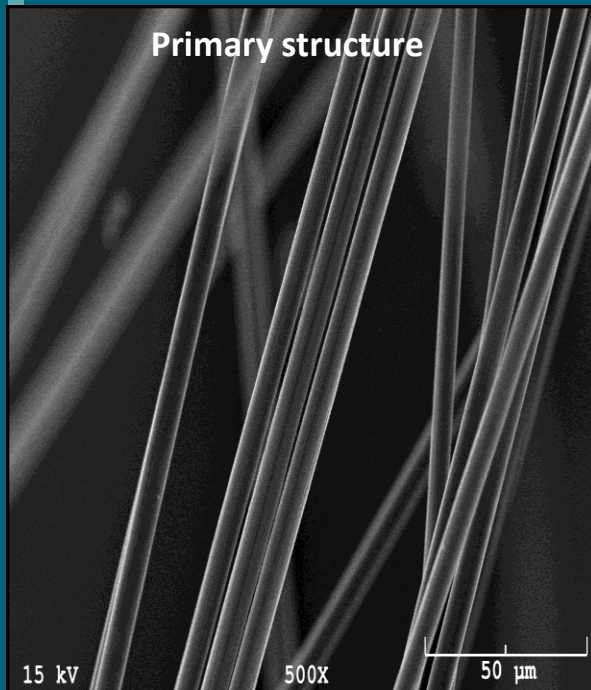
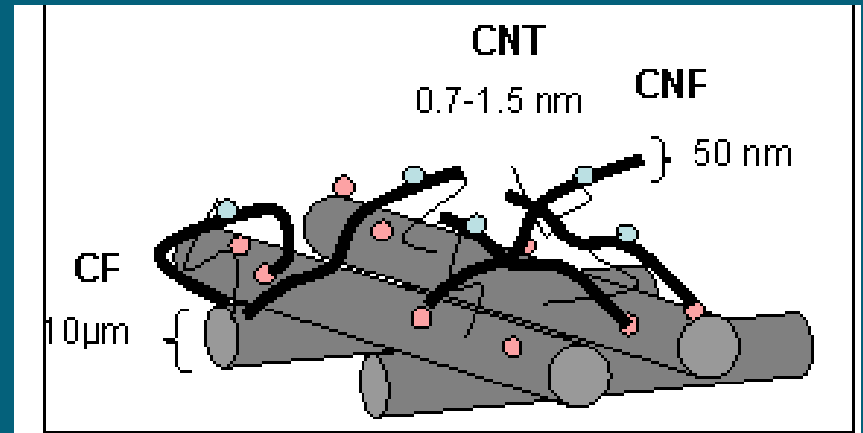


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Introduction



Nanoscale reinforcement is locally segregated at the microscopic scale with controlled orientation



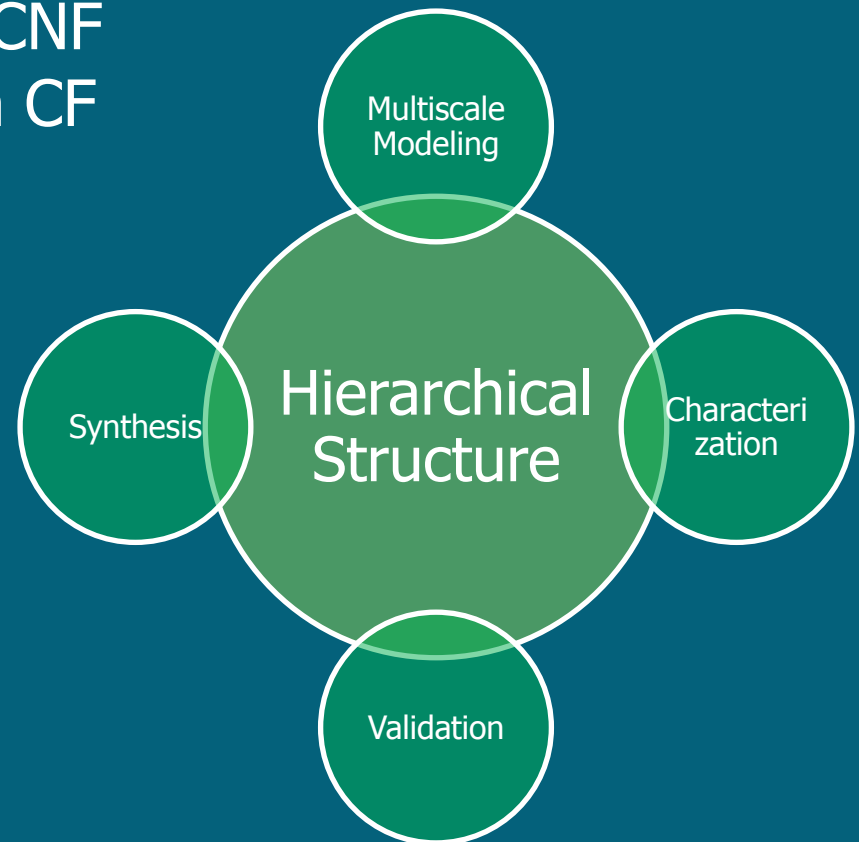


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Objectives and Approaches



- Synthesis and investigate of the growth morphology of CNF and CNT nanostructures on CF
- Investigate the process parameters affecting nanostructure morphology
- Investigate the growth on mechanical properties and thermal conductivity
- Investigate heat transport behavior using multi-scale modeling approach

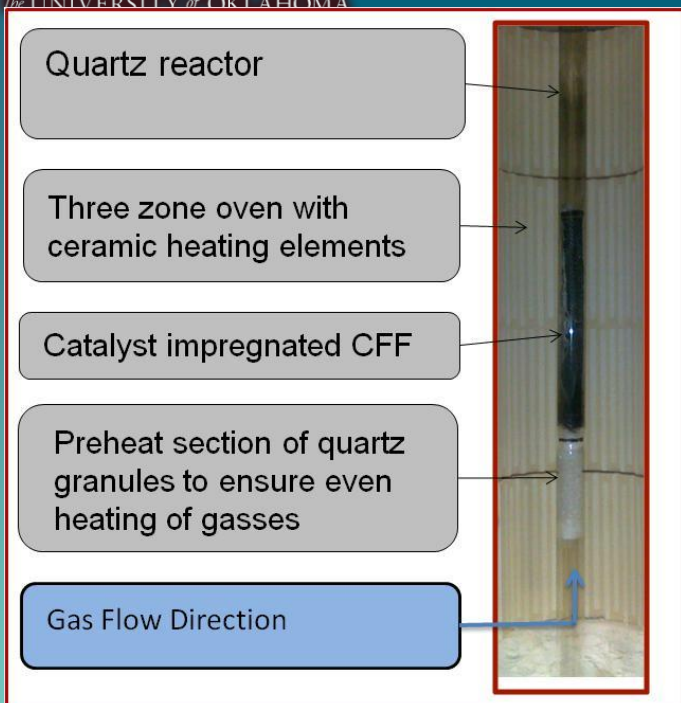




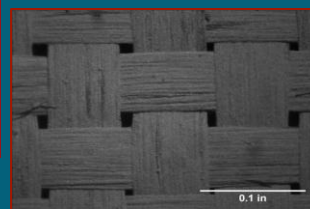
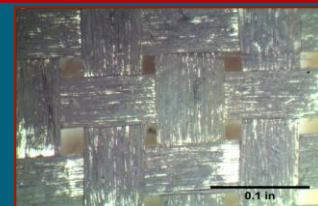
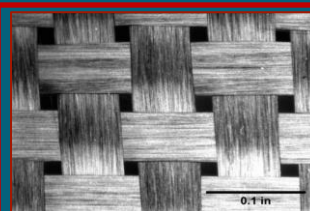
Synthesis of CNF on CF Using CVD



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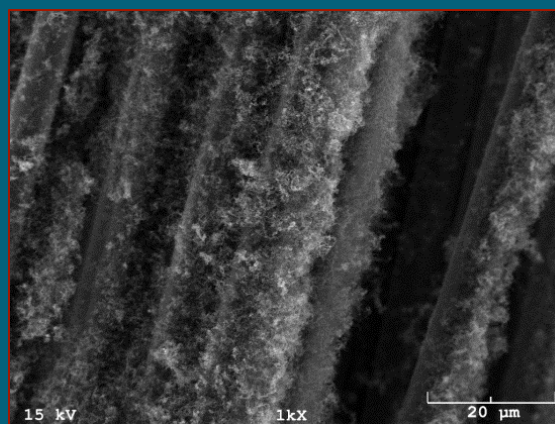


2.5" x 6" CF

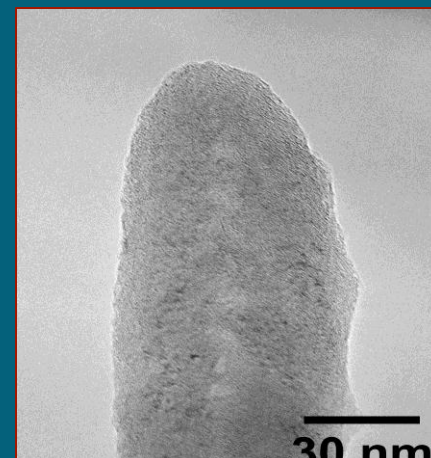


CFF with (top) 0, 30% and (bottom) 80% growth

- *Precursors:* $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$
- $\text{Cu:Ni} = 1:9$
- *Deposition:* Ion exchange vs. Spray
- *Calcination:* 300°C for 1 hr in Air
- *Reduction:* 500°C for 30 min in Hydrogen
- *Reaction :* 750°C for 30 minutes in Ethylene



SEM showing CNF growth

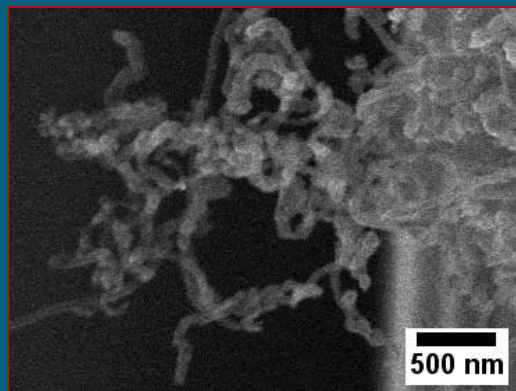
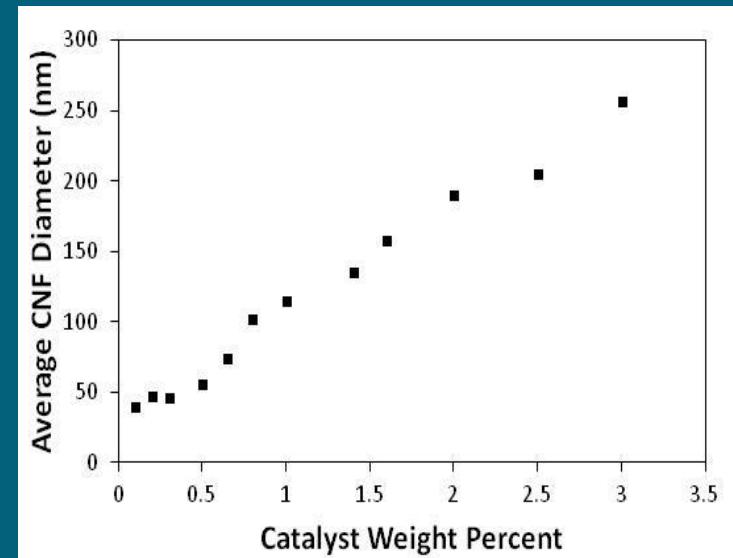
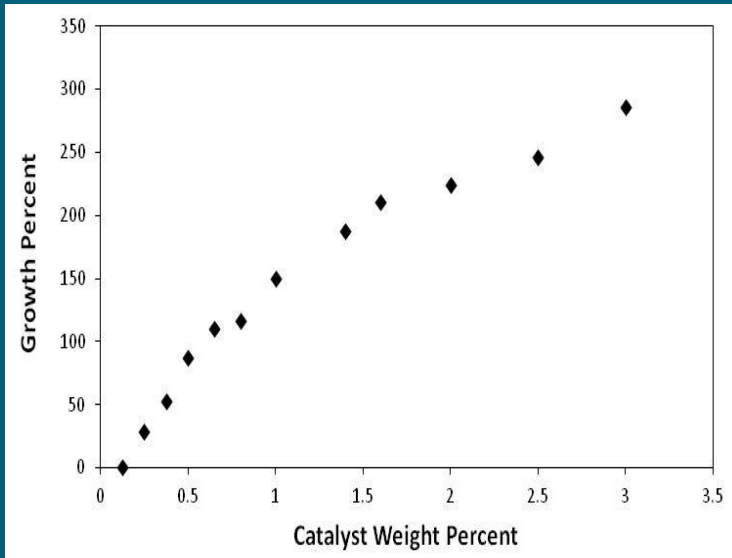


TEM confirms CNF

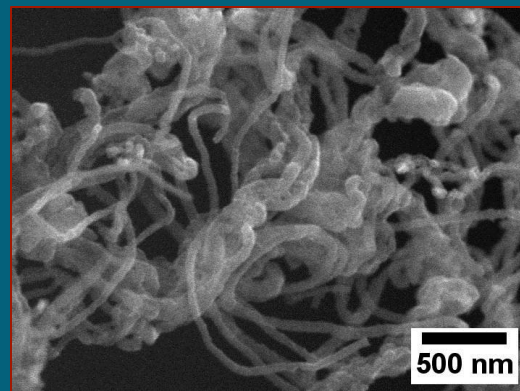


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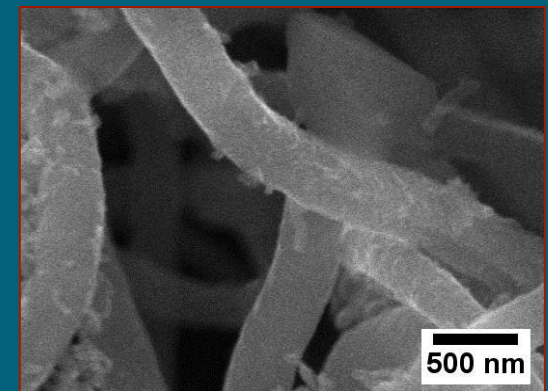
Catalyst Loading on CNF Growth



0.1 wt% catalyst



0.3 wt% catalyst

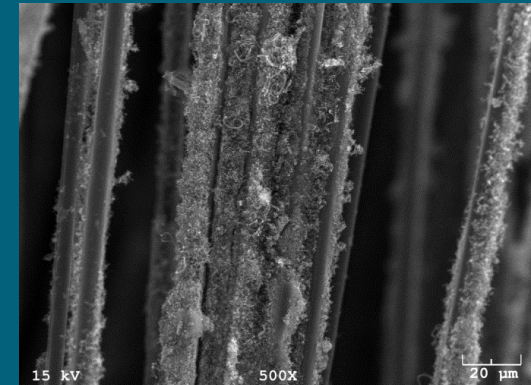
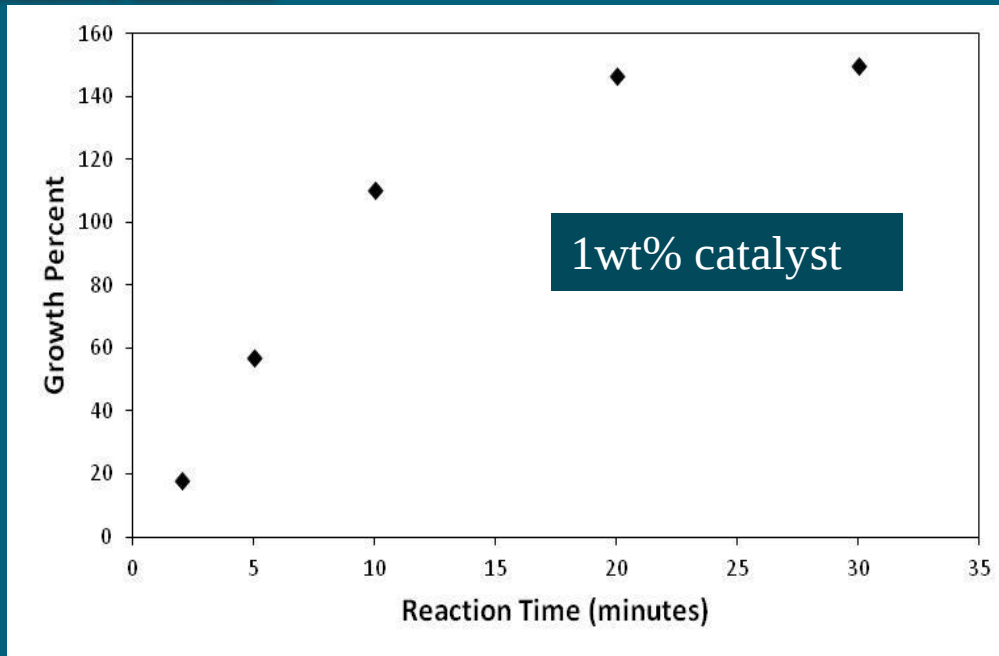


3.0 wt% catalyst

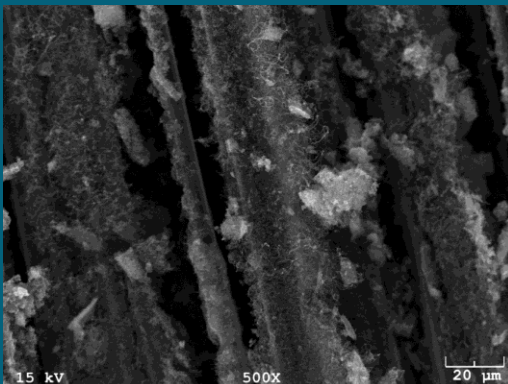


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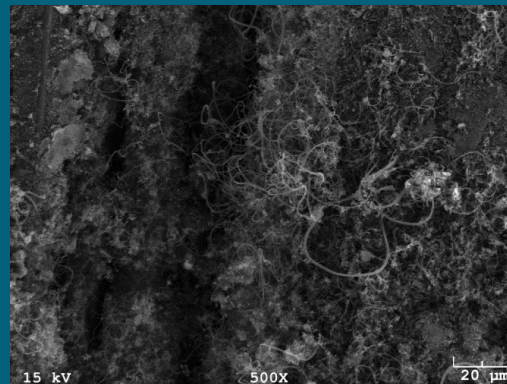
Reaction Time on CNF Growth



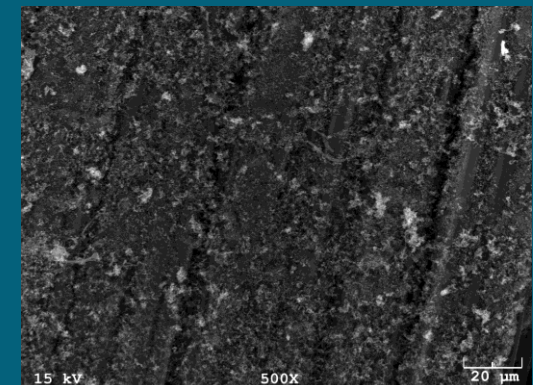
2.5, minutes



5 minutes



20 minutes

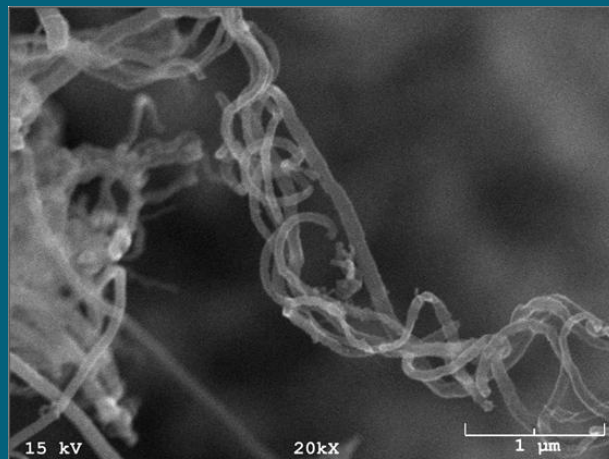
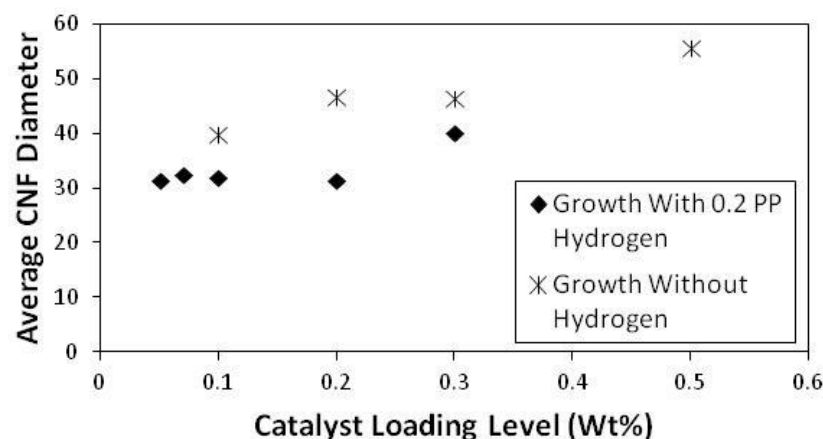
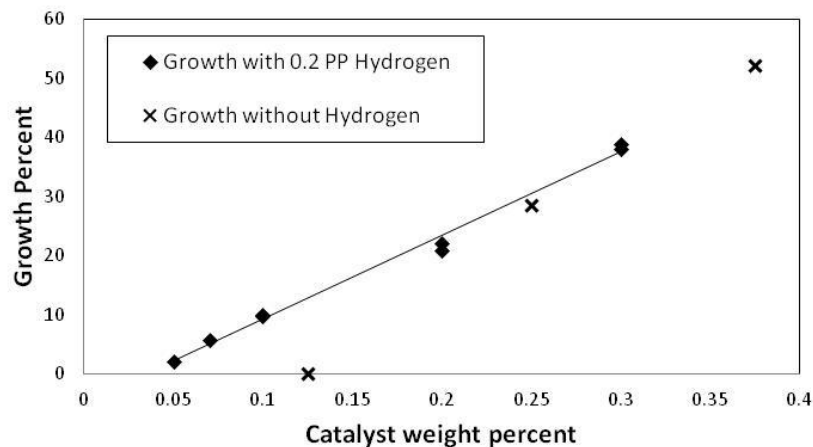


30minutes

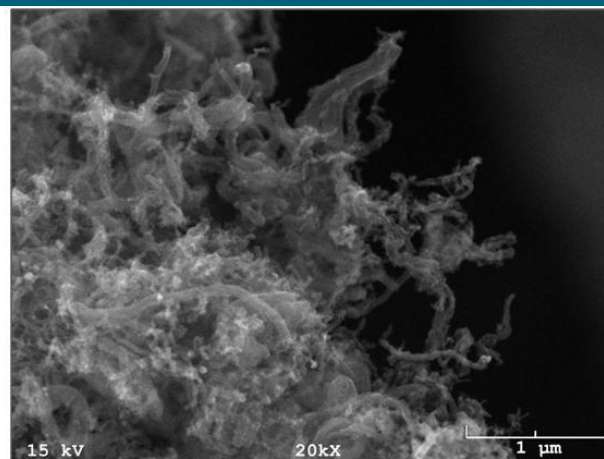


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Hydrogen Dilution on CNF Growth



SEM image of growth from pure Ethylene



SEM image of growth from Ethylene/Hydrogen mix



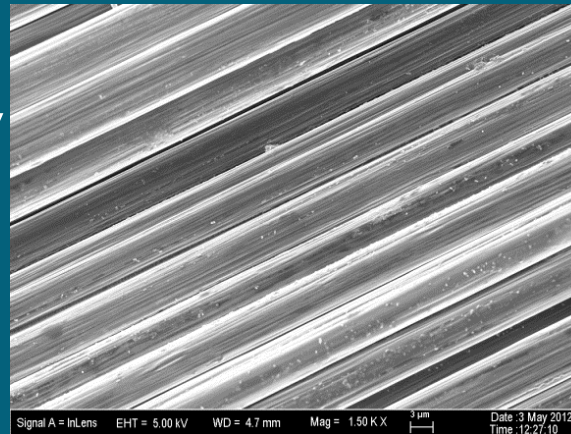
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CVD of CNT Growth on CFs

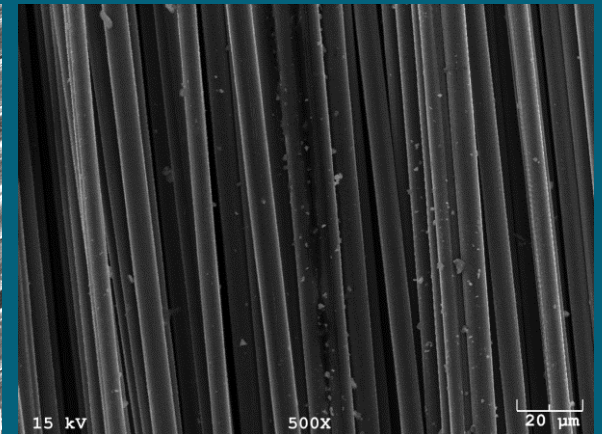


SEM images at different stages of the growth process

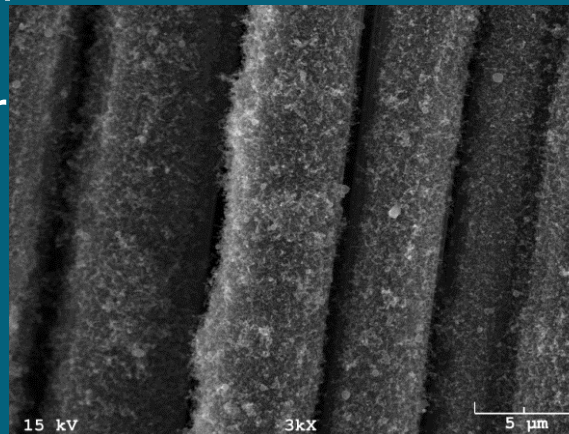
- *Precursors:* $\text{Fe}(\text{NO}_3)_3$, $(\text{NH}_4)_2\text{MO}_2\text{O}_7$
- Fe:MO= 2:1
- Hand Spray
- *Calcination* : 300°C for 1 hr in Air
- *Reduction* : 500°C for 30 min in Hydrogen
- *Reaction* : 750°C for 30 minutes in Ethylene



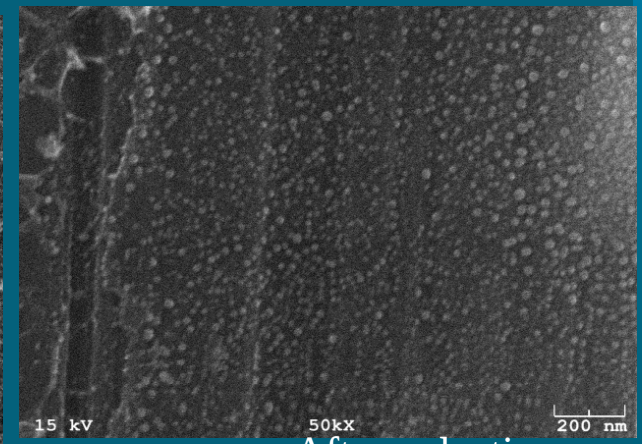
Before calcination



After calcination



After growth



After reduction

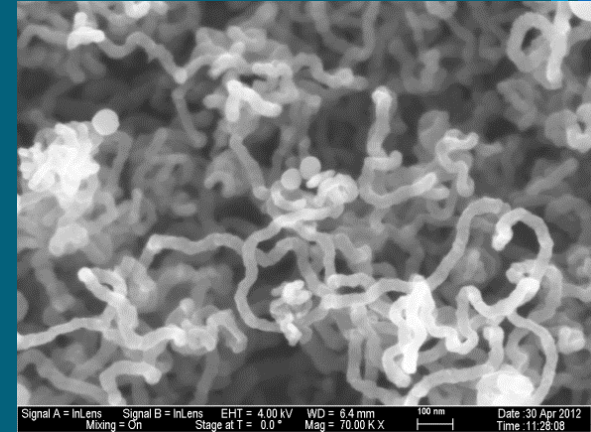
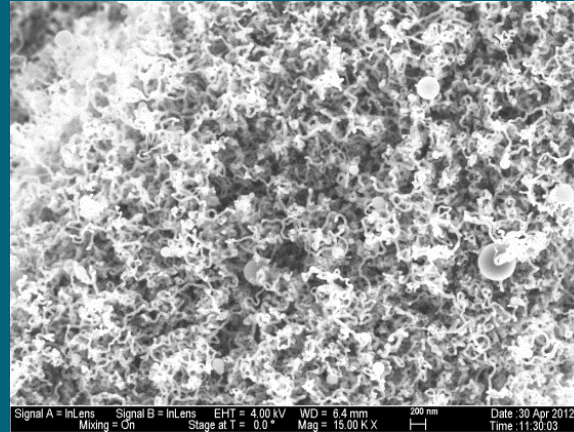
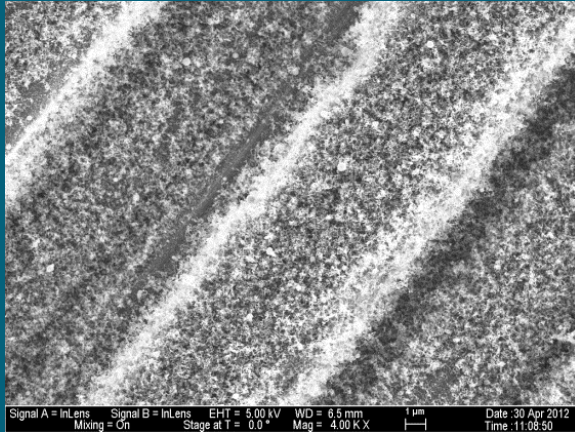


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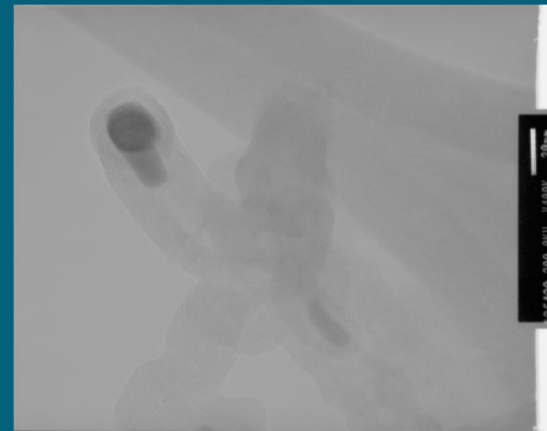
CVD of CNT Growth on CFs



CNT growth performed at 750°C



SEM images showing CNTs growth at different magnification



TEM images confirm CNTs structure with tip growth



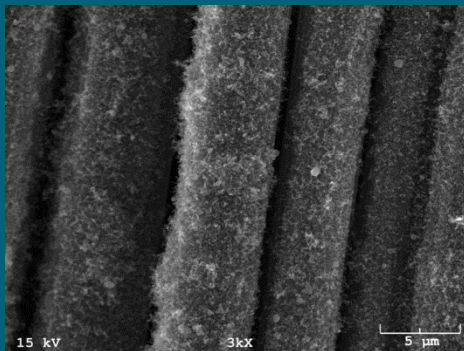
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CVD of CNT Growth on CFs

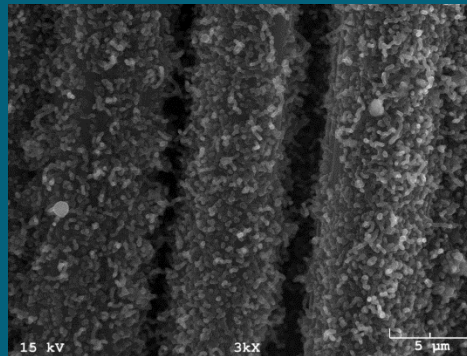


Comparison of two methods of catalyst deposition

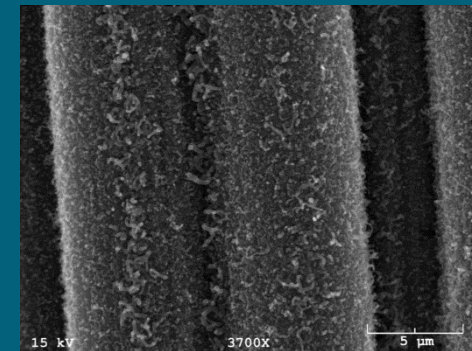
Spray



750°C

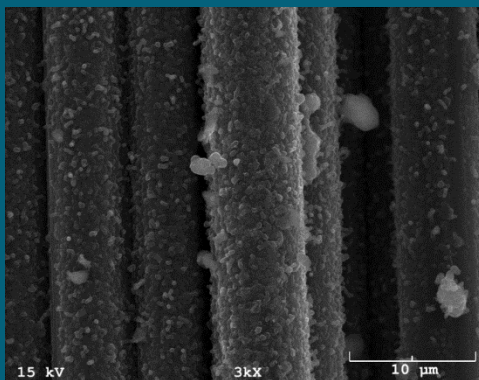


780°C

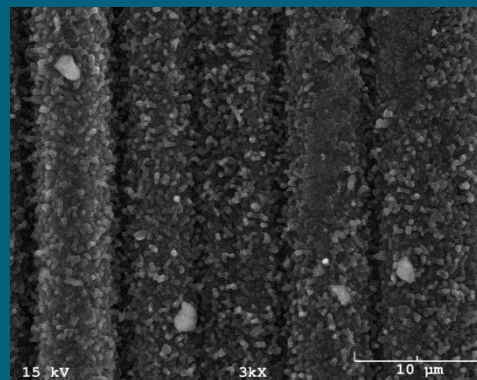


800°C

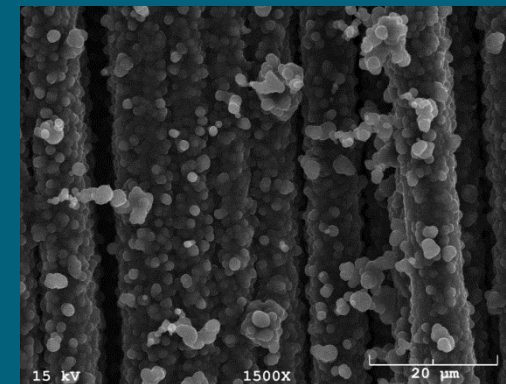
Ultrasonic Atomizer



750°C



780°C

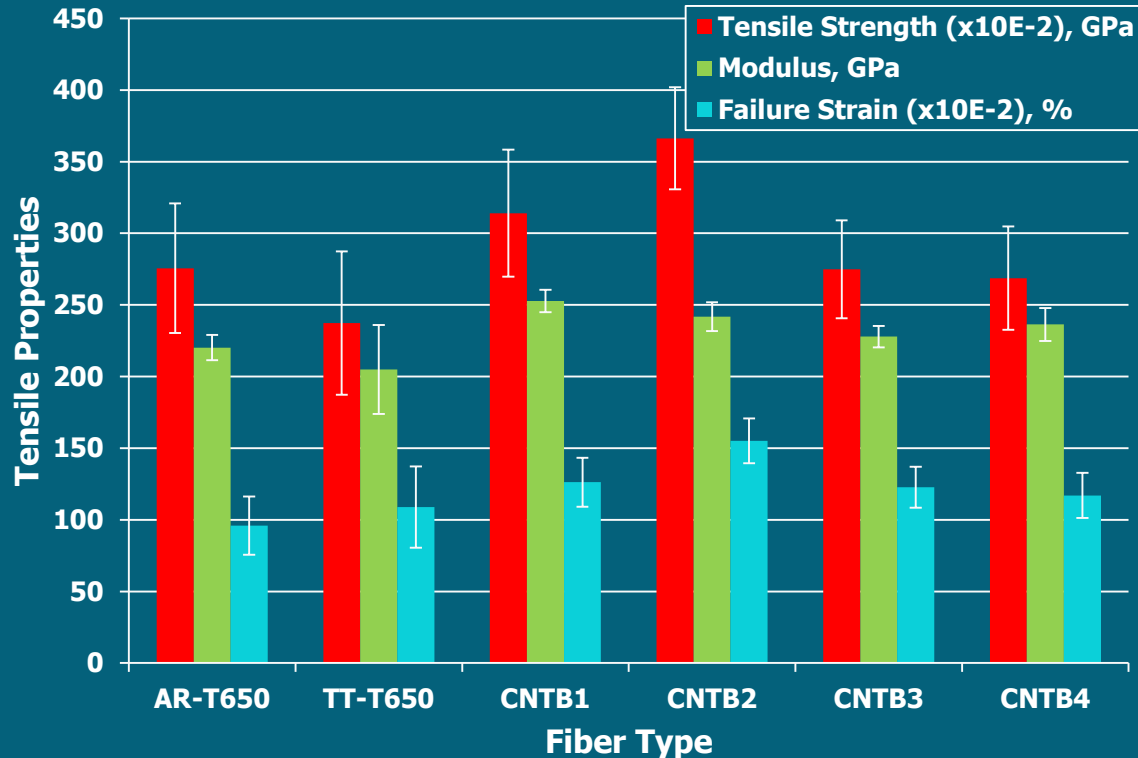


800°C



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Effect of CNTs on Tensile Properties of Carbon Fiber



CNTB1- AR-Spray; CNTB2- AR-Dip
CNTB3- TT-Spray; CNTB4- TT-Dip

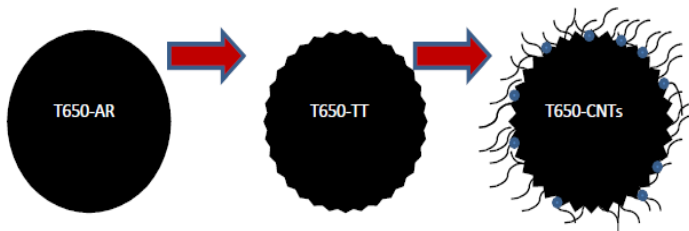
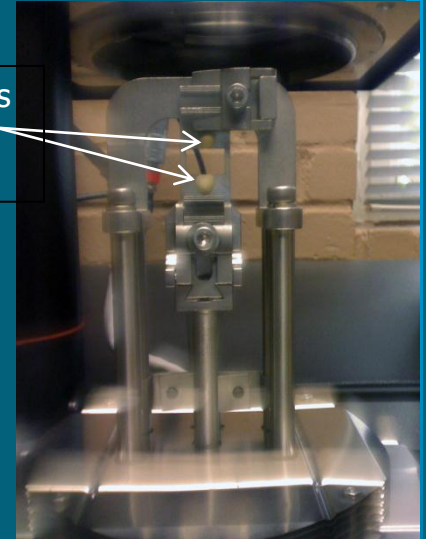


Illustration of fiber surface flaws/irregularities filled with catalyst metals and/or CNTs

Bonded ends of the steel frame



DMA Q800



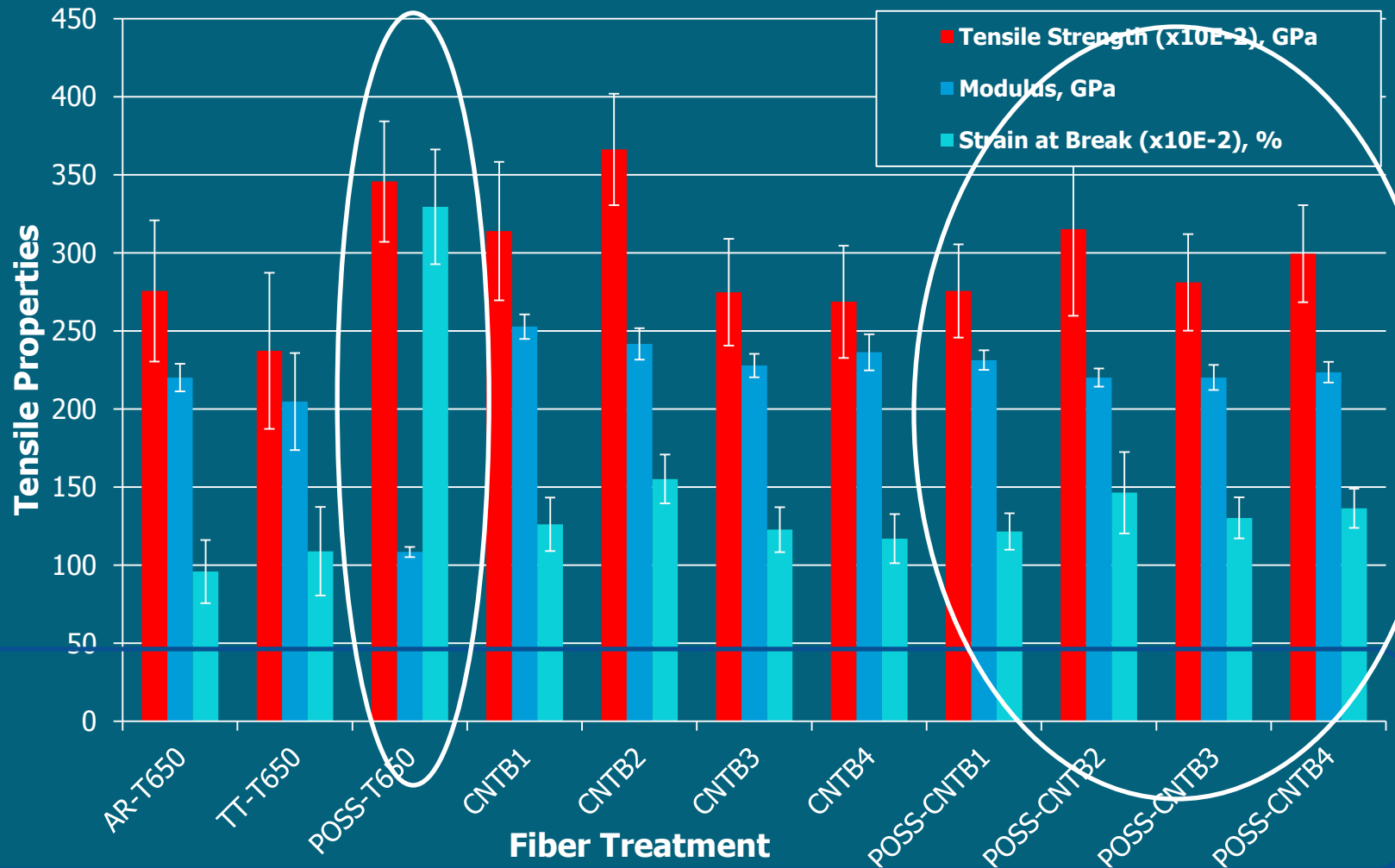
Steel shim frames used for mounting the fibers



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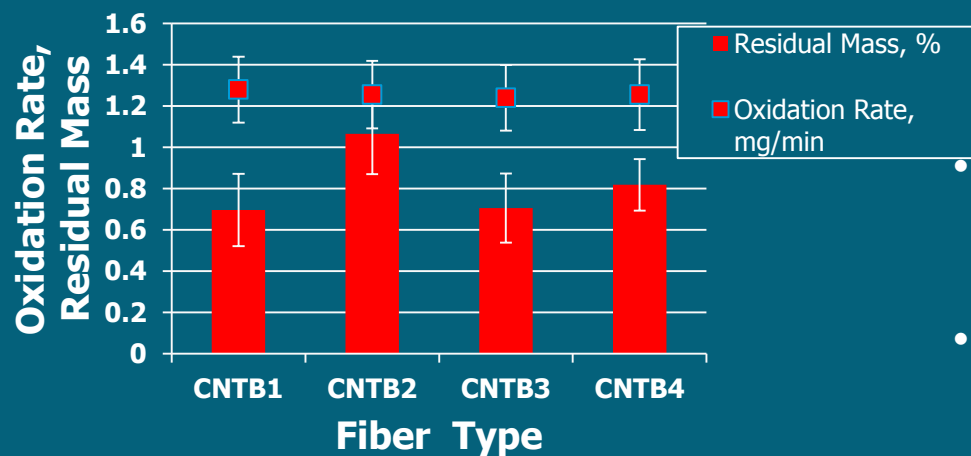
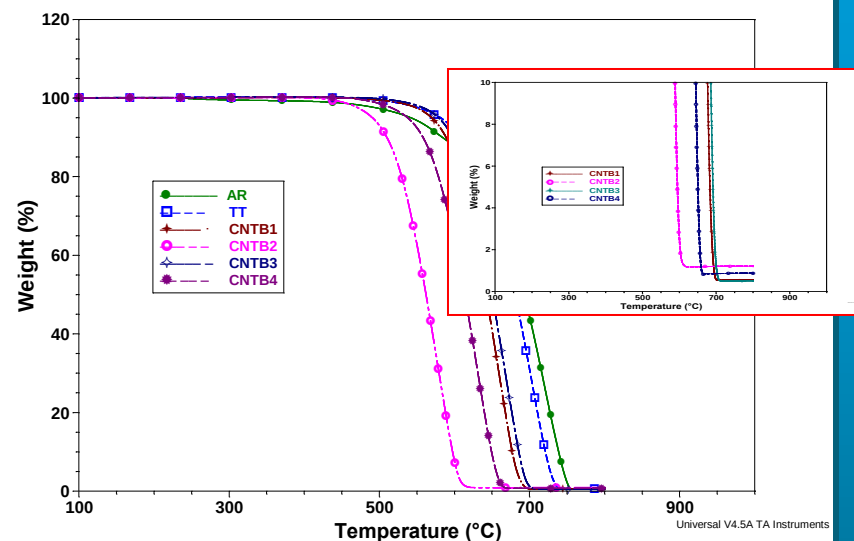
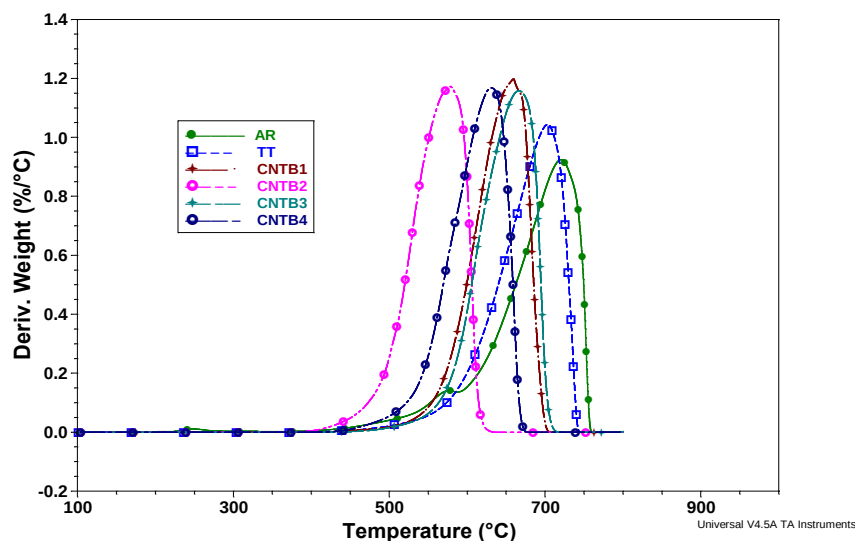
Effect of POSS Coating





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CNT Characterization using TGA



TGA Q50 ceramic pan (500 μ L)

Sample: 18-20mg

- Heated up to 100°C and maintained at this set point for 30 min.
- Ramped to 800 °C at 2°C/min and air flow rate was maintained at 30mL/min

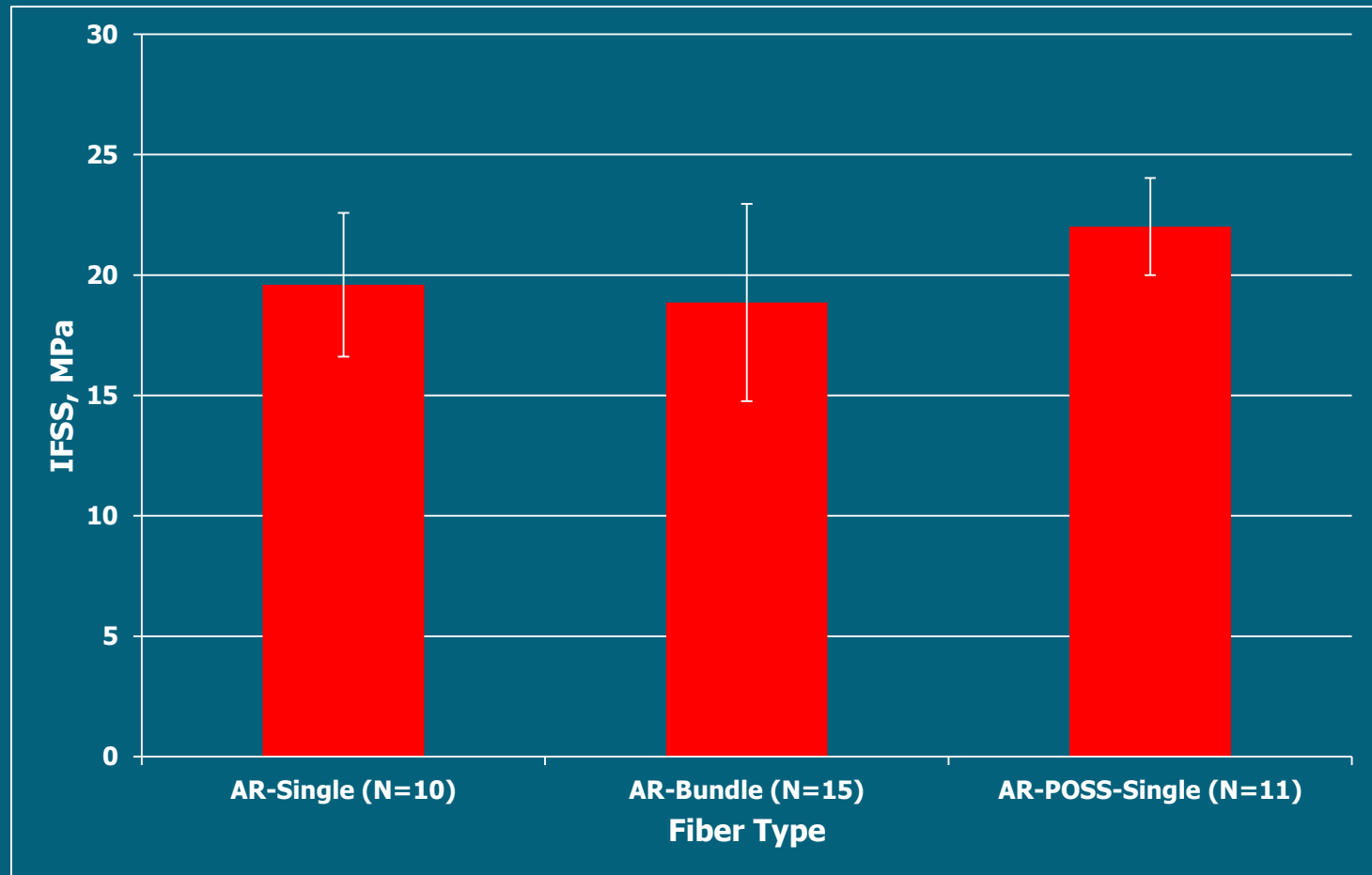


-
- Side view*
- Diagram illustrating the side view of the repair assembly. The assembly consists of a Steel frame (0.102 mm thick) with a Carbon fiber strip (12.70 mm long) bonded to it using Resin and Superglue. The Carbon fiber strip is 0.3 mm* thick. The Superglue layer is 0.57 mm thick. The assembly is secured with a Magnetic strip (1.5 mm wide) and a Resin layer (1.5 mm wide).



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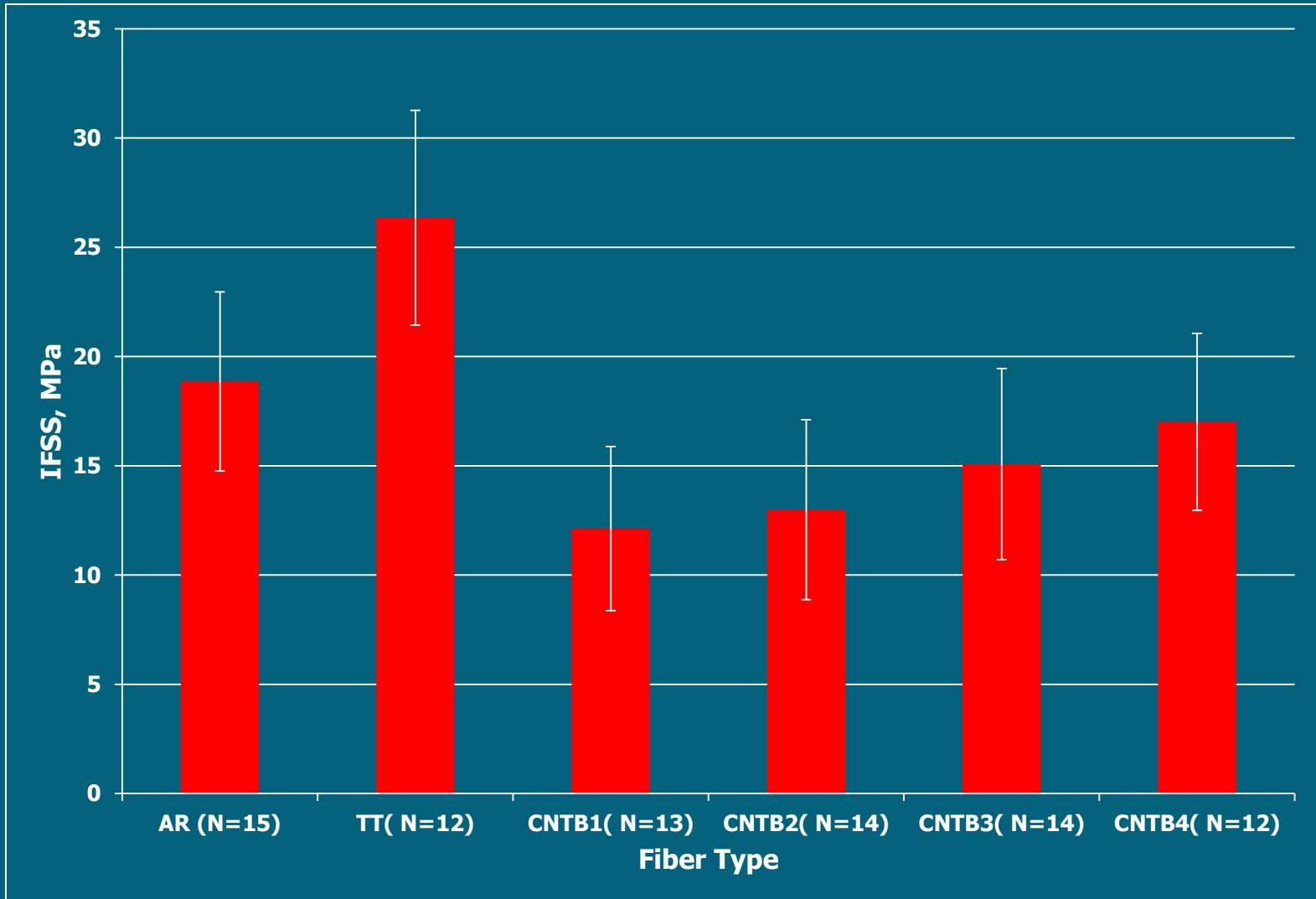
Single Fiber vs. Fiber Bundle





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Effect of CNTs on Interfacial Properties



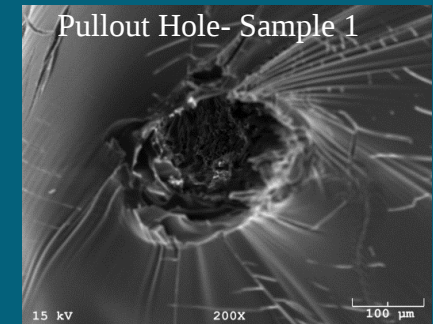
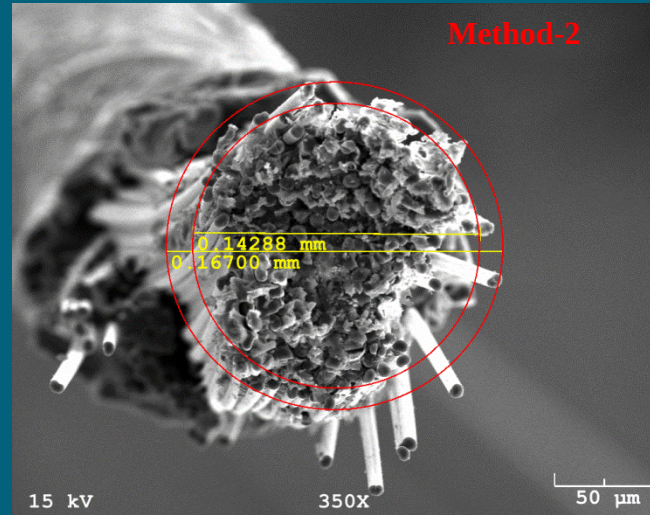
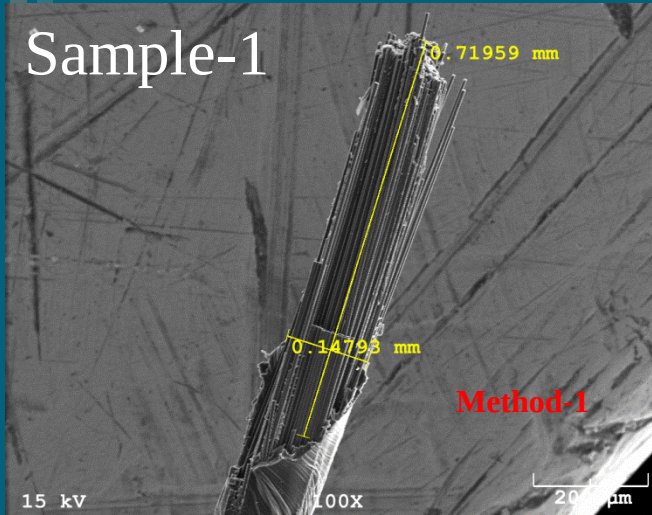


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Diameter and Embedded Length Measurement

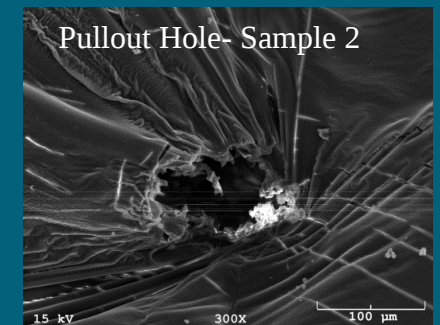
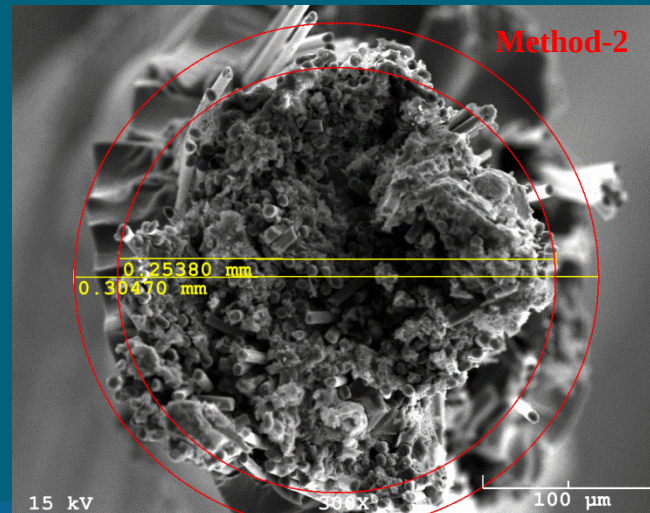
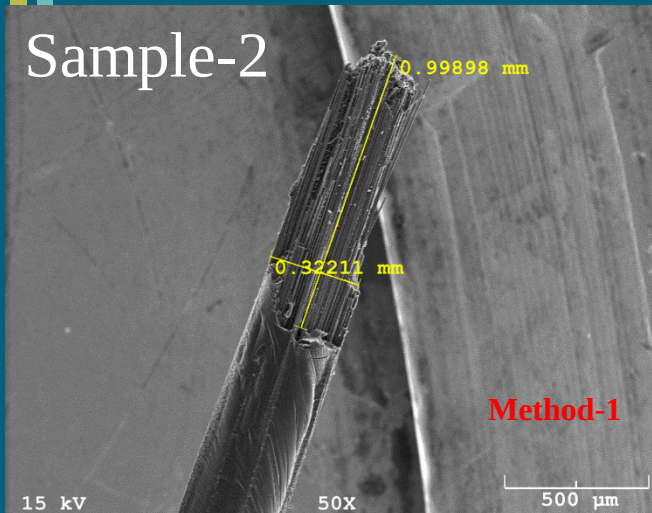


Sample-1



Sample#1 Diameter:
Method 1= 0.14793 mm
Method 2= 0.15494 mm

Sample-2

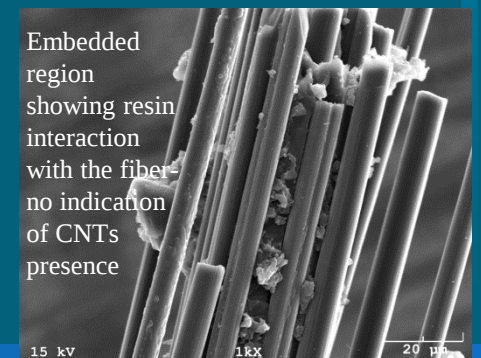
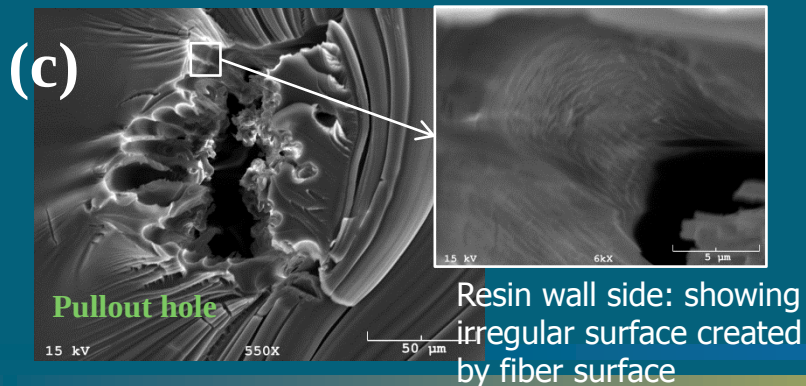
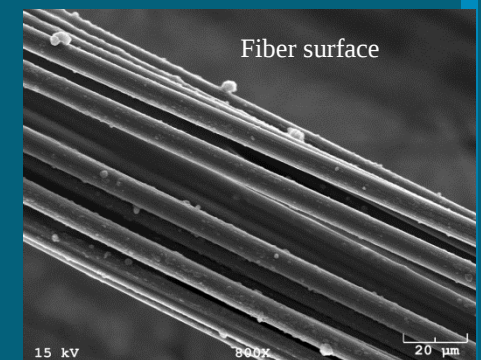
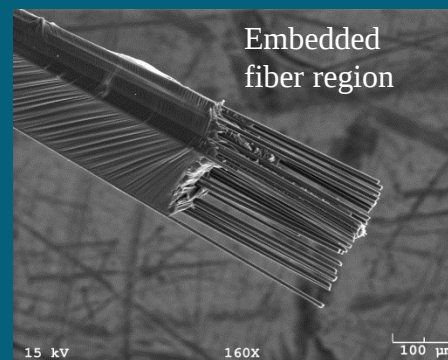
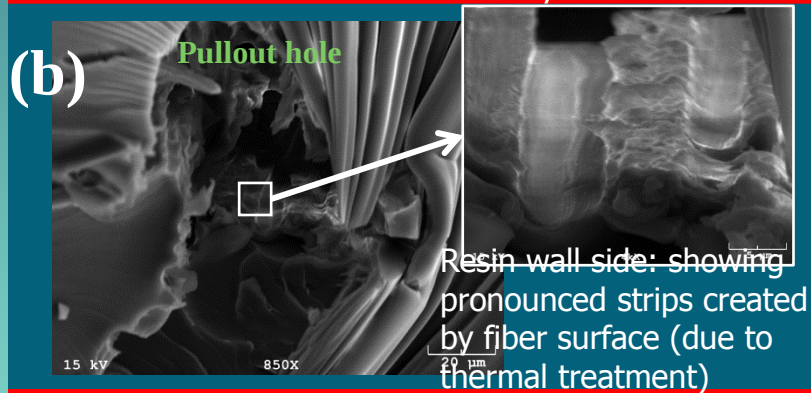
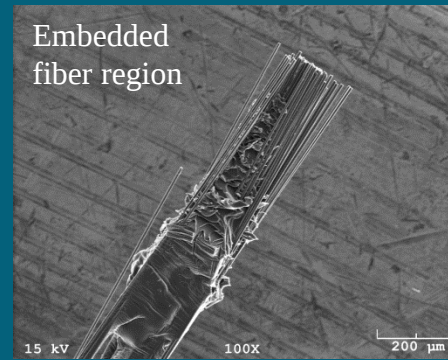
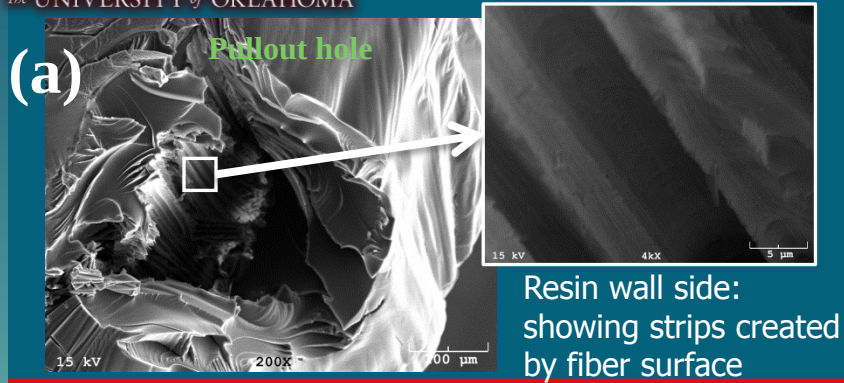


Sample#2 Diameter:
Method 1= 0.32211 mm
Method 2= 0.27925 mm



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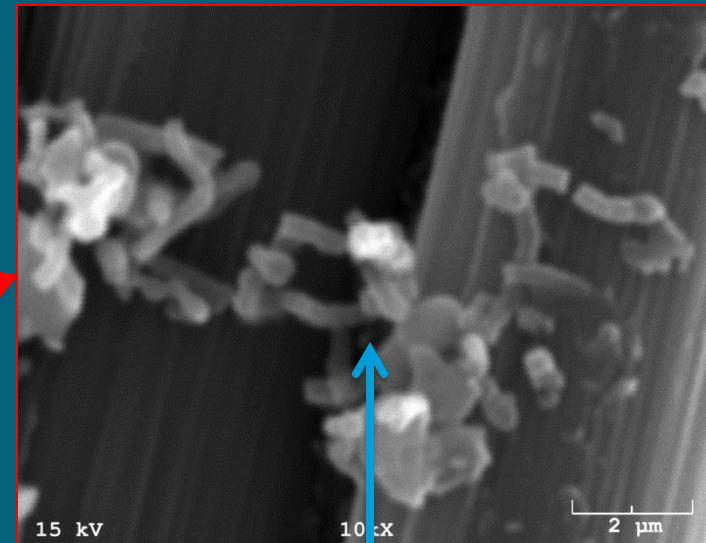
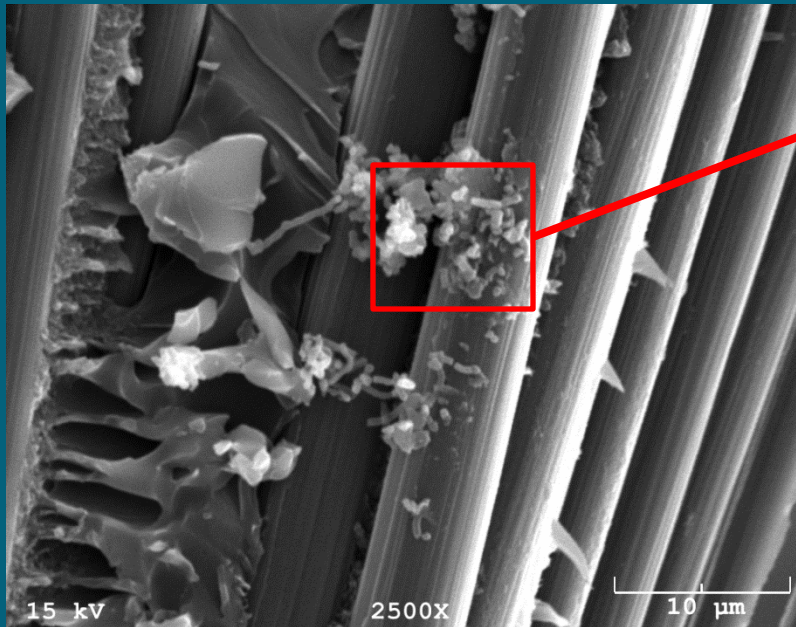
SEM Micrographs showing the pullout hole and the embedded bundle fiber length: (a) AR (b) TT and (c) CNTF





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SEM Investigation of Pullout Fiber Bundle



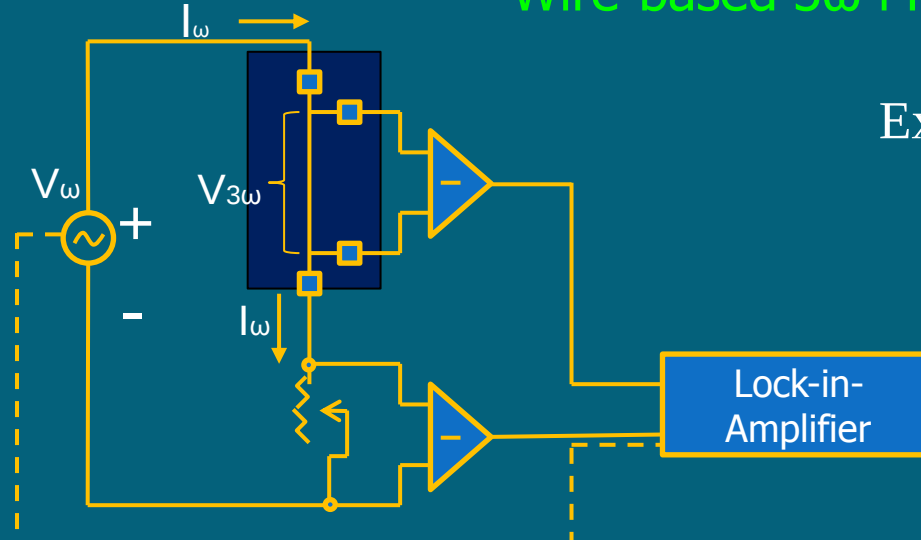
Remains of CNTs on the
fiber after the pullout



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Thermal Conductivity Measurement

Wire-based 3 ω Method



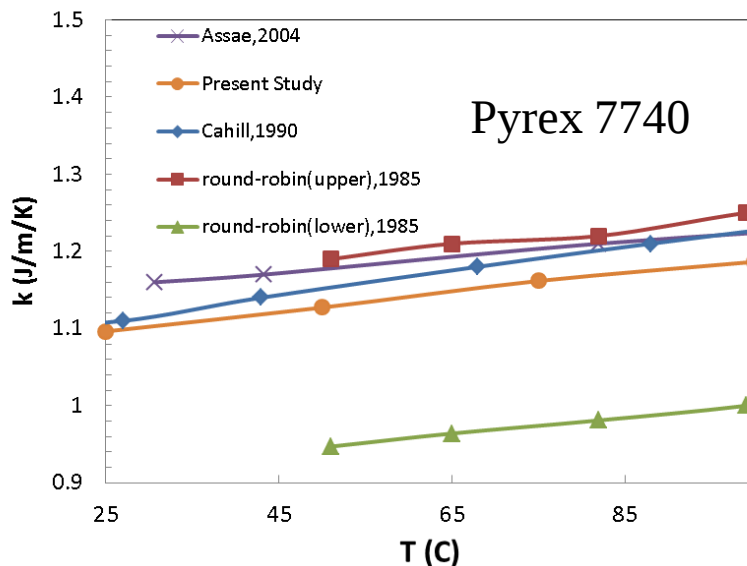
Experimental thermal impedance

$$T = QZ$$

$$Z = -\frac{4R^2 bL}{V_{rms}^3 \frac{\partial R}{\partial T}} V_{3\omega_rms}$$

Analytical thermal impedance

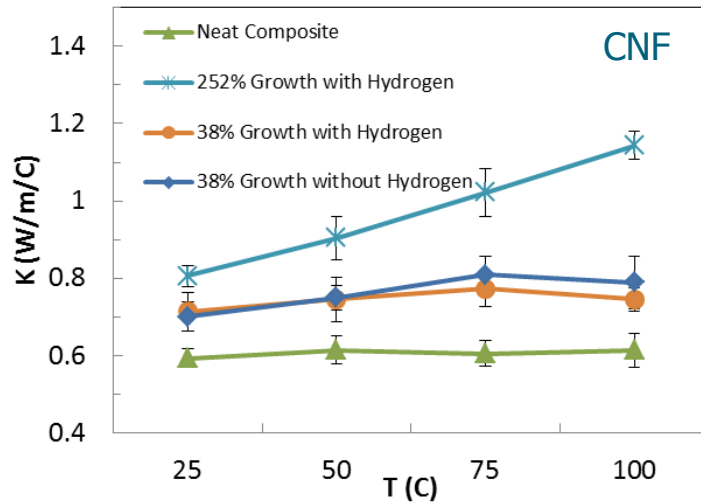
$$\hat{Z} = \int_{4\pi}^{4\pi} \frac{\sin(\chi)}{\chi^2} \frac{-b}{k_y \sqrt{\frac{k_x}{k_y} \chi^2 + \frac{i4\pi f b^2}{\alpha}}} d\chi$$



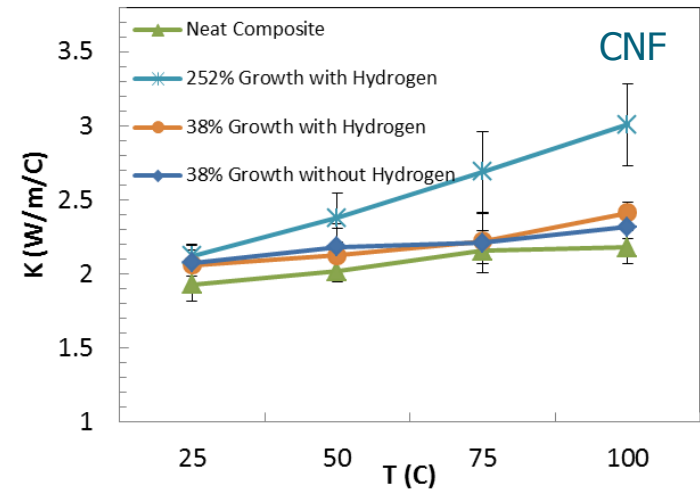


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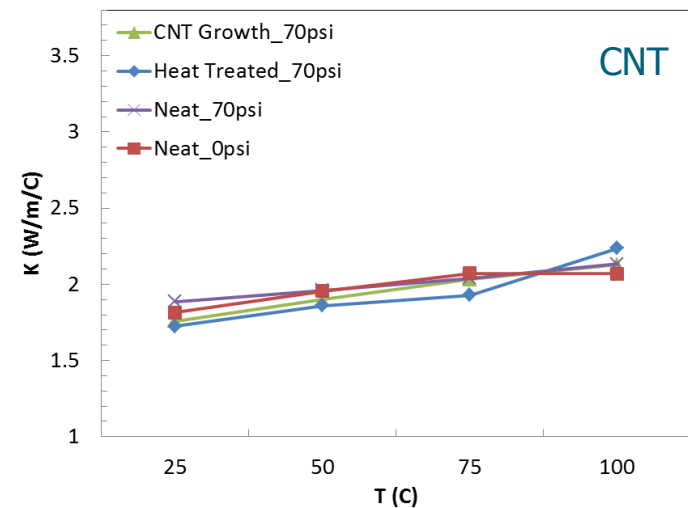
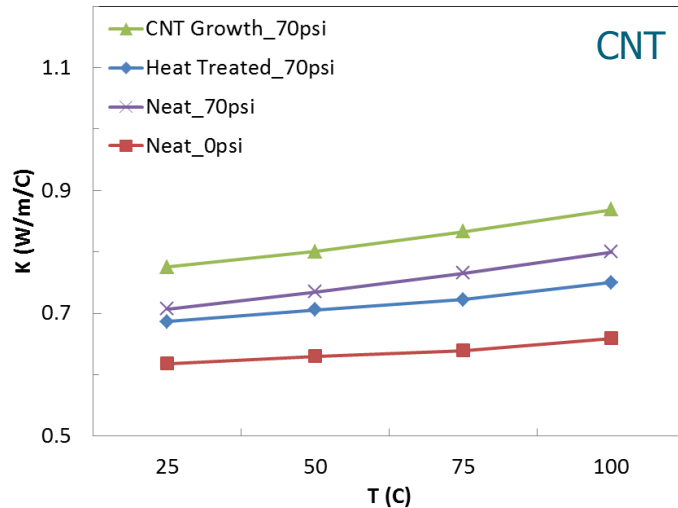
Thermal Conductivity of Composites



Through-thickness direction



In-plane direction



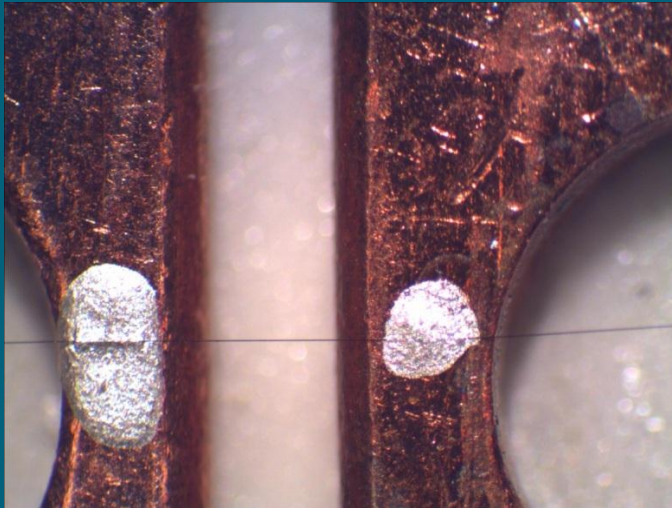


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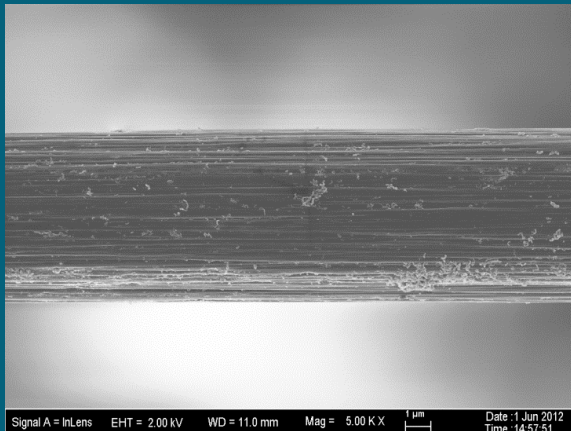


Thermal Conductivity of Single fiber

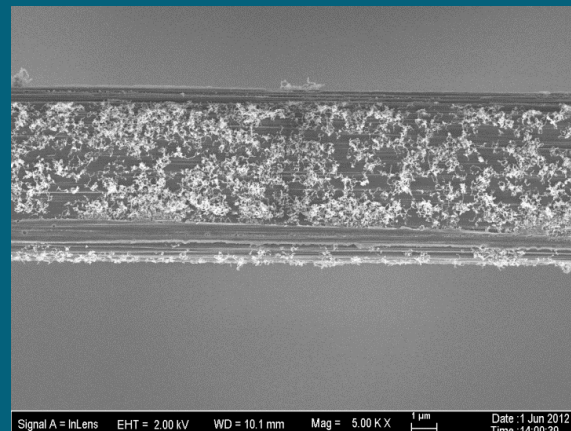
- Lu's model (Lu *et al* 2001)



	K (W/mK)
Neat	14.4
Heat Treated	15.5
CNT Growth	18.1



TC = 15.03 W/mK



TC = 21.06 W/mK

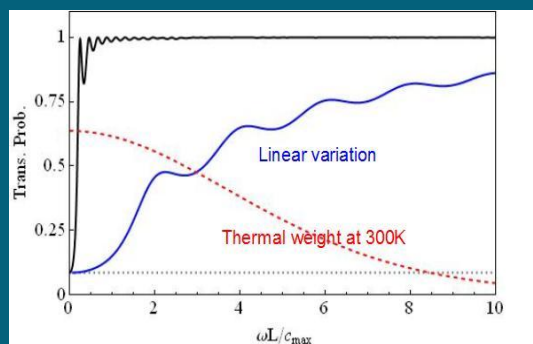
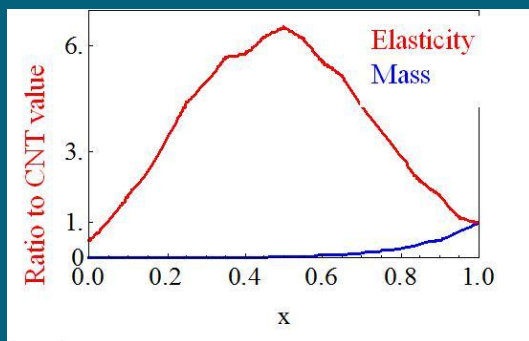


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Effect of CNT Interface on TC

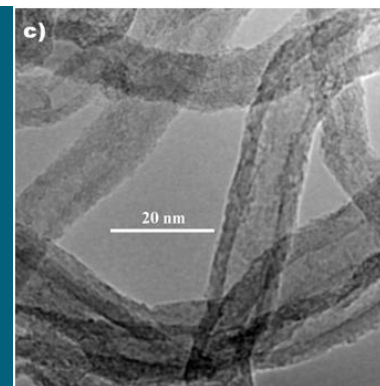
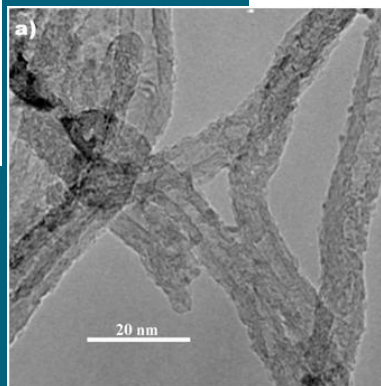
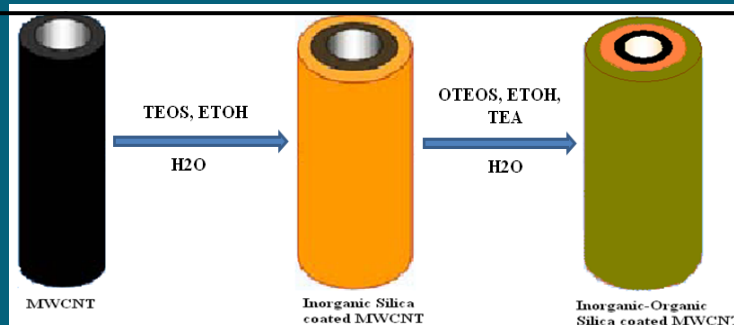


Functionalize the end of 1-D CNT structure with molecular chains of varying stiffness and mass density



An interface with the optimal variation of elasticity and mass as a function of position (top) transmits nearly all phonons (black line, bottom) better than either an abrupt interface (dotted line) or a linear variation (blue line)

Unit (nm)	Pristine	One-layer coating	Two-layer coating
Avg. Diameter	9.1 ± 3.1	10.4 ± 3.8	11.7 ± 4.2
Maximum	20.0	24.5	27.6
Minimum	3.0	4.2	4.8



Pristine MWCNTs

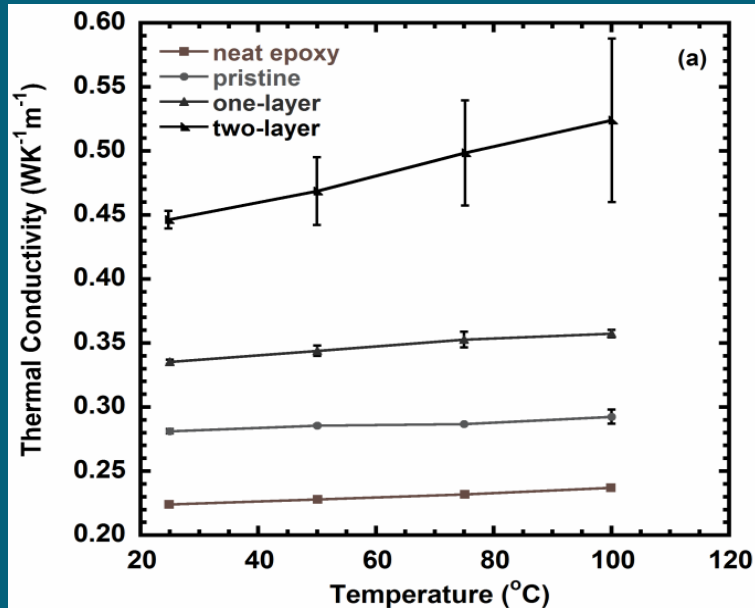
One-layer coating

Two-layer coating

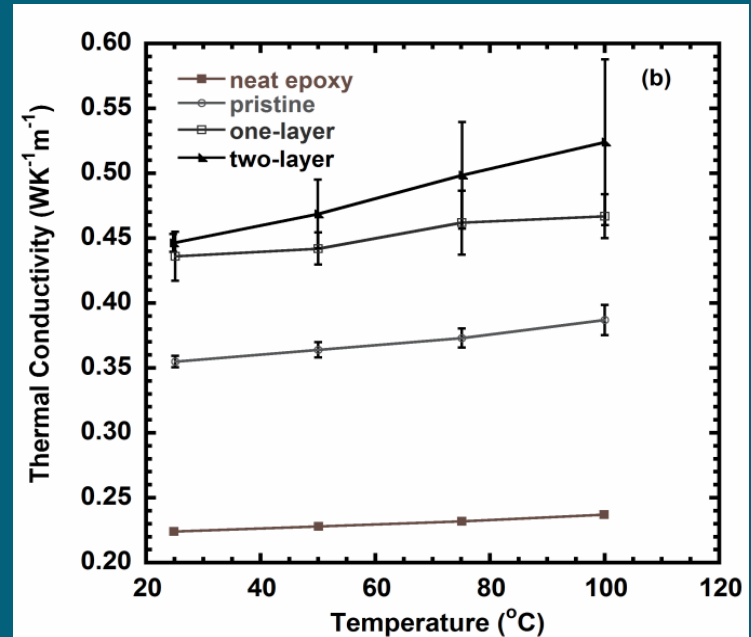


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Effect of CNT Interface on TC



Amount of pristine, one-layer and two-layer of MWNTs is 0.5, 0.83 and 1.0 wt%, respectively, corresponding to 0.5wt% nanotube on nanotube basis



Amount of filler is 1.0 wt% for all three types of MWNTs on a total filler basis

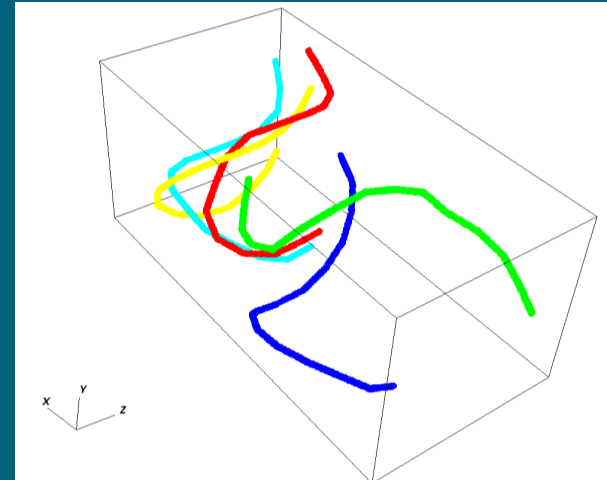
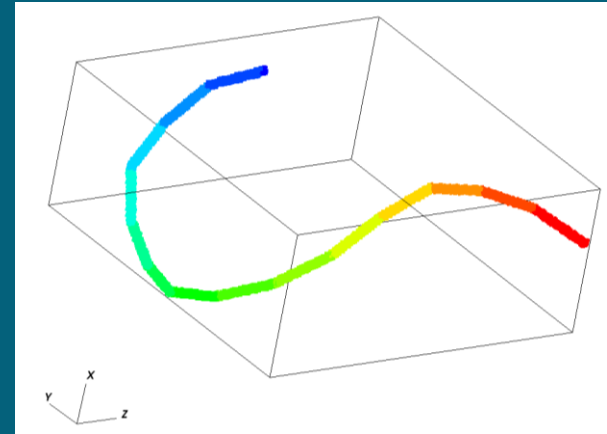
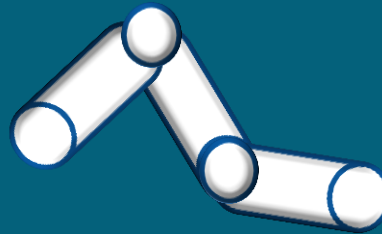
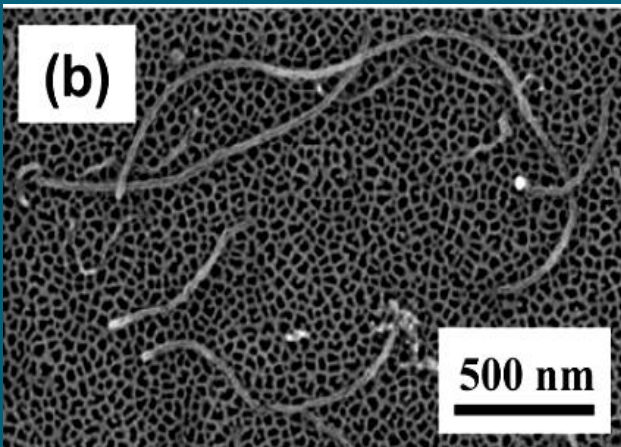
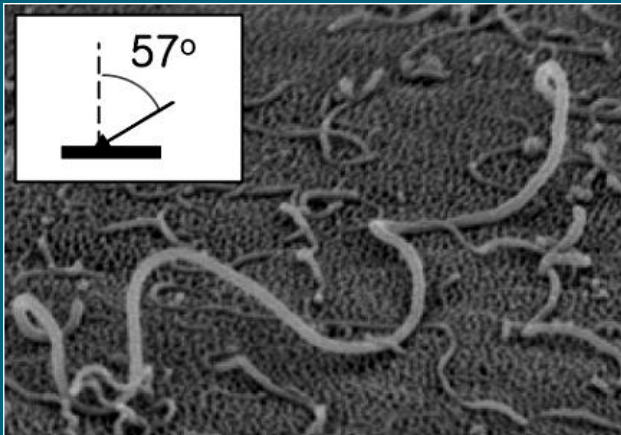


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Mesoscale Modeling of Thermal Conductivity (Monte-Carlo)



Worm-like CNTs in 3D



SEM of MWCNTs on ceramic filter.
Lee *et al.*, *JPCC* 111(51) 2007

Configuration of CNTs inside the computational box:
random placement and random oriented



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Modeling of Thermal Conductivity

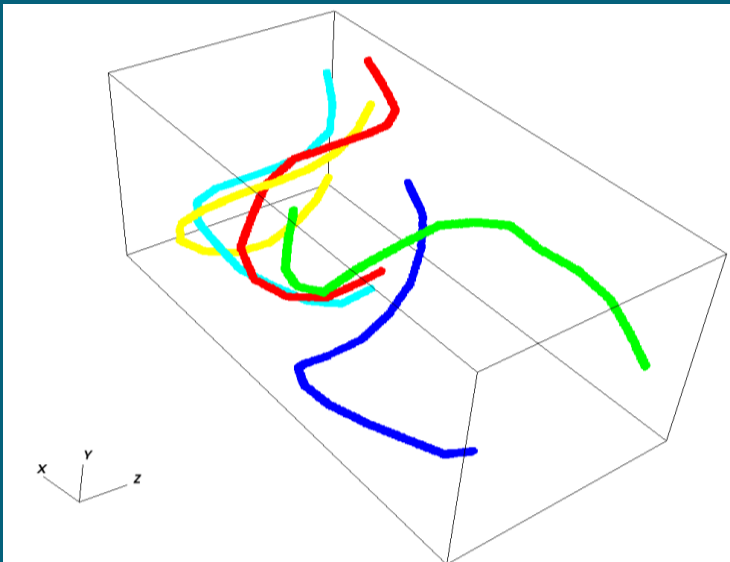
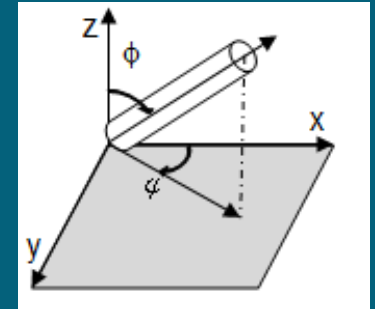
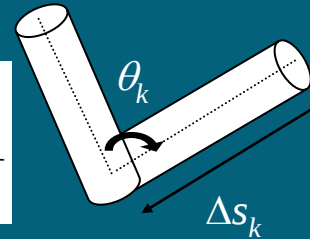


Persistence length, L_p :

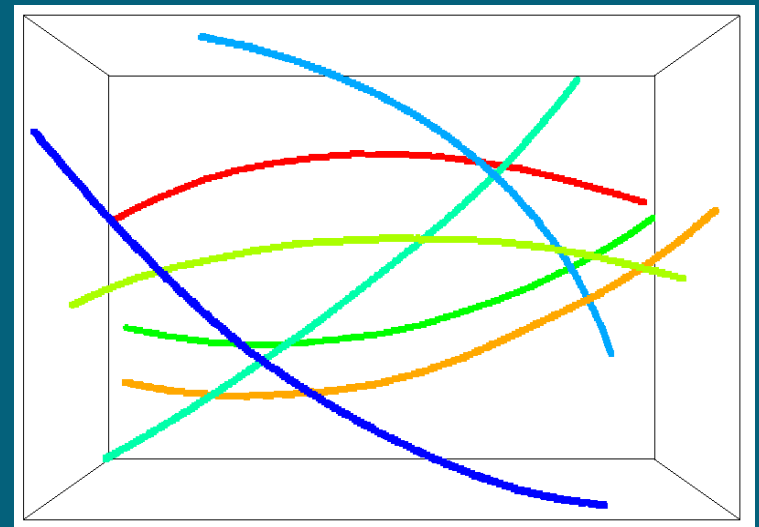
$$L_p = \frac{L^2}{(N-1)^2 \pi^2 \text{var}(a_n)}$$

$$a_n \cong \sqrt{\frac{2}{L}} \sum_{k=1}^N \theta_k \Delta s_k \cos\left(\frac{n\pi}{L} s_k^{\text{mid}}\right), n = 1, \dots, N-1$$

Gittes F. *et al.*, J. Cell Biology 1993, 120, 923-934



$L_p < L$



$L_p \approx L$



Modeling of Thermal Conductivity



L_p of pristine and 2-layer coating MWCNTs

Sample	pristine	2-layer coating
Average L_p (nm)	294.25	273.46
Stdev (nm)	174.90	195.21

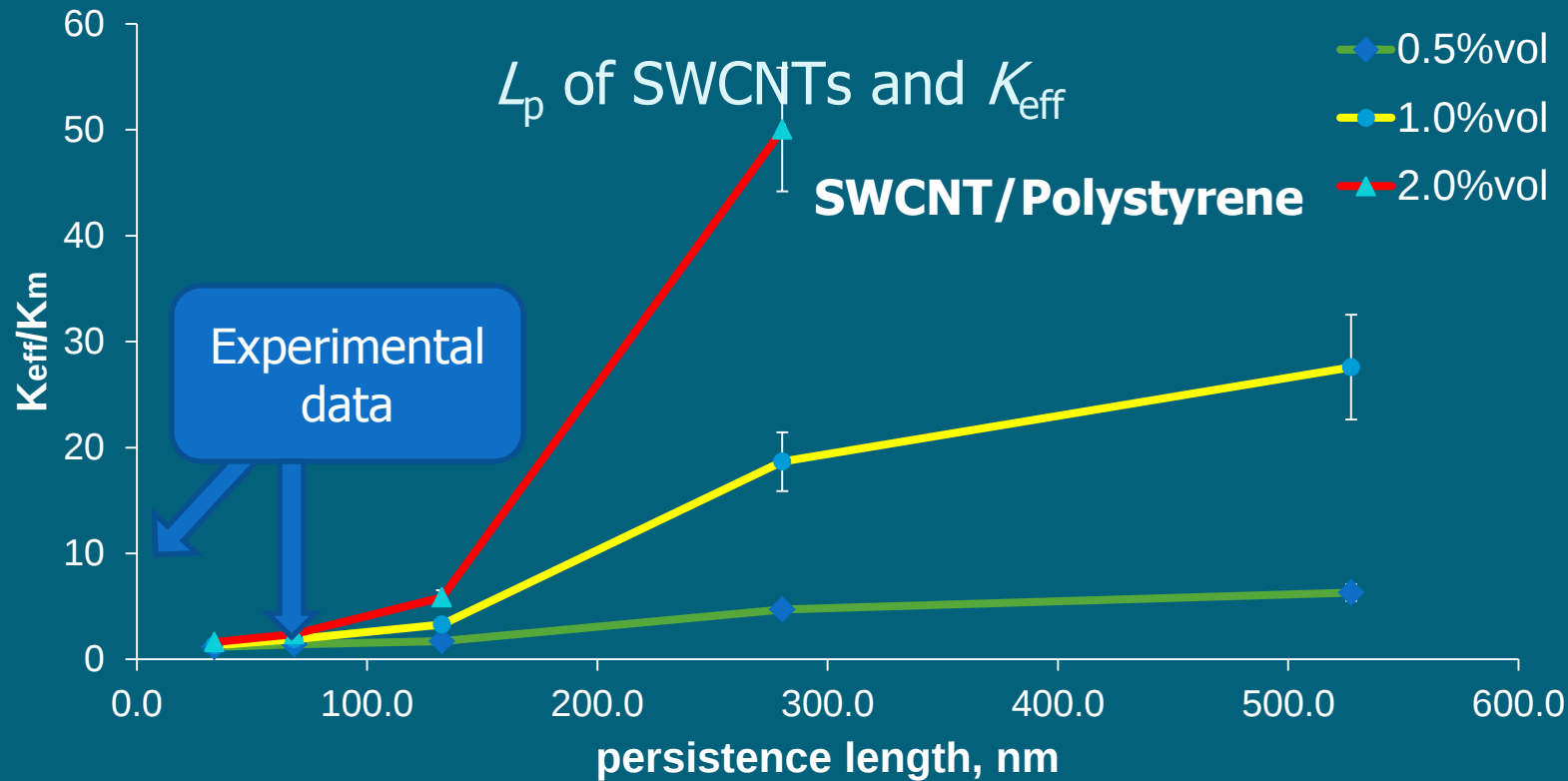
L_p MWCNTs $\approx$ 271nm, Lee *et al.*, JPCC 111(51) 2007

=> The SiO₂ coating did not alter the persistence length of MWCNTs



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Modeling of Thermal Conductivity Monte-Carlo method



Average L_p (nm)	33.6	68.4	132.6	280.3	527.4
Critical angle (degree)	90	43.2	21.6	10.8	5.4



Effect of End-to-End Length



Average L_e (nm)	155	218	321	289	149
Average L_p (nm)	30	55	179	398	812
L_{contour} (nm)	750	600	450	300	150
Average K_{eff}/K_m	1.79	2.74	6.94	2.96	1.14
$\text{Var}(K_{\text{eff}}/K_m)$	0.42	0.39	1.09	0.41	0.03

$L_{\text{end-to-end}} = f(L, L_p)$ is the key nanotube length that affects the effective thermal conductivity (K_{eff}).



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Summary



- Uniform growth of CNFs and CNTs was achieved on large carbon fabric
- Catalyst loading, reaction time, catalyst deposition, and hydrogen dilution were found to affect the growth morphology
- Carbon fiber with CNT showed slight increase in tensile properties and thermal conductivity at both fiber and composite levels
- However, slight decrease in interfacial properties of CNT-grown fibers were due to non-uniform growth
- Step gradient interface modification of CNT showed slight improvement in thermal conductivity
- Effect of CNT wavyness seemed to affect thermal conductivity of nanocomposites



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