

# Effect of Electron Beam Irradiation on the Tensile Properties of Carbon Nanotube Sheets and Yarns

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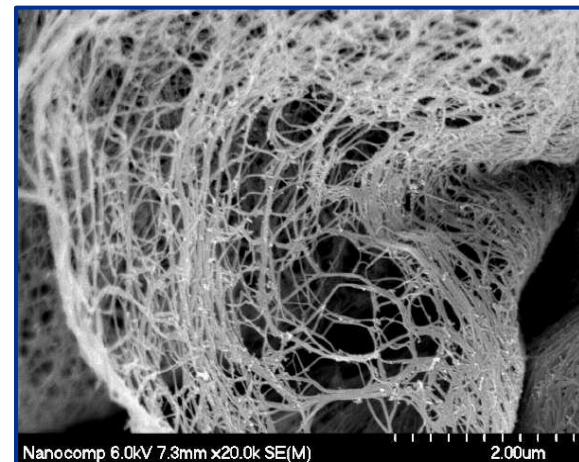


# Presentation outline

- Background and Motivation
- Experimental
- Results and Discussion
- Conclusions

# Background and Motivation

- Lightweight materials and structures
  - Reduced vehicle mass
  - Incorporation of nanostructured reinforcement could decrease aircraft and spacecraft weight by one-third
- Strength of carbon nanotubes (CNTs)
  - 1 TPa  $E'$  and 100 GPa tensile strength (SWNTs via arc discharge)
- Properties much lower in commonly used nanomanufacturing methods
- Weakness attributed to entanglements, slippage of CNTs, van der Waals forces



SEM image of Nanocomp CNT sheet

**Goal is to investigate various routes to introduce covalent crosslinks in CNTs via e-beam irradiation for increased tensile strength**

# Crosslinking of CNTs

- **Common irradiation methods<sup>1-4</sup>**
  - Microwave irradiation
  - Electron beam energy
- Electron beam irradiation usually carried out using TEM
- Covalent crosslinking in CNTs is believed to take place at sites where vacancy defect edges face each other
- E-beam irradiation introduced defects (loose or dangling bonds) that can lead to crosslinking

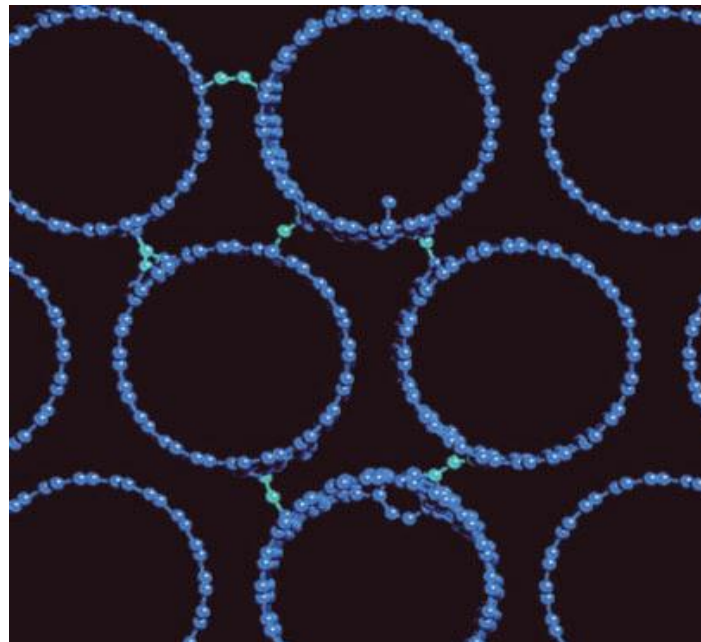


Image taken from Thess, A., *et. al*, Crystalline Ropes of Metallic Carbon Nanotubes, *Science* **273**, 483-487 (1996) and Ajayan, P. Banhart, Nanotubes Strong Bundles, *Nature Materials* **3**, 135-136 (2004)

<sup>1</sup>Vázquez, E., Prato, M., Carbon nanotubes and microwaves: interactions, responses, and applications, *ACS Nano*, vol. 3, no. 12, 2009, 3819-3824

<sup>2</sup>Banhart, F., Irradiation of carbon nanotubes with a focused electron beam in the electron microscope, *Journal of Materials Science*, 2006, 41, 4505-4511

<sup>3</sup>Wang, S., Liang, Z., Wang, B., Zhang, C., High-strength and multifunctional macroscopic fabric of single-walled carbon nanotubes, *Advanced Materials* 2007, 19, 1257-1261

<sup>4</sup>Duchamp, M., Meunier, R., Smajda, R., Mionic, M., Magrez, A., Seo, J.W., Forro', L., Song, B., Toma'nek, D., Reinforcing multiwall carbon nanotubes by electron beam irradiation, *Journal of Applied Physics* 108, 2010, 084314-1—084314-6

# Electron beam irradiation setup

## • Materials

- CNT sheets (Nanocomp)
  - As received
  - Functionalized
  - Stretched
- CNT yarns (General Nano and Nanocomp)
- Northeast Ohio (NEO) Beam Facility (Middlefield, OH)

• Energy of electrons: 2 MeV

• Beam current: 36 mA

• Irradiation time: 20-90 min. (fluence  $4.8 \times 10^{16}$  –  $2.2 \times 10^{17}$  e/cm<sup>2</sup> )

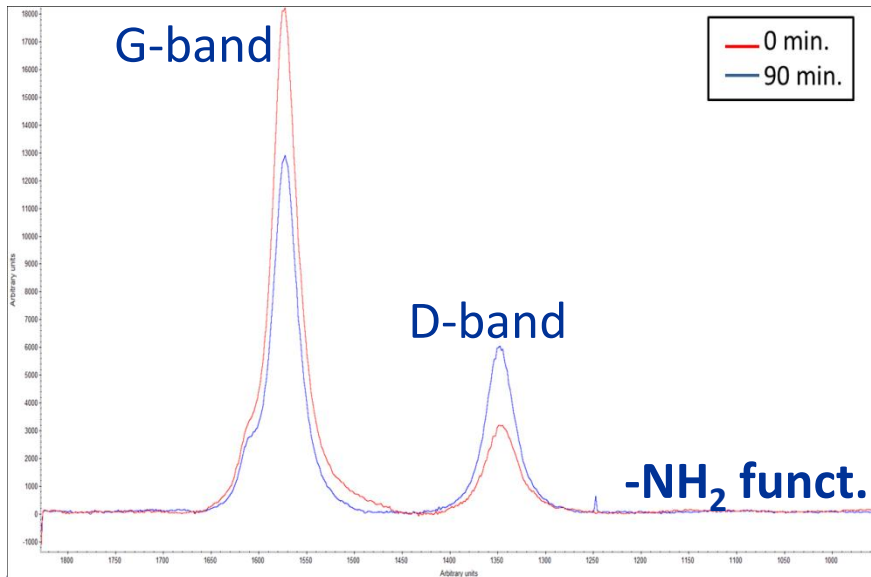
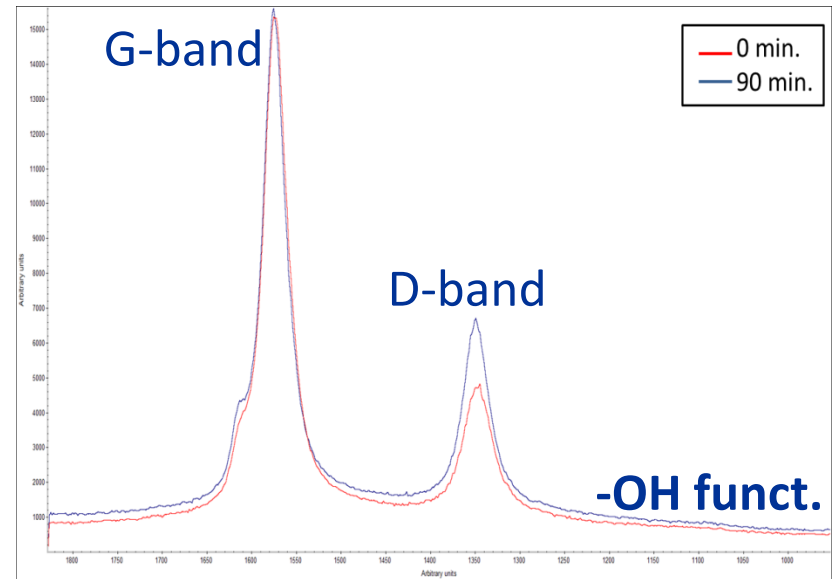
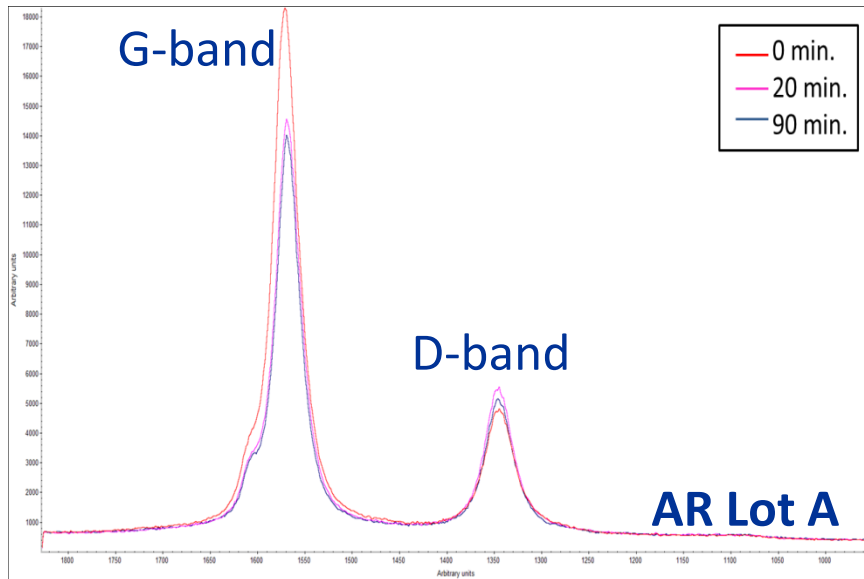
• Irradiated in air



Sample stage  
(water cooled)

CNT samples

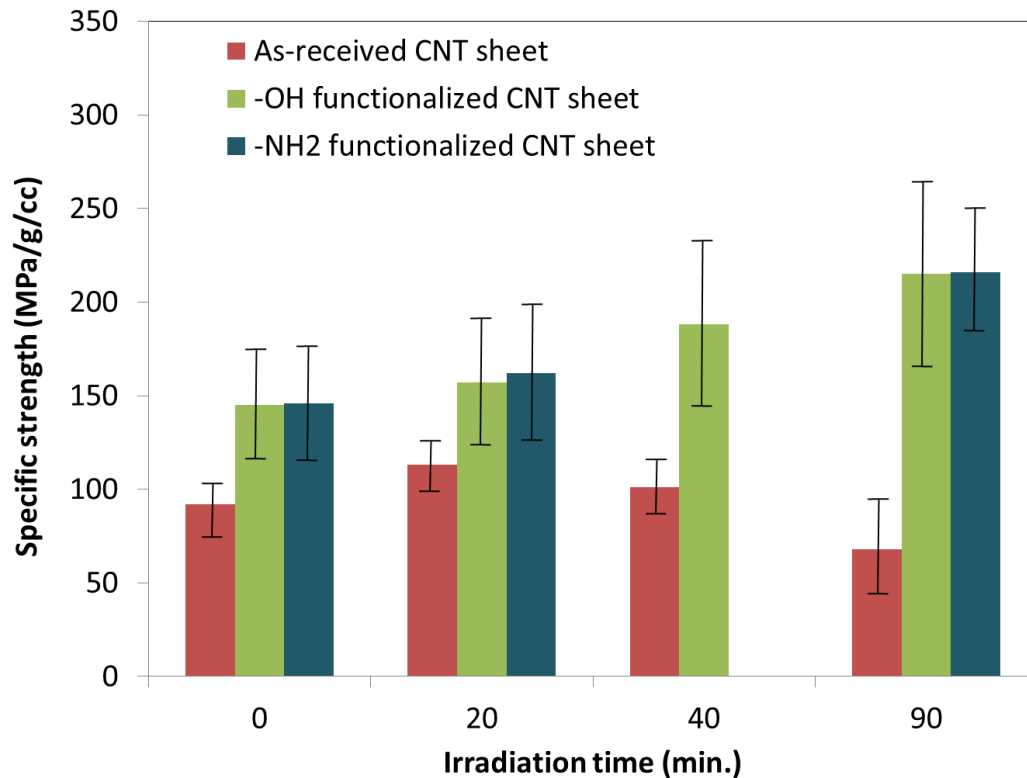
# Effect of irradiation on the structure of CNT sheets



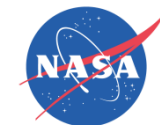
D/G ratio increased in functionalized CNT sheets as the irradiation time/dosage increased



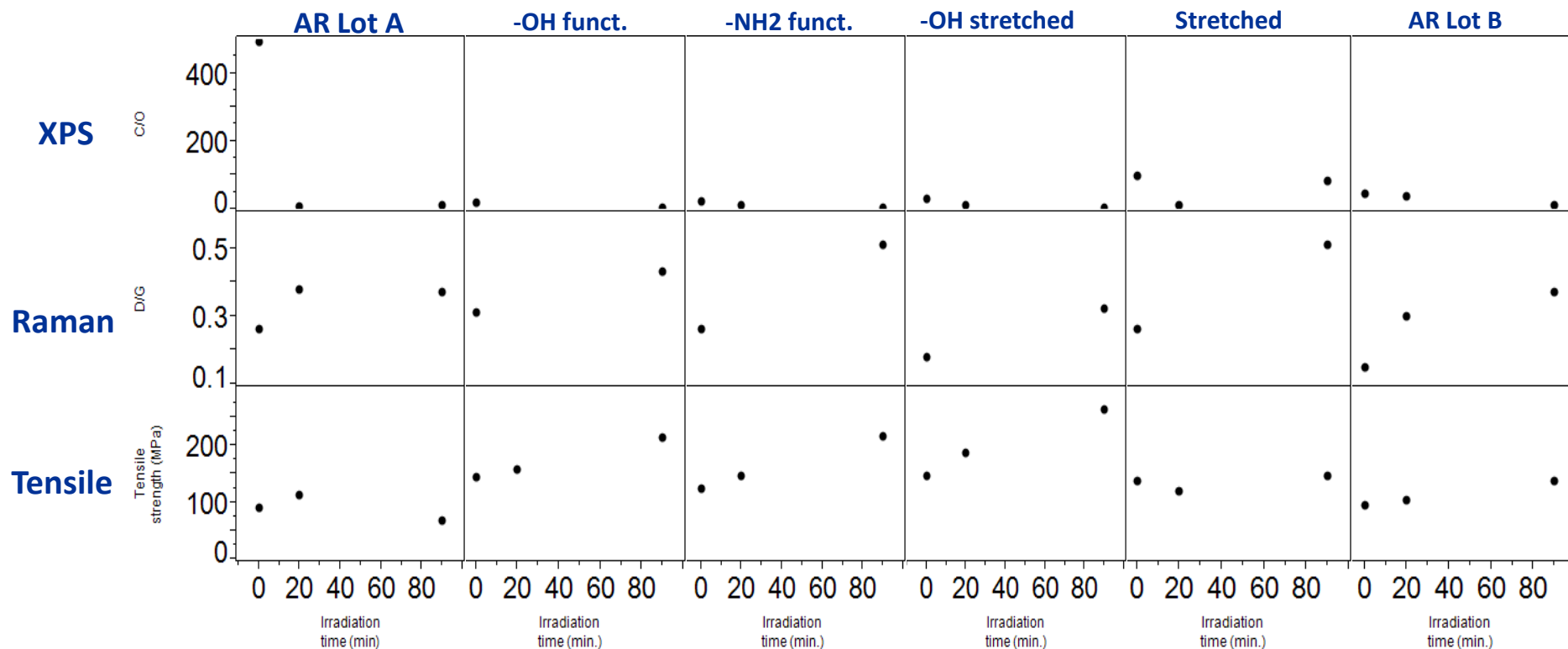
# Functionalization and irradiation effects on tensile properties of CNT sheets



- As-received sheets showed minimal change in tensile strength with increasing e-beam irradiation dosage
- Higher tensile strength observed in -OH and -NH<sub>2</sub> functionalized irradiated sheets
- Irradiation increased tensile strength by approx. 57%
- Over 200% increase in tensile strength in functionalized, irradiated sheets compared to unfunctionalized, irradiated CNT sheets



# Structure-to-property relationship comparison of irradiated CNT sheets

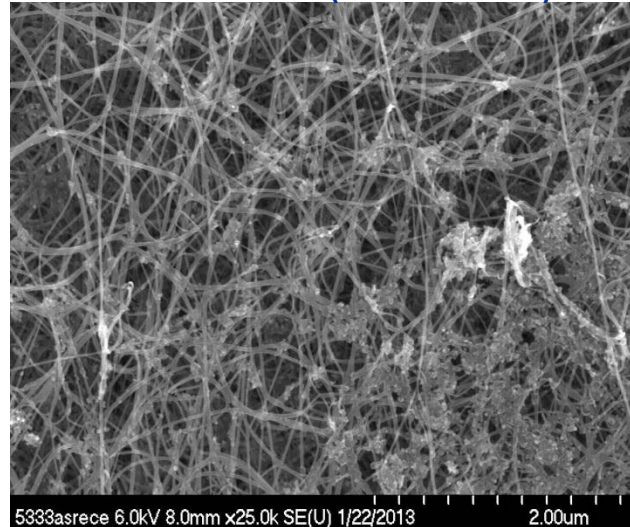


D/G ratio and tensile strength increase with increasing irradiation dosage/time  
 C/O ratio generally decreased with increasing irradiation dosage/time

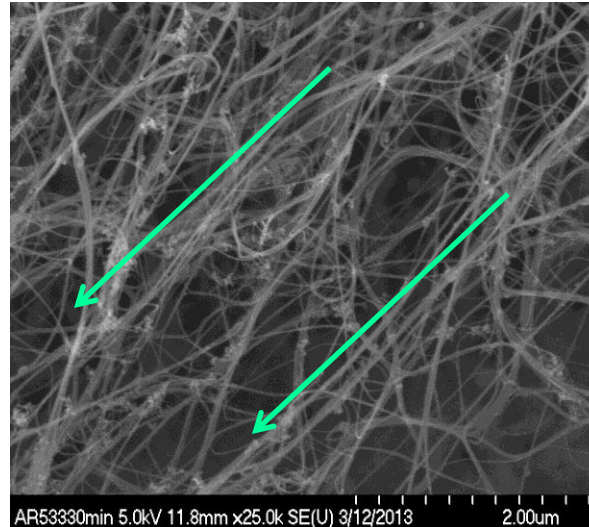


# Surface of irradiated CNT sheets (before and after tensile failure)

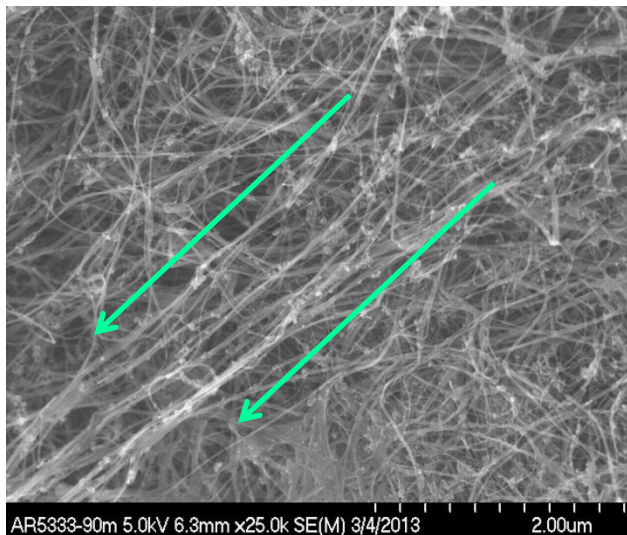
As-received (not tested)



As-received tensile tested



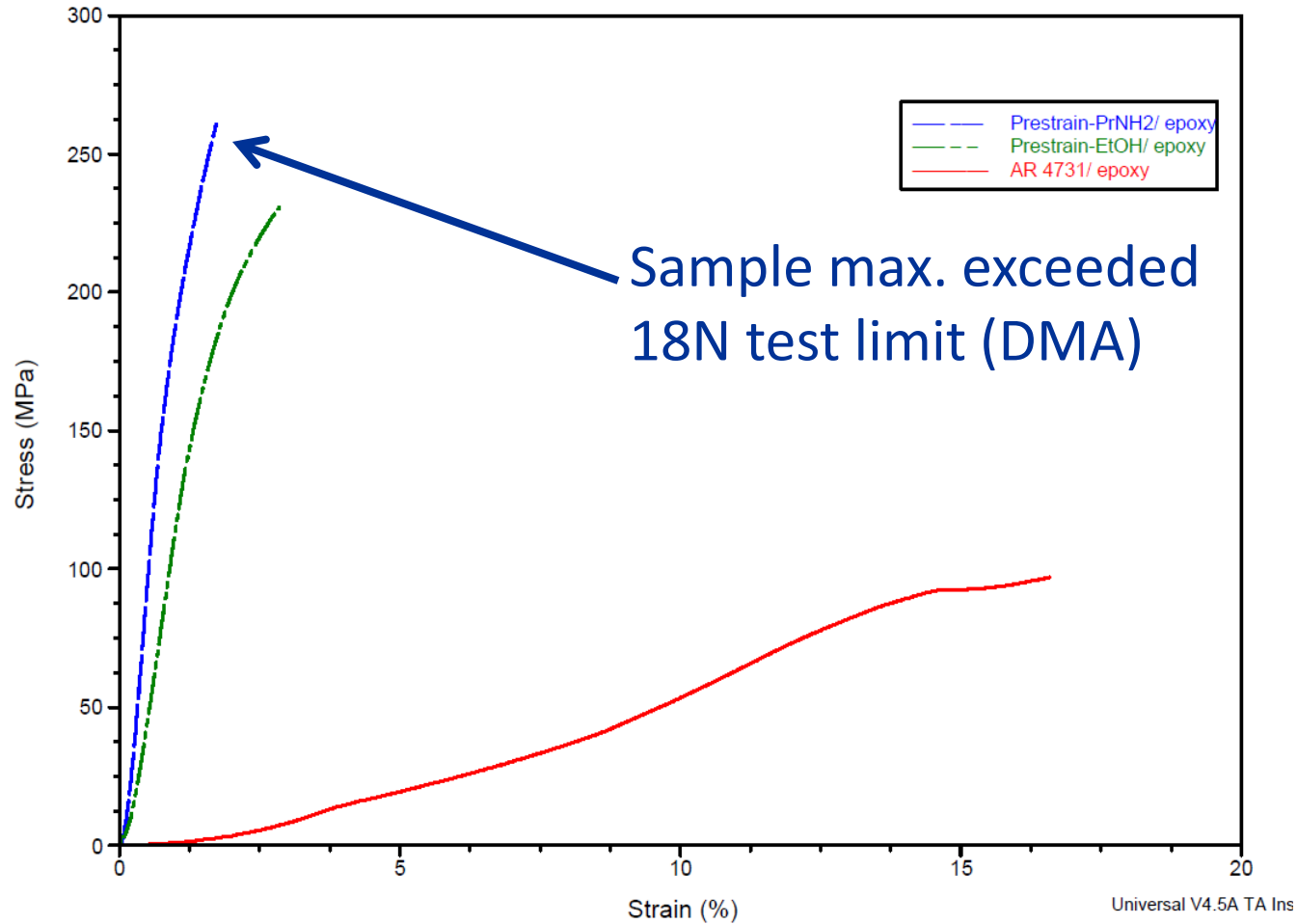
- Random orientation prior to tensile testing
- Sheets could be strained up to 25% in as-received sheets. Lower strain in irradiated sheets
- No visible changes in failure or orientation when irradiating up to 90 min



90 min irradiated tensile tested



# Effect of functionalization on tensile properties of resin infused composites (DMA)

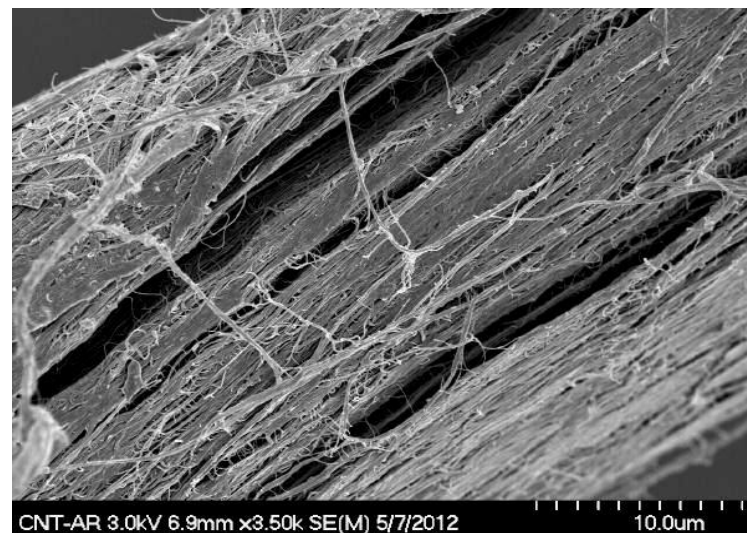
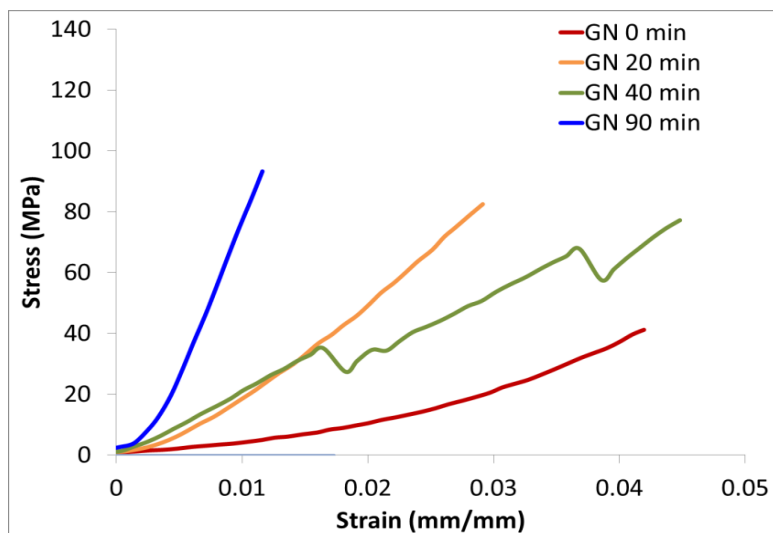
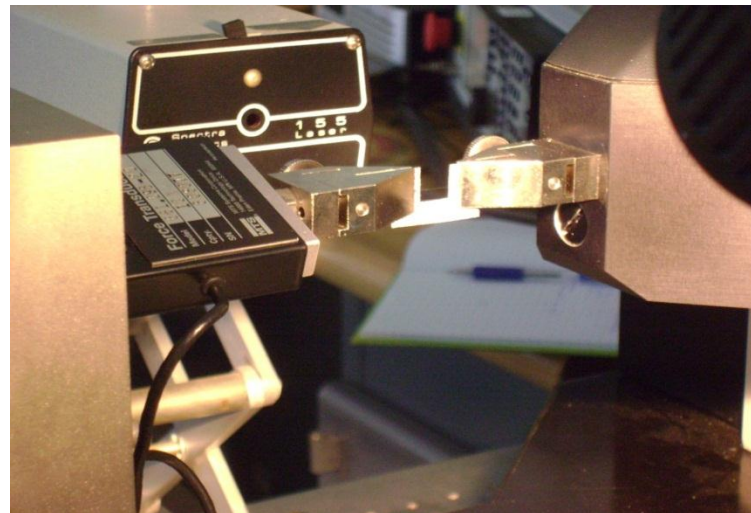


**At least 160% improvement in tensile stress**

**Lot B CNT sheets**

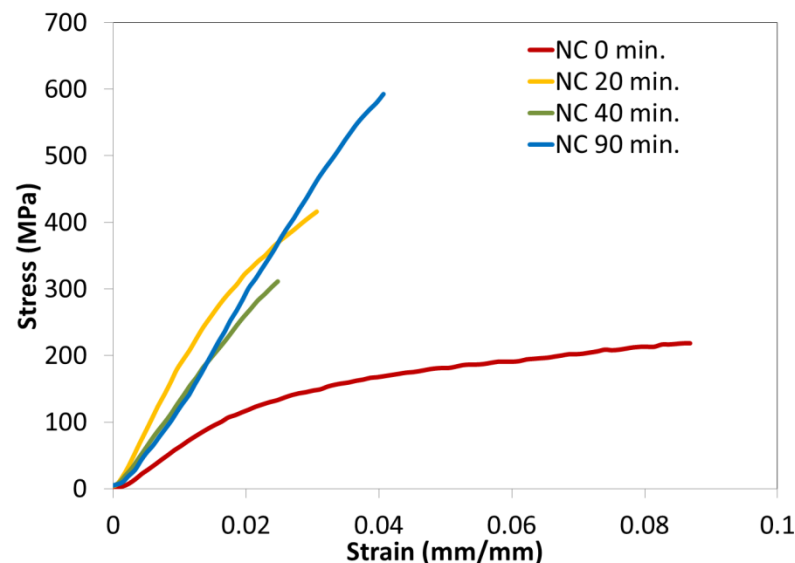
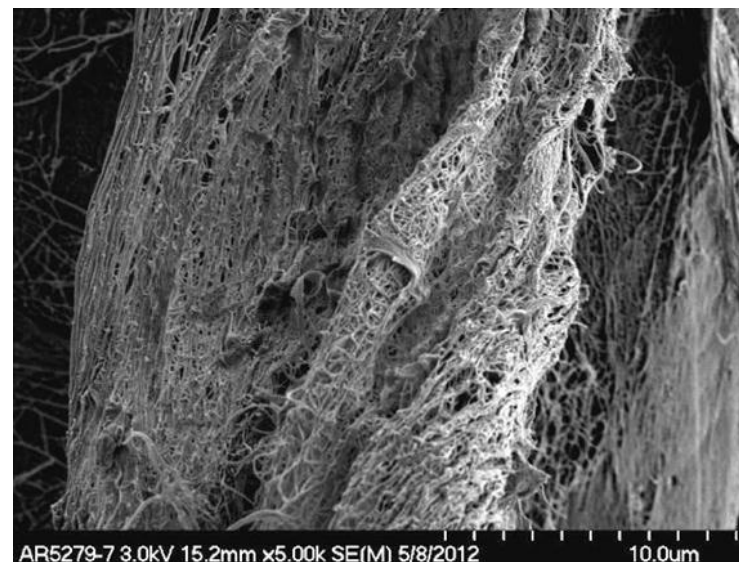
# Effect of irradiation on the tensile properties of CNT yarns (General Nano)

- Mounted on paper brackets
- Tested using Tytron Microtester
- 25 N load cell
- 7-10 specimens/ sample
- Strain rate: 7.5 mm/min



# Effect of irradiation on the tensile properties of CNT yarns (Nanocomp)

- Tensile stress increased with longer irradiation times
- Strain % decreased as irradiation time increased
- Tighter CNT packing in wires was believed to help with crosslinking in unfunctionalized CNT wires



# Tensile properties of irradiated CNT yarns

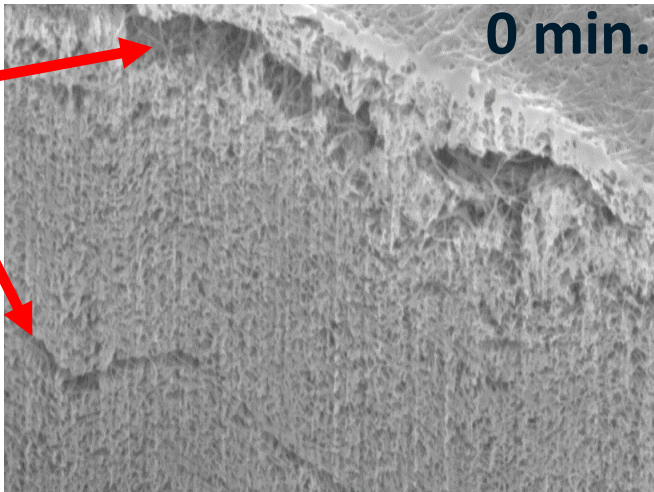
General Nano	Time (min.)	Tensile stress (MPa)	Stress (N/tex)
	0	$54.4 \pm 20.1$	$0.21 \pm 0.05$
	20	$67.9 \pm 24.6$	$0.28 \pm 0.1$
	40	$56.1 \pm 33.9$	$0.20 \pm 0.1$
	90	$90.9 \pm 53.0$	$0.16 \pm 0.08$
Nanocomp			
	0	$202.0 \pm 28.2$	$0.39 \pm 0.04$
	20	$394.5 \pm 56.5$	$0.69 \pm 0.06$
	40	$319.9 \pm 148.1$	$0.6 \pm 0.1$
	90	$587.7 \pm 300.1$	$0.97 \pm 0.1$



Large variation in diameter  
measurements

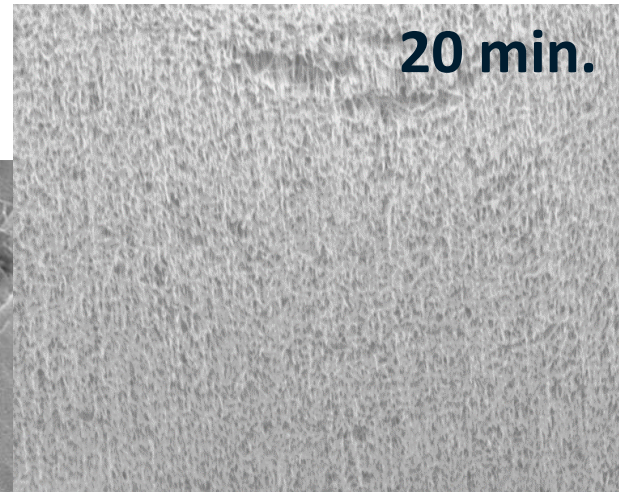
# Irradiation effects on CNT yarns (Nanocomp)

**Voids**



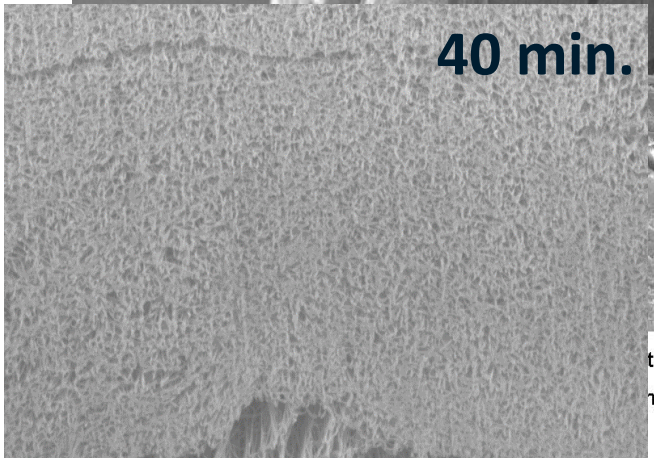
0 min.

Mag = 25.00 KX WD = 5.1 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00  $\mu$ m FIB Probe = 30KV:50pA  
1  $\mu$ m FIB Imaging = SEM EHT = 5.00 kV Tilt Angle = 54.0  $^{\circ}$  Pixel Size = 11.87 nm System Vacuum = 5.60e-006 Torr



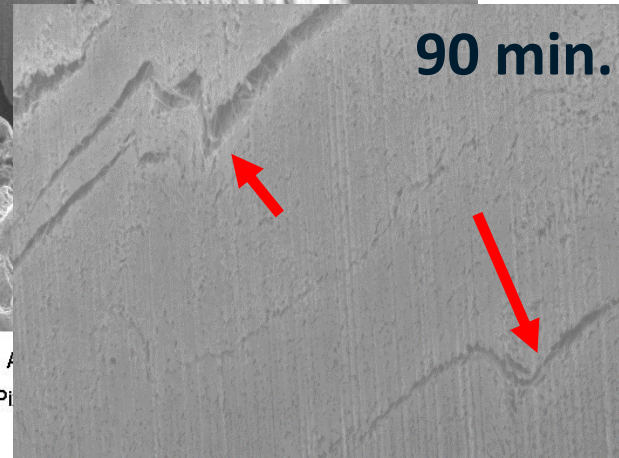
20 min.

Mag = 25.00 KX WD = 5.0 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00  $\mu$ m FIB Probe = 30KV:50pA  
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40 min.

Mag = 25.00 KX WD = 5.1 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00  $\mu$ m FIB Probe = 30KV:50pA  
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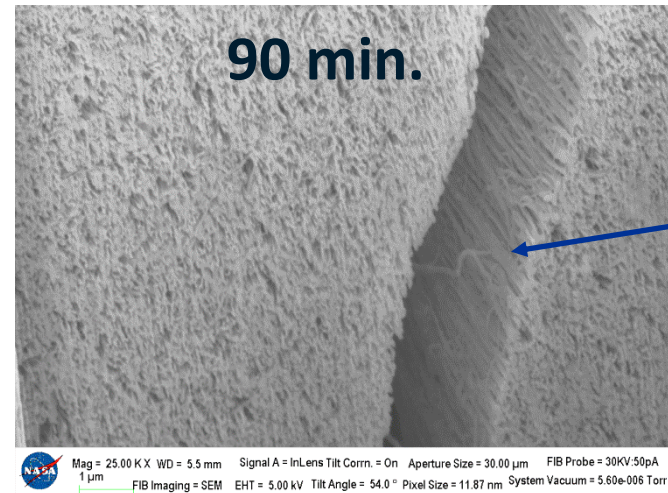
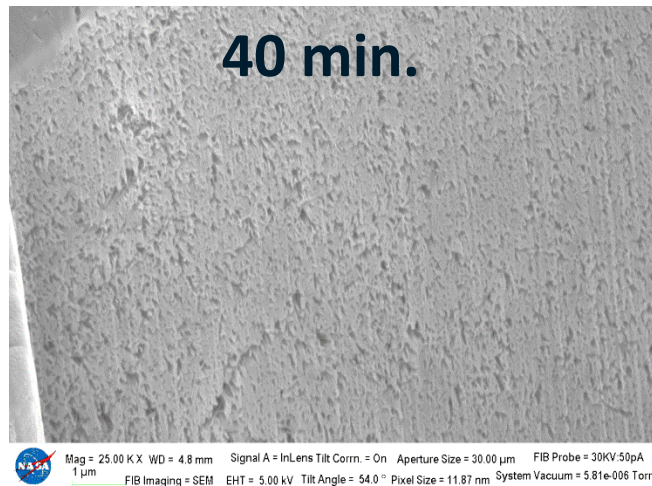
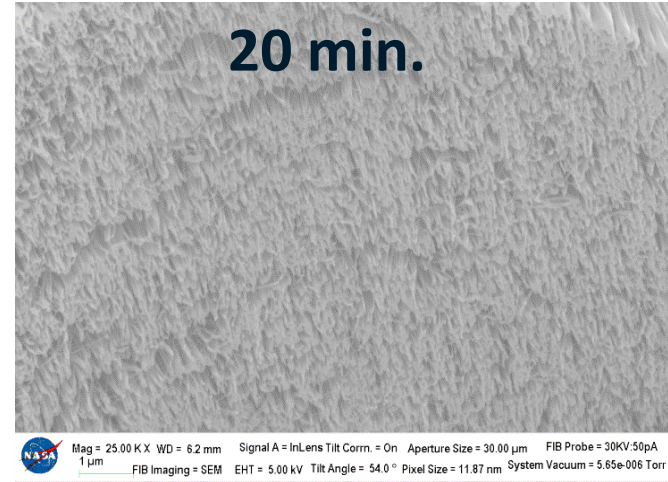
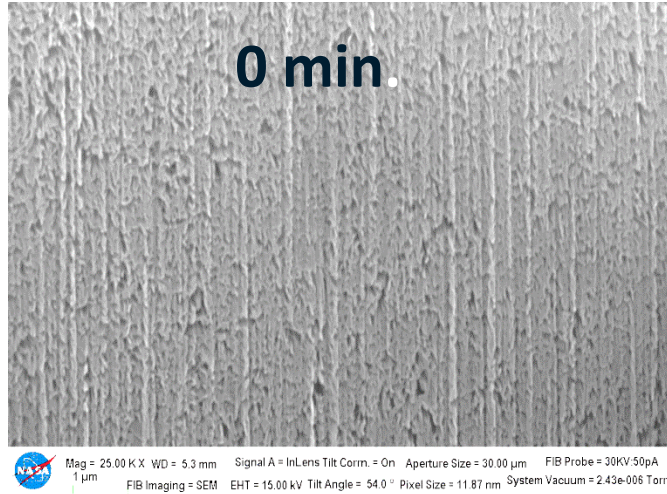
90 min.

Mag = 25.00 KX WD = 5.1 mm Signal A = InLens Tilt Corr. = On Aperture Size = 30.00  $\mu$ m FIB Probe = 30KV:50pA  
1  $\mu$ m FIB Imaging = SEM EHT = 5.00 kV Tilt Angle = 54.0  $^{\circ}$  Pixel Size = 11.87 nm System Vacuum = 5.70e-006 Torr

**Tighter CNT packing as irradiation time increases**



# Irradiation effects on CNT yarns (General Nano)



**Voids**



## Conclusions

- Irradiating for 90 minutes led to at least a 47% increase in tensile strength for untreated CNT sheets
- Significant increase in tensile strength observed in resin infused composites containing functionalized CNT sheets compared to unfunctionalized CNT sheets
- FIB microscopy revealed CNTs in wires became denser with increasing irradiation dosage





# Acknowledgements

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