INCREASED TENSILE STRENGTH OF CARBON NANOTUBE YARNS AND SHEETS THROUGH CHEMICAL MODIFICATION AND ELECTRON BEAM IRRADIATION

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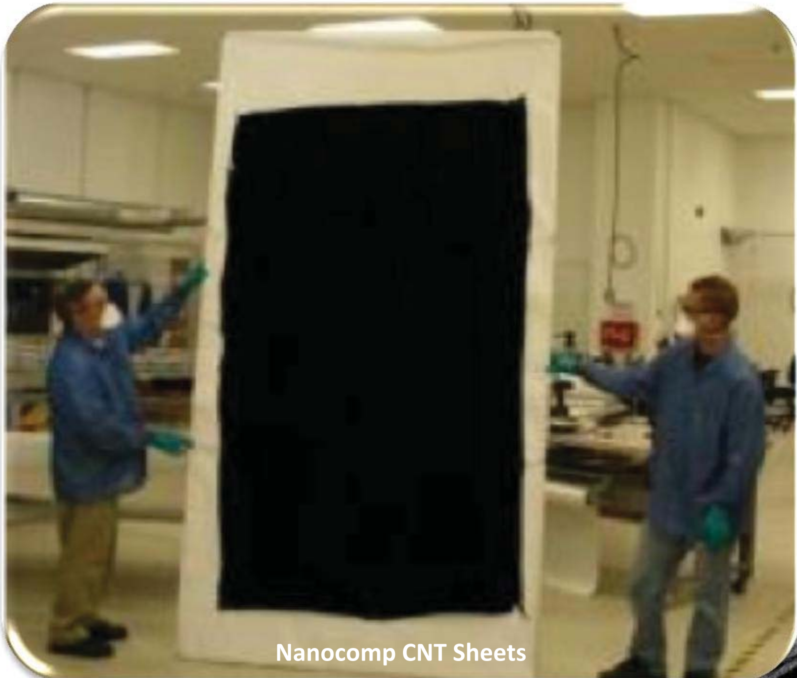
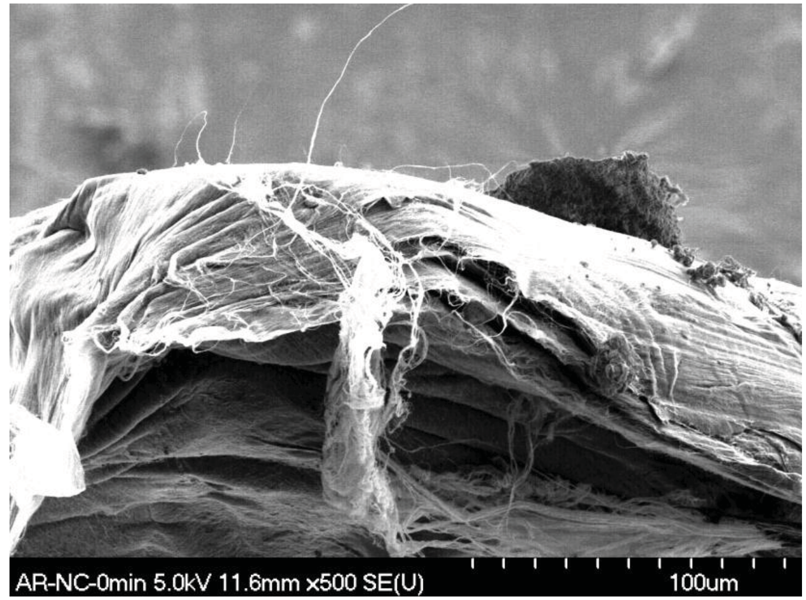
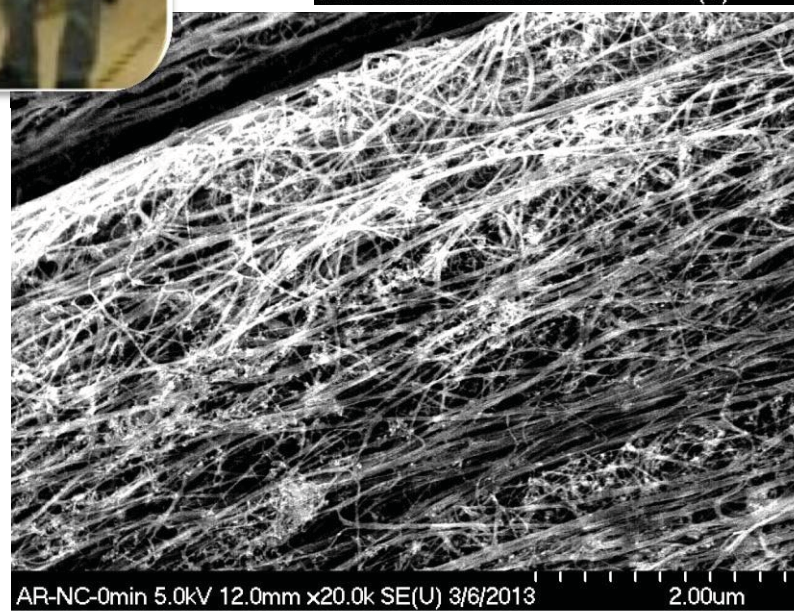
Background

- Individual single wall carbon nanotubes (SWCNTs) have been widely investigated for weight reduction in aerospace structures owing to a theoretical tensile strength of 75 – 135 GPa for an individual SWCNT, and a measured tensile strength of up to 100 GPa.
- Recent focus has moved toward fabrication of CNT sheets and yarns with projected application as a drop-in replacement for carbon fiber in composite structures.
- The inherent limitation of macro-scale CNT material strength resides in weak intra-tube (shell to shell) and inter-tube shear interactions. Therefore, increasing material strength at both of these levels is crucial to development of high strength CNT material forms.
- We have investigated the combined effects of small molecule functionalization together with e-beam generated cross-linking in an attempt to further increase the tensile properties of CNT sheets and yarns.

CNT Sheet Material

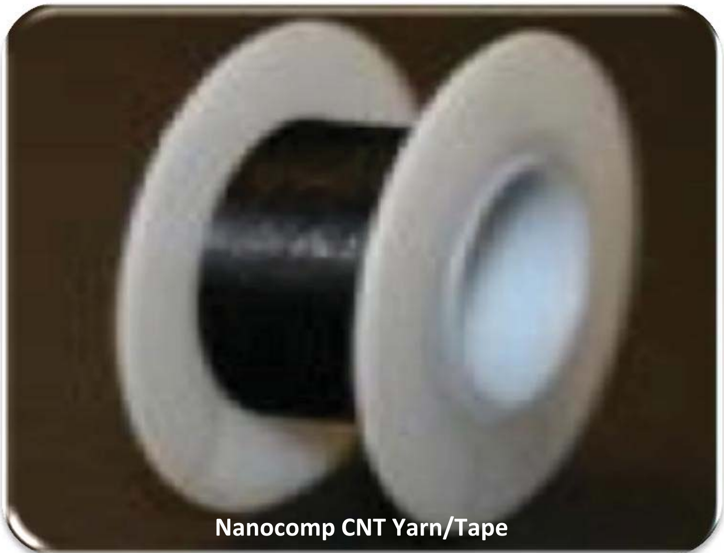


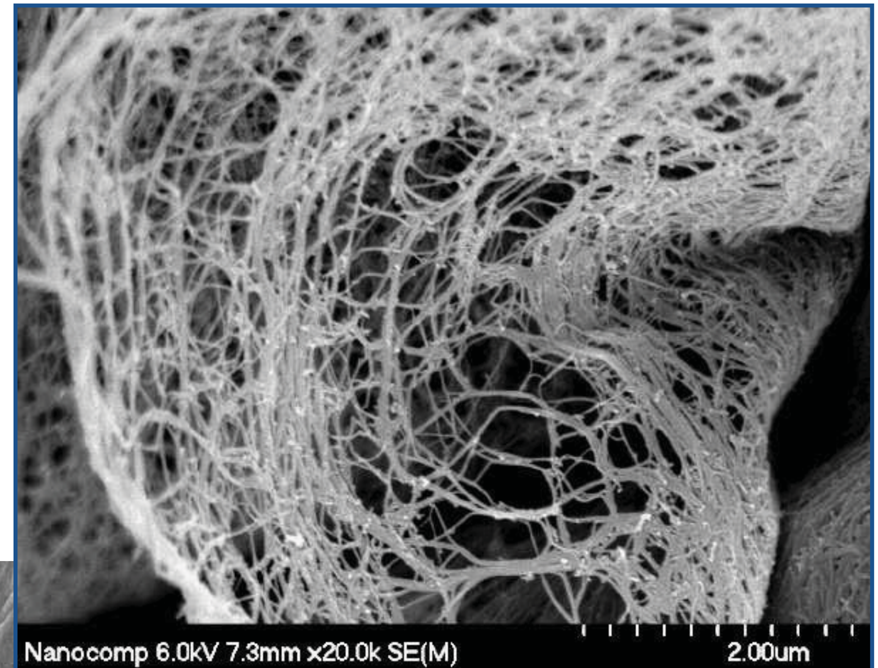


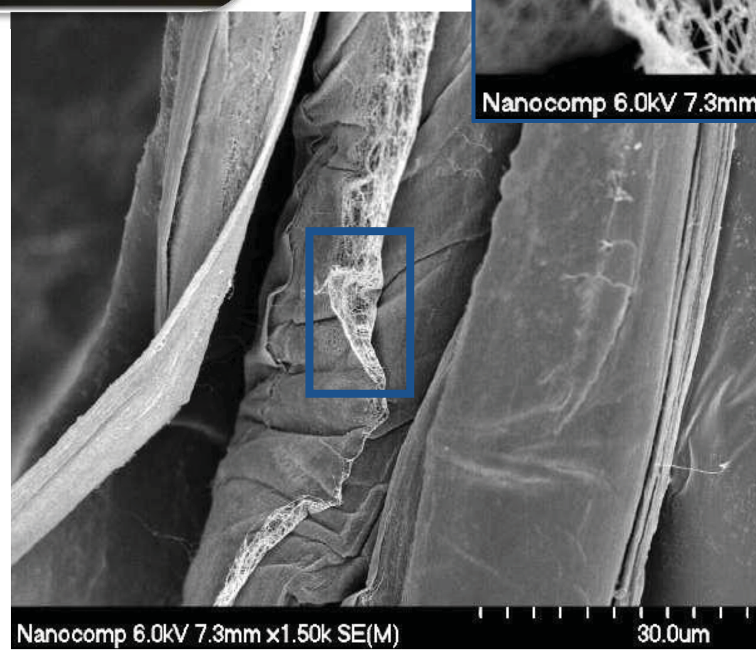


- As-received sheets composed of several compacted layers of CNT sheets.
- Preferential CNT orientation induced during manufacture.

CNT Yarn Material



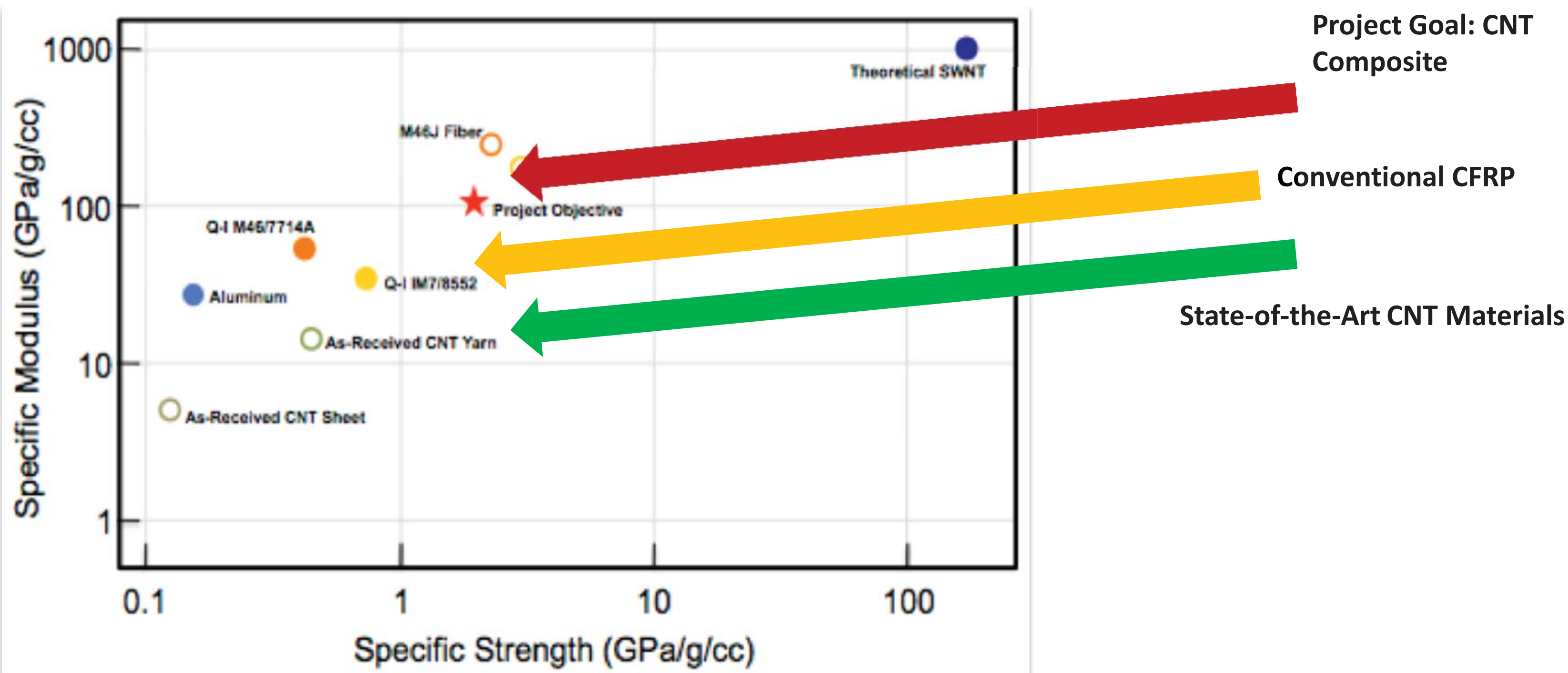




- Relatively greater alignment observed in CNT yarn.
- Entanglement and alignment of CNTs in yarn bundle facilitates crosslinking.

Post-Processing Methodology

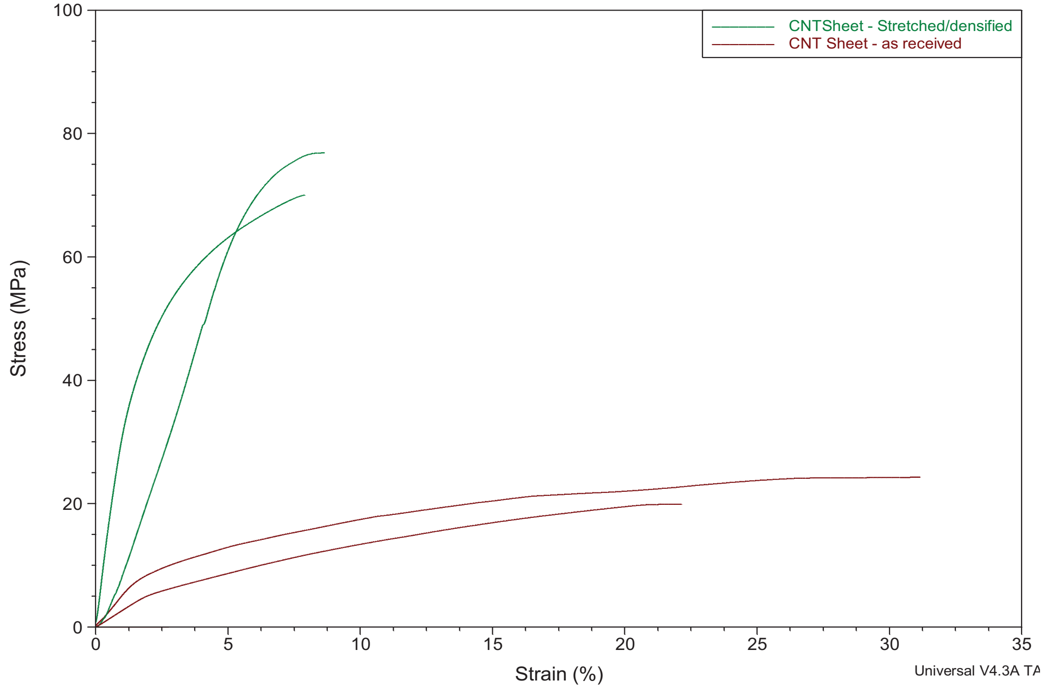
- Pre-strain to increase CNT packing density and alignment.
- Small molecule functionalization
- Electron Beam Crosslinking

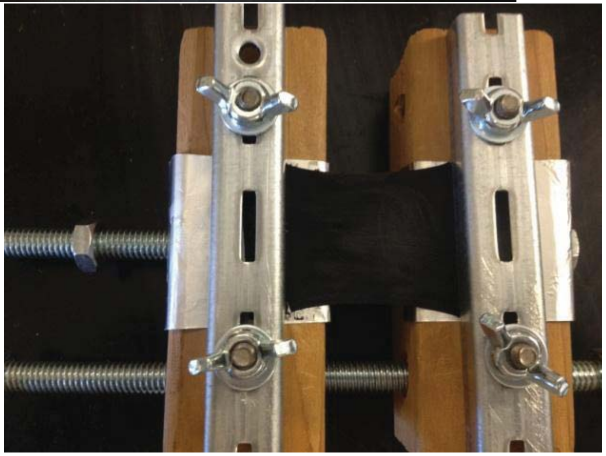


Post Processing- Strain

DMA Tensile Data Following Stretching/ Densification

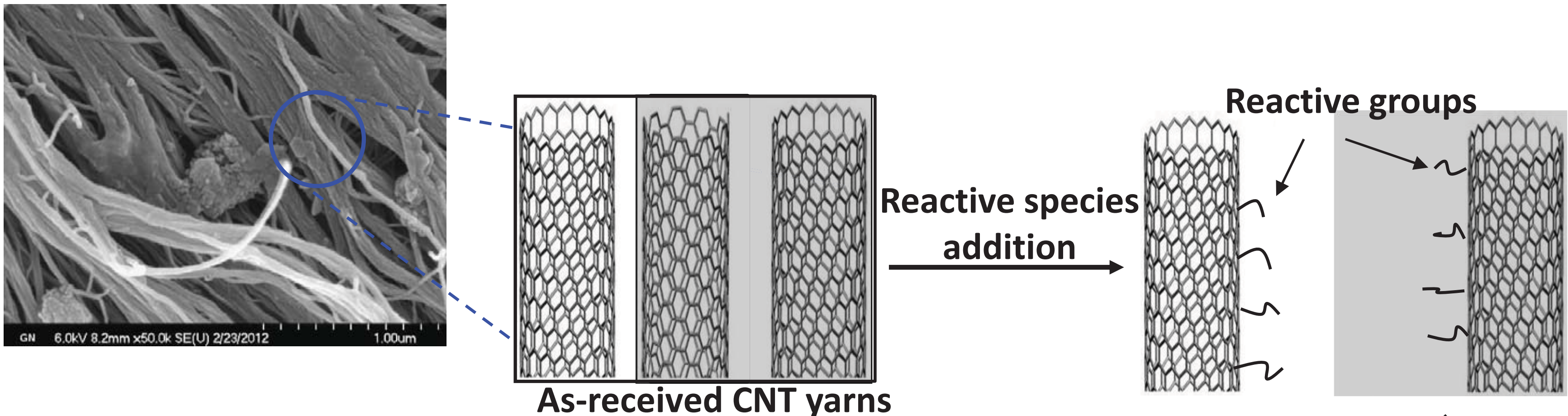
Tensile stress of the CNT Sheet after stretched (ca. 12%) and densification (using acetone) had an increase >200%.



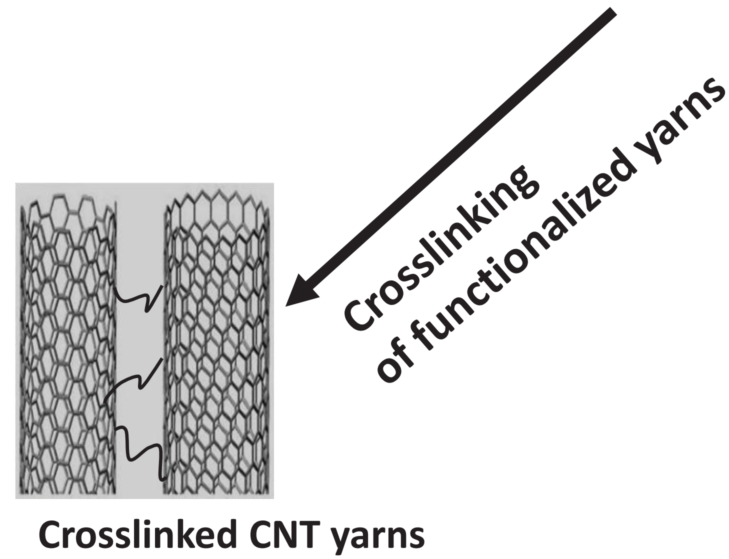


Tensile Stress, MPa	
CNT Sheet as received	CNT Sheet after stretched and densification
22.09 ± 3.08	73.47 ± 4.84

Post Processing- Small Molecule Functionalization



CNT were functionalized with (1) amine and (2) hydroxyl reactive sites. These were chosen to bond with the epoxy matrix that will be used to make composite materials.



Post Processing- Electron Beam Exposure

Exposure levels

- 1×10^{15} e/cm^2
  - 90 sec
- 4.8×10^{16} e/cm^2
  - 20 min
- 9.6×10^{16} e/cm^2
  - 40 min
- 2.2×10^{17} e/cm^2
  - 90 min

Intermediate exposure levels also investigated.

Water cooled Aluminum Plate

CNT material held in place with Kapton tape

Post Modification Characterization

Thickness/Diameter Measurement

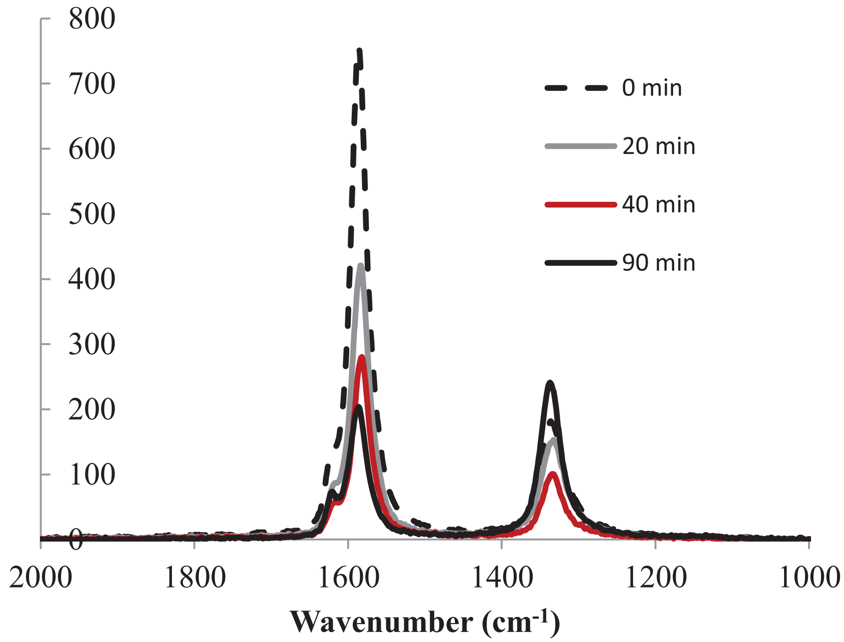
Sheet Thickness/ E-beam exposure time	As Received (mm)	Amine Functionalized (mm)	Hydroxyl Functionalized (mm)
0 min	16.8 ± 3.1	18.0 ± 2.1	15.8 ± 2.9
20 min	20.0 ± 2.2	18.3 ± 2.1	18.7 ± 1.3
40 min	20.3 ± 2.6	15.4 ± 3.0	16.1 ± 1.9
90 min	20.5 ± 3.4	18.0 ± 1.8	17.0 ± 1.7
Yarn Diameter/ E-beam exposure time	As Received (mm)	Amine Functionalized (mm)	Hydroxyl Functionalized (mm)
0 min	67.0 ± 5.0	63.0 ± 5.4	66.7 ± 10.7
20 min	63.2 ± 8.3	66.3 ± 8.3	64.7 ± 6.7
40 min	62.2 ± 3.4	64.5 ± 3.7	73.6 ± 6.3
90 min	60.0 ± 4.8	65.8 ± 4.1	63.4 ± 5.0

Post Modification Characterization- RAMAN and XPS

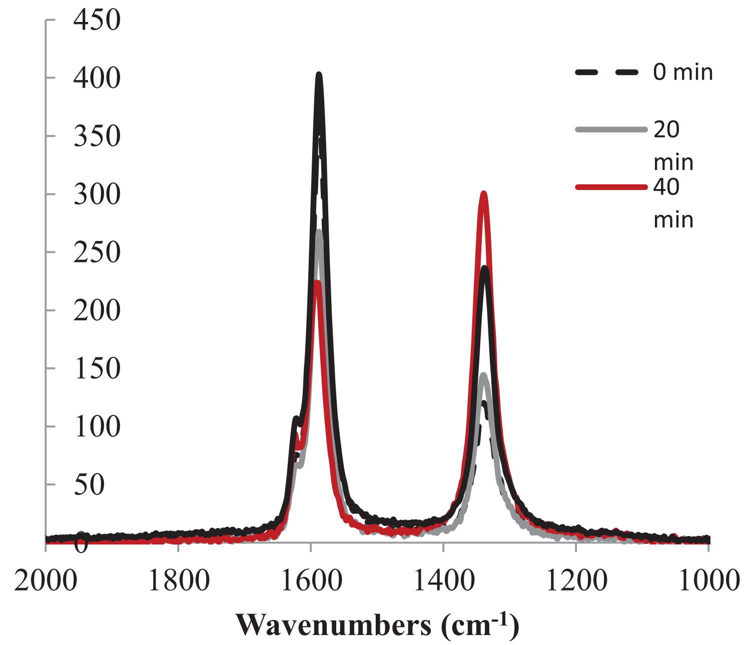
SHEET	Un-functionalized		Amine Functionalized		Hydroxyl Functionalized	
	$I_{G/D}$	C/O	$I_{G/D}$	C/O	$I_{G/D}$	C/O
0 min	3.0 ± 0.2	44.0	2.3 ± 0.2	23.4	3.3 ± 0.5	17.0
20 min	1.5 ± 0.5	37.2	1.7 ± 0.1	10.4	1.5 ± 0.1	10.5
40 min	1.7 ± 0.7	6.5	0.7 ± 0.1	6.5	1.3 ± 0.5	5.4
90 min	0.9 ± 0.2	9.6	1.4 ± 0.1	5.2	0.8 ± 0.1	4.8

YARN	0 min	20 min	40 min	90 min
As- Received	4.8 ± 1.7	1.7 ± 0.2	1.5 ± 0.1	1.0 ± 0.1
Hydroxyl Functionalized	5.2 ± 1.6	1.6 ± 0.7	2.1 ± 0.2	1.4 ± 0.1
Amine Functionalized	2.2 ± 0.8	2.4 ± 0.3	1.3 ± 0.1	1.1 ± 0.1

Post Modification Characterization
RAMAN

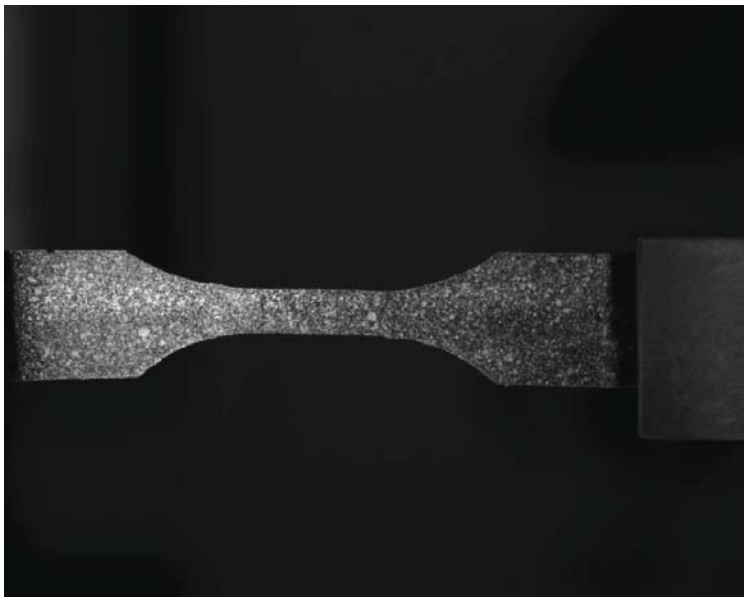


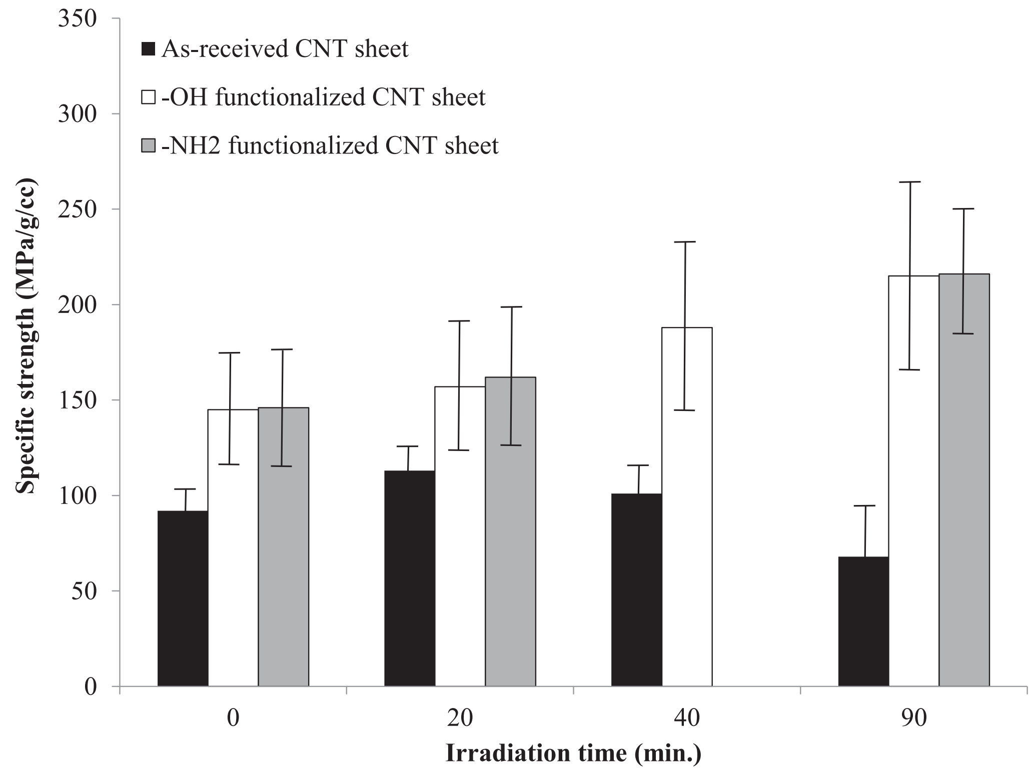
Effect of e-beam irradiation on the G/D ratio of as-received CNT sheet.



Effect of e-beam irradiation on the G/D ratio of 3-aminopropyl functionalized CNT sheet.

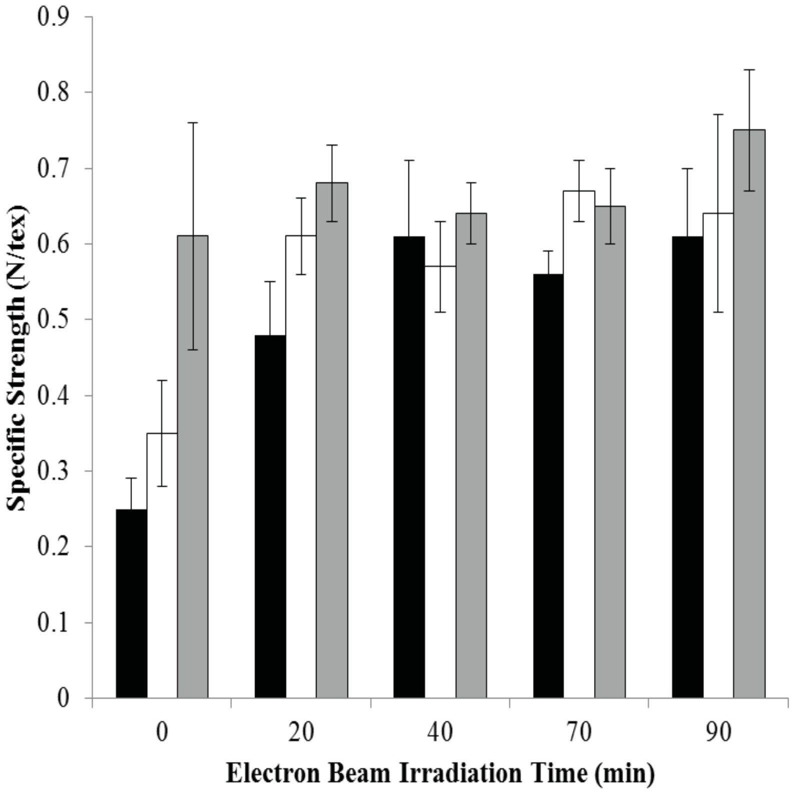
Tensile Test Showed Trend of Increasing Strength with Irradiation and Functionalization

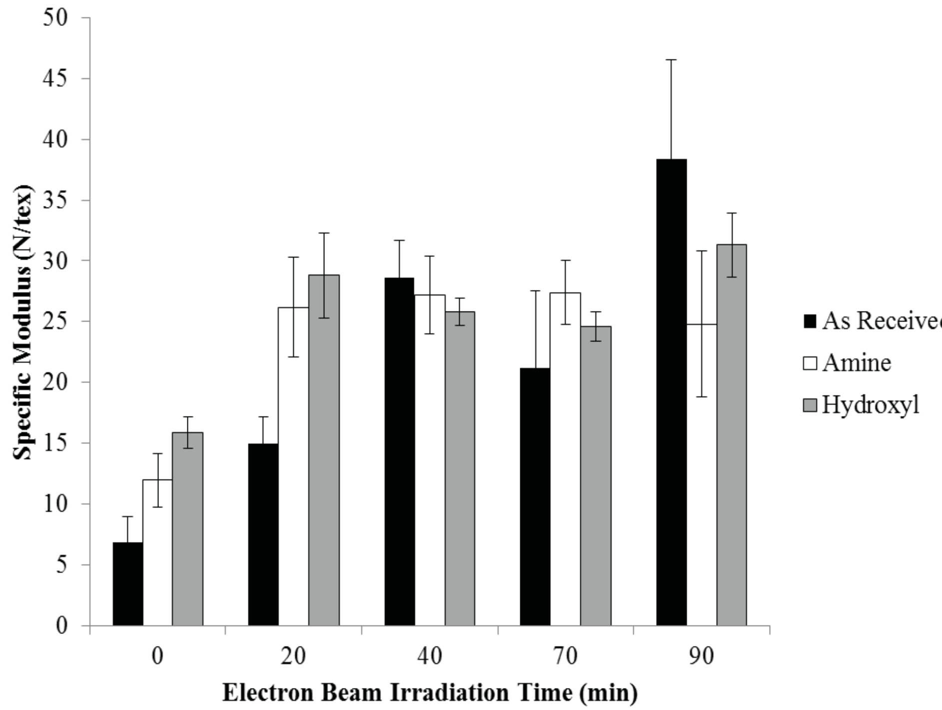




Functionalized sheet material strength was increased with all irradiation doses. The un-functionalized material demonstrated a limit below 90 min of exposure. Sheets were pre-strained.

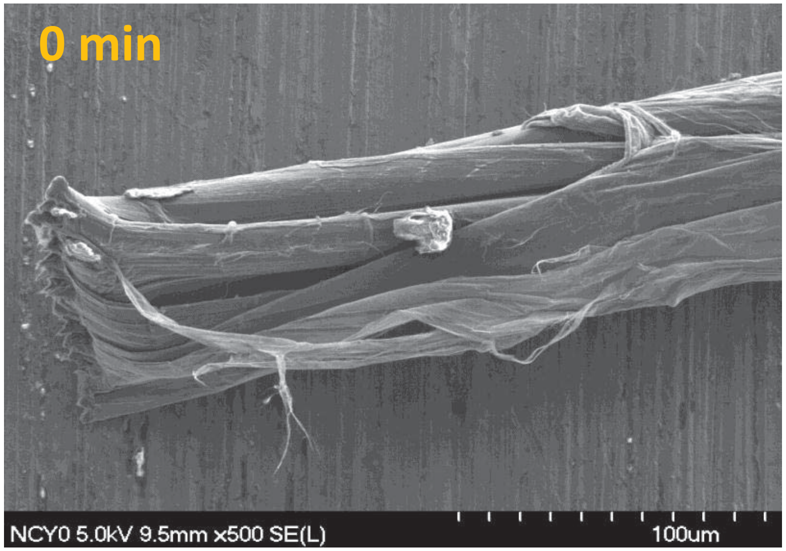
Tensile Tests of Yarn Material

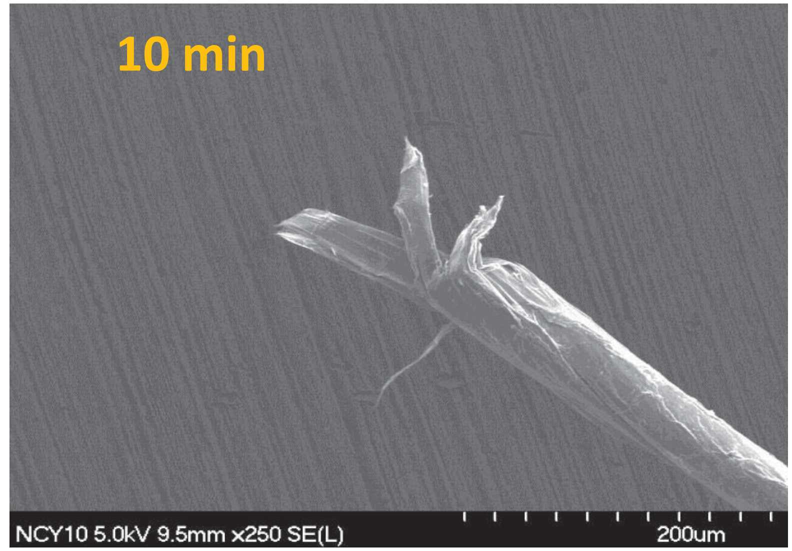


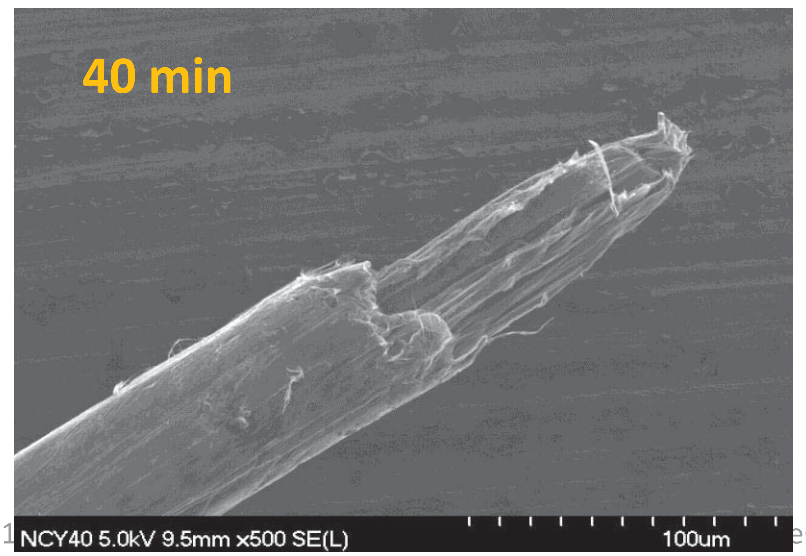


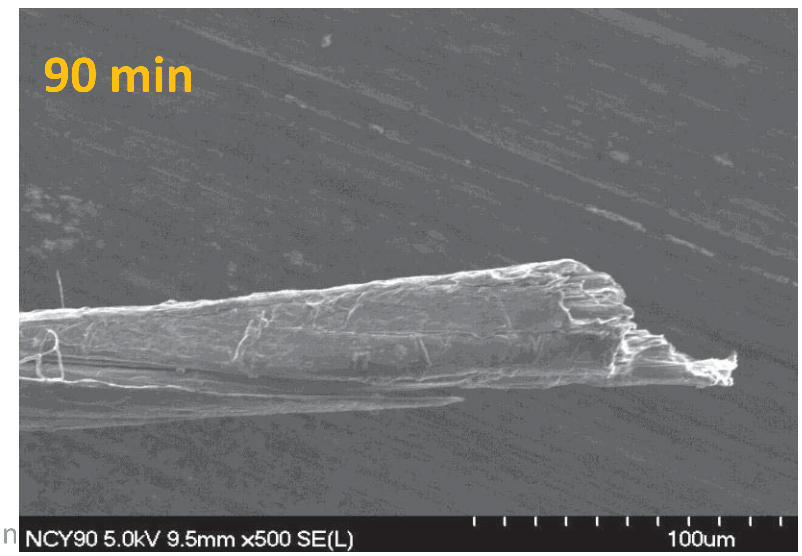
Both strength and modulus increased with functionalization and irradiation time. This was attributed to greater CNT alignment and entanglement within the yarn material relative to the sheet form.

SEM Characterization of Yarn Fracture Surface

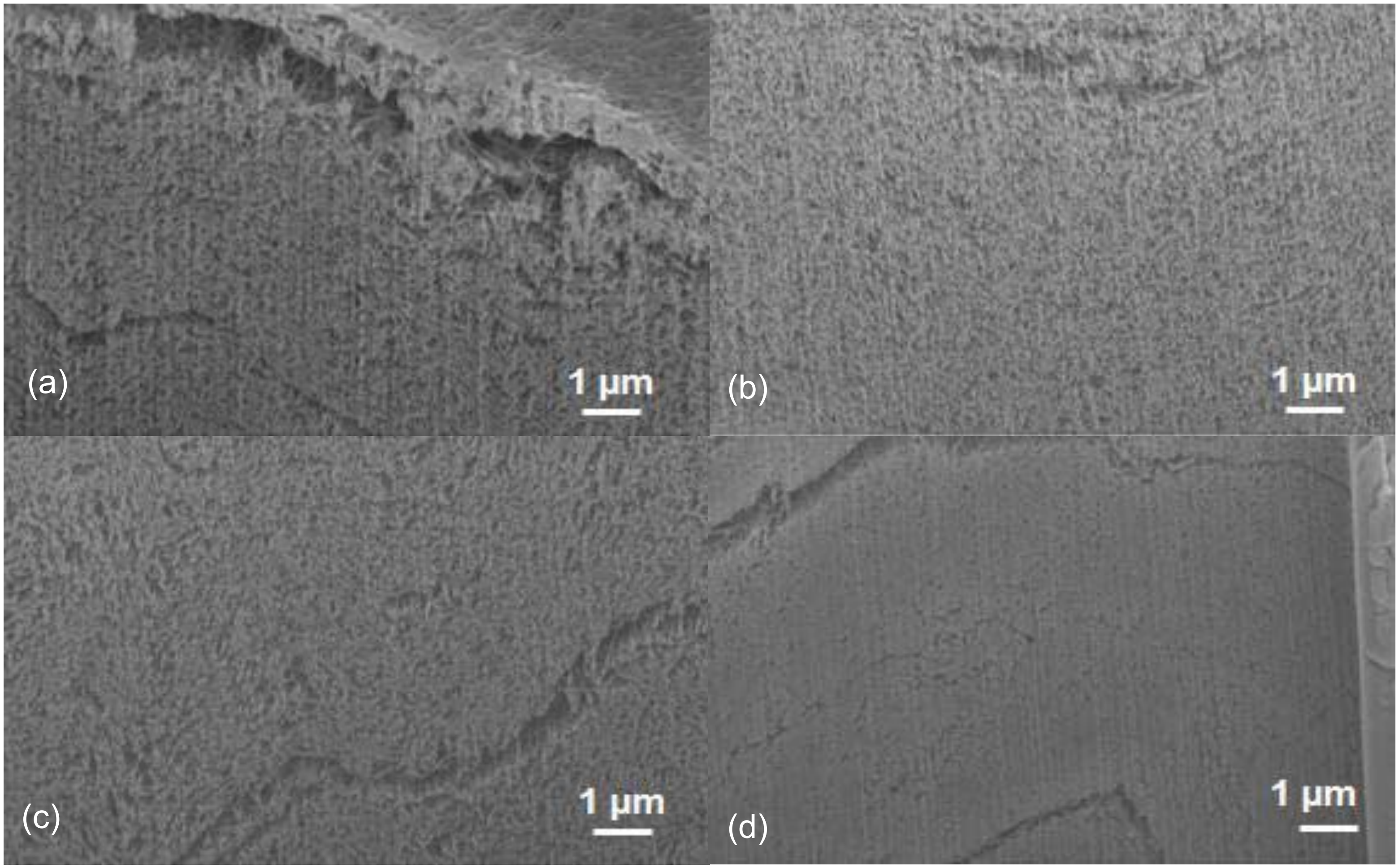






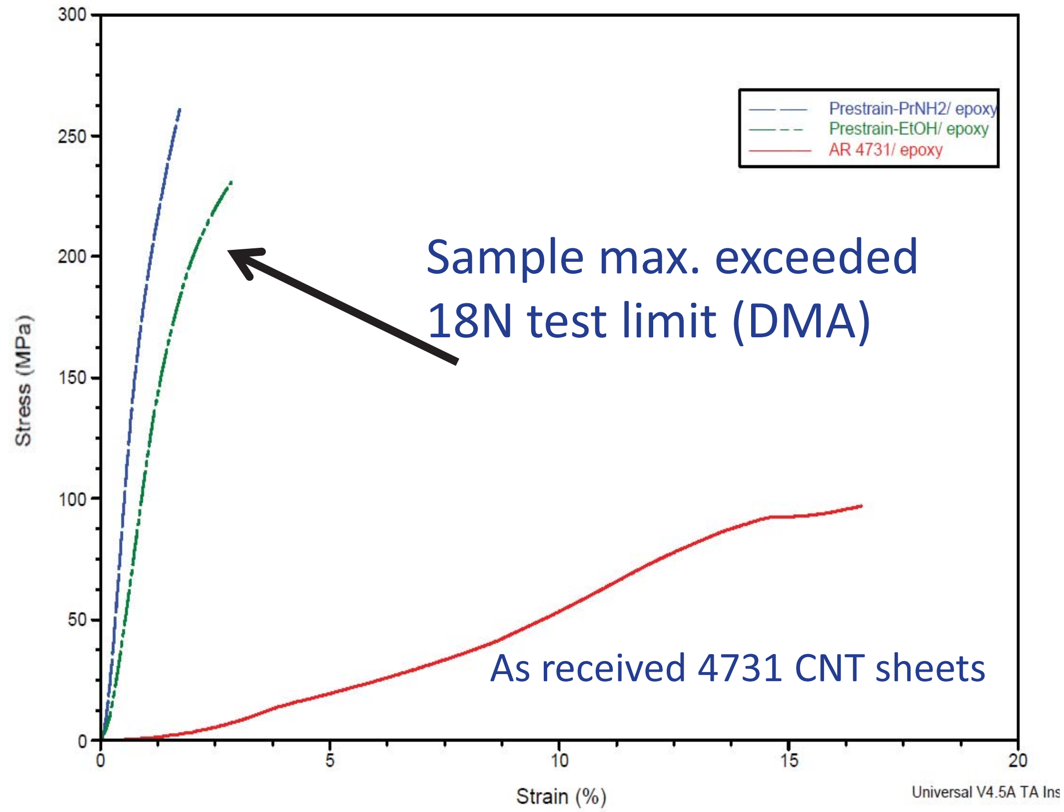


Focused Ion Beam Images Show CNT Yarn Morphology



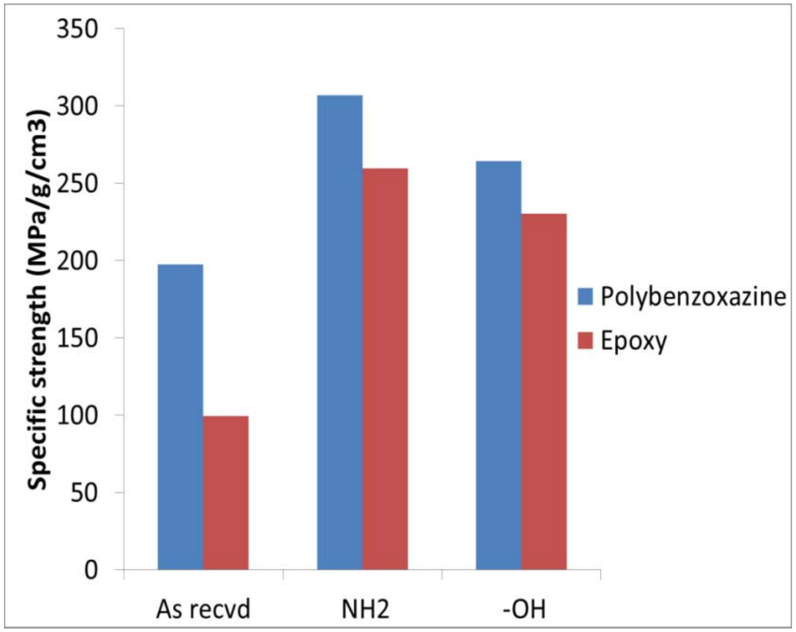
FIB microscopy images of CNT yarn interior morphology following irradiation at (a) 0 min. (b) 20 min., (c) 40 min., and (d) 90 min.

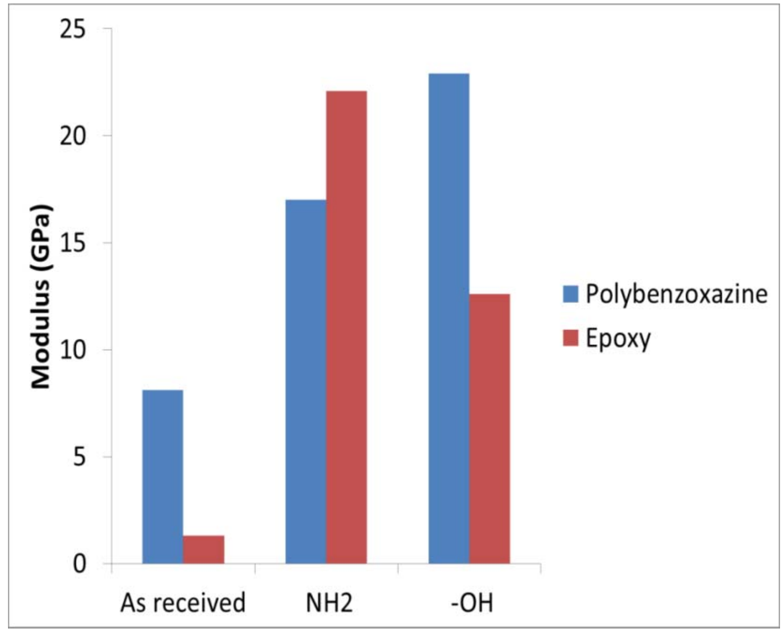
Influence of Resin Infiltration and Tensile Testing

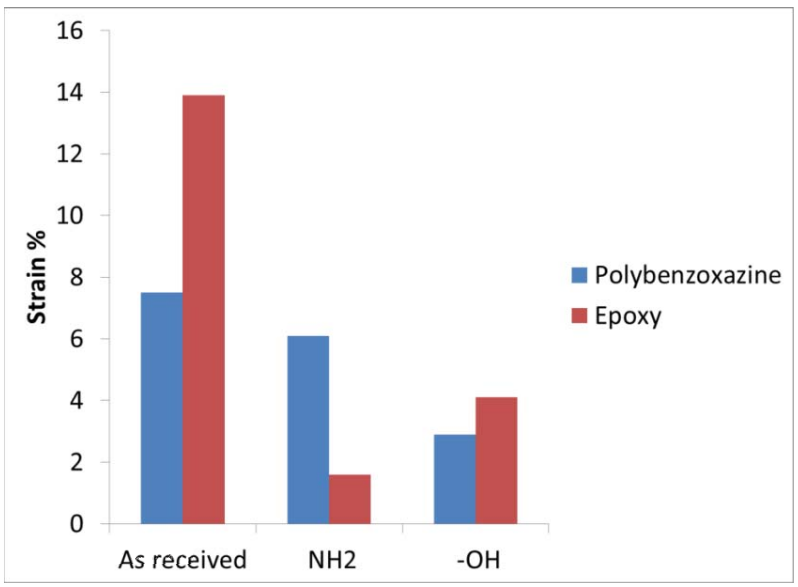


Solvent casting of epoxy into single ply CNT sheets: Dichloromethane was used as the solvent for the resin film casting. The polymer solution was dispensed over the CNT sheet, and a metal block was placed over the CNT sheet during curing. (This sheet was not pre-strained prior to testing)

Single Ply Composite Tensile Tests







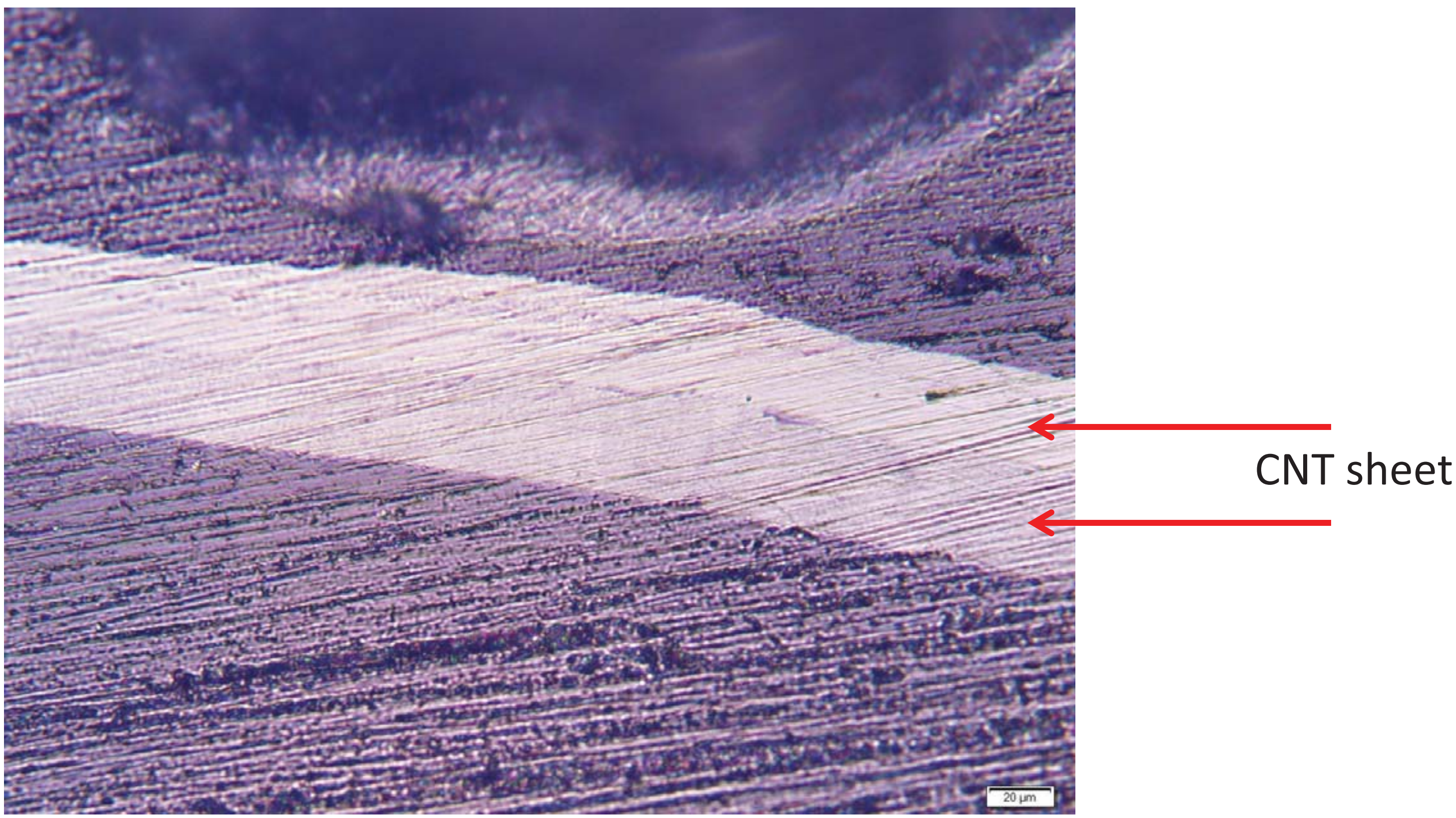
The specific strength of polybenzoxazine- as received CNT sheet composites was 98% higher than that of epoxy- as received CNT sheet

Functionalization of CNT sheets resulted in at least a 130% improvement in specific tensile strength compared to samples that were not functionalized

Functionalization of CNT sheets resulted in a significant increase in the modulus of polybenzoxazine and epoxy resin infused nanocomposites

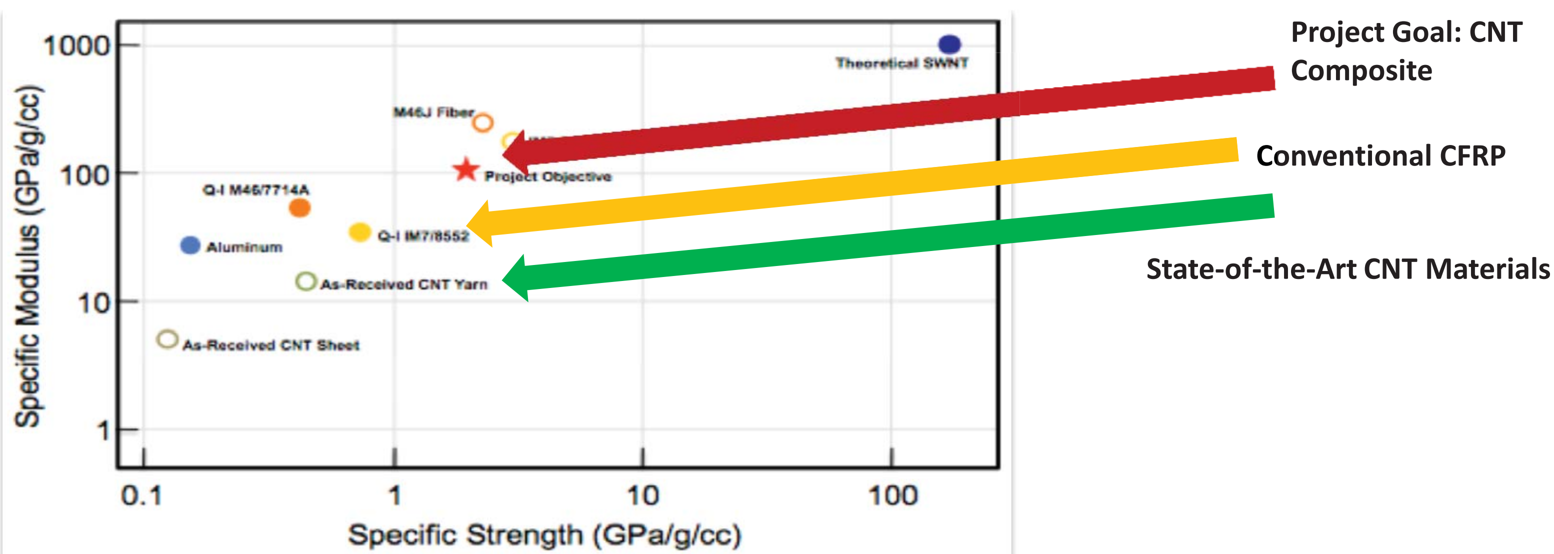
Characterization of CNT Sheet Consolidation Following Resin Infusion

Two stretched CNT sheets were infiltrated with a polybenzoxazine resin and stacked to prepare a 2-ply laminate. Resin content was ~45%. The cross-section was examined by optical microscopy to detect consolidation issues such as voids in the inter-ply region. The panel appeared well consolidated and additional panels will be fabricated with functionalized sheets.



Summary

- The influence of small molecule modification and e-beam irradiation on CNT sheet and yarn material was evaluated.
- Both processes tended to reduce the $I_{G/D}$ ratio due to disruption of the sp^2 hybridization of the pristine CNT material.
- E-beam irradiation of an as-received, bulk CNT sheet material negatively impacted the material tensile strength when exposed to an e-beam flux of 2.2×10^{17} e/cm^2 (90 min). However the same exposure increased the specific strength of the functionalized materials by nearly 60%.
- Irradiation of as-received yarn, led to an increase in tensile strength, through tube alignment and entanglement.



Acknowledgements

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