Improved Composites Using Crosslinked, Surface-Modifed Carbon Nanotube Materials

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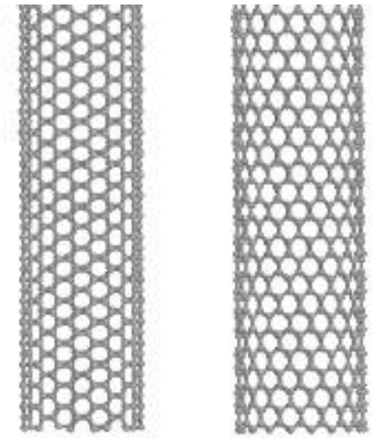
SWCNT



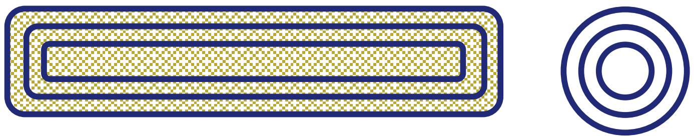
Source: Dai, H. *Acc. Chem. Res*, **2002**, *35*, 1035

Cylindrical structure of *sp*^{2} hybridized carbon atoms

Diameters- 1-50 nm
Lengths- 100nm- ~1 mm

Single-walled (SWCNT) or Multi-walled (MWCNT)

MWCNT



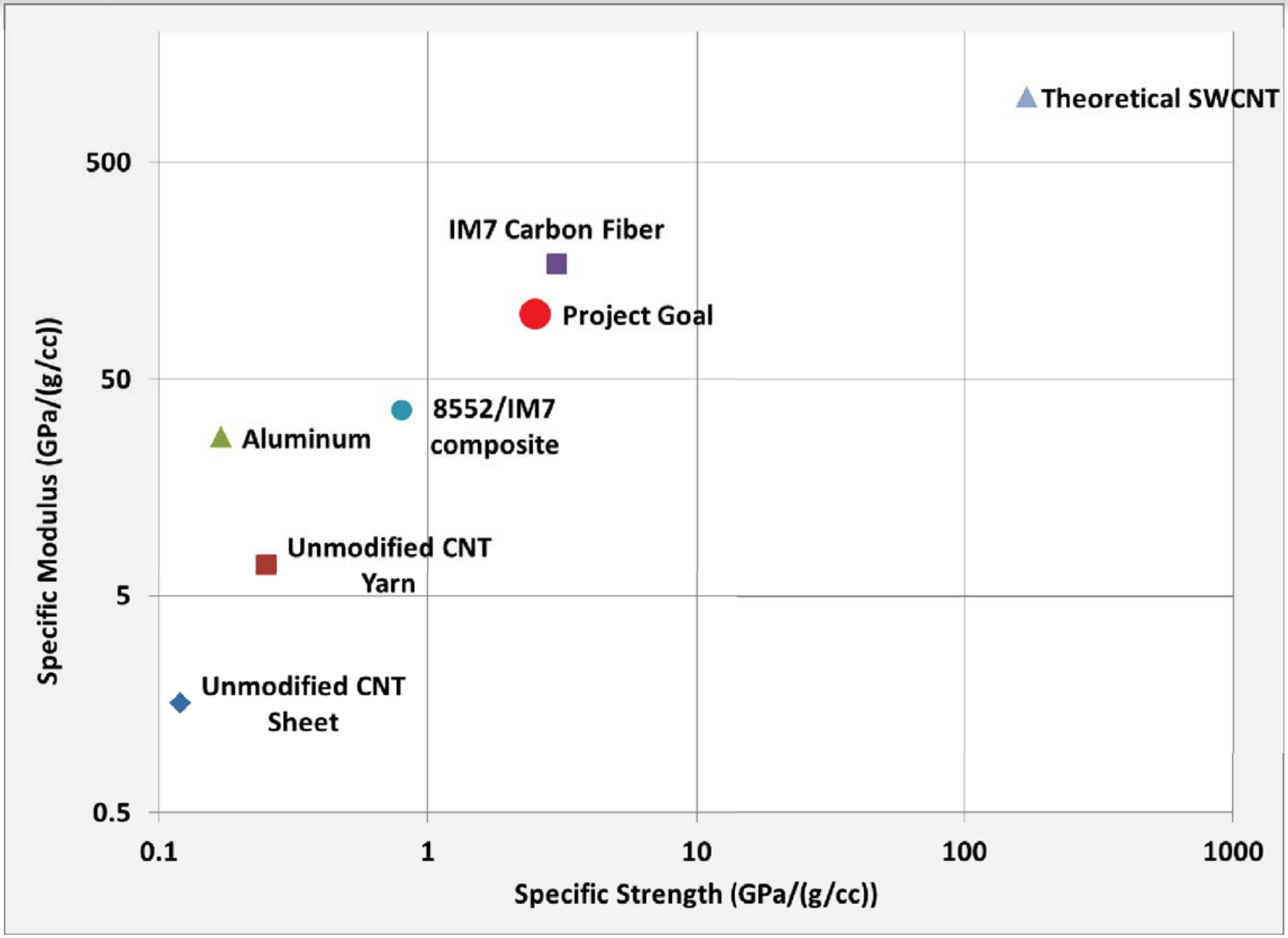
Properties:

- High strength and stiffness
- Low density (~1.6-2.2 g/cm^3)
- Good thermal and electrical conductivity
- High thermal stability

Naraghi, M.; Filleter, T.; Moravsky, A.; Locascio, M.; Loutfy, R.; Espinosa, H. *ACS Nano*, **2010**, *4*, 6463-6476
Lu, W.; Zu, M.; Byun, J-H.; Kim, B-S.; Chou, T-W. *Adv. Mater.*, **2012**, *24*, 1805-1833

Project Goal

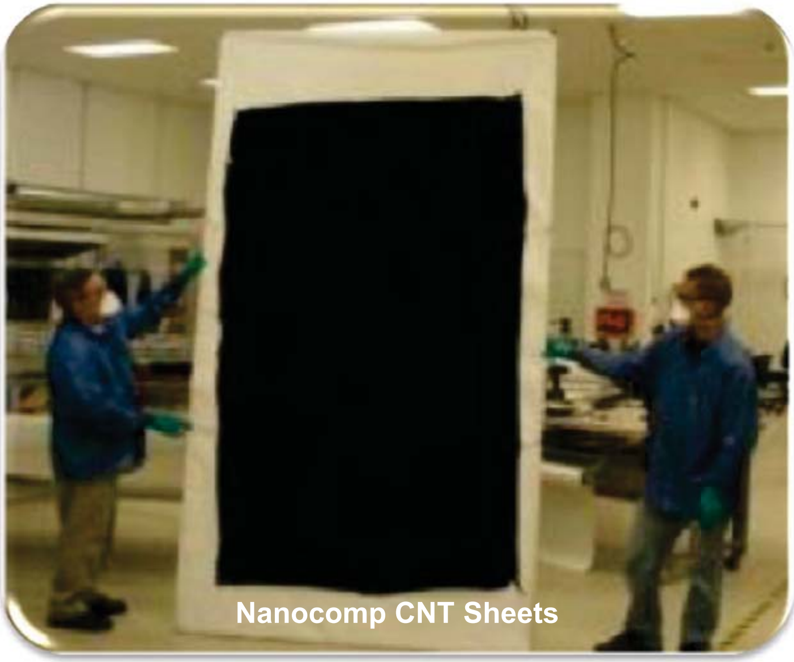
GAME CHANGING DEVELOPMENT PROGRAM

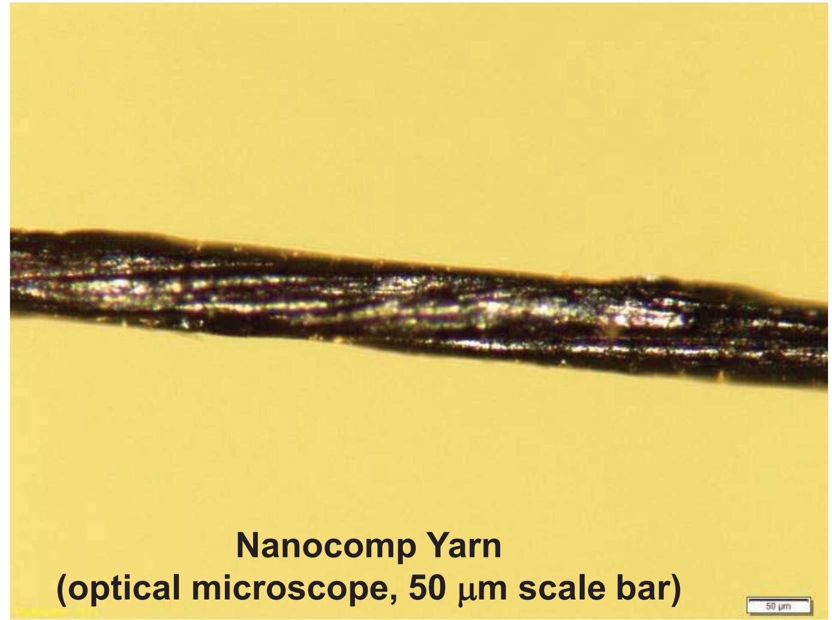


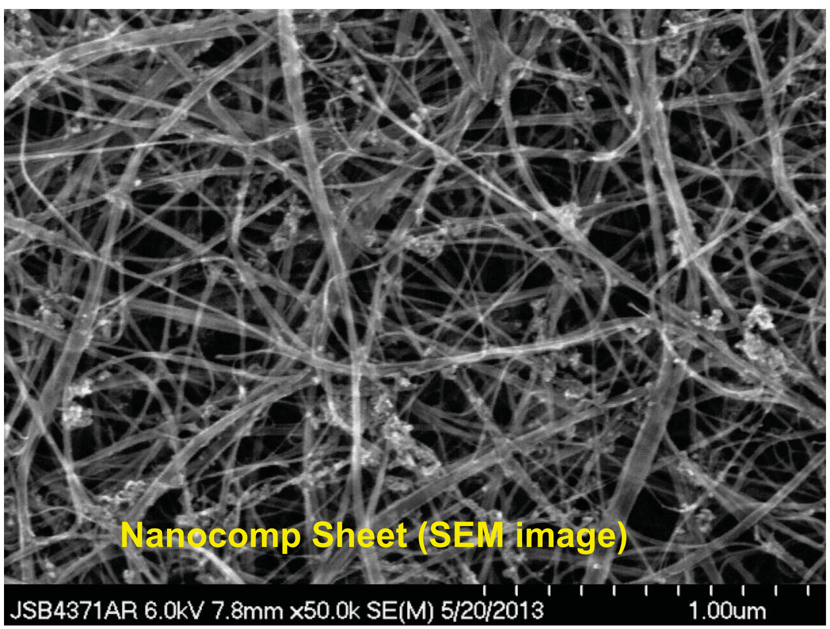
Improve strength to weight ratio of polymer matrix composite materials

- Reduce vehicle dry weight
  - ✓ Increase payload capacity
  - ✓ Lower fuel consumption

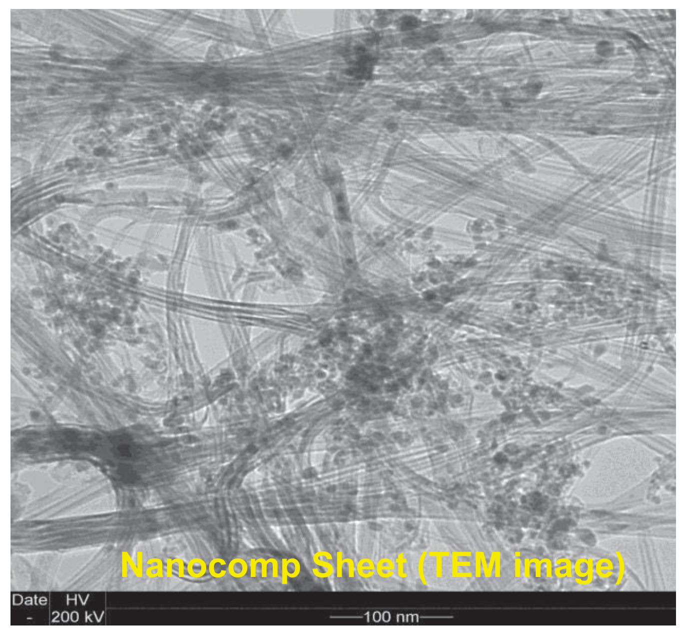
Carbon Nanotube Materials


Nanocomp CNT Sheets


Nanocomp Yarn
(optical microscope, 50 μm scale bar)

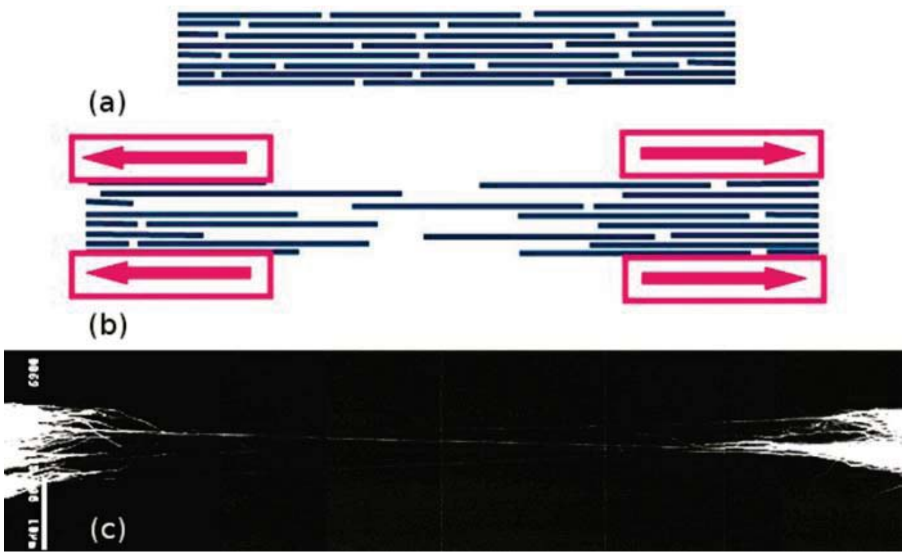


Nanocomp Sheet (SEM image)



Nanocomp Sheet (TEM image)

Carbon Nanotube Yarns



Source: Vilatela,J.; Elliott, J.; Windle, A. *ACS Nano* **2011,** *3*, 1921-27

Carbon Nanotube tensile strength ~10-100 GPa

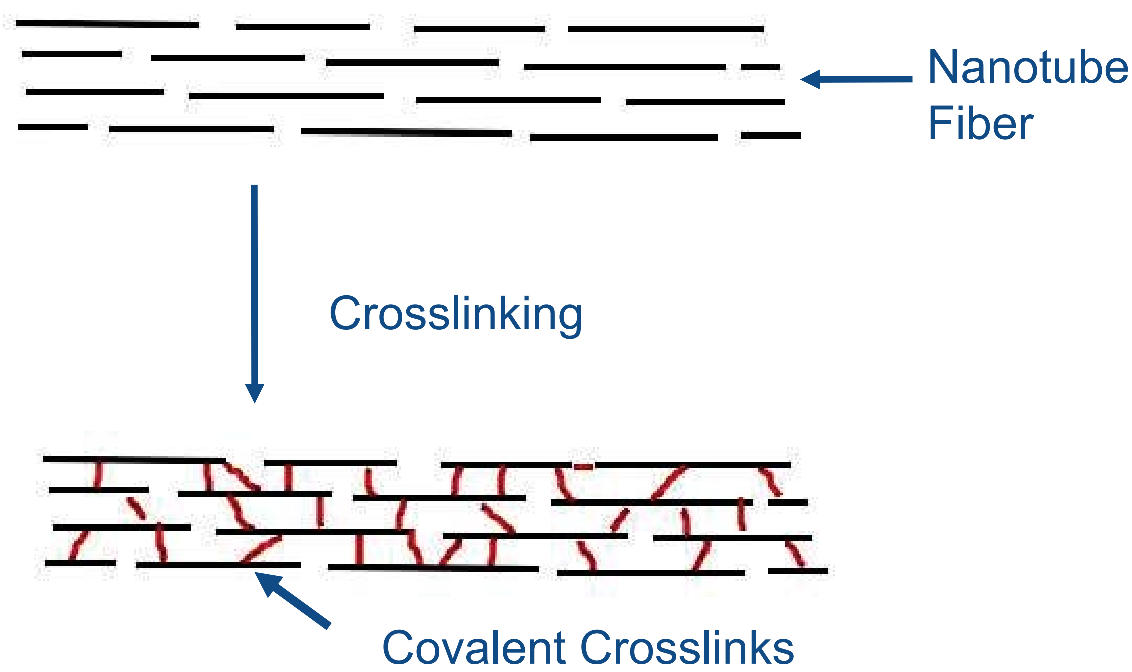
State-of-the-art carbon nanotube yarns ~3 GPa

Failure from slippage of nanotubes/bundles, not breakage of nanotubes

Other Factors:
Imperfect nanotubes
Less than optimal packing

Windle, *et al.* (*Adv. Mater.*, **2010**, 4959; *ACS Nano*, **2011**, 9339)

Our Proposed Solutions



Create covalent, inter-tube bonds to prevent tube-tube sliding.

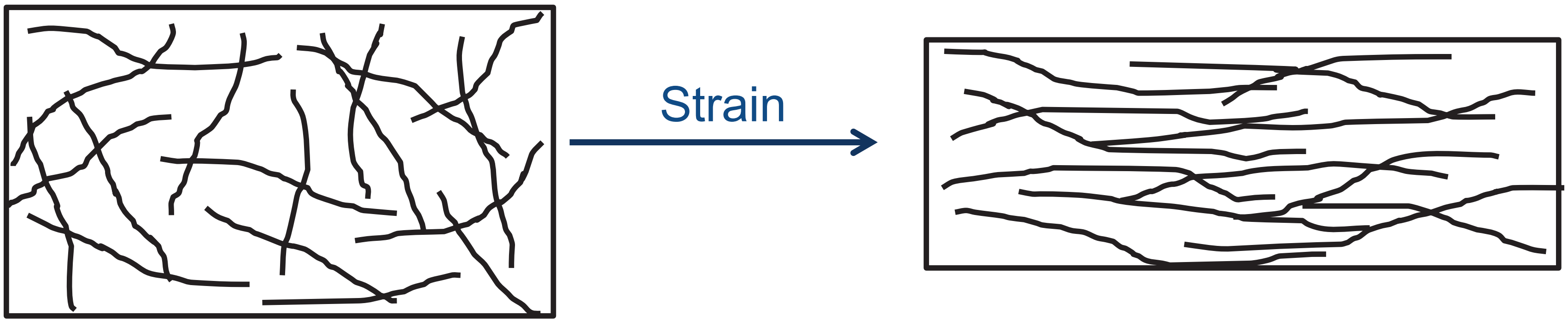
- Chemical modification
- Surface functionalities

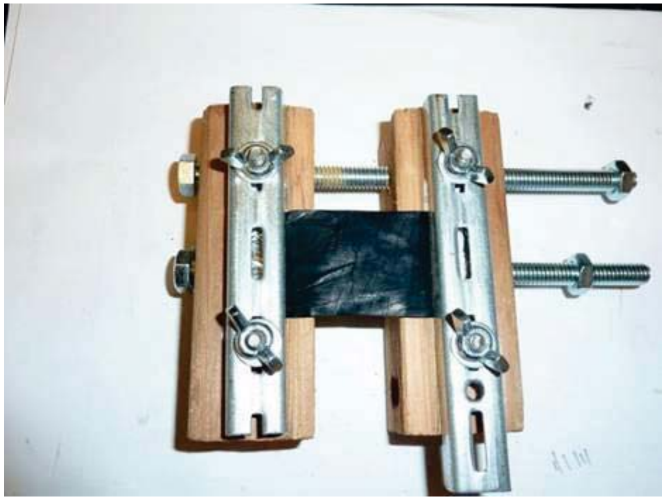
Increase inter-tube contact and alignment

- Solvent densification
- Stretching

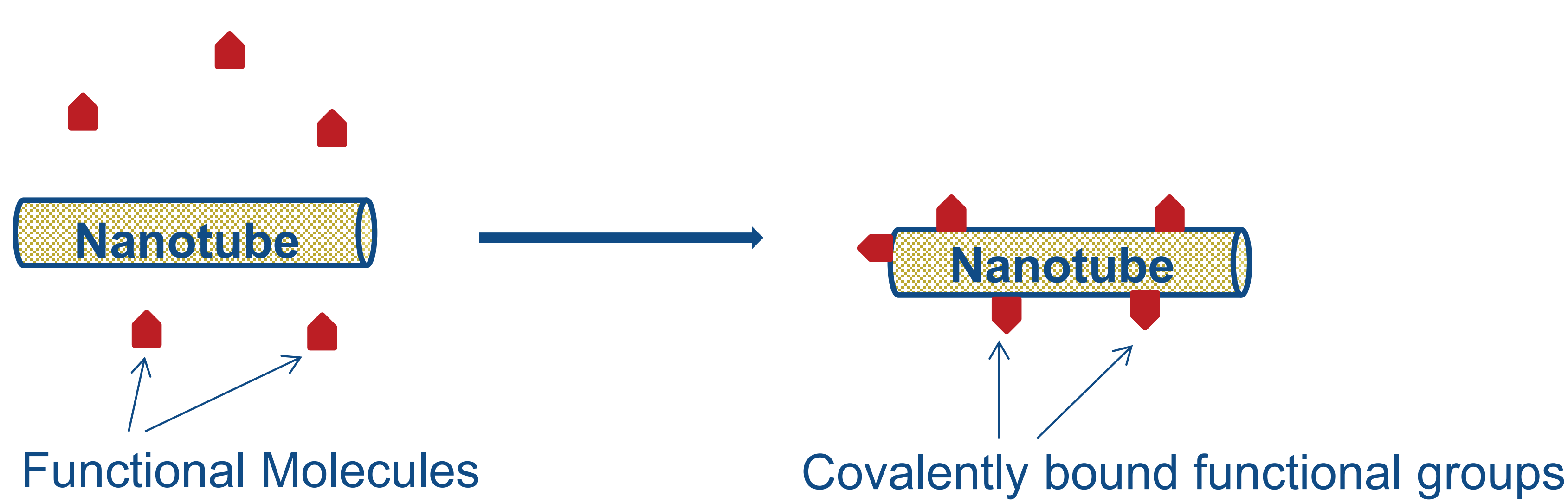
Minimize damage to nanotubes during modification

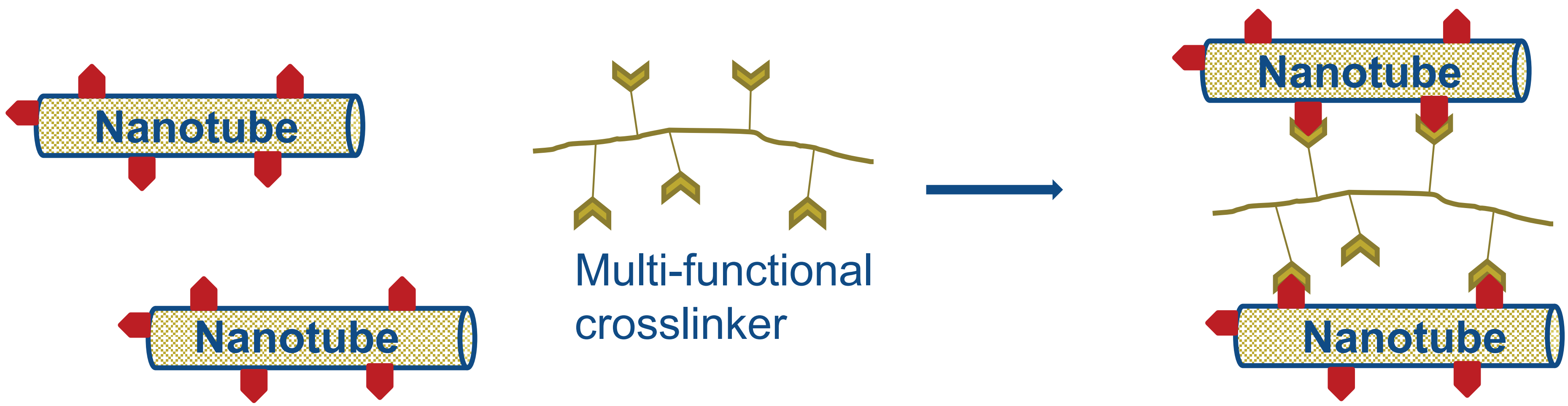
Uniaxial stretching to improve CNT bundle packing and alignment





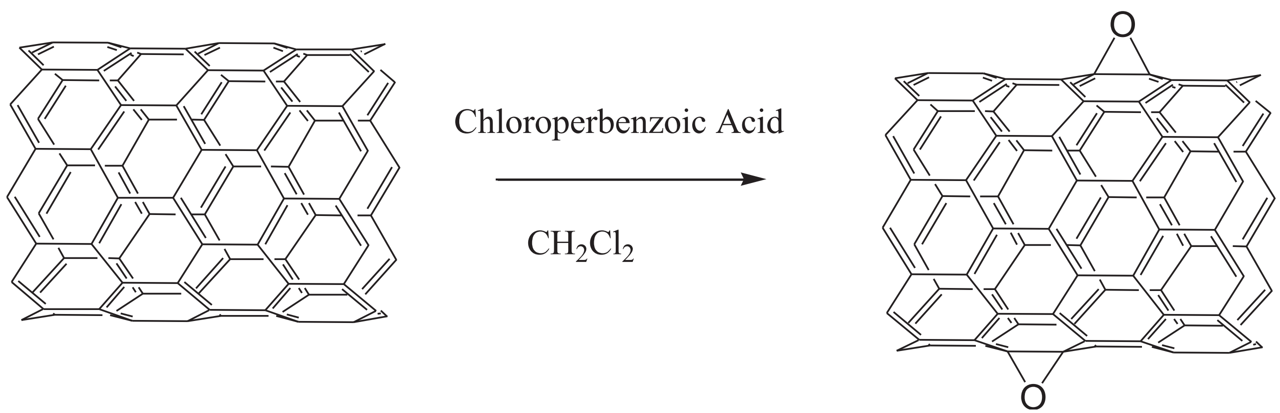
Chemical Crosslinking





Epoxide Functional Nanotubes

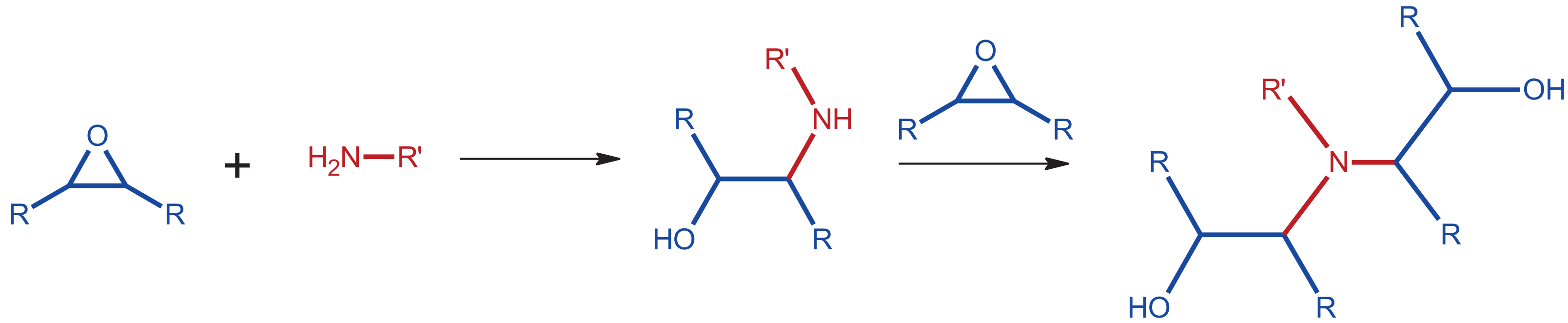
- Reaction with chloroperbenzoic acid (Prilezhaev reaction) can introduce epoxy rings on the nanotube surface (*JACS*, **2006**, 11322; *Small*, **2010**, 763)

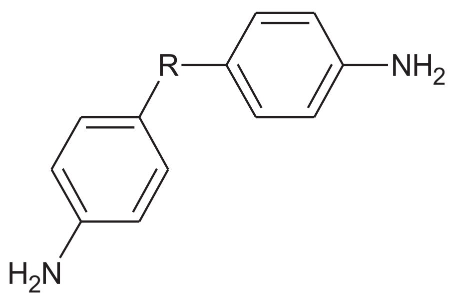


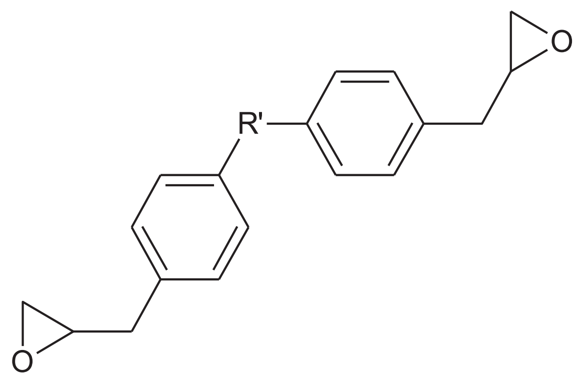
Laing, *et al* (FSU): epoxidized CNT sheet/BMI composites approx. double tensile strength of non-functional CNT sheet/BMI

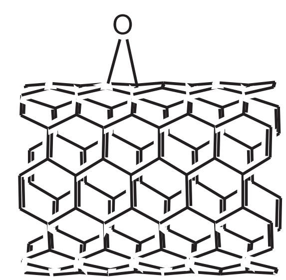
Cheng, Q.; Wang, B.; Zhang, C.; Liang, Z. *Small*, **2010**, *6*, 763

Epoxide Functional Nanotubes





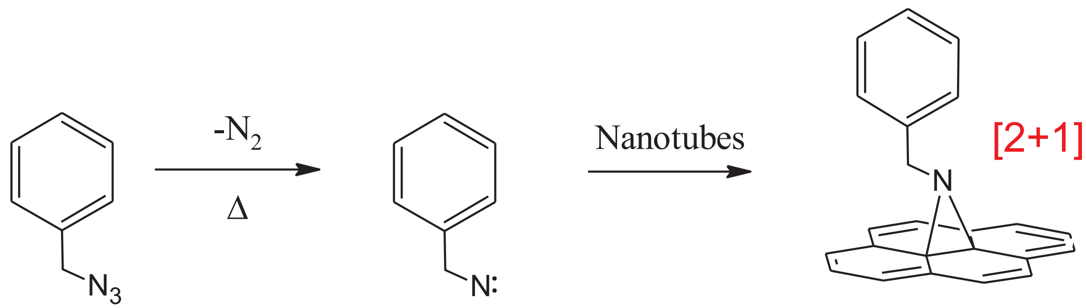




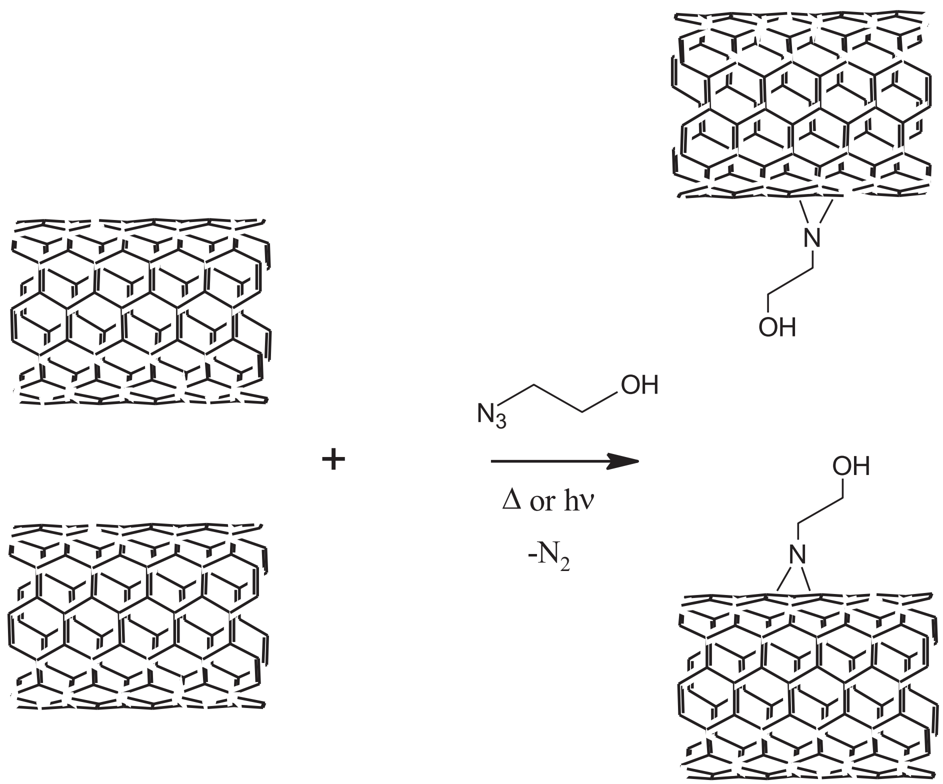
Epoxide rings on nanotubes can react with diamine during resin curing

- covalent attachment of nanotubes to resin matrix

Functionalization Using Nitrenes

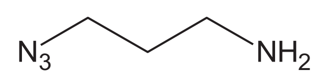


[2+1] cycloaddition of nitrene to nanotube walls



Hydroxyl Functional Nanotubes (CNT-NEtOH)

Similar route for amine (CNT-NPrNH$_2$)



Holzinger, M.; et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 4002; *JACS*, **2003**, *125,* 8566
Gao, C.; He, H.; Zhou, L.; Zheng, X.; Zhang, Y. *Chem. Mater.*, **2009**, *21*, 360

Functionalized Nanotube Sheet Tensile Properties

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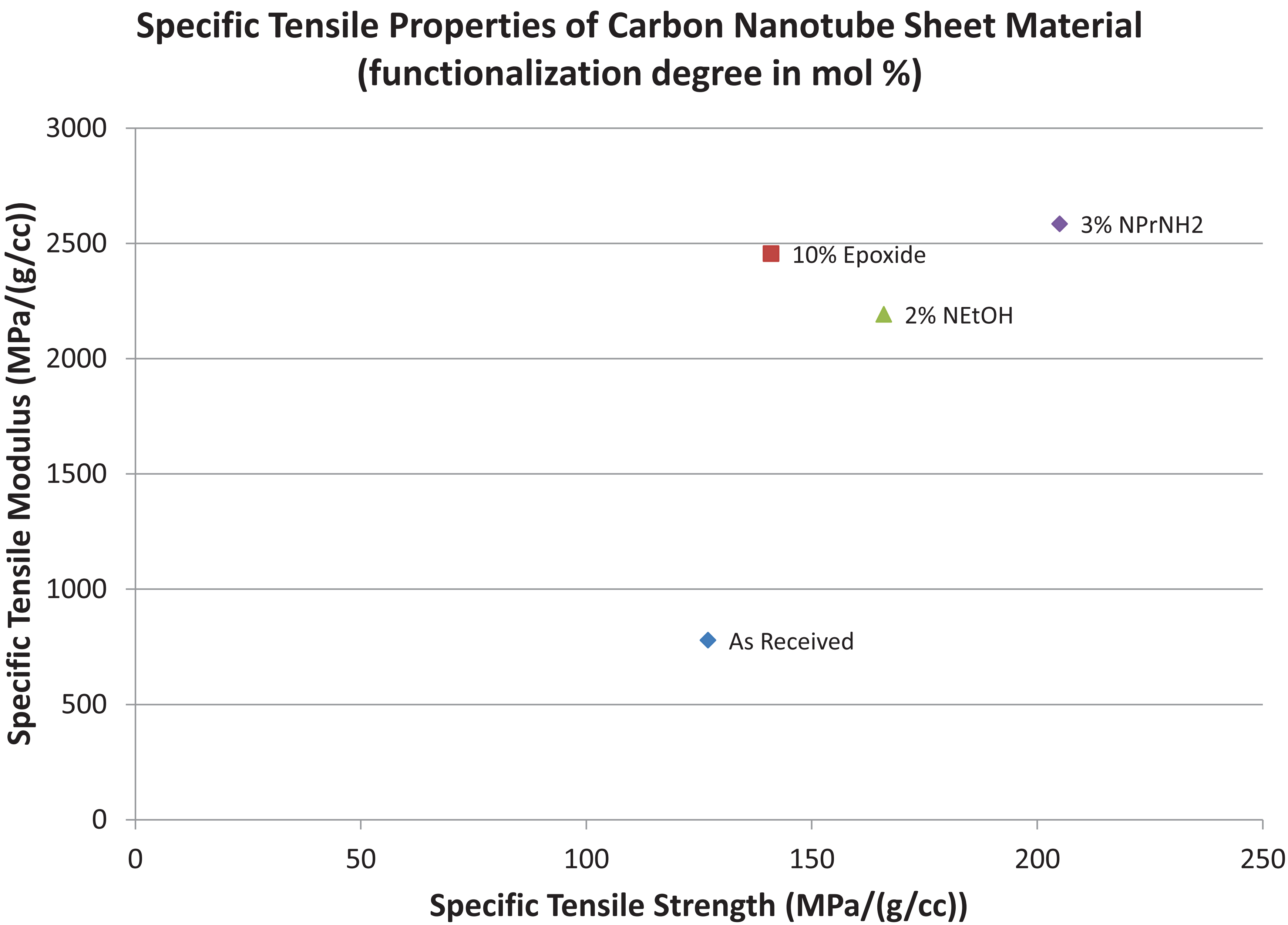

Functionalized and Prestrained Sheet

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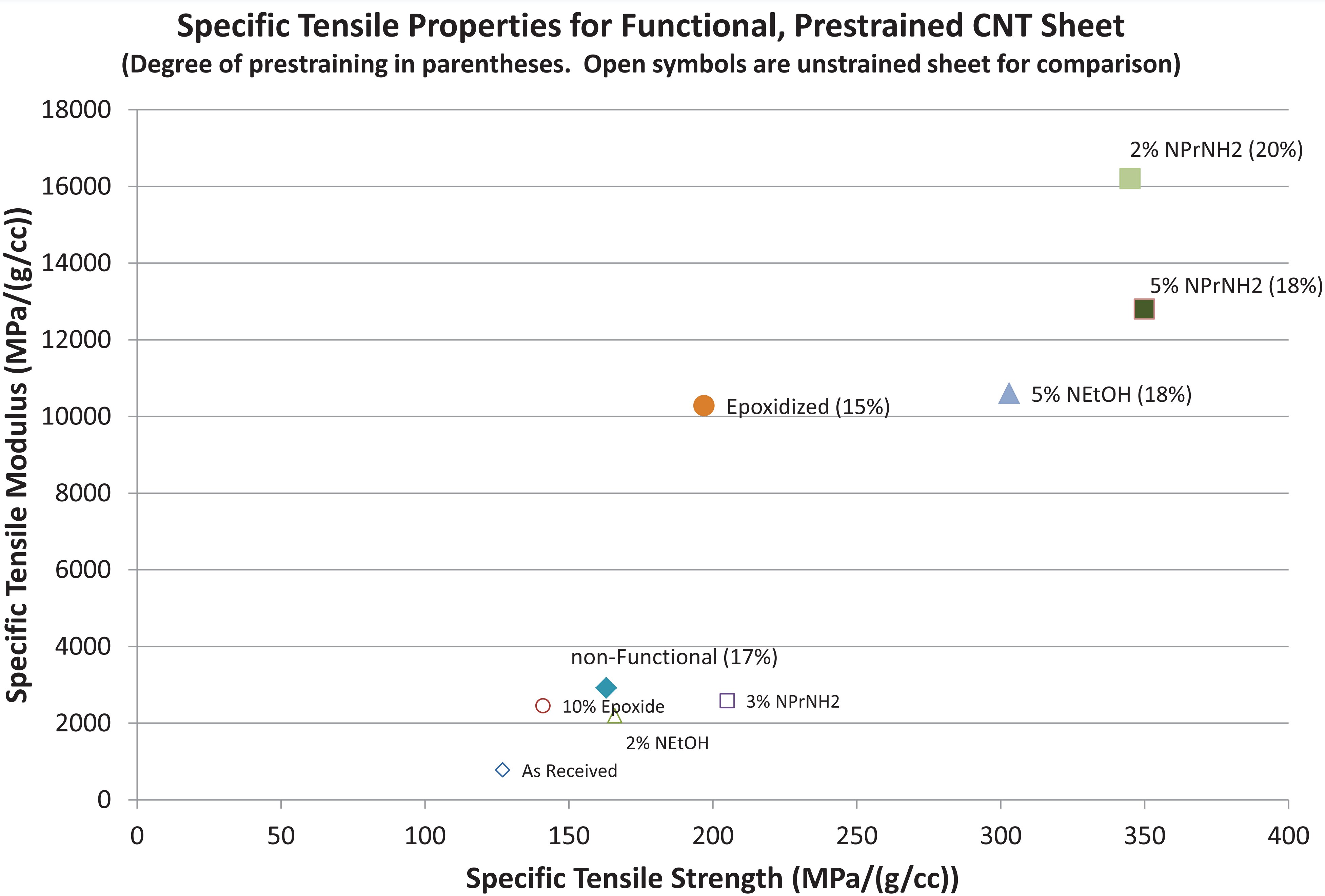
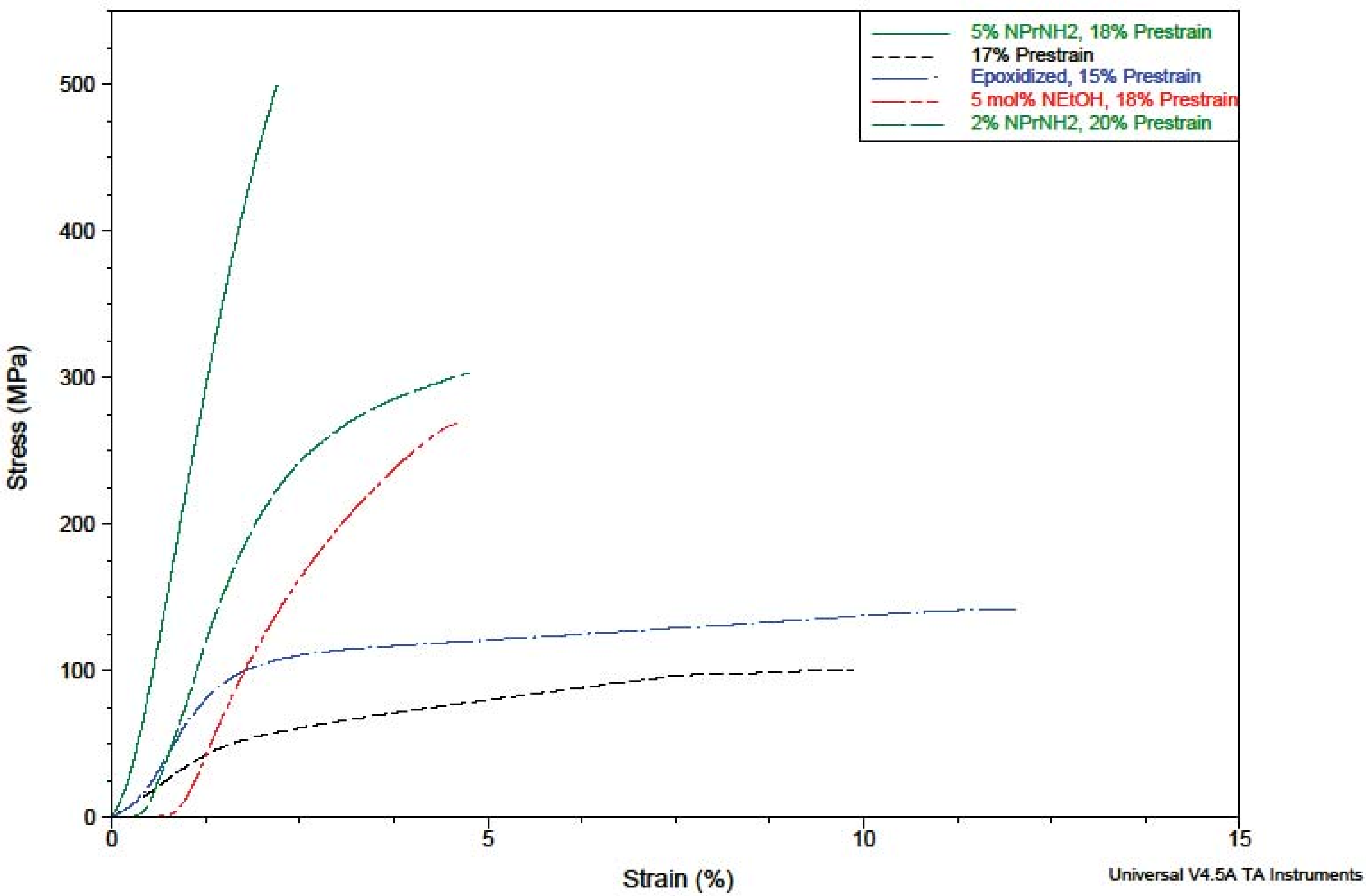


Stress-Strain Traces for Prestrained, Functionalized CNT Sheet



Epoxy Resin/CNT Sheet Composites

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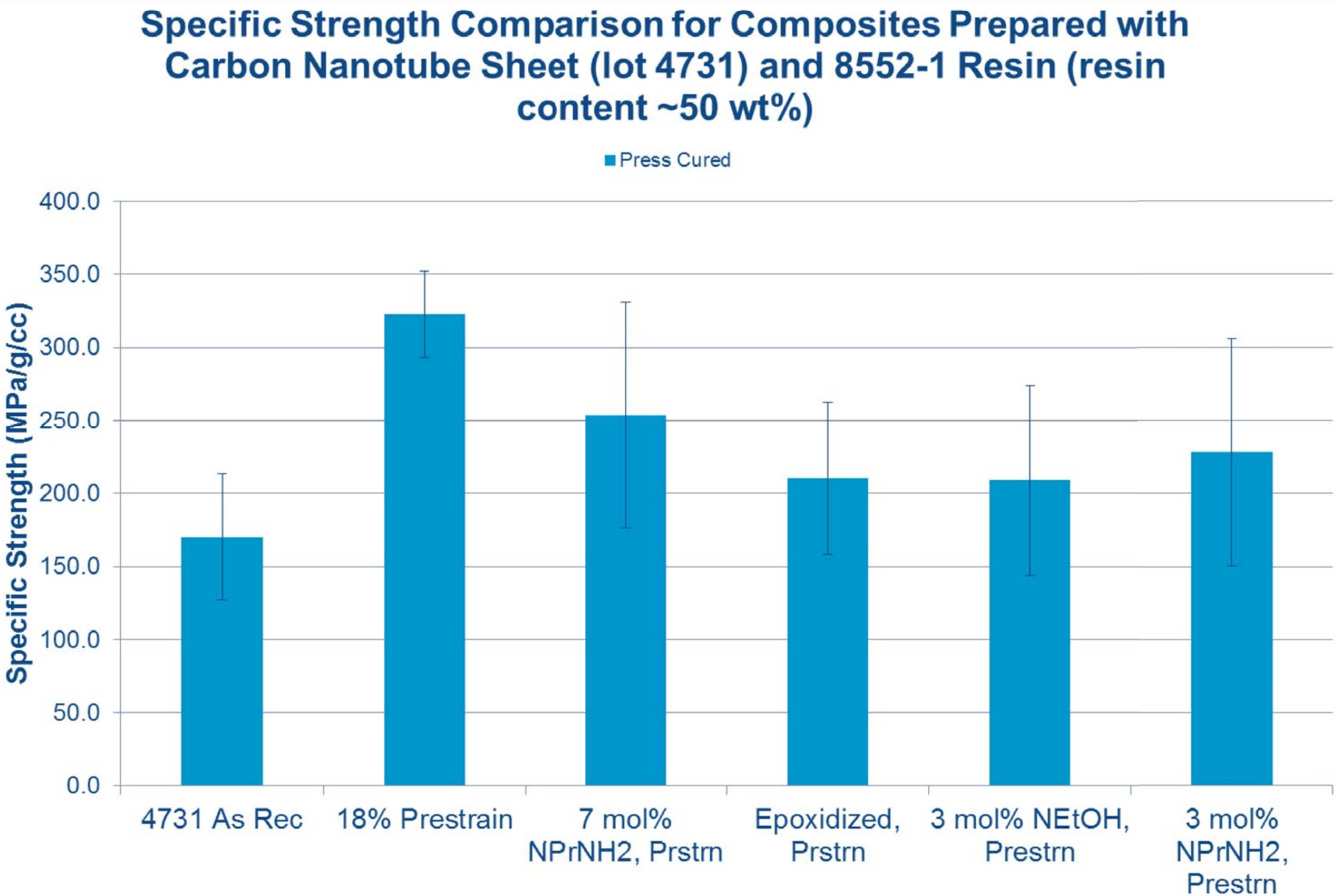
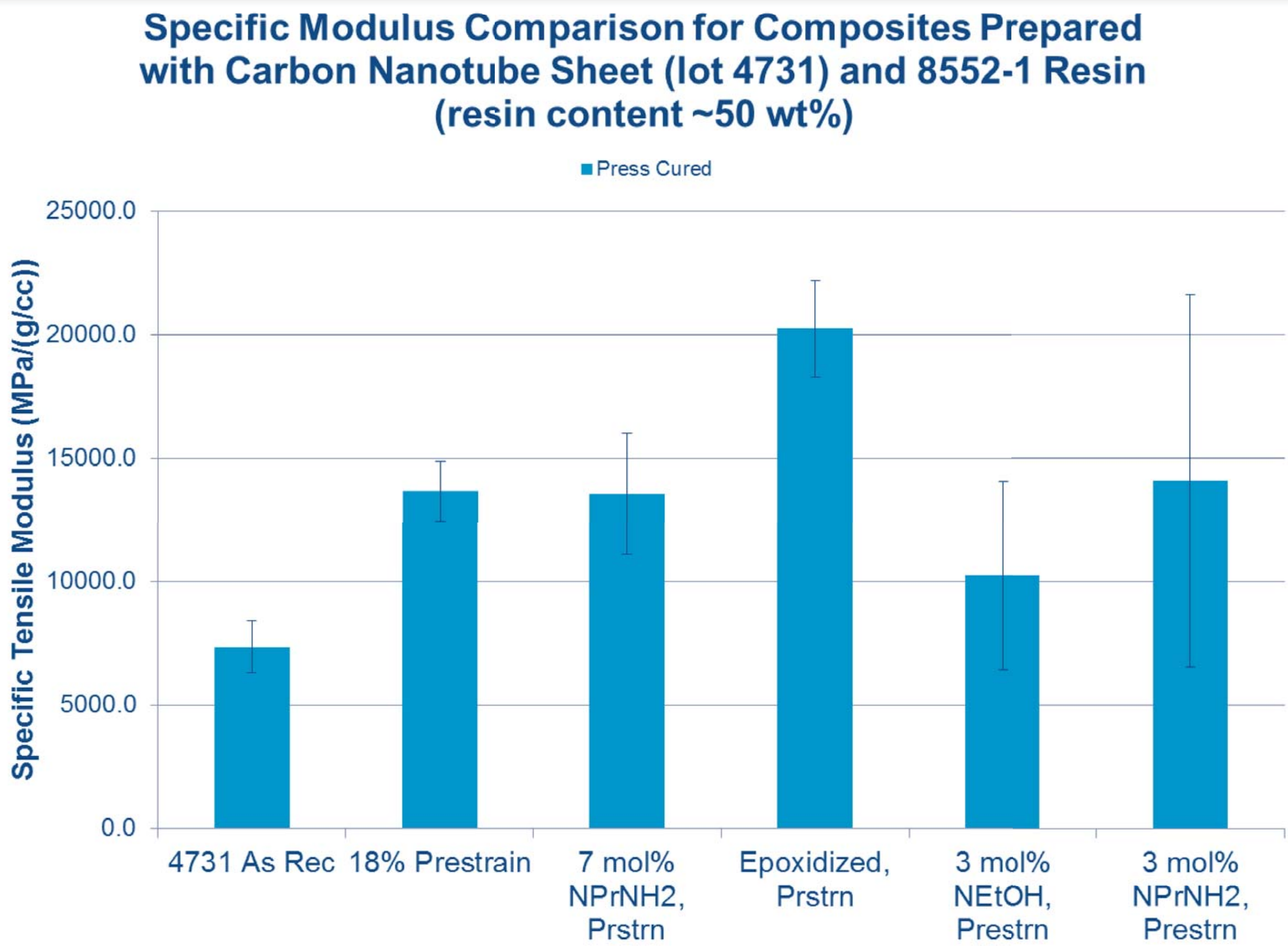


Epoxy Resin/CNT Sheet Composites



Polybenzoxazine/CNT Sheet Composites

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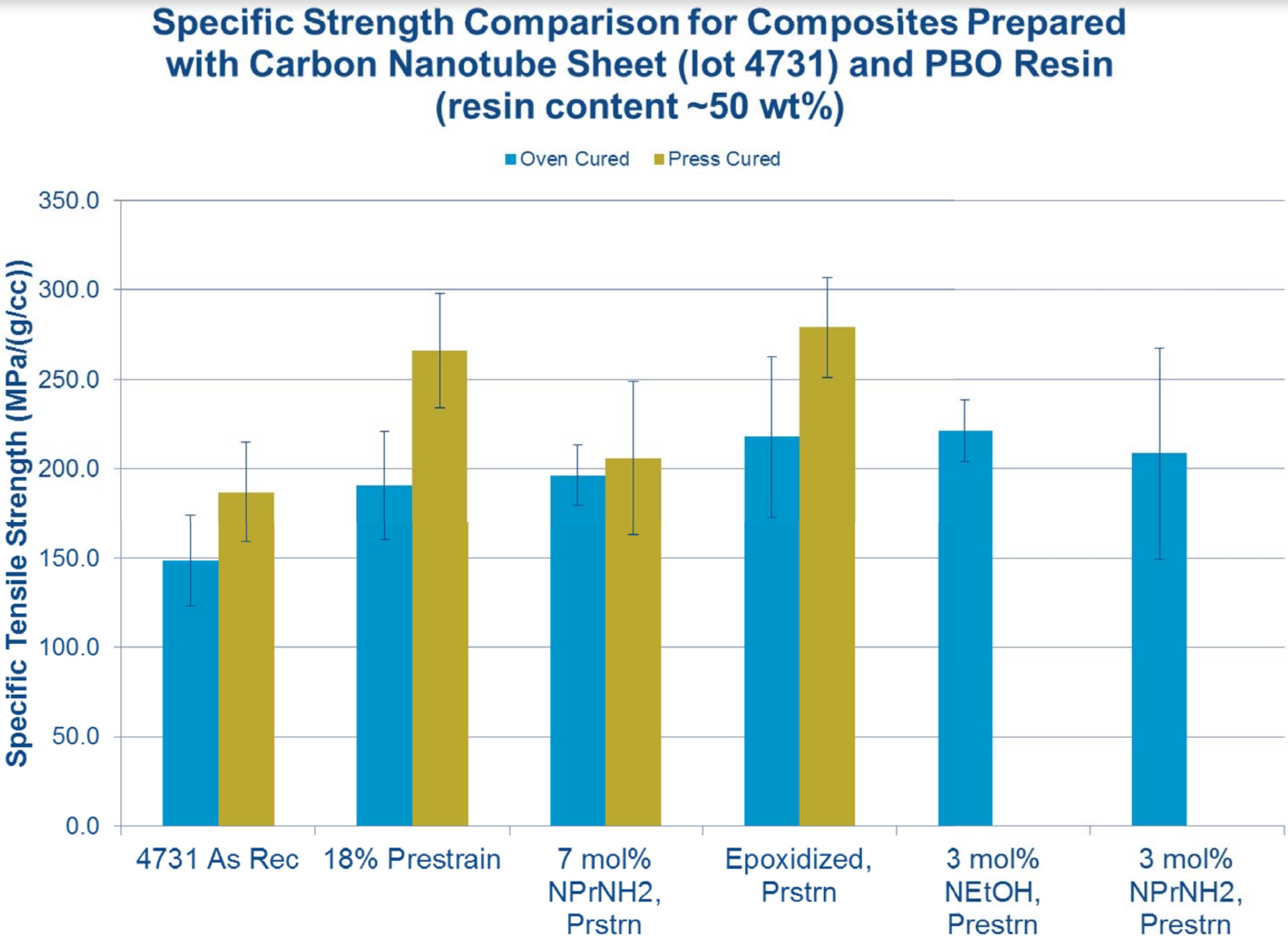
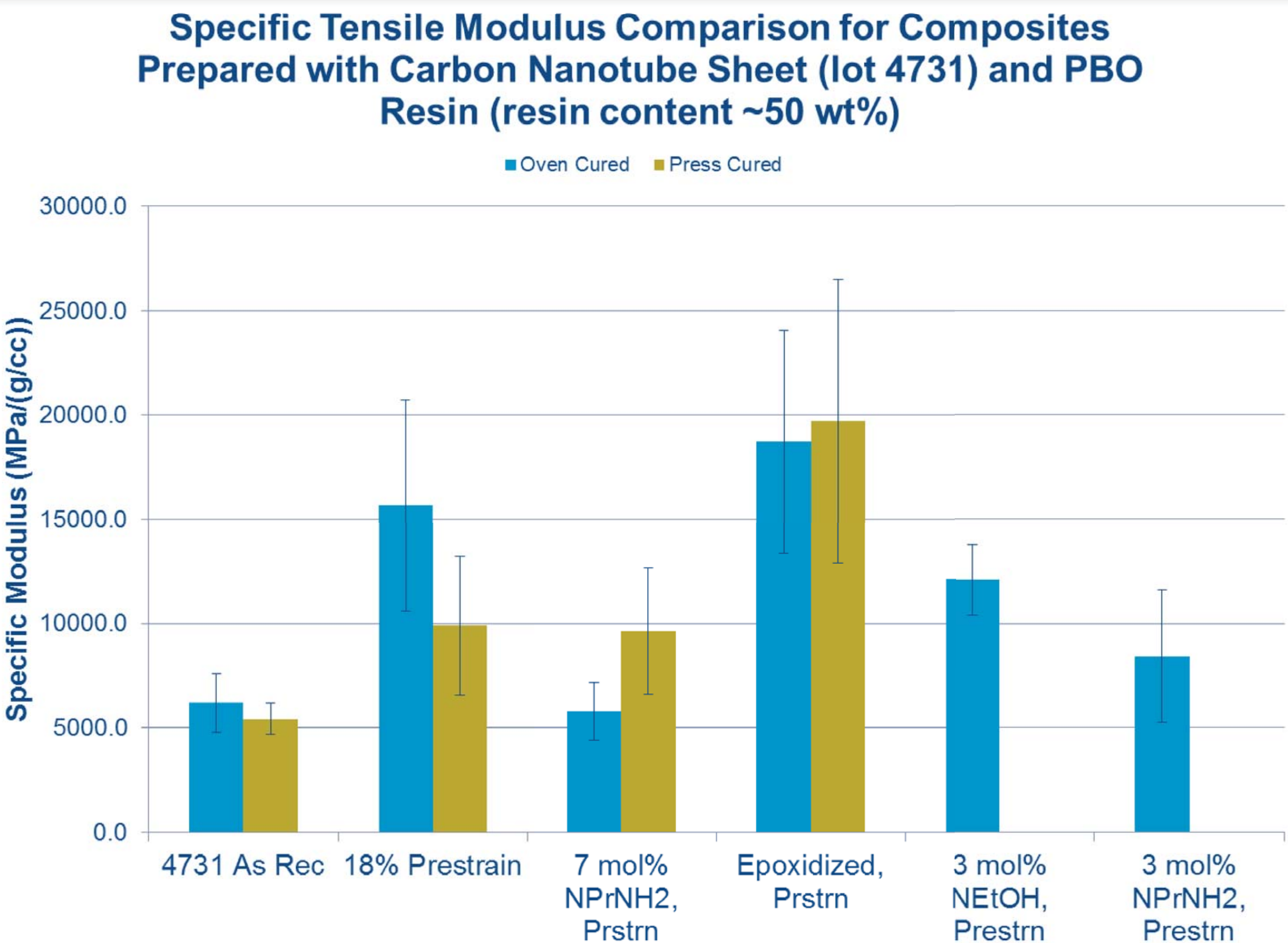
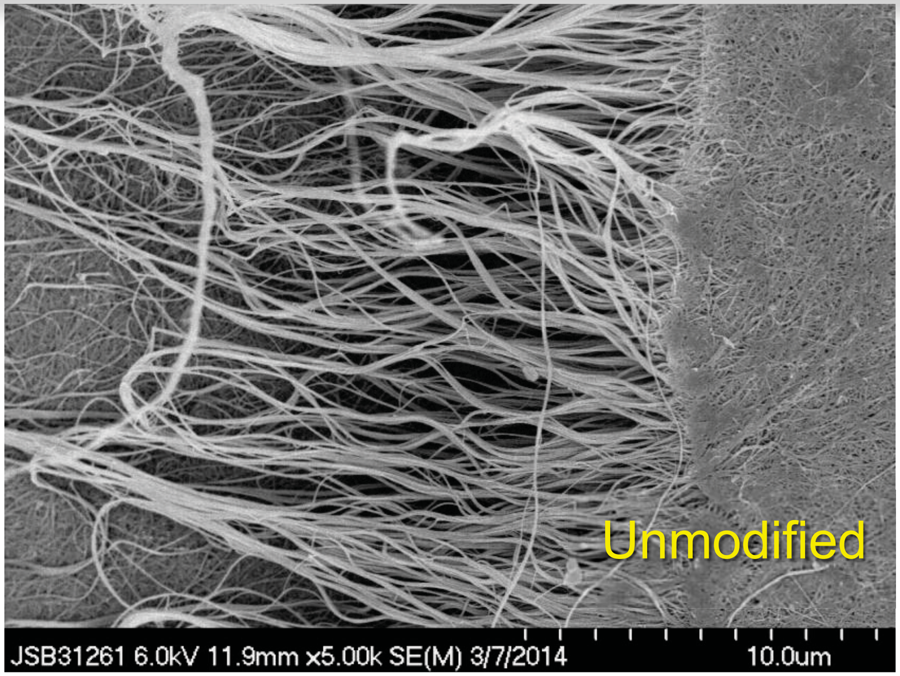


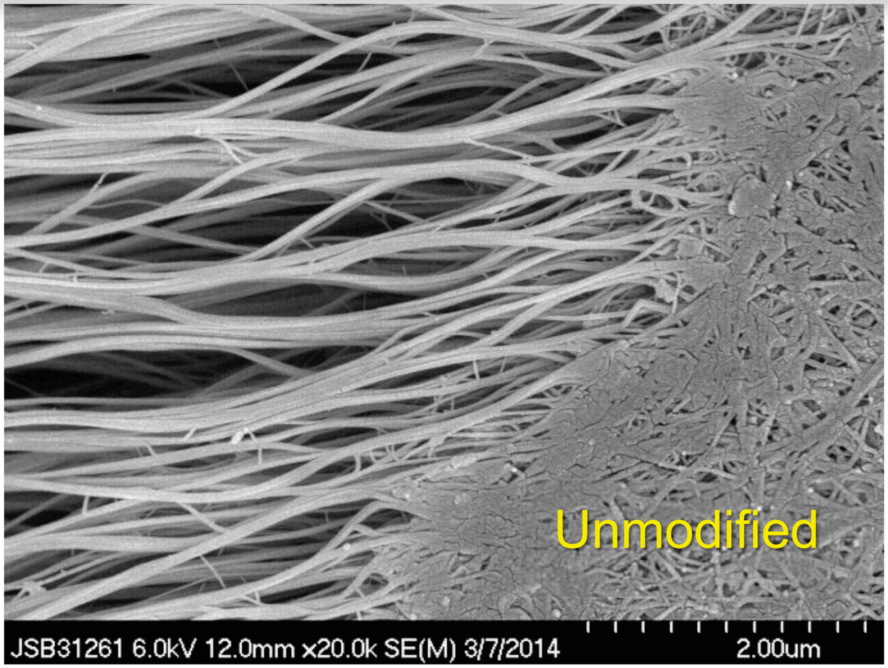
Polybenzoxazine/CNT Sheet Composites

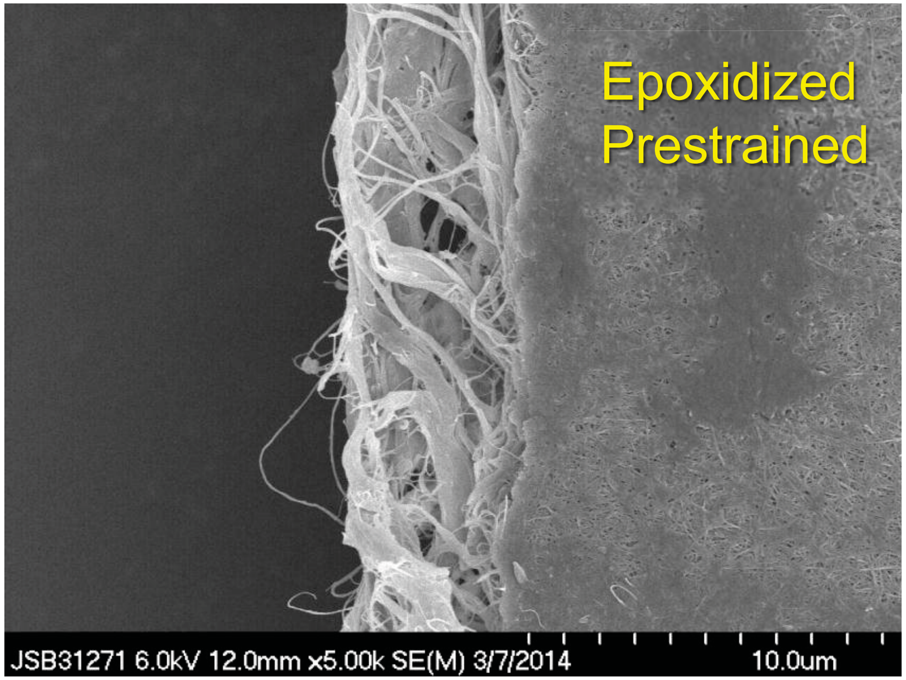


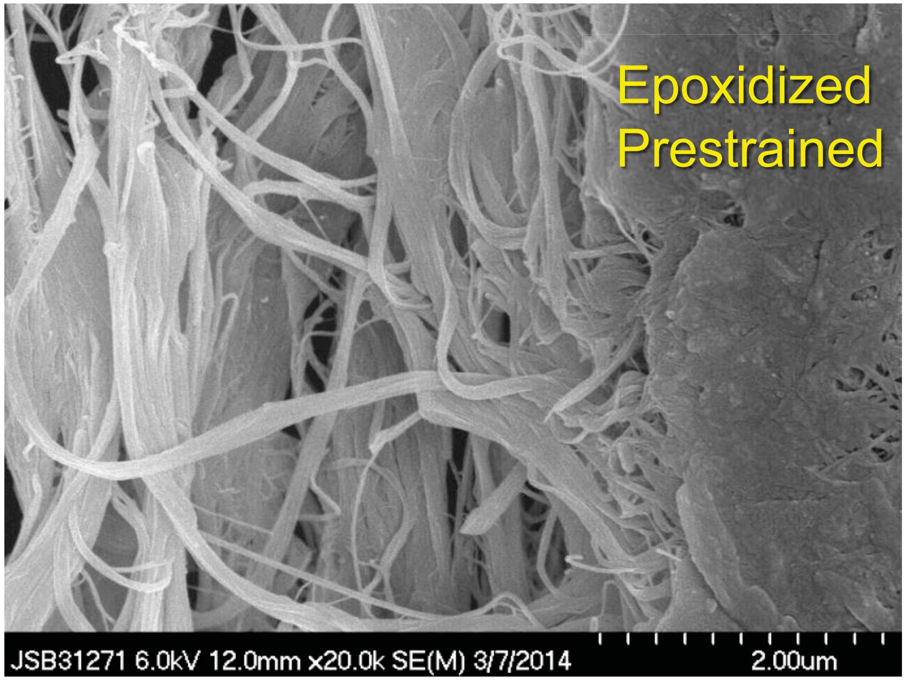
Epoxy Resin Composite Fracture Surface SEM Images

GAME CHANGING DEVELOPMENT PROGRAM

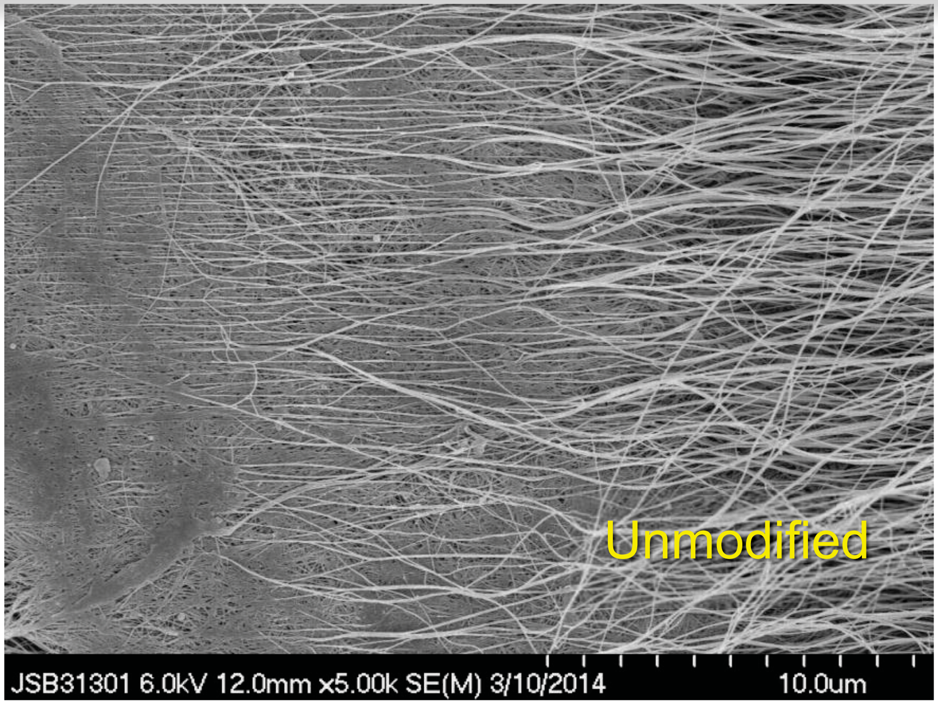


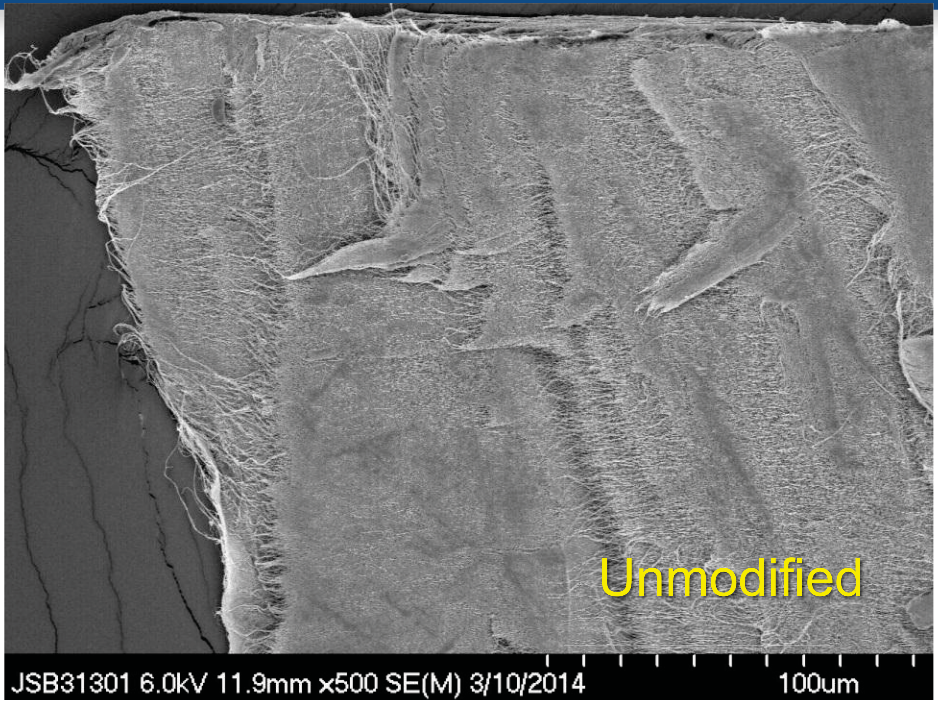


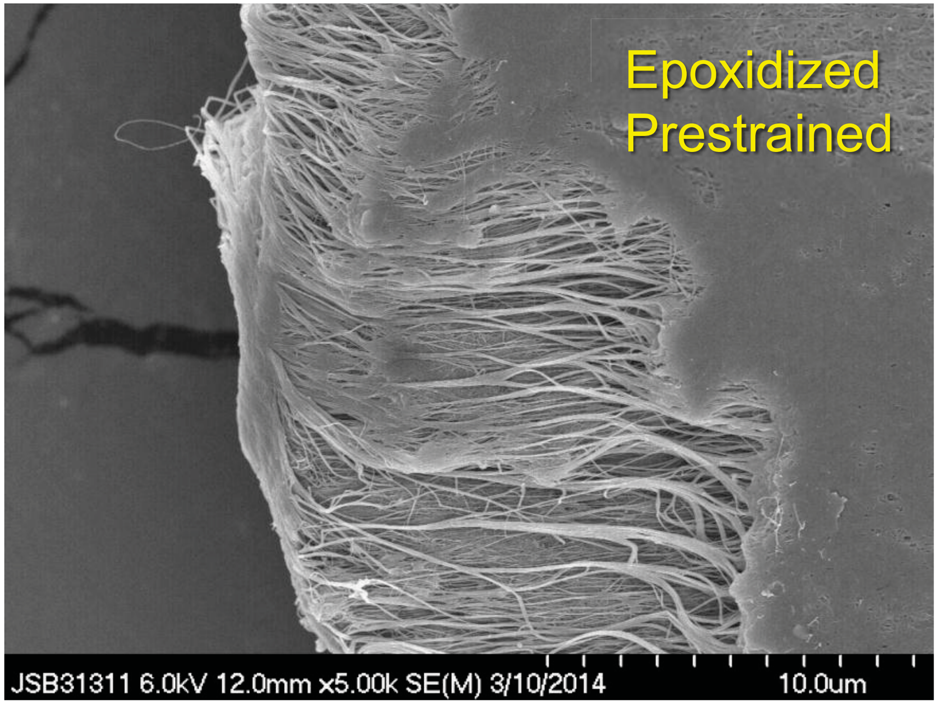


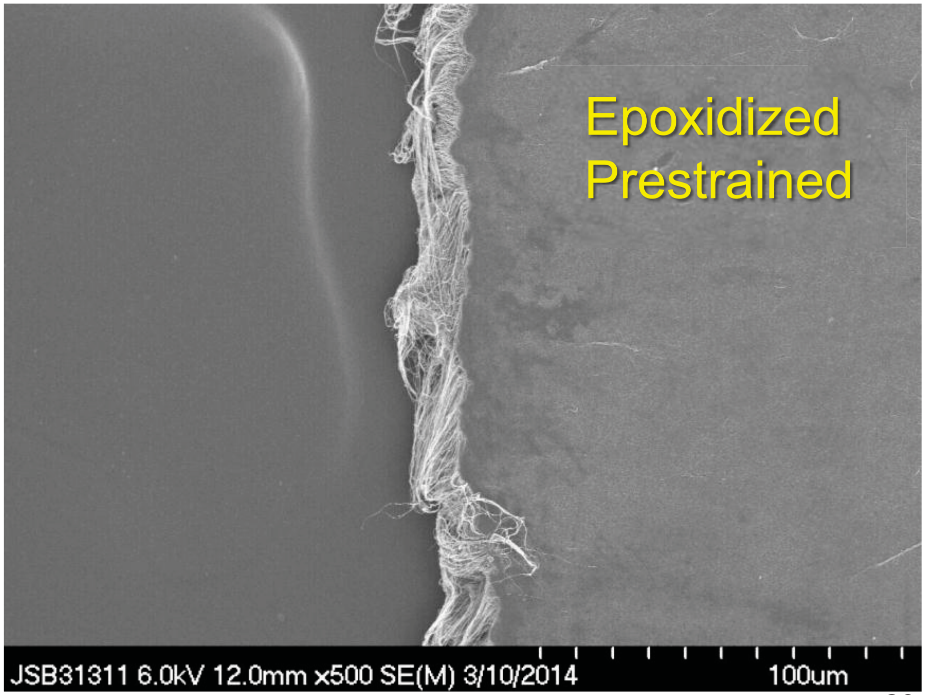


PBO Resin Composite SEM Images









Summary

- Significant improvement in CNT sheet tensile strength and modulus by prestraining
- Covalent functionalization also increases strength and modulus of prestrained sheet
  - Increase of 20% in specific strength and tripling of modulus for epoxidized
  - Doubling of specific strength and 4-5 factor increase in modulus for aminopropylaziridino functional
- Composites prepared from the functional CNT sheets did not exhibit the expected tensile enhancement
  - Composites with functional, prestrained sheet were no stronger than ones with non-functional, prestrained sheet
  - Functional sheets did exhibit cleaner fracture surfaces and resin adhered to CNT bundles by SEM analysis
  - High void volumes, uneven wetting out of resin led to poor composites

What next?

- Optimize resin infiltration and curing conditions
  - Longer low-temp hold times, vacuum bagging
- Composites from functional, non-strained sheet (remove variation in prestraining as a factor)

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