Covalent Crosslinking of Carbon Nanotube Materials for Improved Tensile Strength

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Carbon Nanotubes

Cylindrical structure of $sp^2$ hybridized carbon atoms

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

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

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


Project Goal

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

Carbon Nanotube tensile strength $\sim$10-100 GPa

State-of-the-art carbon nanotube yarns $\sim$3 GPa

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


Carbon Nanotubes

Nanotube tensile strength~ 10-100 GPa

Inter-tube shear force= 0.5-10 MPa

Ease of sliding leads to poor load transfer between nanotubes

Need to increase inter-nanotube forces to take full advantage of nanotube tensile properties

Our Proposed Solutions

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

- Chemical modification
- Electron beam irradiation

Increase inter-tube contact and alignment

- Solvent densification
- Stretching

Minimize damage to nanotubes during modification
Electron Beam Crosslinking

Irradiation of carbon nanotubes with high-energy particles can produce inter-shell or inter-nanotube covalent bonds

Filleter, T.; Espinosa, H. *Carbon*, **2013**, *56*, 1-11
Prestraining

Drawing of yarns during spinning leads to improved nanotube packing and alignment

- Apply same principle to sheet material
Chemical Crosslinking

Nanotube

Functional Molecules

Covalently bound functional groups

Nanotube

Multi-functional crosslinker

Nanotube
Aryl Diazonium


- Use of para-functional anilines allows introduction of functional groups

- Using a di- or multi-amines should allow crosslinking of tubes
Aryl Diazonium
Epoxide Functional Nanotubes

- Reaction with chloroperbenzoic acid (Prilezhaev reaction) can introduce epoxy rings on the nanotube surface (JACS, 2006, 11322; ACS Appl. Mater. Interfaces, 2012, 2065)
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-OH)

Similar route for amine (CNT-NH₂)

Nanotube Crosslinking Through Multifunctional Linkers

[Diagram showing the process of crosslinking nanotubes using multifunctional linkers.]
Functionalization results in:

- Higher tensile strength
- Higher tensile modulus
- Lower strain at break
Effect of Degree of Functionalization

Optimal degree of functionalization is 5-10 mol% for best strength:weight ratio

‘PS’ indicates 14% prestrained
Hydroxyl functional material prepared by reaction with azido ethanol (nitrene route)
E Beam irradiation, 90 min exposure, 2.2 x 10^{17} e^-/cm^2 total fluence

Tensile Strength Comparison for Various Treatments of Carbon Nanotube Sheet (lot 5333)

Hydroxyl functional material prepared by reaction with azido ethanol (nitrene route)
E Beam irradiation, 90 min exposure, 2.2 x 10^{17} e^-/cm^2 total fluence
Specific Modulus and Specific Strength Comparison for Functional Carbon Nanotube Sheets (lot 5333)

- 14% Prestrain, 5 mol% OH, Ebeam
- 5 mol% OH Func, Ebeam
- 14% Prestrain, Ebeam
- 14% Prestrain, 5 mol% OH
- 5 mol% OH Func
- As Rec., Ebeam
- As Received
SEM Micrographs of Nanotube Sheet

A. As Received

B. 14% Prestrain, 5 mol% OH

C. 14% Prestrain, 5 mol% OH, 90 min E Beam
SEM Micrographs of Nanotube Sheet

A. As Received
B. 14% Prestrain, 5 mol% OH
C. 14% Prestrain, 5 mol% OH, 90 min E Beam
Summary

Several methods were examined that resulted in improved tensile properties for the carbon nanotube sheet material

- Covalent functionalization and crosslinking
- Electron beam irradiation
- Uniaxial prestraining

Generally, the methods evaluated resulted in an increase in material tensile strength and modulus and a decrease in strain at failure

Combination of these methods resulted in the largest improvement

14 % prestrain, 5 mol% OH, 90 min E Beam resulted in ~150% increase in specific strength and >10-fold increase in specific modulus over the as-received material

Currently evaluating performance of functional nanotube sheet material in polymer matrix composites
Acknowledgements

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- Project Funding- NASA Space Technology Game Changing Development Program
SEM Micrographs of Nanotube Sheet

A. As Received
B. 14% Prestrain, 5 mol% OH
C. 14% Prestrain, 5 mol% OH, 90 min E Beam
EtOH functionalized (#5333)
PrNH2 Functionalized (#5333)

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Unfunctionalized 15% Prestrain (#5333)

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EtOH 13.5% Prestrain (#5333)

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AR 4371 (CNT sheets for panel fab)

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