Covalent Crosslinking of Carbon Nanotube Materials for Improved Tensile Strength

September 9, 2013

James S. Baker, Sandi Miller, Tiffany Williams, Michael Meador

Postdoctoral Research Fellow

NASA Glenn Research Center, Cleveland, Ohio
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 Sheet (SEM image)

Nanocomp Sheet (TEM image)

Nanocomp Yarn (optical microscope, 50 µm scale bar)
Carbon Nanotube Yarns

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


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


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

- Commonly used method for covalent functionalization of nanotubes

- 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

\[ \text{[2+1] cycloaddition of nitrene to nanotube walls} \]

Hydroxyl Functional Nanotubes (CNT-OH)

Similar route for amine (CNT-NH\(_2\))

References:
Nanotube Crosslinking Through Multifunctional Linkers

Nanotube Crosslinking Through Multifunctional Linkers
Stress vs. Strain Comparison for Various Treatments of Carbon Nanotube Sheet (lot 5333)

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, $2.2 \times 10^{17}$ e$^-$/cm$^2$ total fluence

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

- **As Received**
- **5 mol% OH Func**
- **14% Prestrain**
- **14% Prestrain, 5 mol% OH**

**Legend**
- No EBeam
- 90 Min EBeam
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

- Dr. Michael Meador
- Dr. Sandi Miller
- Dr. Tiffany Williams
- Dr. Francisco Sola-Lopez
- Dr. Marisabel Lebron-Colon
- Dr. Jim Gaier
- Daniel Scheiman, Nate Wilmoth, Linda McCorkle
- Prof. Roberto Uribe (Kent State), NEO Beam electron beam facility
- Fellowship Funding - NASA Postdoctoral Program administrated by Oak Ridge Associated Universities
- 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
### Table

<table>
<thead>
<tr>
<th>AR 5333</th>
<th>Time (min)</th>
<th>Disorder Band</th>
<th>G-band Location</th>
<th>D/G</th>
<th>A (G-band)</th>
<th>A (D-band)</th>
<th>A_D/A_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>G band (~1570 cm⁻¹)</td>
<td>D band (~1350 cm⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>18286.1</td>
<td>4830.6</td>
<td>1570.8</td>
<td>0.264</td>
<td>674830.0</td>
<td>137498.6</td>
<td>0.204</td>
</tr>
<tr>
<td>20</td>
<td>14534.4</td>
<td>5479.4</td>
<td>1569.7</td>
<td>0.377</td>
<td>528274.4</td>
<td>171094.2</td>
<td>0.323</td>
</tr>
<tr>
<td>90</td>
<td>13998.4</td>
<td>5140.9</td>
<td>1569.2</td>
<td>0.367</td>
<td>488926.5</td>
<td>145357.8</td>
<td>0.297</td>
</tr>
</tbody>
</table>
# EtOH functionalized (#5333)

<table>
<thead>
<tr>
<th>EtOH</th>
<th>JSB 11391</th>
<th>Time (min.)</th>
<th>G band (~1570 cm⁻¹)</th>
<th>D band (~1350 cm⁻¹)</th>
<th>G-band location</th>
<th>D/G</th>
<th>A (G-band)</th>
<th>A (D-band)</th>
<th>A_D/A_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>0</td>
<td>15330.3</td>
<td>4718.8</td>
<td>1573.8</td>
<td>0.308</td>
<td>598052.7</td>
<td>141972.4</td>
<td>0.237</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>90</td>
<td>15606.3</td>
<td>6699.2</td>
<td>1575.8</td>
<td>0.429</td>
<td>557340.1</td>
<td>189818.6</td>
<td>0.341</td>
</tr>
</tbody>
</table>
### PrNH2 Functionalized (#5333)

<table>
<thead>
<tr>
<th>PrNH2</th>
<th>Time (min.)</th>
<th>G band (~ 1570 cm⁻¹)</th>
<th>D band (~1350 cm⁻¹)</th>
<th>G-band location</th>
<th>D/G</th>
<th>A (G-band)</th>
<th>A (D-band)</th>
<th>A₀/A₀/A₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>JSB11471</td>
<td>0</td>
<td>20435.0</td>
<td>5324.6</td>
<td>1572.3</td>
<td>0.261</td>
<td>735678.1</td>
<td>117483.5</td>
<td>0.160</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>14246.4</td>
<td>7280.9</td>
<td>1572.3</td>
<td>0.511</td>
<td>523149.3</td>
<td>222635.6</td>
<td>0.426</td>
</tr>
</tbody>
</table>
Unfunctionalized 15% Prestrain (#5333)

<table>
<thead>
<tr>
<th>15% Prestrain JSB11652</th>
<th>Time (min.)</th>
<th>G band (~1570 cm⁻¹)</th>
<th>D band (~1350 cm⁻¹)</th>
<th>G-band location</th>
<th>D/G</th>
<th>A (G-band)</th>
<th>A (D-band)</th>
<th>A₀/A₀</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>18113.4</td>
<td>4642.4</td>
<td></td>
<td>0.256</td>
<td>667741.2</td>
<td>132089.3</td>
<td>0.198</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>15015.8</td>
<td>7636.5</td>
<td></td>
<td>0.509</td>
<td>532588.3</td>
<td>231963.9</td>
<td>0.436</td>
</tr>
</tbody>
</table>
EtOH 13.5% Prestrain (#5333)

<table>
<thead>
<tr>
<th>EtOH 13.5% Prestrain JSB11611 Time (min.)</th>
<th>G band (~1570 cm⁻¹)</th>
<th>D band (~1350 cm⁻¹)</th>
<th>G-band location</th>
<th>D/G</th>
<th>A (G-band)</th>
<th>A (D-band)</th>
<th>A₀/A₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19842.3</td>
<td>4546.0</td>
<td>1575.3</td>
<td>0.230</td>
<td>665729.8</td>
<td>116935.8</td>
<td>0.176</td>
</tr>
<tr>
<td>90</td>
<td>12306.5</td>
<td>3960.5</td>
<td>1576.4</td>
<td>0.322</td>
<td>492436.8</td>
<td>159288.9</td>
<td>0.323</td>
</tr>
</tbody>
</table>
AR 4371 (CNT sheets for panel fab)

<table>
<thead>
<tr>
<th>AR 4371</th>
<th>Time (min.)</th>
<th>G band (~ 1570 cm⁻¹)</th>
<th>D band (~1350 cm⁻¹)</th>
<th>G-band location</th>
<th>D/G</th>
<th>A(G-band)</th>
<th>A(D-band)</th>
<th>A_D/A_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>19993.2</td>
<td>2979.7</td>
<td></td>
<td>1573.9</td>
<td>0.149</td>
<td>736802.9</td>
<td>84292.9</td>
<td>0.114</td>
</tr>
<tr>
<td>20</td>
<td>16064.6</td>
<td>4804.8</td>
<td></td>
<td>1566.4</td>
<td>0.299</td>
<td>614848.9</td>
<td>147794.5</td>
<td>0.240</td>
</tr>
<tr>
<td>90</td>
<td>18539.3</td>
<td>6846.4</td>
<td></td>
<td>1569.5</td>
<td>0.369</td>
<td>685277.1</td>
<td>196265.6</td>
<td>0.286</td>
</tr>
</tbody>
</table>