Improved Composites Using Crosslinked, Surface-Modified Carbon Nanotube Materials

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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/cm³)
- Good thermal and electrical conductivity
- High thermal stability


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

![Graph showing specific modulus and strength of different materials including IM7 Carbon Fiber, 8552/IM7 composite, Aluminum, Unmodified CNT Yarn, Unmodified CNT Sheet, and Theoretical SWCNT. The project goal is represented by a red dot within the graph.](image)
Carbon Nanotube Materials

Nanocomp CNT Sheets

Nanocomp Sheet (SEM image)

Nanocomp Yarn
(optical microscope, 50 µm scale bar)

Nanocomp Sheet (TEM image)
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

Other Factors:
Imperfect nanotubes
Less than optimal packing


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
Prestraining

Uniaxial stretching to improve CNT bundle packing and alignment
Reaction with chloroperbenzoic acid (Prilezhaev reaction) can introduce epoxy rings on the nanotube surface (*JACS*, 2006, 11322; *Small*, 2010, 763)


Cheng, Q.; Wang, B.; Zhang, C.; Liang, Z. *Small*, 2010, 6, 763
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-NPrNH₂)

Functionalized Nanotube Sheet Tensile Properties

Specific Tensile Properties of Carbon Nanotube Sheet Material (functionalization degree in mol %)

Specific Tensile Modulus (MPa/(g/cc))

Specific Tensile Strength (MPa/(g/cc))

- As Received
- 10% Epoxide
- 2% NEtOH
- 3% NPrNH2
Stress-Strain Behavior

Stress-Strain Traces for Prestrained, Functionalized CNT Sheet
Specific Strength Comparison for Composites Prepared with Carbon Nanotube Sheet (lot 4731) and 8552-1 Resin (resin content ~50 wt%)
Specific Modulus Comparison for Composites Prepared with Carbon Nanotube Sheet (lot 4731) and 8552-1 Resin (resin content ~50 wt%)
Specific Strength Comparison for Composites Prepared with Carbon Nanotube Sheet (lot 4731) and PBO Resin (resin content ~50 wt%)
Specific Tensile Modulus Comparison for Composites Prepared with Carbon Nanotube Sheet (lot 4731) and PBO Resin (resin content ~50 wt%)

- Oven Cured
- Press Cured

<table>
<thead>
<tr>
<th>Material Description</th>
<th>Specific Modulus (MPa/g/cc)</th>
</tr>
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<tbody>
<tr>
<td>4731 As Rec</td>
<td>5000.0</td>
</tr>
<tr>
<td>18% Prestrain</td>
<td>6000.0</td>
</tr>
<tr>
<td>7 mol% NPPrNH2, Prstrn</td>
<td>10000.0</td>
</tr>
<tr>
<td>Epoxidized, Prstrn</td>
<td>25000.0</td>
</tr>
<tr>
<td>3 mol% NEtOH, Prestrn</td>
<td>11000.0</td>
</tr>
<tr>
<td>3 mol% NPPrNH2, Prestrn</td>
<td>9000.0</td>
</tr>
</tbody>
</table>
Epoxy Resin Composite Fracture Surface SEM Images

Unmodified

Epoxidized Prestrained

Unmodified

Epoxidized Prestrained
PBO Resin Composite SEM Images

Unmodified

Epoxidized Prestrained

Unmodified

Epoxidized Prestrained
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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