Mechanical properties of carbon nanotube webs

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The ANAM Initiative.

Broad collaboration between Cambridge Engineering and Materials Science Departments, and Ulster University, and several industrial partners.

Focus on direct-spun CNT materials, made by the Windle Process.
Carbon Nanotubes: Intrinsic Properties

Individual Tubes: MWNT
wall structural properties

\[ E = 1 \text{ TPa} \]
\[ \sigma_f > 100 \text{ GPa} \]
\[ \rho \sim 2200 \text{ kg/cm}^3 \]


Good **understanding** of mechanics with **strong theoretical validation**

Yu et al (2000)
Wang et al (2010)
Zhang et al (2014)

Electrical Conductivity: \( 2 \times 10^5 \text{ s/cm} \)
Thermal Conductivity: \( 3500 \text{ W/mK} \)

- Can we realise the properties of CNTs in **Direct-spun Mats** and other **Bulk CNT Materials**?
- If not, **why**?
Carbon Nanotubes: Intrinsic Properties

[Graph showing specific properties of materials, including specific Young's Modulus, specific strength, and specific electrical conductivity.]

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Production and Microstructure of direct-spun CNT Mat & Fibre from the ‘Windle Process’

CNT Mat

Typical Microstructure

Tension during winding

CNT Aerogel “Sock”

Aerogel Formation by CNT Agglomeration

T ~ 1300°C

Methane, Ferrocene, Thiophene

1μm

Interconnected Bundle Network

Detail of Network Junctions: Bundles branch and Cross

Cross-section of Bundle Microstructure

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Bulk CNT Materials: *methods of manufacture*

- Forest and densified pillars
- Fibre spun from Forest
- Mat drawn from Forest

**Buckypaper from filtration**

**Wet spinning from solution**

**CNT Foam**

**Diffusion of solvent out of fibre**

**CNT Fibre**

**Coagulant**

**Tension**
The Properties of Bulk CNT Materials: Mechanical
The Properties of Bulk CNT Materials: Electrical & Thermal

<table>
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<th>ρ (kg/m³)</th>
<th>Electrical Conductivity (s/cm)</th>
<th>Thermal Conductivity (W/mK)</th>
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<td>1000</td>
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</tbody>
</table>

[Diagram showing various categories of CNT materials and their properties, with labels for different types of materials and their respective electrical and thermal conductivities.]
The Properties of a Direct-spun CNT Mat: Uniaxial Response, composition, and electrical properties

Fracture and Delamination

Out of Plane Response

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Direct-spun CNT Mat: In-Plane Piezoresistivity, and Unloading

\[ \sigma_{11}(\text{MPa}) \]

\[ \epsilon \]

\[ R/R_0 \]

\[ \sigma_{11}(\text{MPa}) \]

\[ R/R_0 \]

\[ E_U (\text{GPa}) \]

\[ \text{GF} \]

\[ \epsilon \]
In-Situ Tensile Testing

CNT Mat Sample

0% Strain

10% Strain

12% Strain

5 μm

500 μm
Microstructural change during the uniaxial response
• Rope-like CNT bundles form random interlinked bundle network
• Network deforms like a foam, with transverse deflection of struts.

Direct-Spun Mats: the story

0% Strain
1. Bundle straightening
2. Network Alignment
3. Bundle bending/kinking

10% Strain
1
2
3

Loading

\( \sigma \) (MPa)

\( \epsilon_{11} \)

\( 0 \) | \( 0.05 \) | \( 0.1 \) | \( 0.15 \) | \( 0.2 \) | \( 0.25 \) | \( 0.3 \)

0 5 10 15 20 25 30 35 40 45

0 Degrees
45 Degrees
90 Degrees

3\mu m

3\mu m

CNT Mat

Interconnected Bundle Network

Detail of Network Junctions: Bundles branch and Cross

Cross-section of Bundle Microstructure
Micromechanical Model for direct-spun mat

CNT Bundles are Anisotropic:
- $E_{11} = 680 \text{ GPa}$
- $G_{12} = G_{23} = 9.5 \text{ GPa}$
- $E_{22} = E_{33} = 50 \text{ GPa}$
- $\nu_{12} = \nu_{13} = \nu_{23} = 0.3$

1. Network structure causes foam-like network deformation.
2. Bundles are rope-like.

Modulus below that of CNTs because…

Approximate network with a periodic honeycomb unit cell.
Micromechanical Model for direct-spun mat

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Approximate network with a periodic honeycomb unit cell

Macroscopic yield dictated by the shear strength of CNT bundles.

Network reorientation causes hardening
Routes for Improvement...

Therefore, improvement in mechanical properties can come from **ALIGNMENT** of **CNT BUNDLE MICROSTRUCTURE**

For $G_B \ll E_B$:

$$E_{Network} = \bar{\rho} \cdot \frac{2^{\frac{2}{3}}kG(1+\sin \theta)^2}{\cos^2 \theta}$$
Response in Fluids

- Chlorosulfonic acid lowers $\sigma$ and $E$ by over an order of magnitude.
- $\varepsilon$ increases to $\approx 1.4$ at same rate.
Response in Fluids

Immiscion in chlorosulfonic acid results in creep at low stresses.

Electrical resistance also affected by fluid immersion… but mechanical behaviour is time invariant.
Debundling/debonding upon CSA Immersion

\[
\text{[HSO}_3\text{Cl]}_n + C_x \rightleftharpoons [C_x\text{H}_n^+] + [\text{ClSO}_3^{-}]_n
\]

Dry state: CNTs are closely bundled due to strong van-der-Waals bonds.

After acid infiltration, protonation separates adjacent CNTs.
Debundling/debonding upon CSA Immersion

The presence of **adsorbed ions** at the CNT wall, and in the **solution** screen the positive charge upon the CNT walls, and overcome the **van-der-Waals** attraction.
Fluid Processing in superacid solutions

Ductility and drawing stress controlled by the concentration of a superacid solution.

Drawing process to enhance alignment

1. Acetone Condensation
2. Super-acid Immersion and Stretching
3. Coagulation: acid removal
4. Air Drying
5. Heat Treatment
6. Acetone Condensation

Questions:
- Effect of Acid Treatment
- Effect of Stretch in Acid
- Effect of tension in coagulation
Properties of drawn fibres

- All properties improved significantly.
- Change in ultimate specific strength and conductivity a factor of 3.
- Larger change in stiffness due to switch away from bending.
Summary

- The properties of direct-spun carbon nanotube materials (and CNT materials in general) vary across a wide range of density.
- The stiffness and strength of direct-spun mats is reduced by the CNT bundle network of low nodal connectivity, and by the rope-like structure of the CNT bundles.
- Mechanical and electrical properties of direct-spun CNT mats are enhanced by tensile drawing in different fluids, particularly in superacids.