Tough Materials: Shear Bands & Crazes

Polycarbonate

Applied stress is vertical: horizontal *Crazes* and 45 deg *Shear Bands*

Fatigue crack propagation in polycarbonate Craze and crack moving to the right, Generating shear bands at the craze tip

Images removed due to copyright restrictions.

Please see, for example,
http://www.doitpoms.ac.uk/miclib/micrograph.php?id=559
http://www.doitpoms.ac.uk/miclib/micrograph.php?id=592
The Future - SWCNTs:  
*the ultimate polymer?*

Space Tether

\[ E = 1 \text{ TPa} \]  
(expt and calc)

\[ \sigma_f \sim 50 \text{ GPa} \]  
(calc)

Values for individual tubes

Image removed due to copyright restriction.  
Please see the cover of *American Scientist*,  
July/August 1997.
SWNTs: The Perfect Material

- SWNTs are unique:
  - Polymers of pure carbon
  - High aspect ratio (>1000:1)
  - Unique electron configuration

- SWNTs have extraordinary properties
  - Strength (~100x steel)
  - Electrical conductivity (~Copper)
  - Thermal conductivity (~3x Diamond)
  - Accessible surface area (theoretical limit)
  - Thermal stability (~500 °C air, ~1400 °C anaerobic)

- SWNTs can be customized via organic chemistry
  - Modification of properties
  - Compatibilization with other materials

A new backbone polymer
The most inherently conductive organic molecule
The most thermally conductive material
The strongest, stiffest, toughest molecule there will ever be
The best field emitter
The ultimate engineering polymer

A whole new branch of chemistry!
Strength of commercial organic fibers

Fiber tensile strength (GPa)

- Natural Fibers
- Wet Spun Cellulose
- Melt Spun Nylon
- Kevlar
- PBO

Adapted from NRC Report NMAB-458, April 1992.
TYPES OF NANOTUBES

Carbon nanotubes are basically sheets of graphite rolled up into a tube. Hence, the hexagonal two dimensional lattice of graphite is mapped on a one-dimensional cylinder of radius \( R \) with various helicities characterized by the **rolling vectors** \((n,m)\).

- **(n,0)** zigzag nanotube
- **(n,n)** armchair nanotube
- **(n,m)** chiral nanotube
<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Carbon Fibres</td>
<td>~10,000</td>
</tr>
<tr>
<td>Carbon Nanotubes (Multi-walled)</td>
<td>~10</td>
</tr>
<tr>
<td>Carbon Nanotubes (Single-walled)</td>
<td>~1</td>
</tr>
<tr>
<td>Polymethylmethacrylate (PMMA)</td>
<td>~0.7</td>
</tr>
</tbody>
</table>

Aspect ratio L/D: C60 ~ 1; SWNT ~ 1000; MWNT ~ 2000

Credit:

A. Windle, Cambridge University - about the next 15 slides

Courtesy of Alan Windle. Used with permission.
Electrical Conductivity of Carbon

- CNT Fibre: $2.9 - 8.3 \times 10^5 \, \Omega^{-1}m^{-1}$
- Conventional Carbon fibre: $\sim 1 \times 10^5 \, \Omega^{-1}m^{-1}$
- Commercial graphite: $0.3 - 2 \times 10^5 \, \Omega^{-1}m^{-1}$
- Copper: $6.0 \times 10^7 \, \Omega^{-1}m^{-1}$

Source: Intro. To Mat. Sci. and Eng, W.D. Callister

Courtesy of Alan Windle. Used with permission.
Carbon Nanotubes
long before the ‘nano’ word

T. Baird, J R Fryer and B Grant, *Carbon* 12, 591 (1974)


Courtesy of Alan Windle. Used with permission.
Synthesis of MWCNT “carpets”

- Quartz reaction tube and substrates
- 14 mm and 65 mm diameter reactors
- Quartz slide inserted to collect carpet
- Reaction time 0 to 10 hrs: Longer experiment → longer carpet

200 °C 760 °C

2 to 9.6 wt% ferrocene in toluene

Courtesy of Alan Windle. Used with permission.
Catalyst on substrate: MWCNT Carpet

Images removed due to copyright restrictions.

Courtesy of Alan Windle. Used with permission.
Multi-walled nanotubes: MWCNT

Large Hollow Core plus nested graphene shells

TEM: beam perpendicular to nanotube axis

TEM: beam parallel to nanotube axis (chance)

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Please see http://endomoribu.shinshu-u.ac.jp/research/cnt/images/mwcnt.jpg

Courtesy of Alan Windle. Used with permission.
Direct CNT Fibre Process (A. Windle)

- Continuous process
- Wide range of organic feed stocks work
- Feedstock to product in 10cm at 1200°C
- Both MWNT’s and SWNTs
- Never have to handle nanotube powder, therefore reduced health risks
- Mechanical properties, so far average but for high volume fractions of highly aligned nanotubes prospects are good
- Feedstock costing 0.1 cents/gram converted continuously to CNTs currently marketing at $100/gram: mark-up of $10^5

Courtesy of Alan Windle. Used with permission.
High Temperature Continuous Film Process

@ 1100 C, clean walls, nanotubes only stick below 200°C

Courtesy of Alan Windle. Used with permission.
CVD synthesis of Carbon Nanotubes

Fe

Growth

~10nm

750°C

Courtesy of Alan Windle. Used with permission.
Continuous Wind Up: Film

Feedstock

- Hydrocarbon Feedstock +
- Thiophene +
- Ferrocene

1100 to 1200 °C

H₂ carrier gas

Images removed due to copyright restrictions.
Please see Fig. 1 in Li, Ya-Li, et al. “Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis.” Science 304 (April 9, 2004): 276-278.

Courtesy of Alan Windle. Used with permission.
Images removed due to copyright restrictions.

Please see Fig. 3a in Li, Ya-Li, et al. “Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis.” *Science* 304 (April 9, 2004): 276-278.

Ya-Li Li, Ian Kinloch and Alan Windle, *Science*, 304, p 276, 9 April 2004

Courtesy of Alan Windle. Used with permission.
Multi-wall CNTs: Variable Product Microstructure

Fibre diameter of 20 to 50 μm

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Please see Fig. 3b, c, d in Li, Ya-Li, et al. “Direct Spinning of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis.” *Science* 304 (April 9, 2004): 276-278.

Image analysis

Fibre diameter of 20 to 50 μm

Courtesy of Alan Windle. Used with permission.
Reaction conditions: Ethanol feedstock

- **MWNTs**
  - 2.3 wt% ferrocene
  - 1.5 % thiophene
  - H₂ flow 400 to 800 ml/min
  - Temperature 1100 to 1180 °C

- **SWNTs**
  - 2.3 wt% ferrocene
  - 0.5 wt% thiophene
  - 1200 ml/min H₂
  - 1200 °C

*SWNTs need greater dilution of Fe by carrier gas*

Courtesy of Alan Windle. Used with permission.
SWNT (and DWNTs): 
~ often mixed in with some MWNTs

Diffraction Contrast

Catalyst Particles

Images removed due to copyright restrictions.
Please see Fig. 2c and d in Motta, Marcelo, et al. “Mechanical Properties of Continuously Spun Fibers of Carbon Nanotubes.” Nano Letters 5 (August 2005): 1529-1533.

Courtesy of Alan Windle. Used with permission.
Single Wall CNT Fibres

(A) Courtesy of Alan Windle. Used with permission.

The range of diameters along a fibre occurs due to differences in the local packing density of nanotubes and/or instabilities in the gas-phase reaction.

\[
TEX = \frac{g}{km}
\]

\[
\frac{\text{Force}}{TEX} \times \text{Density} = \text{Stress}
\]

Images removed due to copyright restrictions. Please see Fig. 1 in Motta, Marcelo, et al. “Mechanical Properties of Continuously Spun Fibers of Carbon Nanotubes.” *Nano Letters* 5 (August 2005): 1529-1533.

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