Catalytic Nanoparticle Growth and Nanotube Morphology in a Continuous Gas Phase Process for Carbon Nanotube Synthesis

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Carbon nanotubes (CNTs) have exceptional mechanical, thermal and electrical properties at the nanoscale. These properties can be extended to a macroscopic scale by assembling the CNTs into a fiber with the nanotubes oriented parallel to each other and to the fiber axis …

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Wall Nanotube</td>
<td>1054</td>
<td>150</td>
<td>1.4</td>
<td>3500 (along axis)</td>
</tr>
<tr>
<td>Multi Wall Nanotube</td>
<td>1200</td>
<td>150</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>600</td>
<td>130</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Kevlar</td>
<td>186</td>
<td>3.6</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Steel</td>
<td>208</td>
<td>1.0</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>16</td>
<td>0.008</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT fiber from CVD reactor</td>
<td>50 – 150</td>
<td>0.5 – 1.5</td>
<td>0.28</td>
<td></td>
</tr>
</tbody>
</table>

Table: Mechanical properties of individual carbon nanotubes.
## Knot Test

### Knot Test Results

<table>
<thead>
<tr>
<th>Material</th>
<th>As-supplied strength (GPa/SG)</th>
<th>Knotted strength (GPa/SG)</th>
<th>Knot efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT Fibre</td>
<td>1.22</td>
<td>1.2</td>
<td>98</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>2.2</td>
<td>0.4</td>
<td>17</td>
</tr>
<tr>
<td>Dyneema</td>
<td>3.6</td>
<td>1.9</td>
<td>53</td>
</tr>
<tr>
<td>T300 carbon fibre</td>
<td>2.3</td>
<td>0.026</td>
<td>1</td>
</tr>
<tr>
<td>Cotton</td>
<td>-</td>
<td>-</td>
<td>91</td>
</tr>
<tr>
<td>Nylon</td>
<td>-</td>
<td>-</td>
<td>99</td>
</tr>
</tbody>
</table>

*Courtesy Tortech Nanofibres*
Introduction – The CNT-Fiber-Spinning-Process

This process allows a continuous collection of:

- CNT fibers - Individual solvent-condensed filaments. 
  *Spinning rates of ~20 m/min which correspond to 1 – 5 g/day are achieved*

- Uncondensed aerogel – CNT sheets

The production cost is comparable to the production of synthetic amorphous carbon (~1 USD/kg)

Introduction – The CNT-Fiber-Spinning-Process

- Typically gaseous source of **Carbon**
- Ferrocene to supply **Iron** (~2%)
- Thiophene to supply **Sulfur** (~0.3%)

- Ferrocene decomposes and **Iron** nanoparticles nucleate and grow via condensational and collisional processes
Introduction – The CNT-Fiber-Spinning-Process

- Ferrocene decomposes and **Iron** nanoparticles nucleate and grow via condensational and collisional processes
- **Sulfur** conditions the particle surface

‘Nanotube smoke’ or ‘aerogel’
Introduction – From Nanotube to Fiber

Carbon Nanotube Chirality

Bundle of Carbon Nanotubes

Carbon Nanotube (single and double walled)

Carbon Nanotube Fiber
Introduction – From Nanotube to Fiber
Hypotheses

• Carbon nanotube production rate as well as CNT quality is primarily driven by ‘idealized’ catalyst nanoparticles
  - CNT diameter, chirality, number of walls and therefore its mechanical properties are influenced by catalyst particle diameter
  - Typically only ~1% of produced catalyst nanoparticles contribute to CNT growth

• ‘Delivery’ of catalyst nanoparticles at a temperature where optimal catalytic cracking of carbon source occurs is important
Goal

Develop a mechanistic understanding of the catalyst formation, CNT growth and aerogel formation.

Objectives

• Analyze the growth of the catalyst nanoparticles along the furnace axis by means of an SMPS sampling system
• Determine the evolution of CNT growth by characterizing deposits and web along the furnace axis by means of SEM
• Develop a technique for optical analysis (spectroscopy and light-scattering) of the CNT-aerogel-formation process
Methods – Experimental Setup – Reactant-Injector System

- **Experimental Setup**
- **Reactant Injector System**

**Carbon source:**
- e.g. methane (CH\(_4\), \(~20\) ml/min)

**Bulk H\(_2\)-flow**
- \((\sim0.25-5\) l/min)

**H\(_2\) carrier gas for ferrocene**
- \((\sim40\) ml/min)

**Iron source:**
- solid ferrocene, sublimes at 70 °C

**Furnace tube, 40 mm inner diameter**

**Sulfur source:**
- thiophene (C\(_4\)H\(_4\)S)
  - cooled down in ice-water to 0.1 °C

**H\(_2\) carrier gas for thiophene**
- \((C_4H_4S, \sim5\) ml/min)

**Different injector designs – here:**
- schematic of showerhead design
Methods – Experimental Setup – Particle/CNT-Sampling System

To FTIR and vent flow

N₂ for dilution
Orifice
Ejector

SMPS

To particle (SMPS) and TEM sampler

HEPA filter

Sampling Probe System

To FTIR and dilution vent flow

H₂ diluted in N₂ and air (~0.5 l/min)

Compressed air at ~1.2 bar

H₂ sensor
4 to 20 mA output
~0 to 2,000 ppm H₂

R = 100.0 Ω
12 VDC

Vent flow
Results – Analysis along Tube Axis

- 500 ml/min
- Re~25<<2300
- Reactor tube, 40 mm inner diameter, length: 700 mm

Temperature distribution ($T_{\text{max}} \sim 1500$ K)
Results – Analysis along Tube Axis
Results – Analysis along Tube Axis

Temperature distribution

Investigations by K. Kuwana et al. and D. Conroy et al.  

Particle size distributions along the furnace axis in ferrocene and thiophene added to the system and at a H₂ bulk flow rate of 500 ml/min (alumina worktube, maximum count ~10⁸).
Results – Analysis along Tube Axis

Wall Temperature [K]

Resistance between Wall and Exit Wall

Resistance [Ω]

Length of Tube [mm]
Results – Analysis along Tube Axis

[Images of micrographs showing analysis along tube axis with labeled measurements and electron beam settings.]
Results – Analysis along Tube Axis
Results – Analysis along Tube Axis
Results – Analysis along Tube Axis
Introduction of CVD process that has the potential to produce (oriented) CNTs at a rate and a price comparable to the production of synthetic amorphous carbon.

Particle appearance and disappearance observed in both SEM images and SMPS measurements was shown.

Catalyst nanoparticles stick to initially grown CNTs and may act as a growing point of a new CNT.

Different ‘quality’ of produced web was shown by means of SEM.

During the synthesis process, CNTs mostly assemble into bundles.
Gaining optical access to the process …
Thank you...

Questions?
Introduction – From Nanotube to Fiber
Results – Analysis along Tube Axis

Particle size distributions along the furnace axis measured for ferrocene and thiophene added to the system and at a H₂ bulk flow rate of 500 ml/min (alumina worktube).
Results – Blockage of Furnace Tube
• No ‘web’ growth at specific spot
Results – Blockage of Furnace Tube – outer region

- Carbon rods/ CNTs
- Some catalyst particles
Results – Blockage of Furnace Tube – inner region

- Carbon rods
- No catalyst particles
Results – Blockage of Furnace Tube – inner region

- Carbon rods/ CNTs
- Some catalyst particles