Nanofibers
structural & sensoric applications
Outline

1. Introduction to nanofibers
2. Structural properties
3. Sensoric applications
4. Suggestions future research
Introduction: Nanofibers by CVD or Electrospinning

<table>
<thead>
<tr>
<th>FIBER FORM:</th>
<th>SWNT</th>
<th>MWNT</th>
<th>ESNF</th>
<th>Whiskers</th>
<th>Fibers</th>
<th>Wire</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROCESS:</td>
<td>CVD</td>
<td>Electrospinning</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scale (m):</td>
<td>(10^{-10}) atomic</td>
<td>(10^{-9}) nano</td>
<td>(10^{-8}) micro</td>
<td>(10^{-6})</td>
<td>(10^{-5})</td>
<td>(10^{-4})</td>
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<tr>
<td>COMPOSITION:</td>
<td>EELS</td>
<td>AES</td>
<td>XPS</td>
<td>EDX</td>
<td>µ-Raman</td>
<td>µ-FTIR</td>
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<tr>
<td>STRUCTURE:</td>
<td>TEM</td>
<td>STM</td>
<td>AFM</td>
<td></td>
<td>SEM</td>
<td>Light microscopy</td>
</tr>
<tr>
<td>PHYSICAL:</td>
<td>AFM</td>
<td>Nanindentation</td>
<td></td>
<td>MEMS Test Devices</td>
<td>Conventional</td>
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</tbody>
</table>

CVD: low output, expensive
perfect material properties
cnt’s, oxides, metals
short fibers (um’s)

ES: high output, “cheap nano”
less ideal material structure
polymers, oxides, carbon
long fibers (cm range)
# Structural properties high performance fibers

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Weight kg/m³</th>
<th>E-modulus GPa</th>
<th>Strength GPa</th>
<th>Strgth/Wgth MPa.m³/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>7900</td>
<td>200</td>
<td>0,4</td>
<td>0,05</td>
</tr>
<tr>
<td>E-glass</td>
<td>2560</td>
<td>70</td>
<td>2,4</td>
<td>0,9</td>
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<tr>
<td>Aramide</td>
<td>1440</td>
<td>130</td>
<td>3,6</td>
<td>2,5</td>
</tr>
<tr>
<td>Carbon</td>
<td>1800</td>
<td>700</td>
<td>5,0</td>
<td>2,8</td>
</tr>
<tr>
<td>HMPE</td>
<td>980</td>
<td>95</td>
<td>3,0</td>
<td>3,1</td>
</tr>
<tr>
<td>PBO</td>
<td>1550</td>
<td>230</td>
<td>5,8</td>
<td>3,7</td>
</tr>
<tr>
<td>M5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNTpotential</td>
<td>1300</td>
<td>1000</td>
<td>100</td>
<td>76,9</td>
</tr>
<tr>
<td>CNTcurrent</td>
<td>1300</td>
<td>2-4</td>
<td>1,5-3</td>
<td></td>
</tr>
</tbody>
</table>
Carbon Nanotube Reinforced Nanocomposite Fibrils and Yarns

Bridging the Gap between CNT and Macrocomposite Structures

1. Processing
2. Characterization
3. Multifunctional composites

• Exceptional Mechanical Properties:
  – Elastic Moduli: 1-5 TPa
  – Fracture Strains: 6-30%
  – Ultimate Tensile strength: 30-180 GPa

• Novel Electric Properties:
  – Conductivity: 6000 S/cm

• Ultrahigh Surface Area:
  – A_s up to 1500 m²/gram

• Higher Thermal Conductivity
  – The Best Carbon Fibers:
    – 2000 W/m-K

• Diameter: 1-2 nm
• Aspect Ratio : 10³ - 10⁴

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FSU-FAC²T Workshop on Nanotube-Reinforced Composites, March 23-24, 2004
Nanoengineered Materials

- Nanotubes
  - SWNT
  - MWNT (including DWNT)
- Nanoplatelets
  - Graphite (GNP)
  - Montmorillonite (Nanoclay)
- Nanofiber
  - Vapor-grown graphite (Pyrograf)
  - Electrospun/phase separated LC fibers
- Nanocomposite fibers
  - Organic polymer co-electrospun with CNT, GNP, VGNF
  - Inorganic matrix fibril reinforced by CNT, GNP, VGNF
Nanocomposite Fibrils

- Nanotubes and nanoplatelets, which have two and one nano-dimensions, respectively, are highly effective as bulk reinforcing fillers because of their high aspect ratio.
- Further orienting these along a fiber’s length focuses their reinforcing effects.
Electrospinning of CNT/PAN Nanocomposite Fibrils

NASA Program
Ko et al. AIAA Proceedings, 2002
Frank K. Ko, Fibrous Materials Laboratory

Co-electrospinning

Alignment of CNT
- Flow induced alignment
- Charge induced alignment
- Confinement effect

Polymer Solution
Taylor Cone
V
HV
Spinning Drum
Ventilation/Conditioning
Orientation
Attenuation
Twisting
Takeup

Continuous Processing of CNT nanocomposite yarn

CNT Yarn

PAN

CNT/PAN
Polymer CNT Composites

Mechanics:
• reinforcement with 1 % (0.5 vol %) results in 42 % increase in modulus!

• Under stress failure along the weak NT-PS interface together with cracking of NT at defect sites (kinks, catalyst residues)
Polymer CNT Composites
Mechanical Reinforcement

- Epoxy
- PA 6
- iPP

Graphs showing stress-strain relationships and other mechanical properties for different composites.
Bonding issue of CNT in the polymer matrix

*in progress*

- Polymer wrapping
  - plasma deposition of 2-7 nm polystyrene
- Covalent functionalization
  - Epoxide terminated molecule and carboxylated cnt
- Insitu polymerization
  - PMMA
  - PAN
- Etching
  - Plasma
  - Chemical
Baughman Group, Dalton

- poly(vinyl alcohol) fibers
  - containing 60 wt.% SWNTs
- tensile strength of 1.8 GPa
- 80 GPa modulus for pre-strained fibers
- High toughness
  - energies-to-break of 570 J/g
  - greater than dragline spider silk and Kevlar

Kearns, Shambaugh

- SWNT were dispersed into polypropylene
  - via solution processing with dispersion via ultrasonic energy
  - melt spinning into filaments
- 40% increase in tensile strength at 1wt.% SWNT addition, to 1.03 GPa.
- At higher loadings (1.5 and 2 wt%), fiber spinning became more difficult
  - reductions in tensile properties
- “NTs may act as crystallite seeds”
  - changes in fiber morphology, spinning behavior
  - attributable to polymer crystal structure
FEA Prototype
Space Elevator Ribbon Materials

Current Research

- Fiber Composition
  - PMMA/CNT-60
  - PS/CNT-60
- Coatings
  - SiO₂
  - Al 6061-T6

<table>
<thead>
<tr>
<th>Property Name</th>
<th>Unit</th>
<th>PMMA/CNT-60</th>
<th>PS/CNT-60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Modulus</td>
<td>N/m²</td>
<td>601E+9</td>
<td>610E+9</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>N/m²</td>
<td>6.78E+9</td>
<td>8.20E+9</td>
</tr>
<tr>
<td>Mass Density</td>
<td>kg/m³</td>
<td>1256</td>
<td>1200</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>N/m²</td>
<td>60.1E+9</td>
<td>60.1E+9</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>N/m²</td>
<td>1.29E+8</td>
<td>1.3E+8</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>N/m²</td>
<td>6.78E+7</td>
<td>8.2E+7</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W/m K</td>
<td>1200.07</td>
<td>1200.05</td>
</tr>
<tr>
<td>CTE</td>
<td>10⁻⁶/K</td>
<td>86.7</td>
<td>88.5</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Property Name</th>
<th>Unit</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elongation Modulus</td>
<td>N/m²</td>
<td>1000E+9</td>
</tr>
<tr>
<td>Compression</td>
<td>N/m²</td>
<td>1E+9</td>
</tr>
<tr>
<td>Mass Density</td>
<td>kg/m³</td>
<td>1300</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>N/m²</td>
<td>100E+9</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>N/m²</td>
<td>5.3E+9</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W/m K</td>
<td>2E+7</td>
</tr>
<tr>
<td>CTE</td>
<td>10⁻⁶/K</td>
<td>2000</td>
</tr>
</tbody>
</table>

Targetted Mechanical Properties of Polymer/CNT-60 and CNT Fibers

Near-term Efforts
- Interconnects
- Kapton
- Validation Materials
  - Kevlar 49Dupont
Buckypaper laminates (aerospace)

Nanotube Buckypaper Composite Microstructural Characterization

Random Orientation

Magnetically Aligned – 17.3 T

Dr. Liang et al – FAMU-FSU COE

Buckypaper Fabrication

Single Wall Carbon Nanotubes

Dispersion

Filtration and washing

Filtration

Bucky paper

Buckypapers to Nanocomposite Laminates

90 mm

47 mm

25 mm

Resin infusion/hot press process

Dr. Liang et al – FAMU-FSU COE
Conclusions structural properties cnt composites

- Nanotubes are > 150 GPa in strength.
  - Strain-to-break of 10 to 20%
  - Should allow 100 GPa composites
  - At present best results 2-3 GPa
  - Still much room for improvement
- Challenges still exist
  - Stress transfer / straining the tubes
  - Controlling the interface
  - Increase aspect ratio (long fibers)
  - Eliminating defects at high alignment
  - High throughput, low cost processing
- Work is progressing among many groups
Strength of polymer nanofiber fabrics (Tandec, USA)

- 2x increase in tensile strength (660 nm PU)
- 10x increase in tensile strength (68 nm PA)
- thanks to increase in no. fiber-fiber bondings

**Table 3 Normalized Tensile Strength of Meltblown and Electrospun PU Fabrics (10 x 2.5 cm² samples)**

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Basis Weight (g/m²)</th>
<th>Break Elong (%)</th>
<th>Peak Force (N)</th>
<th>Normalized P.F.</th>
<th>S.D.</th>
<th>C.V. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meltblown</td>
<td>27.9</td>
<td>357</td>
<td>5.43</td>
<td>0.194</td>
<td>0.018</td>
<td>9.4</td>
</tr>
<tr>
<td>Electrospun</td>
<td>38.2</td>
<td>163</td>
<td>18.6</td>
<td>0.479</td>
<td>0.066</td>
<td>13.8</td>
</tr>
</tbody>
</table>

**Table 4 Normalized Tensile Strength of Meltblown and Electrospun Nylon Fabrics (10 x 2.5 cm² samples)**

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Basis Weight (g/m²)</th>
<th>Break Elong (%)</th>
<th>Peak Force (N)</th>
<th>Normalized P.F.</th>
<th>S.D.</th>
<th>CV(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meltblown</td>
<td>40.4</td>
<td>24.9</td>
<td>6.24</td>
<td>0.154</td>
<td>0.021</td>
<td>13.6</td>
</tr>
<tr>
<td>Electrospun</td>
<td>7.6</td>
<td>6.8</td>
<td>11.7</td>
<td>1.52</td>
<td>0.09</td>
<td>6.0</td>
</tr>
</tbody>
</table>
**Electrospinning**
- typical 50-100 nm fibers
- various polymers & biopolymers (TNO)
- various metaloxides & ceramics
- carbon
- but also:
  - dual fiber
  - hollow fiber

**Scheme 1.** A schematic drawing of the spinneret constructed from two coaxial capillaries, and the molecular structures of MEH-PPV and PHT.

**electrospinning**

**dual fiber electrospinning**

**hollow nanofibers by electrospinning**
Nanofiber fabric for filters

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>SOLVENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6 and nylon 66</td>
<td>Formic Acid</td>
</tr>
<tr>
<td>Polycrylonitrile</td>
<td>Dimethyl formaldehyde</td>
</tr>
<tr>
<td>PET</td>
<td>Trifluoroacetic acid/Dimethyl chloride</td>
</tr>
<tr>
<td>PVA</td>
<td>Water</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>DMF/Toluene</td>
</tr>
<tr>
<td>Nylon-6-co-polyamide</td>
<td>Formic acid</td>
</tr>
<tr>
<td>Polybenzimidazole</td>
<td>Dimethyl acetamide</td>
</tr>
<tr>
<td>Polyamide</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Polyimides</td>
<td>Phenol</td>
</tr>
</tbody>
</table>

Single Human Hair
Single Pollen Spore
Human Red Blood Cell
Nanofibers
Nanofibers
Nanofibers
Conclusions ES nanofiber (polymer, metal oxide)

- High throughput low cost nanofiber
- “Cheap” large surface area/weight fabric:
  - Absorption, Filtration
  - Catalytic
  - Sensor
- Further exploration needed:
  - Structural applications
    - Reinforcement fiber
    - CNT-polymer composite fiber
  - Insulation
  - Selective gas permeation
CNT Applications: Electronics

- CNT quantum wire interconnects
- Diodes and transistors for computing
- Capacitors and data storage
- **Mechanical (resonator) and electrochemical sensor**
- Field emitters for instrumentation and flat panel displays
- THz oscillators
CNT DNA Sensor
Using Electrochemical Detection

- MWNT array electrode functionalized with DNA/PNA probe as an ultrasensitive sensor for detecting the hybridization of target DNA/RNA from the sample.
  - Signal from redox bases in the excess DNA single strands

- The signal can be amplified with metal ion mediator $\left[ Ru(bPy)_3^{2+} \right]$ oxidation catalyzed by Guanine.
Single-Walled Carbon Nanotubes For Chemical Sensors

- Every atom in a single-walled nanotube (SWNT) is on the surface and exposed to environment
- Charge transfer or small changes in the charge-environment of a nanotube can cause drastic changes to its electrical properties
SWNT Sensor Assembly

- Purified SWNTs in DMF solution
- Cast the SWNT/DMF onto IDE
SWNT Sensor Response to NO$_2$ with UV Light Aiding Recovery

Detection limit to NO$_2$ is 44 ppb.
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  - At present best results 2-3 GPa
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  - Eliminating defects at high alignment
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Industrial Applications of CNT’s

- H-storage: unrealistic
- nanotransitors: a wonderful toy
- cold electron emission: very realistic
- composites for electrical conductivity: realistic
- mechanical composites: still progress needed
- artificial muscles: realistic
- catalysis and catalyst support: realistic
- interconnects, wires in chips: realistic
Electroactive polymers
artificial muscles

CNT’s have piezo activity e.g.:
- CNT – PAN
- CNT – PVDF
Thank you.