Multifunctional Nanocomposites for Aerospace Applications: Overview

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NASA Langley Research Center

Founded in 1917: first civil aeronautical research laboratory
Facilities: $4 billion replacement value
People: 2000 Civil Servants ; 1700 Contractors

All images credit: NASA
Advanced Materials and Processing Branch

Materials Design
- Design
- Processing
- Characterization
- Modeling

Innovative Materials Processing
- CNT
- Nanocomposite

Materials Testing

Advanced Material Systems

Materials for Extreme Environments

All images credit: NASA
Critical Concerns for Aerospace Systems

**Weight**
- Reduced fuel consumption & emissions
- Reduced launch costs
- Enabler for many new vehicles designs

**Functionality/Performance**
- Reduced fuel or power consumption
- Multifunctionality – additional reduced weight

**Durability**
- Safety and reliability
- Maintenance down-time and costs
- Extreme environments

All images credit: NASA
## Design Materials Properties

### Materials Properties to be Tailored
- Electrical Conductivity
- Dielectric Permittivity
- Magnetic Permeability
- Thermal Conductivity/expansion coefficient
- Radiation Shielding
- Mechanical (modulus, strength, toughness...)
- Solar Absorptivity/Thermal Emissivity
- Band gap engineering
- Optical property (transparency, refractive index...)
- Piezoelectricity/Pyroelectricity/Electrostrictive
- Gas/Liquid Permeability
- Anisotropy/orientation

### Design Parameters
- Nano Inclusion type and combination (CNT, BNNT, BCNNT, GP, hBN, NP...)
- Matrix type
- Composition
- Dispersion
- Orientation
- Geometry, Fabrication, Processing...

### Specific Applications
- R2R Printing of Electroactive Polymer Composites: NSF/NASA
- Electroactive properties & Radiation Shielding of BNNT Composites: AFOSR/NASA C&I
- Radiation Detection and Conductivity Control: DOE (ORNL)/NASA
- Solar Absorption and Thermal Emission Control: NASA C&I
- Structural BNNT composites, BNNT fibers and mats: Rice Univ/NASA GCD, B&P, IRAD
- Multiple Metal Infusion for Multifunctionality (S2M2N): NASA IRAD
- Bandgap Engineering of nanotubes: NASA IRAD
- Doped Chiral Polymer Metamaterials (DCPM): NASA IRAD
- Radiation Shielding and Thermal Conduction (Electronic Packaging): NASA IRAD
- Ultralight Flexible Shielding Tension Shell: NASA IRAD
Multifunctional Nanocomposites
  • Nanotube Synthesis: High Temperature-Pressure (HTP) BNNT and BCNNT Synthesis
  • Dispersion
  • Tailoring physical properties of nanocomposites for multifunctions
  • Metallized Nanotube Polymer Composites (MNPC)
  • Doped Chiral Polymer Metamaterials (DCPM)
  • Band Gap Engineering ($B_xC_yN_z$ Nanotubes)

• Sensors/Actuators

• Radiation Shielding

• Summary
Properties of Materials for Vehicle Structure

Baseline Materials
- Baseline Materials
- 5-10 years (TRL = 4-6)
- 10-20 years + (TRL = 1-3)

Charlie E. Harris, M. J. Shuart, H. Gray, NASA/TM-2002-211664

Nanotube values are theoretical.
Properties of Materials for Vehicle Structure

Specific Modulus, GPa/(g/cm³)

Specific Strength, GPa/(g/cm³)

1. BNNT (theoretical)
2. Baseline Materials
3. 5-10 years (TRL = 4-6)
4. 10-20 years + (TRL = 1-3)

Nanotube values are theoretical.
<table>
<thead>
<tr>
<th></th>
<th>Carbon Nanotubes</th>
<th>Boron Nitride Nanotubes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electric Properties</strong></td>
<td>Metallic or semiconducting</td>
<td>Wide band gap (about 6.0 eV band gap)</td>
</tr>
<tr>
<td><strong>Mechanical Properties</strong></td>
<td>1.33 TPa (very stiff)</td>
<td>1.18 TPa (very stiff)</td>
</tr>
<tr>
<td>(Young’s Modulus)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thermal Conductivity</strong></td>
<td>&gt;3000 W/mK (highly conductive)</td>
<td>~300–3000 W/mK (highly conductive)</td>
</tr>
<tr>
<td><strong>Thermal Oxidation Resistance</strong></td>
<td>Stable up to 300-400 °C in air</td>
<td>Stable to over 800 °C in air</td>
</tr>
<tr>
<td><strong>Neutron Absorption Cross-Section</strong></td>
<td>C = 0.0035 barn</td>
<td>B = 767 barn (B \textsuperscript{10} \sim 3800 barn)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N = 1.9 barn (Excellent radiation shielding)</td>
</tr>
<tr>
<td><strong>Polarity</strong></td>
<td>No dipole</td>
<td>Permanent dipole</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Piezoelectric (0.25-0.4 C/m\textsuperscript{2})</td>
</tr>
<tr>
<td><strong>Surface Morphology</strong></td>
<td>Smooth</td>
<td>Corrugated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Provides better bonding for composites, ionic bonding)</td>
</tr>
<tr>
<td><strong>Color</strong></td>
<td>Black</td>
<td>White</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(can be dyed to color)</td>
</tr>
<tr>
<td><strong>Coefficient of Thermal Expansion</strong></td>
<td>-1 x10\textsuperscript{-6} K\textsuperscript{-1} (very low)</td>
<td>-1 x 10\textsuperscript{-6} K\textsuperscript{-1} (very low)</td>
</tr>
</tbody>
</table>
Synthesis Methods of Carbon Nanotubes

- Arc-discharge: solid state carbon precursor
- Laser ablation: solid state carbon precursor
- Chemical vapor deposition (CVD): gaseous carbon precursor/ HiPco (High pressure CO)
- Free Electron Laser (Jefferson Lab): funded by NASA-LaRC C&I
- RF Induction Thermal Plasma (Canadian NRC)

Credit: www.tekna.com

Nano Lett 2, 56 (2002)
BNNT Synthesis History

- First Theoretical prediction: *PRB* **49** 5081–5084 (1994) (UC Berkeley, Cohen), computation


- High pressure


- Ball milling/thermal annealing: *CPL* **74** 2782 (1999) (ASU Australia, Chen) Ball milling of B powder in NH3 gas


High Temperature-Pressure (HTP) BNNT and BCNNT

- Free Electron Laser or CO₂ laser
- No Catalyst, only B and N resource (and C for BCNNT)
- Very long, small diameter, highly crystalline BNNT, BCNNT
• 5 kW of infrared radiation @ 10.6\(\mu\)m
  Heat source for vaporizing Boron feed stock above 3500\(^\circ\)C
• Pressurized with Nitrogen to 200 psi
• LaRC rig operating since May 2012
daily with two operators for 1 shift

Nanotechnology, 20 505604 (2009)
J. Thermophysics and Heat Transfer 27 369 (2013)
Proc. SPIE 9060 906006 (2014)
Cotton-like High Pressure and Temperature (HPT)-BNNT

Benefits
• One-to-few-walled tubes with high crystallinity
• Very long, high-aspect ratio tubes
• High scale-up potential
• No toxic catalysts (only B and N as reactants)
• Standard industrial cutting/welding lasers
• High service temperature (over 800ºC)
• Highly electroactive (due to the B-N polar bond)
• Neutron radiation shielding (due to their B content)

(~ 30 minutes run time)

All images credit: NASA
5 nm dia.

Image: Wei Cao, ODU/ARC

All images credit: NASA
Thermal Stability of BNNT vs. CNT: TGA

BNNT: No Oxidation at 800°C in Air

Remained oxidized BNNT after 1000°C run

Heating rate: 5°C/min
Mechanical Properties of BNNT and BNNT Composites: Processing and Characterization Techniques

Individual BNNT and BNNT Bundles: compressive modulus, tensile modulus and strength, radial modulus

TEM-AFM, TEM-STM Holders  
Credit: NASA LaRC/NIA/Binghamton

3D Nanomanipulator in SEM/FIB  
Credit: SUNY Binghamton

AFM  
Credit: SUNY Binghamton

Small, 8, 116 (2012)  
ACS Nano, 6, 1814 (2012)  
Nanotechnology, 23, 095703 (2012)

BNNT composites and BNNT yarns

Spun yarns: NASA LaRC/NIA (credit)  
Wet spinning/Electrospinning  
Credit: NASA LaRC/NIA

Superacid Spinning  
Credit: Rice U
How to make strong, stiff, tough structural BNNT composite?

**Good tubes:**
- highly crystalline, long, thin BNNTs → Excellent intrinsic BNNT properties

- Longer tube (high aspect ratio) → Greater yarn strength

**BNNT Tensile Test Results (Only for comparison with CNT)**

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Elastic modulus (GPa)</th>
<th>Breaking Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D = 2.5 nm</td>
<td>760-960</td>
<td>14-38</td>
</tr>
</tbody>
</table>

Credit: Prof Ke (SUNY Binghamton)

**Hearle’s Yarn Equation**

\[ \sigma_y \approx \cos \theta (1 - \text{kosec} \theta) \cdot \sigma_f \]

- \( \sigma_y \): yarn strength,
- \( \sigma_f \): fiber (tube) strength
- \( \theta \): helix angle that fibers make with yarn axis

- \( k \): \((dQ/\mu)^{1/2}/3L\), \( d \): fiber diameter
- \( \mu \): coefficient of friction
- \( L \): fiber length
- \( Q \): fiber migration length

\[ \text{If } \sigma_f \uparrow, d \downarrow, L \uparrow, \mu \uparrow \rightarrow \sigma_y \uparrow \]

Credit: Hearle, Structural mechanics of fibers, yarns, & fabrics, (1969)

**High orientation**
- Solution spinning and extrusion

**High interfacial strength**
- BNNT-epoxy and BNNT-PMMA interfacial strength are superior to CNT counterpart

**Longer tube (high aspect ratio)**

*Yakobson 2002*
First BNNT run successfully without optimization July 2013; excellent quality (long, thin, highly crystalline BNNT)

Successful pressure test up to 950 psi (higher pressure leads to better BNNT potentially)

In-situ diagnostic tools installed (planar laser induced fluorescence: PLIF); more tools coming (CARS, pyrography, high speed camera…)

Parallel computational study for nucleation and growth ongoing (both NIA and NASA)

All images credit: NASA/NIA
NIA BNNT Science Chamber

Shadowgraph

Optical Lenses and Mirrors

Pressure Gauge

Nitrogen Feed

Cooling Lines

Cameras

Main Chamber

Optical Filters/ Shutters

All images credit: NASA/NIA

Misang-Hyon Chu (NIA), NIA Nanotechnology Workshop (2014)
In-situ Optical Diagnostics

- Understand chemistry and flow physics of nanotube generation
- Improve and validate simulation/modeling
- Optimize material properties, production rate
- Specific Goals:
  - Determine gas and melt-ball temperatures
  - Determine amount of $B_2$, B, BN, N and $N_2$
- In-situ, on-surface measurement:
  - High speed imaging; high speed (1 kHz) optical pyrometer being developed to study melt-ball dynamics
- Off-surface, gas phase measurement:
  - High-speed, high-resolution imaging
    - Shadowgraph and visible emission
  - Species sensitive imaging (BN PLIF)
  - Temperature measurements (CARS)

All images credit: NASA/NIA

Jennifer Inman, Paul Danehy, Steve Jones, Joe Lee (NASA LaRC), Andrew Cuttler (GWU)

Modeling of Laser Ablation and Plume Chemistry in a Boron Nitride Nanotube Production Rig

Contour lines of temperatures and mass fraction of BN in the plume

Proc. SPIE 9060 906006 (2014)
J. Thermophysics and Heat Transfer 27 369 (2013)

All images credit: NASA
How to disperse Nanotubes?

1) Kinetic Approach
   High shear (stirring, homogenization, speedmix)
   Sonication (cavitational force)
   Melt mixing (twin screw mixer, extruder, calendering, capillary rheometer, fiber spinning)
   In-situ polymerization
   *In-situ polymerization under simultaneous sonication & high shear* (Chem. Phys. Lett. 364, 303 (2002))

2) Thermodynamic Approach (Minimizing free energy of mixing)
   Covalent bonding
     Acid etching
     Stirring, reflux, and soxhlet extraction with H₂SO₄, HNO₃, and HCl
     Functionalization
     Fluorination, reflux with amine, electrochemical (diazonium compound)

   Non-covalent bonding
     Amphiphilic (surfactant), hydrophobic interaction: Water soluble polymers
     Wrapping: PmPV, Polyvinyl pyrrolidone, Polystyrene sulfonate, PPE
     Charge Transfer (Donor-acceptor) (Chem. Phys. Lett. 391, 207 (2004))
     Dispersion Interaction (London force, Permittivity matching)
     Solvent or Co-solvent selection (Hansen solubility parameter, surface energy)
     Similar size/structure to SWCNT
     Zwitterion
     Complex formation
     Nonspecific interaction

\[ \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \]
Using Functionalized AFM tips interaction forces can be directly probed.

<table>
<thead>
<tr>
<th>Alkyl-thiol Endgroup</th>
<th>Experiment Force/Molecule (pN)</th>
<th>Modeling (pN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–OH</td>
<td>9.6 ± 2</td>
<td></td>
</tr>
<tr>
<td>–perfluoro</td>
<td>8.7 ± 3</td>
<td></td>
</tr>
<tr>
<td>–SH</td>
<td>9.2 ± 3</td>
<td></td>
</tr>
<tr>
<td>–CH=CH₂</td>
<td>8.1 ± 2</td>
<td></td>
</tr>
<tr>
<td>–CH₃</td>
<td>7.6 ± 2</td>
<td>1.92</td>
</tr>
<tr>
<td>–COOH</td>
<td>12.2 ± 3</td>
<td></td>
</tr>
<tr>
<td>–NH₂</td>
<td>23.4 ± 4</td>
<td>2.98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aryl-thiol Endgroup</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methylbenzene</td>
<td>18.9 ± 5.7</td>
<td></td>
</tr>
<tr>
<td>4-nitrobenzene</td>
<td>21.8 ± 5.3</td>
<td></td>
</tr>
<tr>
<td>4-aminebenzene</td>
<td>22.6 ± 4.7</td>
<td></td>
</tr>
<tr>
<td>4-bromobenzene</td>
<td>26.9 ± 3.6</td>
<td></td>
</tr>
<tr>
<td>4-hydroxybenzene</td>
<td>32.0 ± 8.4</td>
<td></td>
</tr>
<tr>
<td>4-fluorobenzene</td>
<td>39.5 ± 8.8</td>
<td></td>
</tr>
<tr>
<td>4-methoxybenzene</td>
<td>41.5 ± 10.9</td>
<td></td>
</tr>
<tr>
<td>H-benzene</td>
<td>46.8 ± 11.8</td>
<td></td>
</tr>
<tr>
<td>4-Nitrilebenzene</td>
<td>56.9 ±15.5</td>
<td></td>
</tr>
</tbody>
</table>
Hanson and Hilderbrand Solubility:

\[ \frac{2}{t} = \frac{2}{d} + \frac{2}{p} + \frac{2}{h} \]

@ T = 25°C

\( \delta_d \): dispersion component
\( \delta_p \): polar
\( \delta_h \): hydrogen bond

Code written to plot coordinates \((\delta_d, \delta_p, \delta_h)\) for each solvent and solute and color code good, poor, and unknown solvents.

Michelle Tsui (UC Berkeley, LARSS)
2-D Hansen Plot ($\delta_p$, $\delta_h$ only): Select Good Solvents/Co-Solvents

Hanson and Hilderbrand Solubility:

$$\frac{2}{t} = \frac{2}{d} + \frac{2}{p} + \frac{2}{h}$$

### Diagram

- **Green** – Relatively good solvent
- **Red** – Relatively poor solvent
- **Blue** – Ambiguous or not tested
- ★ - Ratios attempted

Michelle Tsui (UC Berkeley, LARSS)
Building Blocks: SWCNT/Polymer Nanocomposites

Electroactive High Performance Polyimide

\[(\beta\text{-CN})\text{APB/ODPA (}T_g = 220^\circ\text{C)}\]

- Dispersion Interaction
- Donor-Acceptor interaction
- In-situ Polymerization under sonication and shear

Polyimide + SWNT

All images credit: NASA

HRSEM: Well Dispersed SWCNT in Polyimide (2D & 3D)

All images credit: NASA
Tailoring Physical Property for Multifunctions

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<tr>
<td>• Thermal Conductivity/expansion coefficient</td>
<td>• Dispersion</td>
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<td>• Radiation Shielding</td>
<td>• Orientation</td>
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<tr>
<td>• Mechanical (modulus, strength, toughness…)</td>
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<td>• Anisotropy/orientation</td>
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</table>
Versatility of SWCNT Electroactive Polymer Nanocomposites

- In the vicinity of percolation, the composite acts as a dielectric material and yields an enhanced sensor response.
- Above percolation, the composite is conductive (anti-static) and can be used as an electrostatic actuator.
- Well above percolation, the composite is very conductive.


\[
(1 - f)(s_i^{1/s} - s_m^{1/s})/(s_i^{1/s} + A) + \frac{f(s_c^{1/t} - s_m^{1/t})}{s_c^{1/t} + A} = 0
\]

\[
A = \frac{(1 - f)}{f_c}
\]

Alignment Approach

- **SWCNT Reinforced Functional Polymer Composites**

- **Alignment**
  - **High Shear Alignment (Passive)**
    - Extrusion, Pultrusion, Calendering
    - Fiber spinning (melt and wet spinning)
    - Electrospinning

  - **Electric Field Alignment (Active)**
    - AC & DC in a solvent
    - CNT growth w/ EF

  - **Magnetic Field Alignment (Active)**
    - MF in a solvent

- **Aligned SWCNT-Functional Polymer Composites Using Dielectrophoresis**
  Tailoring Physical Properties (Mechanical, Electrical, Dielectric, Thermal…)

[Image: Wet spun fiber 1% SWCNT]

Credit: NASA

[Image: Wet spun fiber 1% SWCNT]


Credit: Krupke Science 301 344 (2003)

[Image: Wet spun fiber 1% SWCNT]

Credit: NASA
Shear Alignment: Extruded Fibers and Films

1% SWNT/Ultem
Shear direction


Poly(p-phenylene benzobisoxazole)

Dry-jet wet spinning
Georgia Tech Fiber

<table>
<thead>
<tr>
<th>Fiber Type</th>
<th>Yield strength (GPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Elongation (%)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBO</td>
<td>2.6</td>
<td>138</td>
<td>2.0</td>
<td>insulating</td>
</tr>
<tr>
<td>5wt% SWCNT/PBO</td>
<td>3.2</td>
<td>156</td>
<td>2.3</td>
<td>insulating</td>
</tr>
<tr>
<td>10wt% SWCNT/PBO</td>
<td>4.2</td>
<td>167</td>
<td>2.8</td>
<td>insulating</td>
</tr>
</tbody>
</table>

Macromolecules 35 9039 (2002)

Percolation concentration of well dispersed SWCNT in a polyimide ≈ 0.05vol%


Volume Fraction Percolation (Conductivity)

Orientation increase

All images credit: NASA
Dielectrophoretic Alignment: Spheres, Platelets, Fibers...
AC Electric Field Alignment

Model for longitudinal and lateral aggregation of inclusions

\[
\beta = \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \right) \text{ or } \left( \frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1} \right)
\]

Figure 14. Optical micrograph of thin section of aligned glass fibers (4.5 vol%). Polymerized after 30 s under 0.81 kV/mm AC.

\[
\frac{a^3(E)^2}{k_B T} > 1 \quad \text{for Alignment}
\]

Davis, J. Appl. Phys. 72, 1334 (1992)
Aligned SWCNT/Polymer Composites: OM and SEM

Cured without electric field
SWCNT loading: 0.03wt%

Cured with electric field (200V_{pp}, 10Hz, 10min)

Effect of Alignment of 0.03% SWCNT/Polymer Composites

0.03% < \( \phi_c \)

Applied Voltage

Frequency

Conductivity (S/cm)

Frequency (Hz)

Applied Voltage

Frequency

Conductivity (S/cm)

Frequency (Hz)

Degree of SWCNT Alignment \( \Rightarrow \) Tailor Physical Properties

Metallized Nanotube Polymer Composite (MNPC) Metal Infusion Process into SWCNT/Polyimide Film

SWCNT/polyimide film formation: good dispersion

Metal-MNPC (Metal/SWCNT/polyimide) film formation: SCF Metal impregnation

> 200 atm
> 100°C
1–6 hr
250°C
1 hr

All images credit: NASA

Ag-MNPC Films with various SWCNT Concentration

0%SWCNT

0.1%SWCNT

2%SWCNT

10%SWCNT

Control

Ag-MNPC

Shiny surfaces
Reflection shielding

All images credit: NASA

Above: Topograph and tunneling AFM images of 10 wt.% SWNT/\(\square\)-CN AO/Ag prepared by 20 % metallization solution.

Conductivity & Toughness increased

Left: HRSEM micrograph of 10 wt.% SWNT/\(\square\)-CN AO/Ag prepared by 20 % metallization solution.

Hydrogen Storage

BNNT enables

Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Systematic Computational and Experimental Study

Electroactive properties of BNNT

B\textsubscript{x}C\textsubscript{y}N\textsubscript{z} Nanotube (BCNNT) Development
Band Gap Measurement: Low Energy EELS (modified BNNT)

Bandgap measurement of BNNT (Low-loss region)

- Band gap 5.74 eV
- Plasmon excitations

Bandgap measurement of C₆₀/BNNT (Low-loss region)

- Band gap 4.1 eV
- Band gap 3.9 eV

Superimposed Low Loss EEL spectra of multi walled Boron nanotubes shown in previous pages

Endo-Doped BNNNT (C₆₀/BNNT, Gd/GNNT) UC Berkeley

- 3 different BNNTs
- Band gap: 5.7-5.8 eV

30 nm

Credit: UC Berkeley; Zettl

All images credit: NASA
Doped Chiral Polymer Metamaterials (DCPM)
Problems of SOA Split Resonance Ring (SRR)

- Special architecture and complex design required
- Difficult to build SRR crystalline structures
- Difficult to scale-up
- Not flexible and difficult to apply for complex structures
- Difficult to reach optical ranges
- Lack of resonance frequency tunability

What is Metamaterial? & Challenges

$n < 1 \rightarrow$ Metamaterials

Metamaterials without special architecture or design (negative permeability) possible for optical ranges?

$n_{eff} = \sqrt{\varepsilon \mu}$
Our Novel Approach: Metamaterial without special architecture and negative permeability

Chiral Metamaterials

$$n_{\text{eff}} = \sqrt{\varepsilon \mu} - \kappa$$

Our Novel Approach

$$n_{\text{eff}} = n_{\text{composite}} - \kappa_{\text{composite}}$$

$$n_{\text{composite}} = n_{\text{host}} - \Delta n_{\text{plasmonic}}$$

- The size of the **helical chiral polymer** is of the order of wavelengths in the optical range
- Self-organization of helical polymer chains
- Incorporating **plasmonic inclusions** lowers the permittivity
- Electronic coupling between plasmonic particles and helical polymer chains enhances chirality
Plasmon NP infusion: *in situ* Direct Mixing & SCF infusion

**In-situ Direct mixing**

- **PBLG**
- **Ag salt**

Supercritical fluid (SCF) CO$_2$ Ag impregnation

- SCF CO$_2$
  - > 345.4 atm
  - > 70°C
  - 1–6 hr

- 200°C
  - 1hr reduction

**Ag/PBLG Film**

All images credit: NASA
Ellipsometry (Index of Refraction): PBLG, DCPM

Drawing of chiral polymer $\rightarrow$ Reduction of index of refraction
Addition of Ag or Au plasmonic nanoparticles $\rightarrow$ Reduction of index of refraction

$n_{PBLG} \approx 1.55$ in visible range

Drawing $\rightarrow$ $n$

Plasmonic Ag $\rightarrow$ $n$

Plasmonic Ag size $\rightarrow$ $n$ changes

Plasmonic Ag, Au $\rightarrow f_{res}$ change

Resonance peak is not from metal coating
Piezoelectric and Electrostrictive Properties for Sensors/Actuators (SWCNT and BNNT Composites)
Actuation Response: SWCNT/Polyimide Composite

Out-of-plane strain Using Fiber Optic Displacement Measurement

Sample

Thickness change

Sample holder

Photonic Sensor

Probe

Cantilever Beam

Sample

High Voltage Amplifier

Stable Stage

Oscilloscope

Function Generator

Lock-in Amplifier

Acousto-Optic Sensors model 201

Angstrom Resolver™

Dilatometer with cantilever

All images credit: NASA
Electrostrictive coefficient

**SWCNT/Polyimide**  \( M_{33} = -3.6 \times 10^{-15} \sim -1.2 \times 10^{-13} \text{ m}^2/\text{V}^2 \)

**Polyurethane**  \( M_{33} = -4.6 \times 10^{-18} \sim -1.6 \times 10^{-17} \text{ m}^2/\text{V}^2 \)

**10^3 – 10^4** times higher

\[
S_{33} = S_E \text{ (Electrostriction)} + S_M \text{ (Maxwell effect)}
\]

\[
S_M = \frac{1}{2Y} \int_0^r E^2 (1 + 2 \sigma) < 0.01\%
\]

Bending Actuation of SWNT Polymer Nanocomposite

$M_{31} = 2.86 \times 10^{-15} \text{ (m}^2/\text{V}^2\text{)}$

Sonic fatigue abatement
Noise transmission attenuation
Wing and panel flutter control
Tail buffet alleviation control
Surface shape control

Multifunctional BNNT Polymer Composites

• Electroactive Properties
• Radiation Shielding Properties
Piezoelectric Properties of BNNTs

Piezoelectric Effect

h-BN plane

BNNT

Zig-zag

Armchair

Molecular Dynamics

- Define forces between atoms using a given interatomic potential (energy)
  \[ U_i = V_{i,j}(r_{ij}) B_i V_A(r_{ij}) \]
  \[ \vec{F}_i = \frac{U_i}{\vec{r}_i} \]
- Evolve atoms according to Newton’s law: \[ \vec{a}_i = \vec{F}_i / m_i \]

Piezoelectric MD

- Introduce dipole term to the interatomic potential (energy)
  \[ U = U_r + U_p; \quad U_p = \sum_{i=B, j=N} U(p_{BN, ij}) \]
  \[ \vec{p}_{BN, ij} = p_0 \left( \frac{r_{BN, ij}}{r_0} - 1 \right) + \frac{1}{2} \cos \theta_{ijk} \]

Induced polarization, \( \vec{p} \), under strain \( \varepsilon_{jk} \): \[ p_i = \varepsilon_{ijk} \varepsilon_k \]
where \( \varepsilon_{ijk} \) - piezoelectric tensor with symmetry:
\[ e_{xxx} = e_{xyy} = e_{yxy} = e_{yyx}; \quad e_{xxx} = 0.086 \quad 0.12 \text{ e/Bohr} \]

The MD model has to reproduce this behavior!

(Sai & Mele, PRB 68, (2003) 241405)
The MD model is successful in representing the piezoelectric properties of BNNTs.

\[ p_z(\text{stretch}) = e_{11} \]
\[ p_z(\text{twist}) = e_{14} \]

Experiment Displacement Study

**Polymer Matrix:**
- Polyimides [CP2, (β-CN)AMPB/ODPA (bCNAO), (β-CN)APB/PMDA (bCNAP)]
- Polyurethane
- PMMA
- Nylon 6,10

**Inclusions:**
- h-BN (hexagonal boron nitride powders)
- BNNT (purchased CVD, large, fat tubes, low quality)
- BNNT (high pressure, high temp, CO2 laser as grown)

**Alignment** (stretched)
No alignment (no stretched) and stretched (up to 100%)

Polyimide (CP2)
Polyimide (bCNAO)
Polyimide (bCNAM) (unstreched and stretched 100%)
5wt%hBN/polyimide (stretched 110%)
5wt%BNNT(CVD)/polyimide
2wt%BNNT(laser)/polyimide (unstreched and stretched 100%)

All images credit: NASA
Pristine and composite films are stretched with a tensile tester (Instron microtest) in an oven at above Tg.

Field induced strain ($\varepsilon_{33}$)

$$\varepsilon_{33} = d_{33} \cdot E + M_{33} \cdot E^2 + \ldots$$

$d_{33}$: piezoelectric (PE)
$M_{33}$: mostly electrostrictive (ES)
Stretched BNNT-Polyimide Nanocomposite

100% Strain,
225°C slightly above Tg
Actuation of Unstretched/Stretched 2% BNNT/Polyimide

Unstretched

100% Stretched @225°C, Annealing

100% Stretched @225°C, Quenching

Origin of Actuation → BNNT
LaRC-ANAS Film

Goal: Flexible, transparent, large actuation, high sensitivity, Mechanically Durable

All images credit: NASA
Field induced strain ($\varepsilon_{33}$)

$$\varepsilon_{33} = d_{33} \cdot E + M_{33} \cdot E^2 + \ldots$$

$d_{33}$: piezoelectric coefficient
$M_{33}$: electrostrictive coefficient
$E$: applied electric field
### Actuation of Unstretched/Stretched h-BN/BNNT Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Inclusions</th>
<th>Polymer</th>
<th>Actuation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide (PI)</td>
<td>None</td>
<td>Polyimide</td>
<td>None</td>
</tr>
<tr>
<td>5%hBN/Polyimide (100% stretched)</td>
<td>5%hBN</td>
<td>Polyimide</td>
<td>None</td>
</tr>
<tr>
<td>5%BNNT (CVD)/Polyimide</td>
<td>5%BNNT (CVD)</td>
<td>Polyimide</td>
<td>None</td>
</tr>
<tr>
<td>Polyimide (100% stretched)</td>
<td>None</td>
<td>Polyimide</td>
<td>None</td>
</tr>
<tr>
<td>2%BNNT (laser)/Polyimide</td>
<td>2%BNNT</td>
<td>Polyimide</td>
<td>✔</td>
</tr>
<tr>
<td>2% BNNT (laser)/Polyimide (100% stretched)</td>
<td>2%BNNT</td>
<td>Polyimide</td>
<td>✔✔</td>
</tr>
<tr>
<td>20%BNNT/Polyurethane</td>
<td>&gt;20% BNNT</td>
<td>Polyurethane</td>
<td>✔✔✔✔✔✔✔✔✔✔✔✔</td>
</tr>
</tbody>
</table>

**Actuation**

- **h-BN** → No Actuation
- **Commercial BNNT (CVD)** → No Actuation
- **Polymer** → No Actuation
- **Stretched Polymer** → No Actuation
- **BNNT (high pressure, high temp laser)** → Origin of the Actuation

All images credit: NASA
Spacecraft data nails down radiation risk for humans going to Mars


Interviewed Sheila Thibeault at NASA Langley about the study published in *Science*

Mars Science Laboratory (MSL) during its cruise to Mars between 6 December 2011 and 14 July 2012 (253 days)

Mars Round Trip Dose Equivalent is around 0.66 Sievert
Neutron Radiation Shielding Study

Materials
- Hydrogen, Boron, Nitrogen
- BN, BNNT, Gd
- Low density polyethylene (LDPE), polyimide (Kapton, CP2, (β-CN)APB/ODPA), polyurethane

Radiation Shielding Structural Materials
- In-situ polymerization under simultaneous sonication and shear
- Supercritical Fluid Infusion

Characterization
- Neutron Radiation Exposure Lab: Source: Am/Be 1 Curie
- Moderated by borated polyethylene cylinder block (44mm thick): 45 mrem/hr thermal neutrons
- Sample: 2 x 2” polymer and BN polymer composites
- Detection Foil: 1.25” Indium Foil (0.5mm, 19 barns)
- RSMES: Radiation Shielding Materials Evaluation Software

Modeling
- OLTARIS


All images credit: NASA
Advanced Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Preliminary Results

Neutron radiation

![Graph showing neutron radiation absorption coefficients for different BNNT concentrations.]

Beta radiation

![Graph showing beta radiation absorption coefficients for different BNNT concentrations.]

Am/Be 1 Curie & moderated by borated PE

0.1 μCi Sr-90: β (Synthesized Apr 2009)

\[ ^{241}_{95} \text{Am} \rightarrow ^{237}_{93} \text{Np} + \frac{4}{2} \text{He}(\alpha) \]

\[ \frac{4}{2} \text{He}(\alpha) + ^{9}_{4} \text{Be} \rightarrow ^{12}_{6} \text{C} + ^{1}_{0} \text{n} + \gamma(5.71 \text{MeV}) \]

\[ ^{90}_{38} \text{Sr} \rightarrow ^{90}_{39} \text{Y} + \beta^-; t_{\text{half}} = 28.8 \text{ y} \]
Materials assumed to have common 30 cm thickness.

BN materials perform better than LH2 and water. BN+5%H performs better than state of art polyethylene.
BN\textsubscript{x}C\textsubscript{y}N\textsubscript{z} Nanotubes (BNNT, BCNNT) were successfully synthesized with High Temperature-Pressure Laser Synthesis method.

Development of multifunctional nanotube polymer nanocomposites with uniform dispersion.

Physical properties of nanocomposites can be tailored over a wide range by fine tuning the type of tubes, concentration, and degree of the alignment of nanotubes.

In-situ diagnostics and modeling were implemented to support study of the BNNT and BCNNT nucleation and growth mechanism.

Multifunctional Nanocomposites can sense strain, stress, pressure, damage, temperature.

Multifunctional Nanocomposites can actuate through piezoelectric and electrostrictive phenomena and generate large strain at low electric fields.

Multifunctional Nanocomposites can shield radiation and high heat flux.
Thank You

All Images Credit: NASA