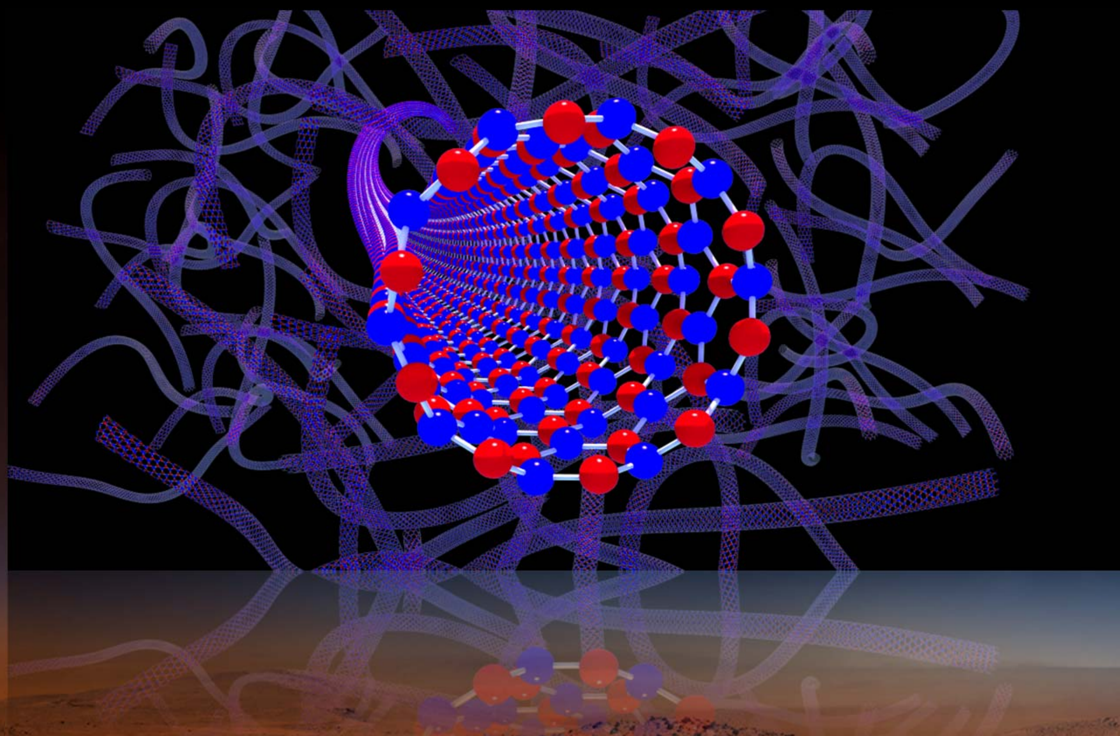
NASA Langley Research Center

Multifunctional Boron Nitride Nanotubes and Nanotube Composites for Extreme Space Environments

Cheol Park, Samuel Hocker, Sang-Hyon Chu*, Vesselin Yamakov*, Catharine Fay

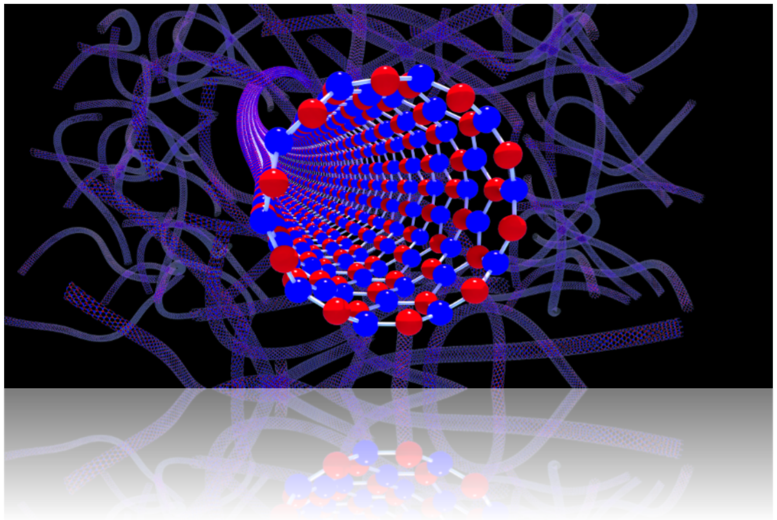


Advanced Materials and Processing Branch, NASA Langley Research Center
**National Institute of Aerospace, Hampton VA USA*

All images credit: NASA

Outline

- Motivation
- BNNT Synthesis (High Temperature Pressure (HTP) Method)
- BNNT and BNNT Composite Applications
- Dispersion
- Mechanical Properties
- Thermal Properties

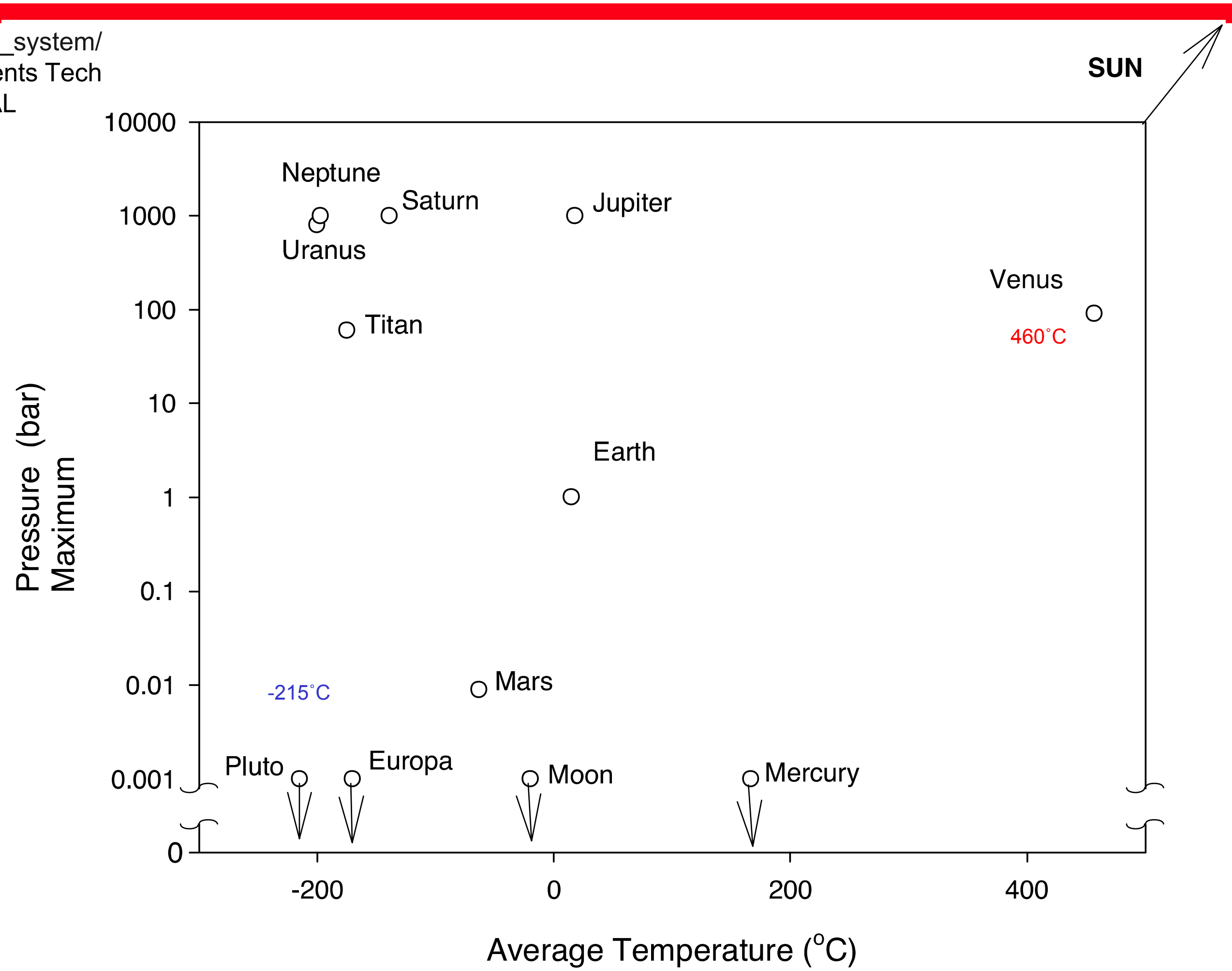


- Multifunctional Properties in Extreme Environments
    - Sensor/Actuator/Energy Harvester (BNNT and CNT Nanocomposites)
    - Radiation Shielding
- Summary

All images credit: NASA

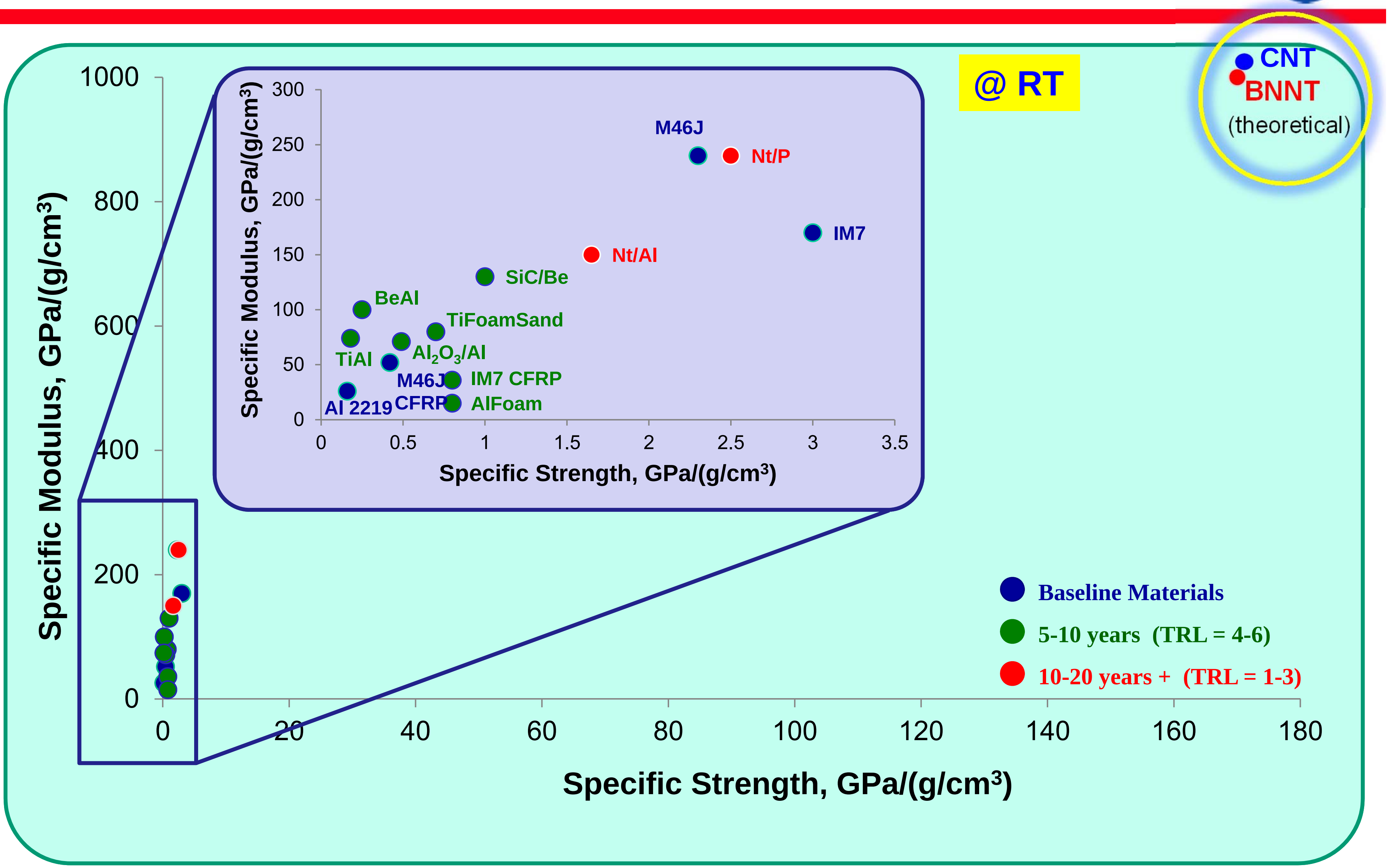
Estimated Pressure Max vs Temp for Selected Missions

http://www.jpl.nasa.gov/solar_system/
17NASA Extreme Environments Tech
Space missions Report FINAL



Heat flux at atmospheric entry: Heat fluxes often exceeding 10's W/cm^2
Hypervelocity impact: Higher than 3 km/sec
Low and high temperature: Lower than −55˚C and Exceeding +125˚C
Thermal cycling: Cycling between temperature extremes outside of the military standard range of −55˚C to +125˚C
High pressures: Exceeding 20 bars
High radiation: Total ionizing dose (TID) exceeding 300 krad (Si), GCR, SPE, Neutron
Low and High gravity: microgravity on comets, 2.5g on Jupiter, launch, entry, descent

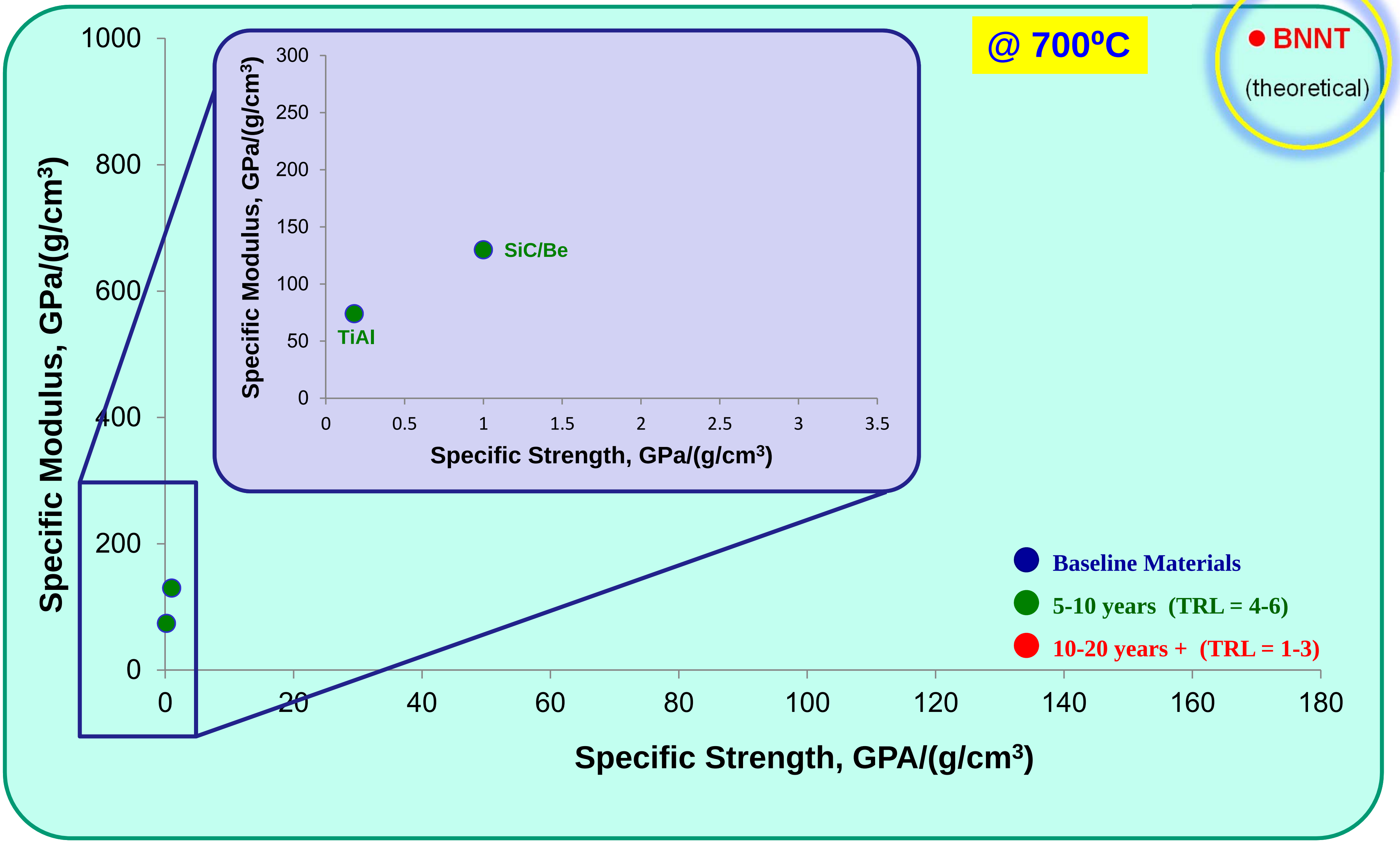
Motivation: Properties of Materials for Vehicle Structure



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

Nanotube values are theoretical.

Motivation: Properties of Materials for Vehicle Structure



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

Nanotube values are theoretical.

Nanotube Comparison (Theoretical)

	Carbon Nanotubes	Boron Nitride Nanotubes
Electrical Properties	Metallic or semiconducting	Wide band gap (about 6.0 eV) Insulation, corrosion resistant
Mechanical Properties (Young's Modulus)	1.33 TPa (very stiff)	1.18 TPa (very stiff)
Thermal Conductivity	>3000 W/mK (highly conductive)	~300–3000 W/mK (highly conductive)
Thermal Oxidation Resistance	Stable up to 300-400 °C in air	Stable to over 900 °C in air
Neutron Absorption Cross-Section	C = 0.0035 barn	B = 767 barn (B^{10} ~3800 barn) N = 1.9 barn Excellent radiation shielding
Polarity	No dipole	Permanent dipole Piezoelectric (0.25-0.4 C/m^2)
Surface Morphology	Smooth	Corrugated Better interfacial strength for composites, ionic bonding
Color	Black	White (can be colored)
Coefficient of Thermal Expansion	-1 $\times 10^{-6}$ K^{-1} (very low)	-1 $\times 10^{-6}$ K^{-1} (very low)

Significance of the BNNT Innovation

- **Structural/Mechanical**: **lightweight** composite armor, thermal protection, engine components, and radiation shielding materials for **extreme environments**.
- **High stiffness as well as high toughness** for spacecraft and space suits, ultrastrong tethers, meteorite impact protection layers, protective gear for astronauts.
- **Space lubricants** without moisture.
- **High temperature** thermal protection systems (**TPS**) used in the **nose cap**, wing **leading edges**, **engine parts**, lubricants, and planetary **Entry, Descent, & Landing** (**EDL)** TPS.
- **Fire resistant and retardant.**
- **High temperature sensor, actuator, energy harvesting devices** in extreme environments.
- **Radiation shielding, UV (ultraviolet) protection,** and electromagnetic transparency while decreasing aircraft weight.
- **Radar transparency** mitigates Electromagnetic Interference (EMI) and Radio Frequency (RF) blackout.
- **Efficient zero-energy water filter and desalination membrane in microgravity**.

All Images Credit: NASA

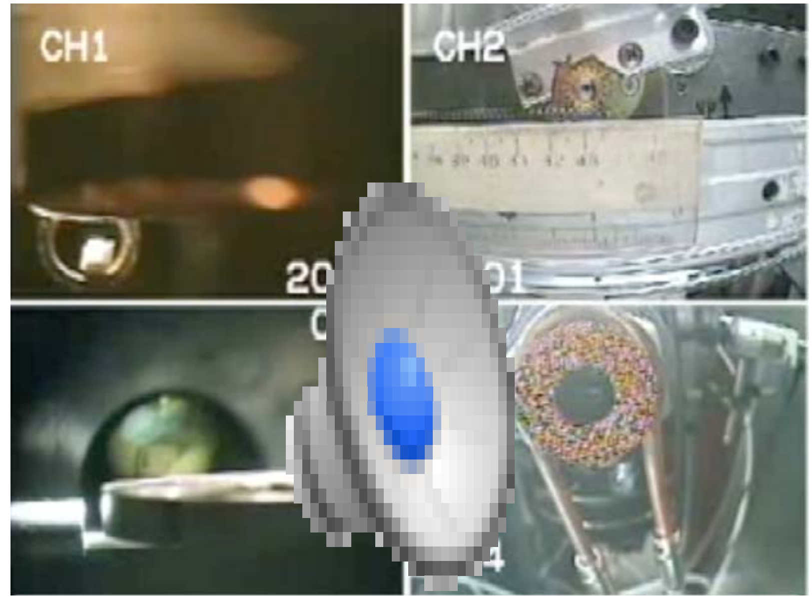
High Temperature-Pressure (HTP) BNNT

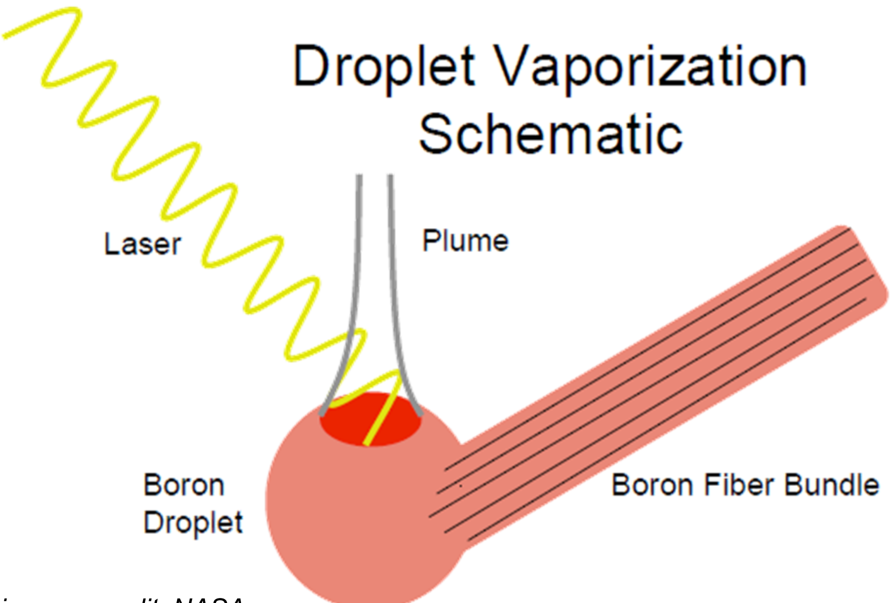
- Free Electron Laser (FEL) or CO_2 laser
- ***No Catalyst, only B and N resource***
- Very long, small diameter, highly crystalline BNNT

Nanotechnology, **20** 505604 (2009)
US Patent 8206674 B2 (2012)

BNNT Synthesis Lab: NASA Langley (1st Gen)

Production Chamber and Laser



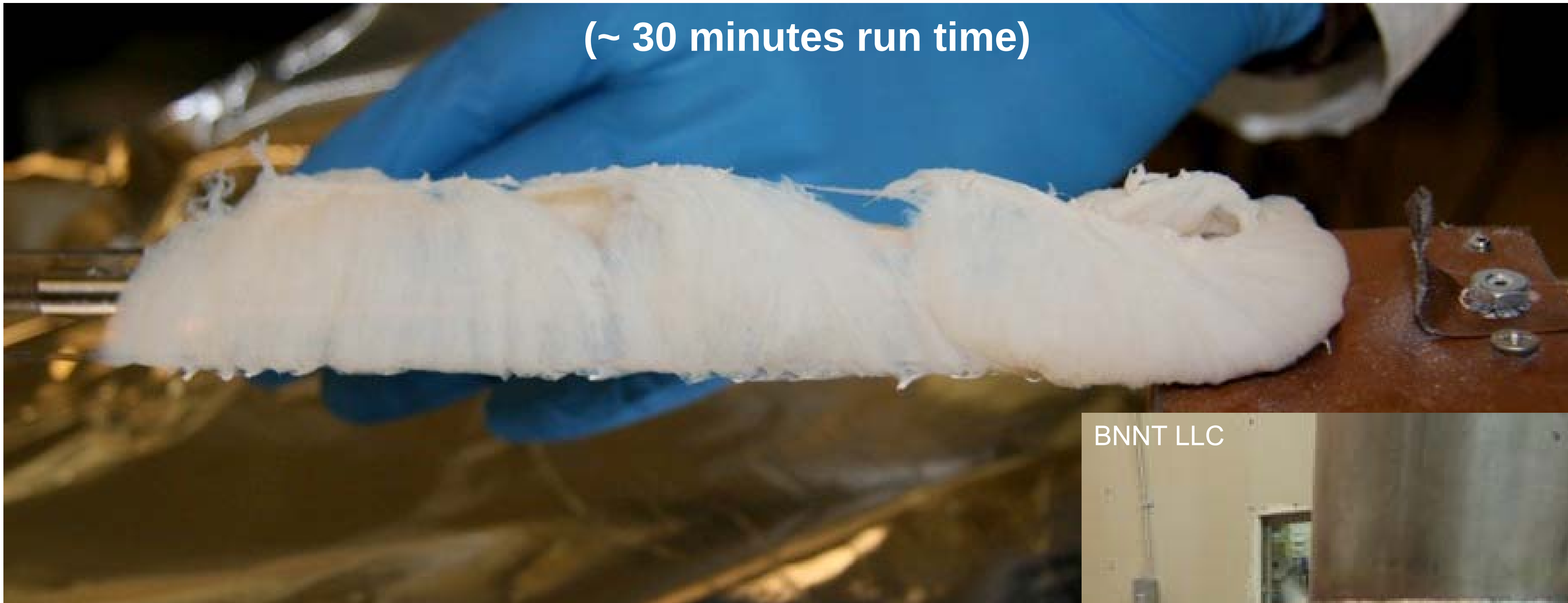


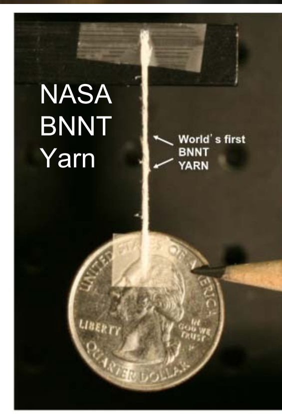
All images credit: NASA

- 5 kW of infrared radiation @ 10.6µm
- Heat source for vaporizing Boron feed stock above 3500ºC
- Pressurized with Nitrogen to 200 psi

Nanotechnology, **20** 505604 (2009)
J. Thermophysics and Heat Transfer **27** 369 (2013)
Proc. SPIE **9060** 906006 (2014)

Cotton-like High Temperature and Pressure (HTP)-BNNT



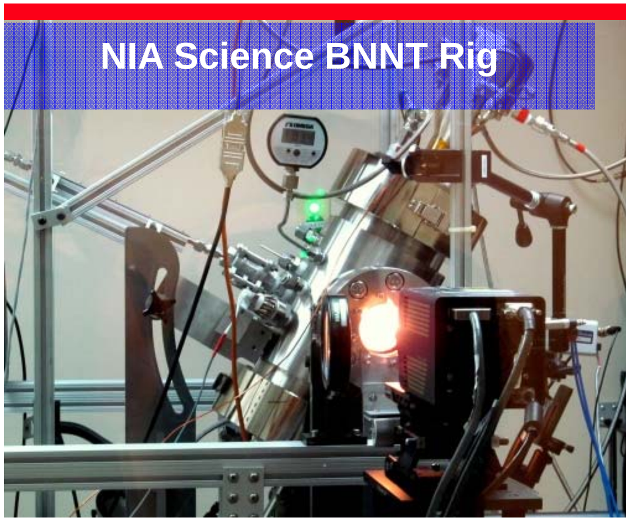


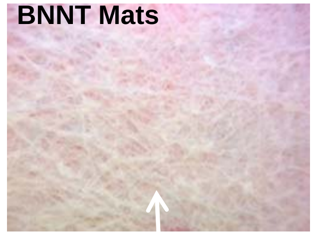
Benefits

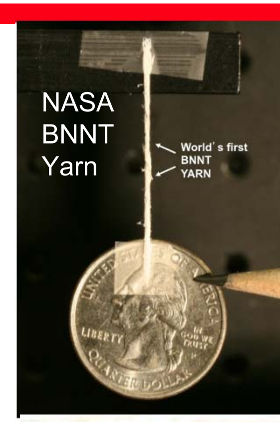
- One-to-few-walled tubes with high crystallinity
- Very long, high-aspect ratio tubes
- High scale-up potential
- No toxic catalysts (only B and N as reactants)
- Standard industrial cutting/welding lasers
- High service temperature (over 800ºC)
- Highly electroactive (due to the B-N polar bond)
- Neutron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

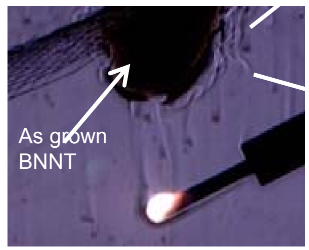
All images credit: NASA, BNNT LLC

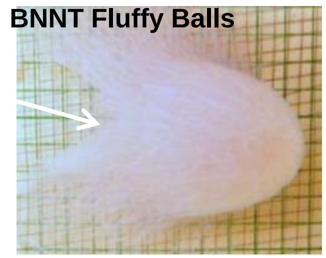
BNNT Scale-Up and Various Forms of BNNT

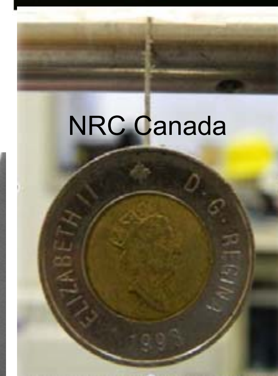


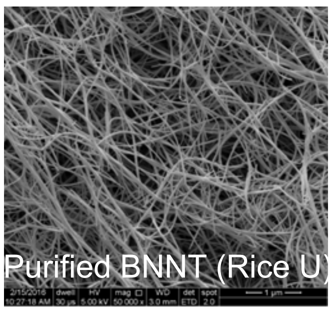


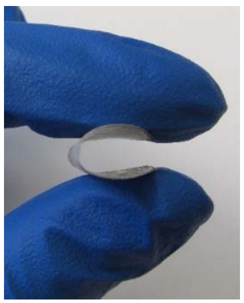


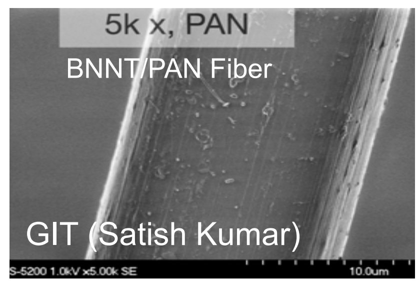






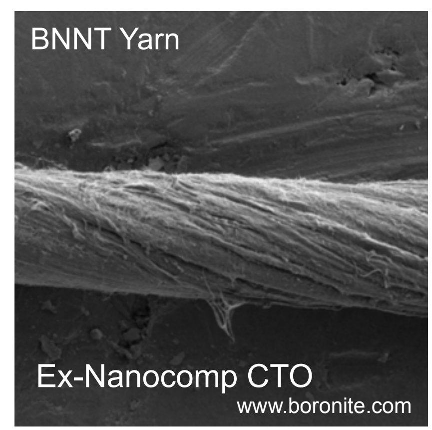






BNNT LLC

NRC Canada (Tekna)



Boronite Corp

Dispersion

Thermodynamic Approach: Effective BNNT Dispersion

Essential for Quality Yarn, Fabric, and Composite Formation

Thermodynamic Approach:
Gibbs Free Energy of Mixing

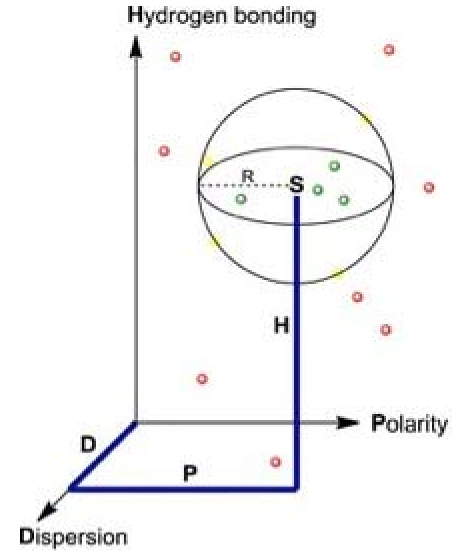
$$\Delta G_{mix} = \Delta H_{mix} - T^* \Delta S_{mix}$$

If ΔG_{mix} is negative, spontaneous mixing happens to form a homogeneous solution

Hansen Solubility Parameters (HSP) $(\delta_d, \delta_p, \delta_h)$: "like dissolves like"

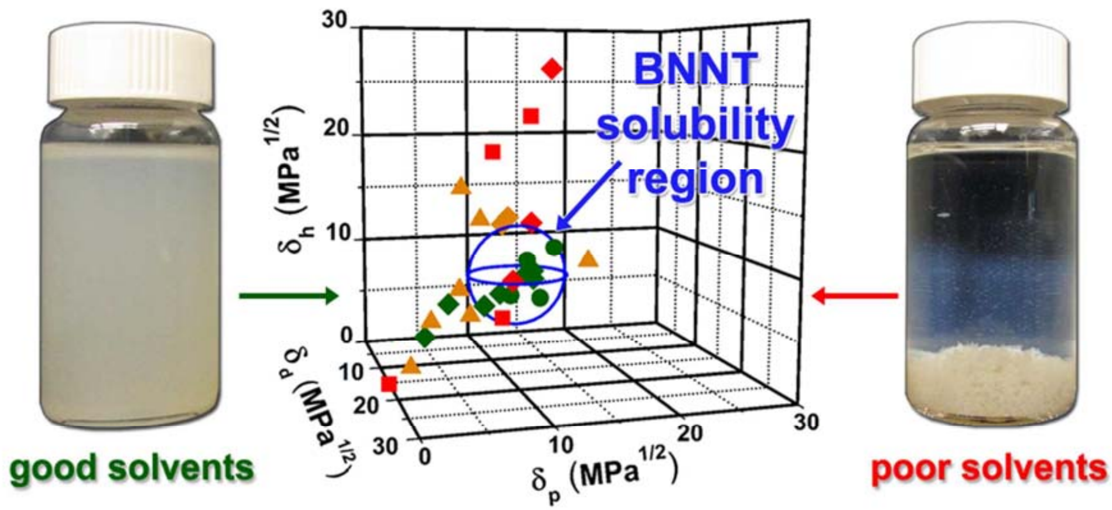
$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

δ_t^2: Hildebrand parameter
δ_d: dispersion component
δ_p: polar component
δ_h: hydrogen bonding component



Example of 3D Hansen space*

Single and Co-solvents



BNNT Hansen Solubility Parameters
$\delta_d, \delta_p, \delta_h$ = 16.8, 10.7, 9.0 MPa$^{1/2}$
δ_t = 21.8 MPa$^{1/2}$

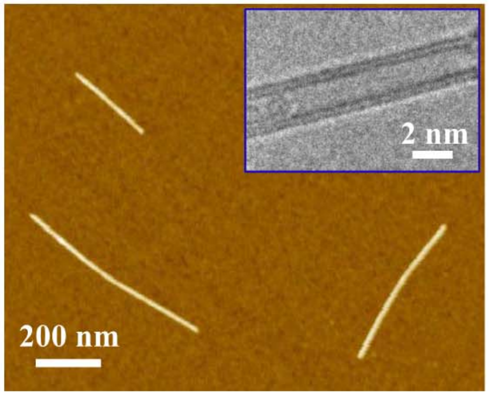
Nanoscale 8 4348 (2016)

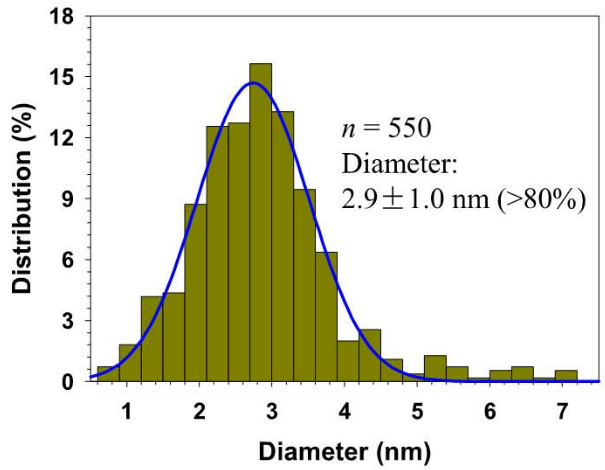
https://www.hansen-solubility.com/

Mechanical Properties

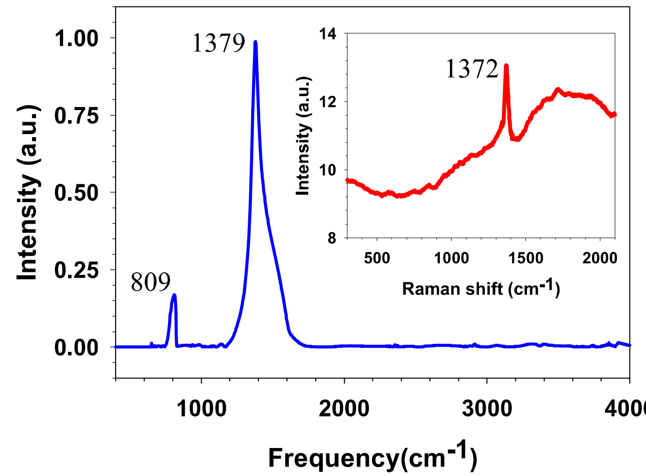
In-situ Single BNNT Test Inside of an SEM

AFM

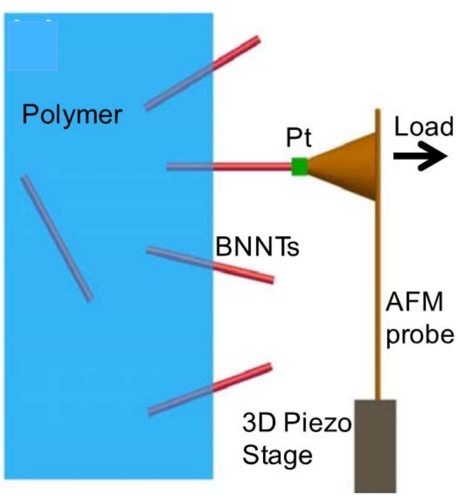




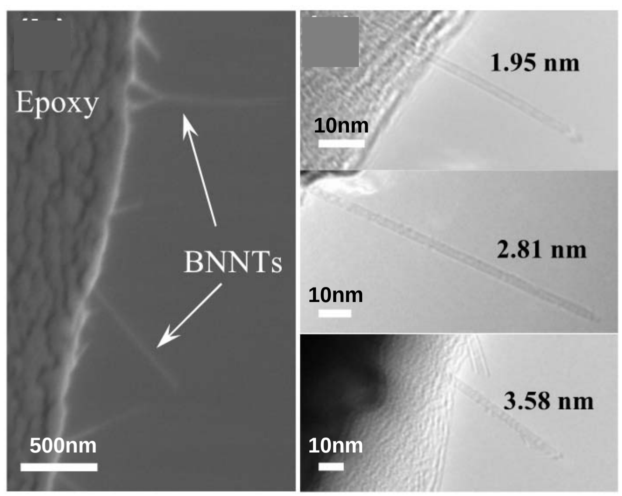
FTIR and Raman



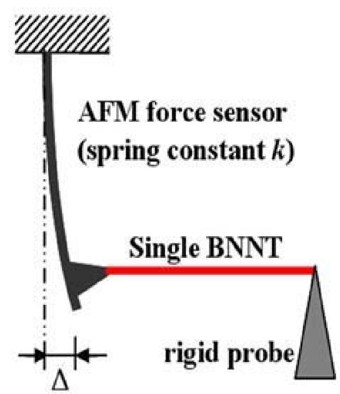
Pull-Out Test

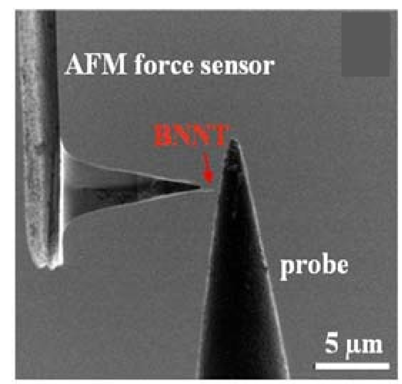


SEM



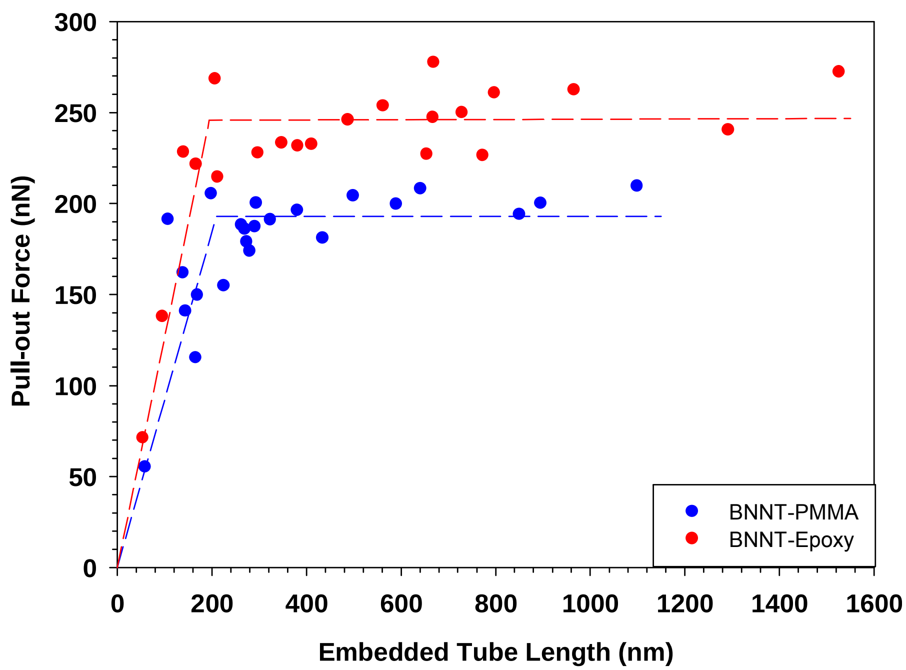
Tensile Test

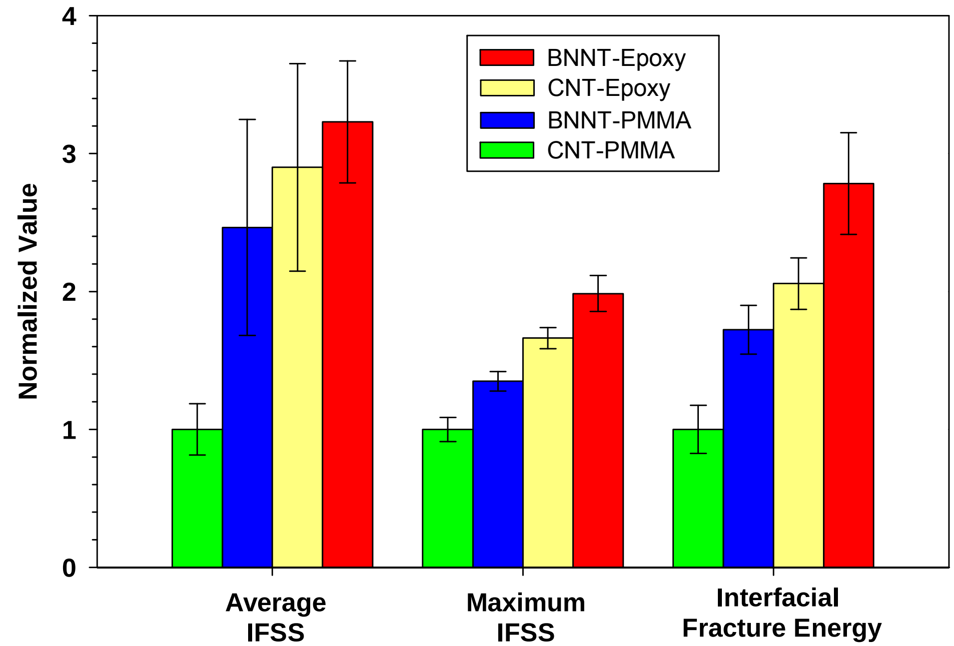


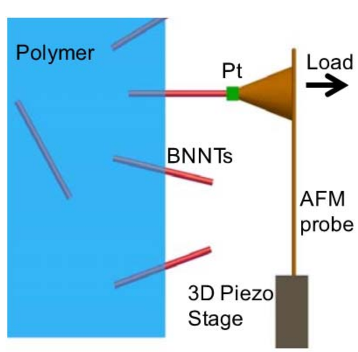


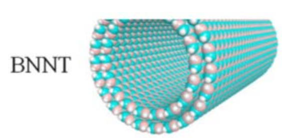
Credit: Prof Ke (SUNY Binghamton) FEI Nanolab 600 *Small* **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)

Interfacial Strength: *In-situ* Single Nanotube Pull-Out Test



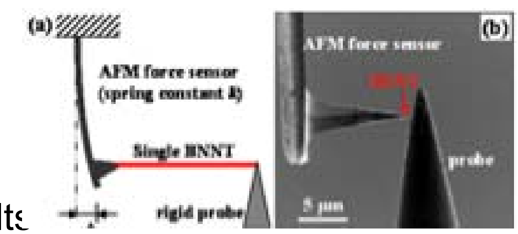






(a)

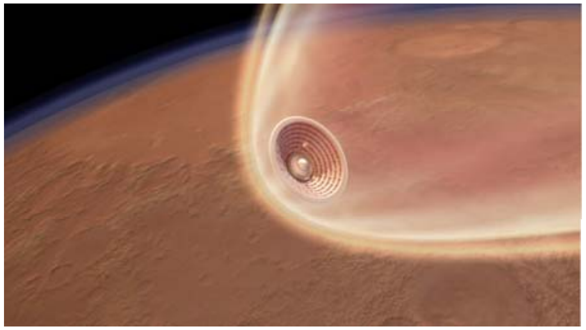
BNNT Tensile Test Results

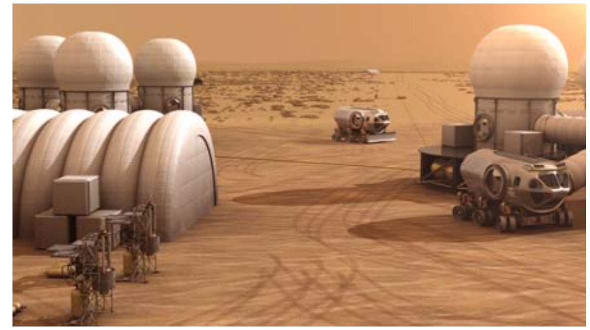


Diameter	Elastic modulus (GPa)	Breaking Strength (GPa)
D = 2.5 nm	760-960	14-38

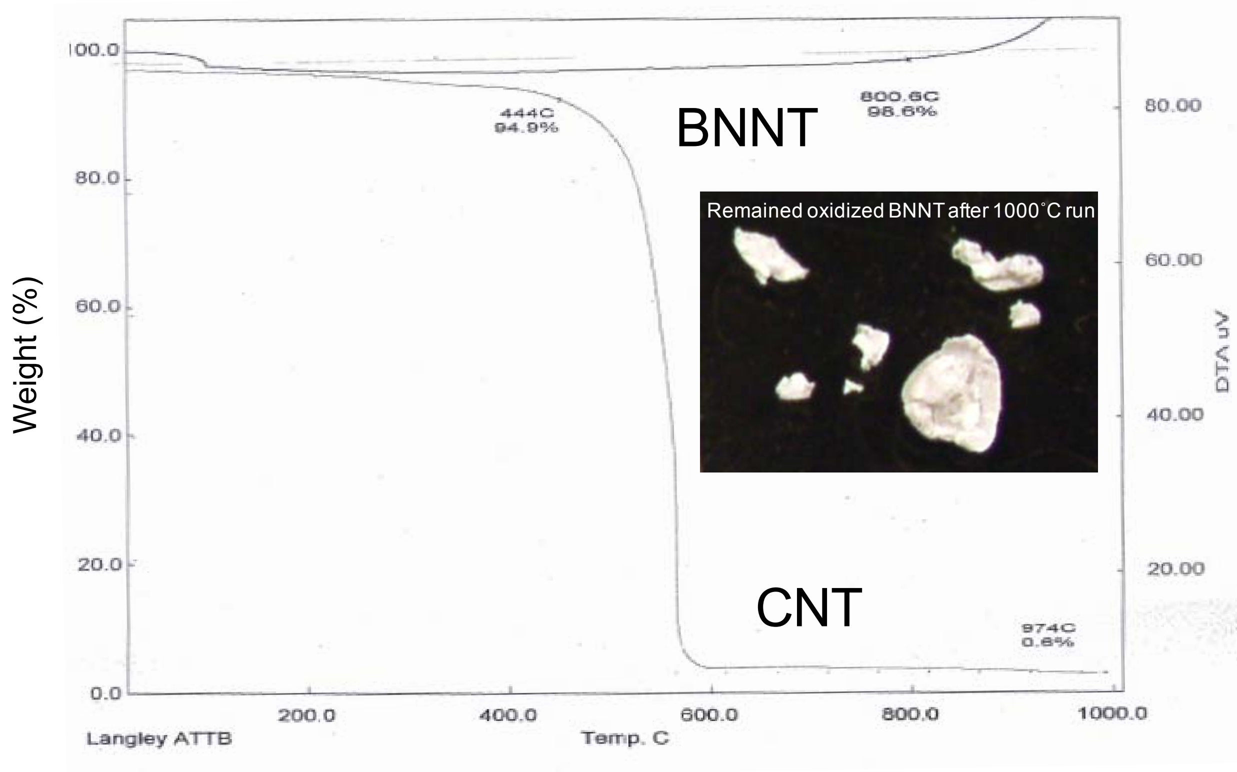
Small **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)

Credit: Prof Ke (SUNY Binghamton)





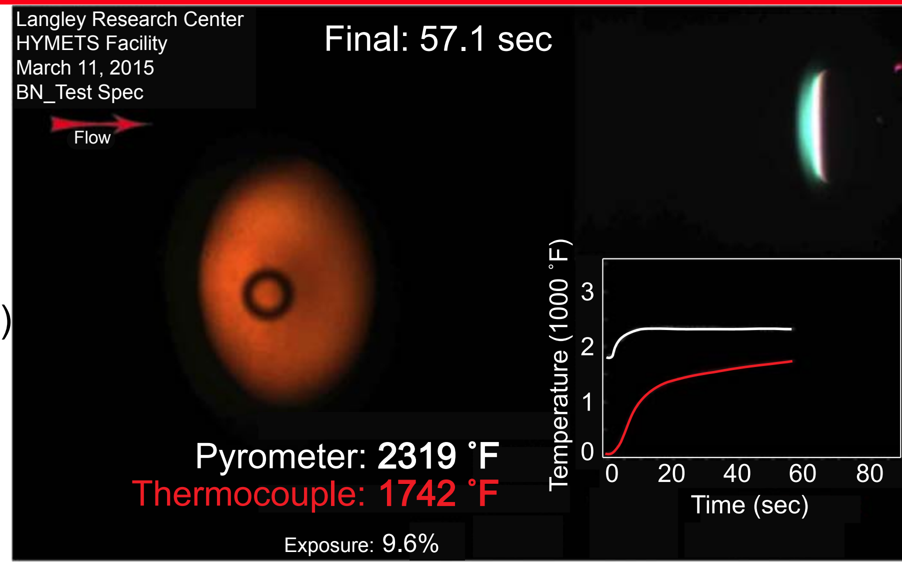
Thermal Properties

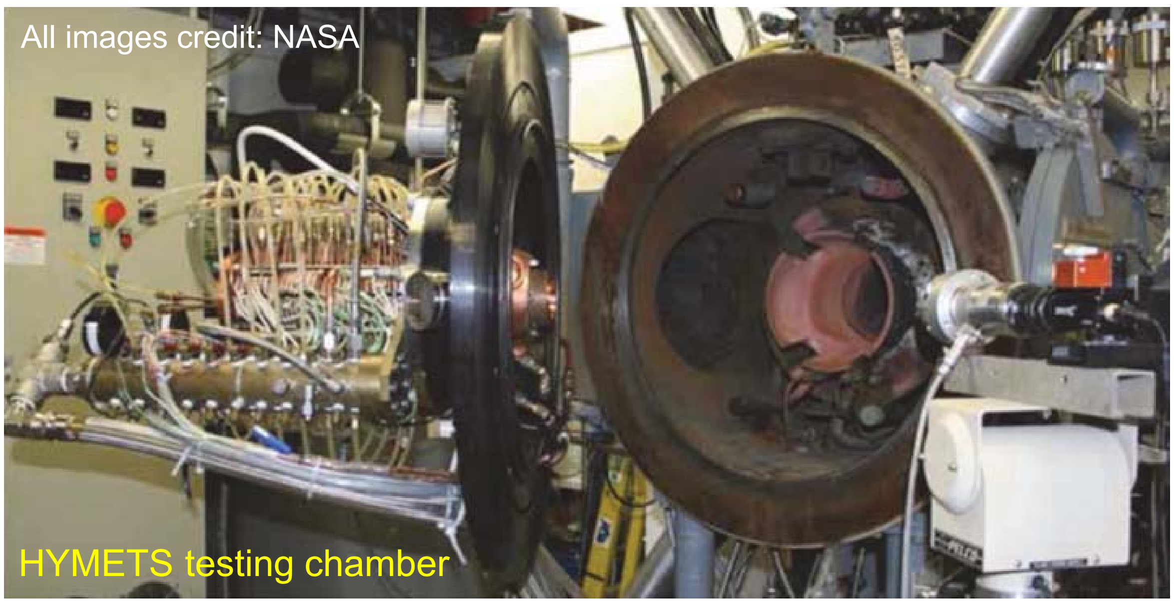


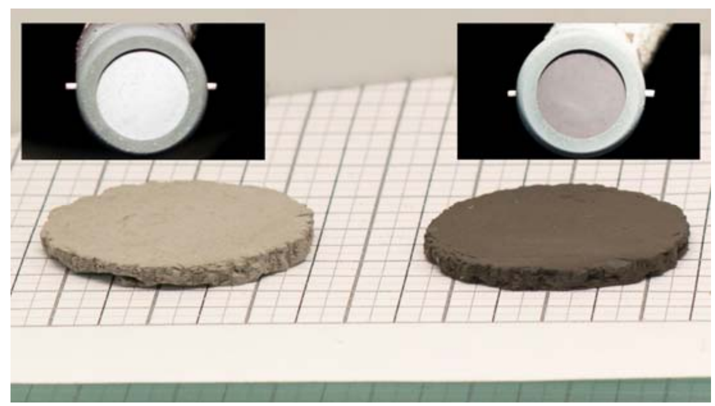
Hypersonic Materials Experiment Test System (HYMETS)

<u>Sample: BNNT Mat</u> <u>(as grown, nonwoven)</u>
- Diameter: 25 mm – 75 mm
- Thickness: 2.1 mm – 20 mm
- Density: 0.2 – 0.35 g/cm^3

<u>HYMETS TEST Info</u>
- Heat flux: Set at about 50 W/cm^2 (2nd Gen MARS EDL)
- Duration: 1 min – 5 min
- Atmosphere: Air (with 5% Ar)
- Cooled under vacuum



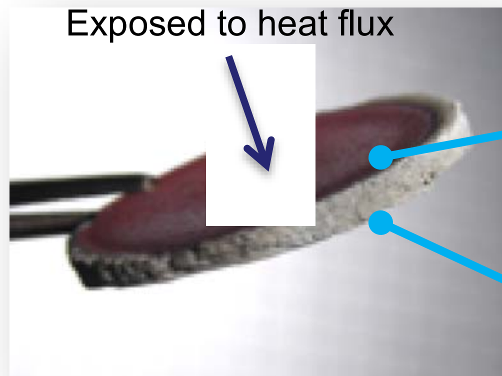

All images credit: NASA
HYMETS testing chamber



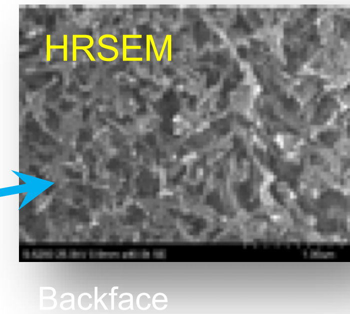
Collaborators: Scott Splinter, Jeff Gragg, Kamran Daryabeigi

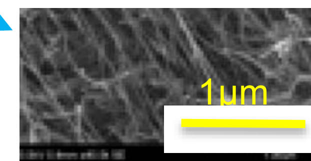
Hypersonic Materials Experiment Test System (HYMETS)
BNNT Non-Woven Mats

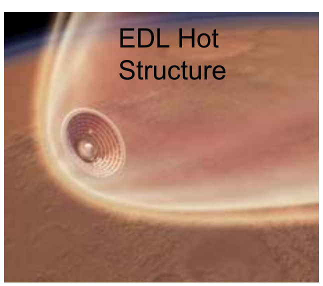
BNNT mat sample **survived** through the hypersonic heat flux (50W/cm²) for 60 sec run with a minimal loss

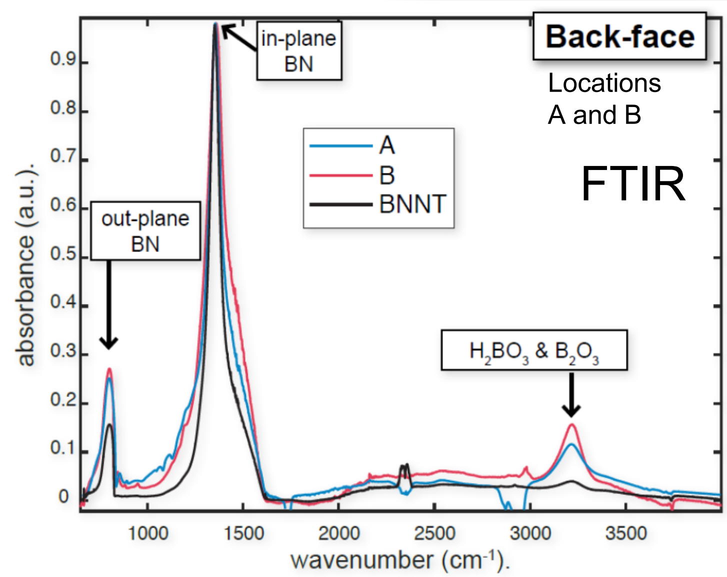


After HYMETS Test





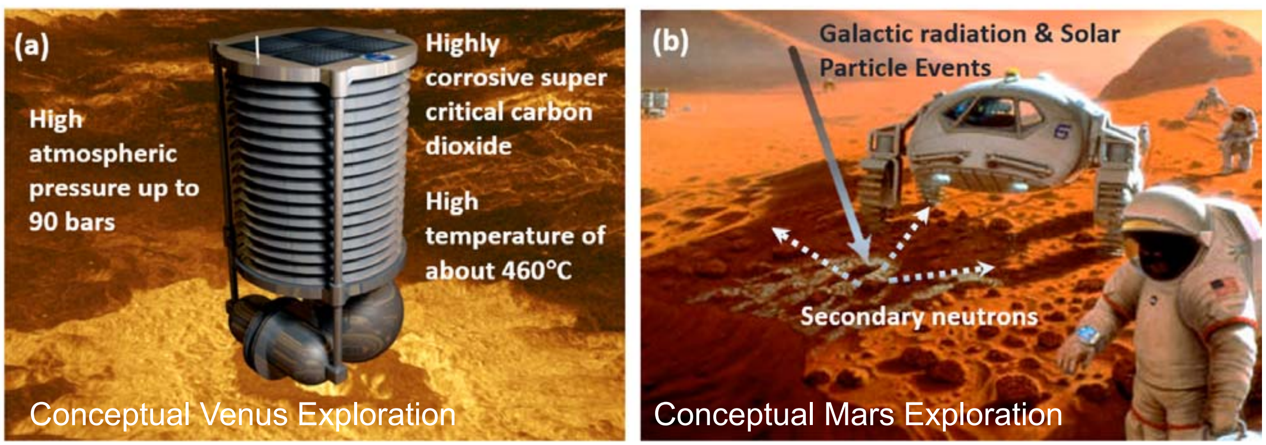




Collaborators: Scott Splinter, Jeff Gragg, Kamran Daryabeigi

Multifunctional BNNT Polymer Composites

- Electroactive Properties
- Radiation Shielding Properties

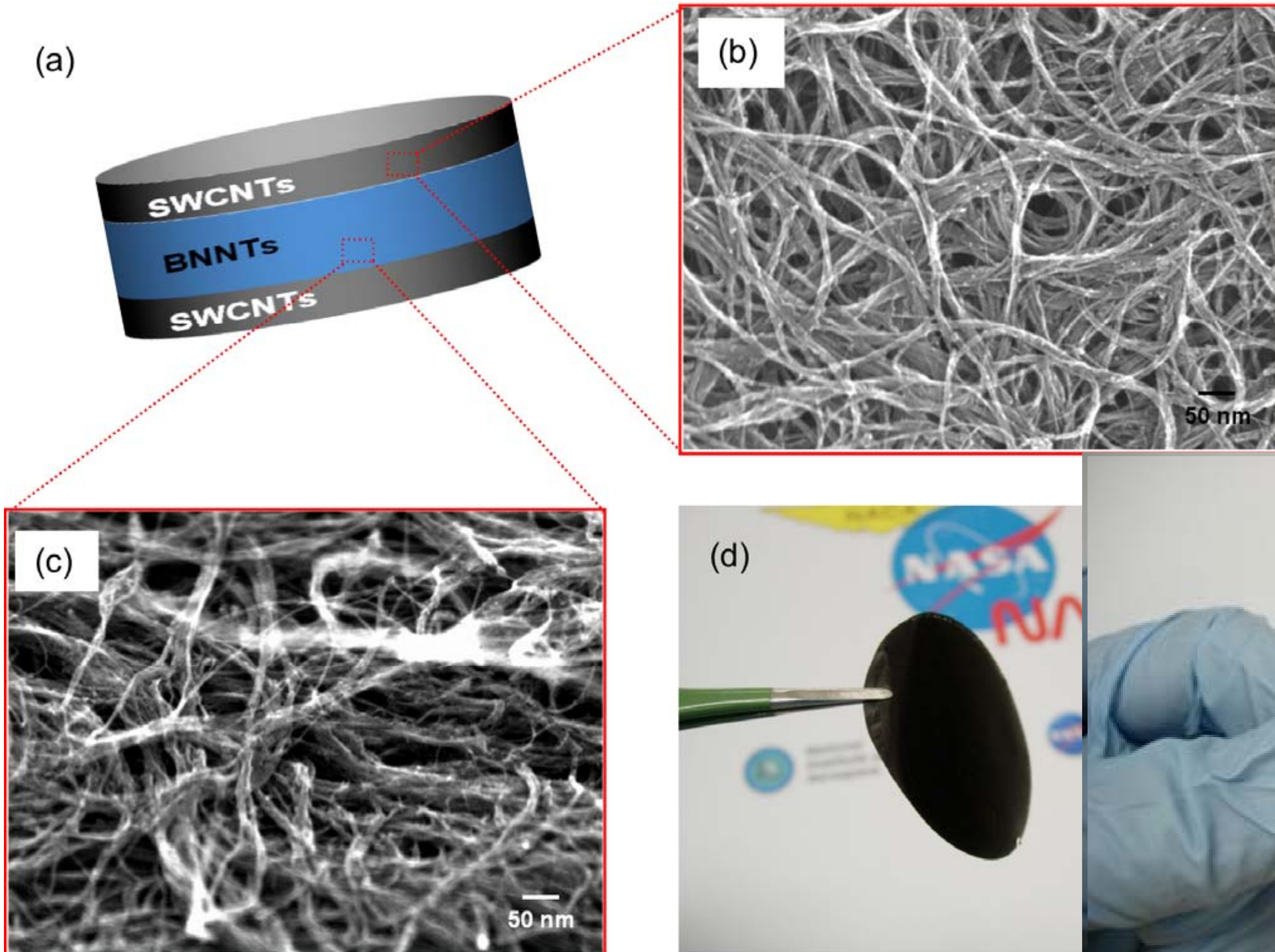


Conceptual Venus Exploration
Conceptual Mars Exploration

All images credit: NASA

Comp. Mater. Sci., **95** 362 (2014)
ACS Nano **9** 11942 (2015)

Langley All-Nanotubes Actuator/Sensor (LaRC-ANAS) Film

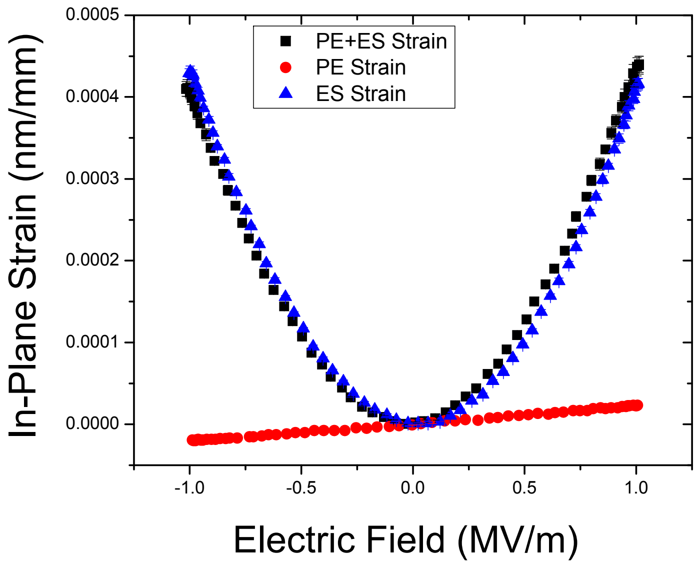


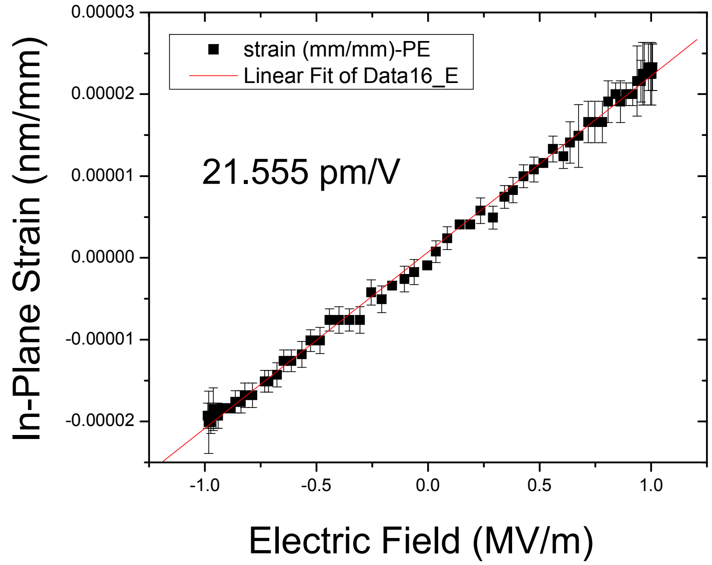
Goal: Flexible, transparent, large actuation, high sensitivity, mechanically durable

All images credit: NASA

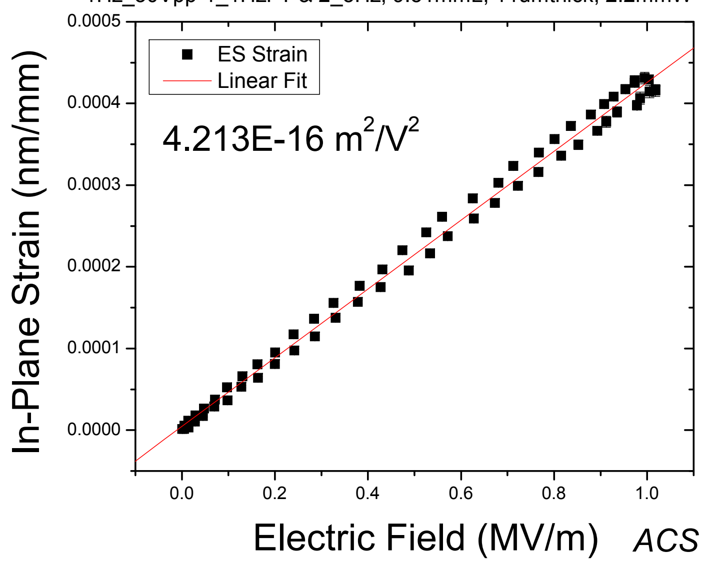
ACS Nano **9** 11942 (2015)

All-Nanotubes Actuator/Sensor Film: In-Plane Strain





JK 919-57-04-A-LaRC ANA-CNT-BNNT+PU film-In Plane Strain-1Hz_30Vpp-1_1HzFT & 2_5Hz, 9.51mmL, 11umthick, 2.2mmW



Field induced strain (ε_{33})

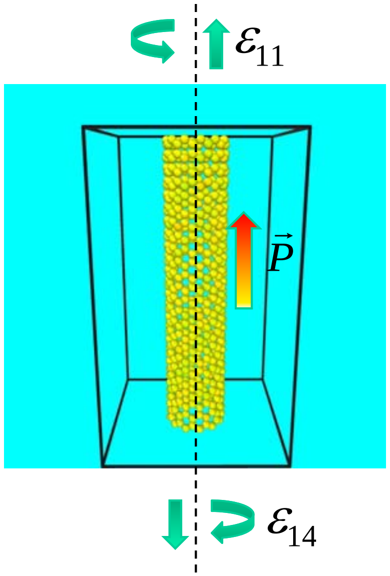
$$\varepsilon_{33} = d_{33} \cdot \boldsymbol{E} + M_{33} \cdot \boldsymbol{E}^2 + \ldots$$

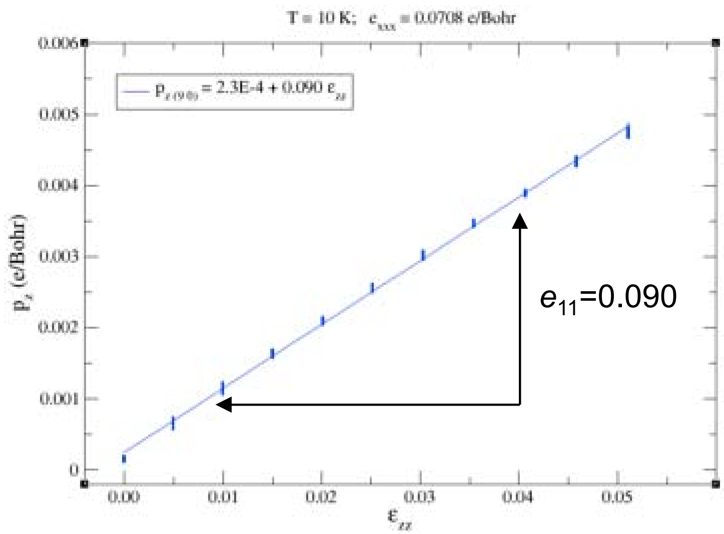
d_{33}: piezoelectric coefficient
M_{33}: electrostrictive coefficient
E: applied electric field

ACS Nano **9** 11942 (2015)

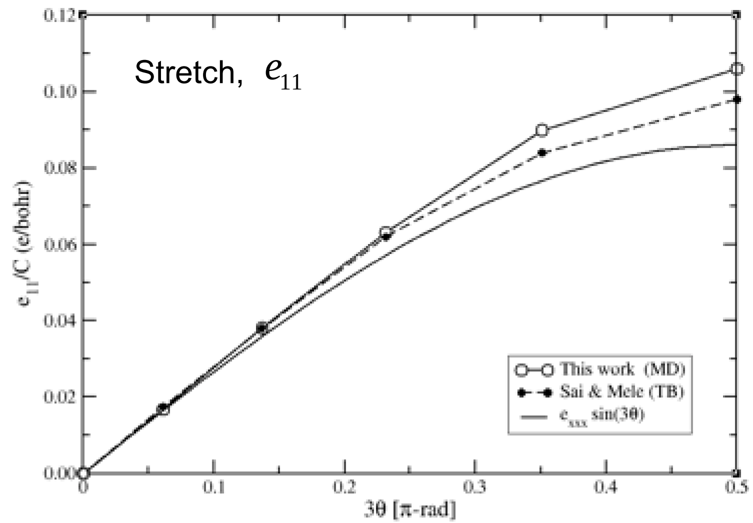
Results: Piezoelectricity under Deformation

Successful Molecular Dynamics (MD) model for piezoelectric properties of BNNTs



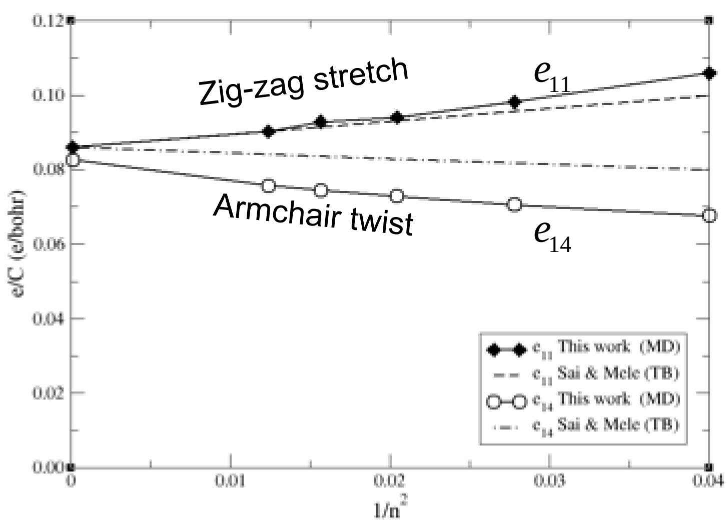


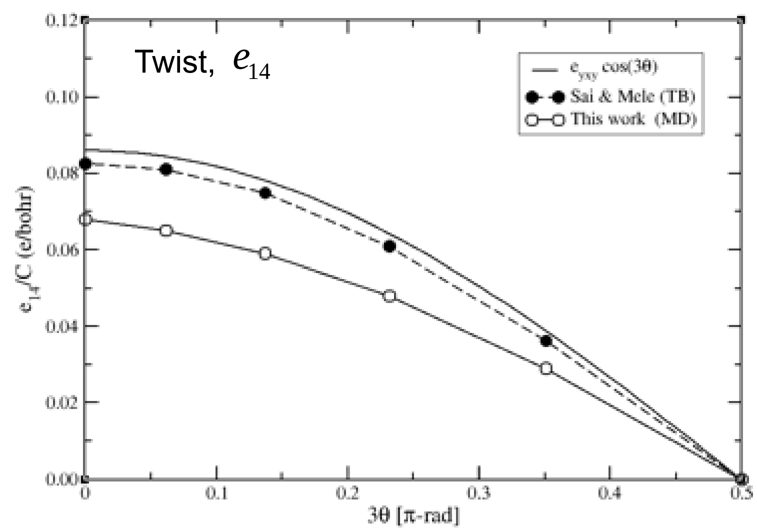
Armchair -> Chiral -> Zig-zag



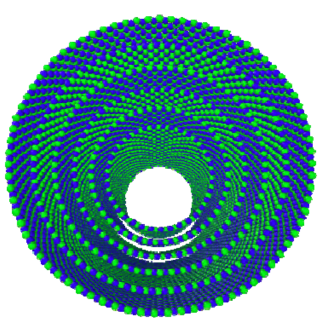
$p_z(stretch) = e_{11}\varepsilon_s$

$p_z(twist) = e_{14}\varepsilon_t$





MWBNNT



Comp. Mater. Sci., **95** 362 (2014)

Radiation Shielding Properties

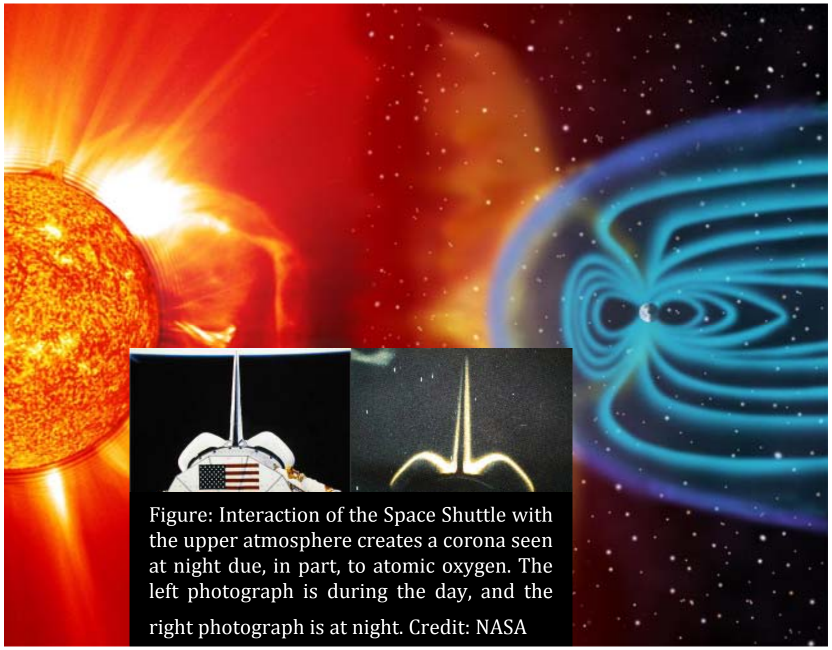
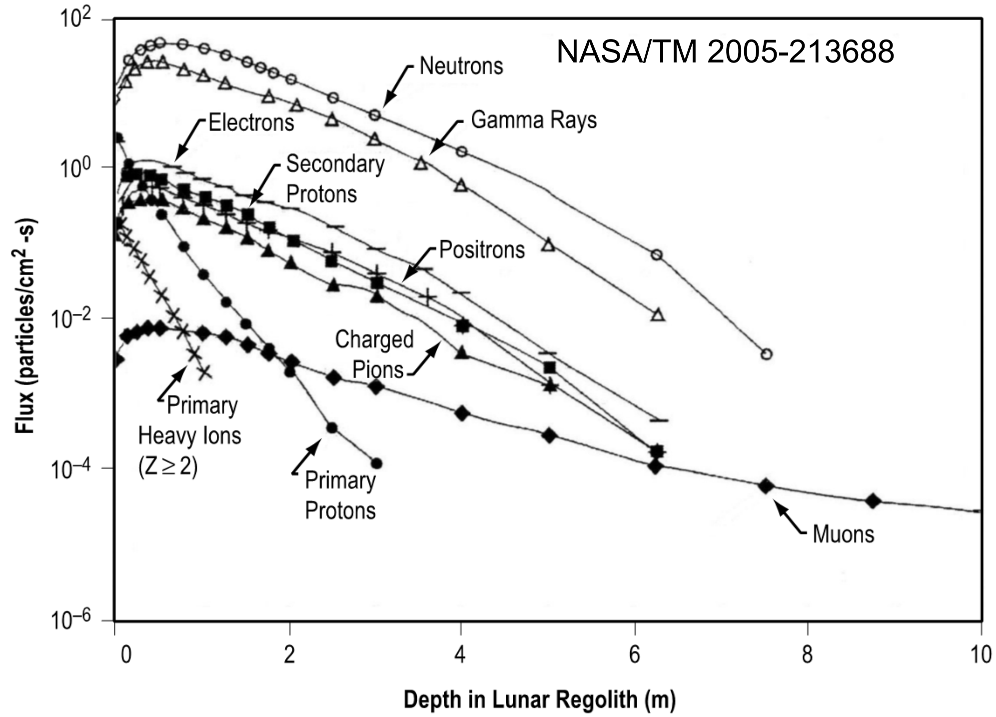


Figure: Interaction of the Space Shuttle with the upper atmosphere creates a corona seen at night due, in part, to atomic oxygen. The left photograph is during the day, and the right photograph is at night. Credit: NASA

Science **340** 1080 (2013)

Primary GCR and produced Secondaries in lunar regolith



Measurements of Energetic Particle Radiation in Transit to Mars on the Mars Science Laboratory

C. Zeitlin,[1*] D. M. Hassler,[1] F. A. Cucinotta,[2] B. Ehresmann,[1] R. F. Wimmer-Schweingruber,[3] D. E. Brinza,[4] S. Kang,[4] G. Weigle,[5] S. Böttcher,[3] E. Böhm,[3] S. Burmeister,[3] J. Guo,[2] J. Köhler,[3] C. Martin,[3] A. Posner,[6] S. Rafkin,[1] G. Reitz[7]

The Mars Science Laboratory spacecraft, containing the Curiosity rover, was launched to Mars on 26 November 2011, and for most of the 253-day, 560-million-kilometer cruise to Mars, the Radiation Assessment Detector made detailed measurements of the energetic particle radiation environment inside the spacecraft. These data provide insights into the radiation hazards that would be associated with a human mission to Mars. We report measurements of the radiation dose, dose equivalent, and linear energy transfer spectra. The dose equivalent for even the shortest round-trip with current propulsion systems and comparable shielding is found to be 0.66 ± 0.12 sievert.

Spacecraft data nails down radiation risk for humans going to Mars

Nature News, May 30, 2013, Ron Cowan
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

All images credit: NASA


Integrated Radiation Protection Strategy Enables Human Mars Exploration
Integration across Research and Technology Required…
National Aeronautics and Space Administration
NASA
Mission and Architecture Systems Analysis
Image credit: NASA
Mars MTV-02
Image credit: NASA
Image credit: NASA
Image credit: NASA/NIAC
Active Shielding Concepts
Environmental Modeling, Monitoring, and Prediction
Predictive Models
Crew Selection and Operations
Integrated Radiation Protection System
Images credit: OLTARIS.nasa.gov (top) and NASA (lower)
OLTARIS
External Environment
Internal Environment
High Energy Nuclear Physics and Transport
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Image: Public Domain
Individualized Risk Assessment
On-board Dosimetry– ISS TEPC
Radiobiology and Biological Countermeasure
NSRL
Image credit: BNL
Track Damage to DNA
with GCR — Mouse Model
Innovative Multi-Purpose Shield Solutions
Image credit: BNL
Inflatable Shield Prototype
Image credit: NASA
Shield Sections
Personal Shielding
Dr. Karl Johnson © 2004
Storage BNNT
Background Image credit: NASA
Credit: Lisa Simonsen (NASA)

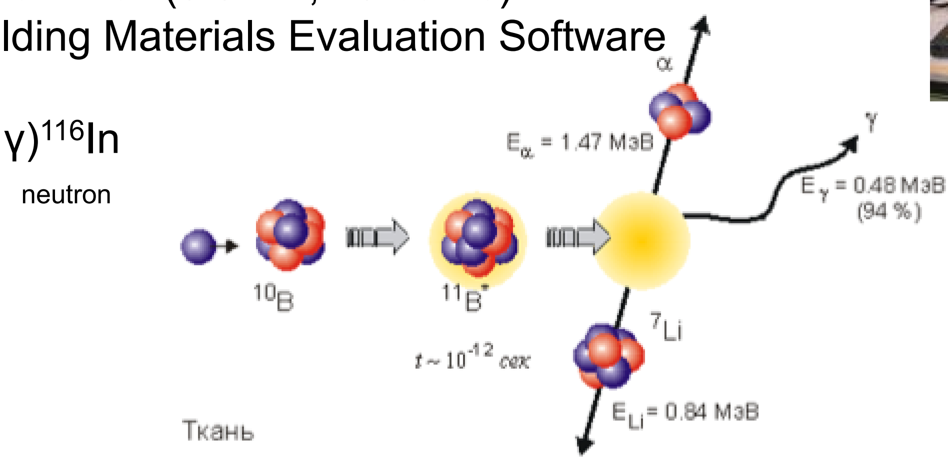
Neutron Radiation Shielding Study

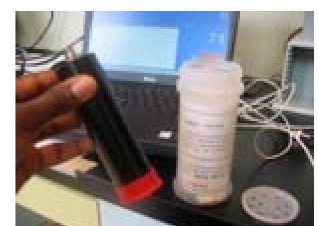
Materials
- Hydrogen, Boron, Nitrogen
- BN, BNNT, Gd
- Low density polyethylene (LDPE), polyimide (Kapton, CP2, (β-CN)APB/ODPA), polyurethane

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

Characterization
- Neutron Radiation Exposure Lab: Source: Am/Be 1Curie
- 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

$^{115}In(n, \gamma)^{116}In$





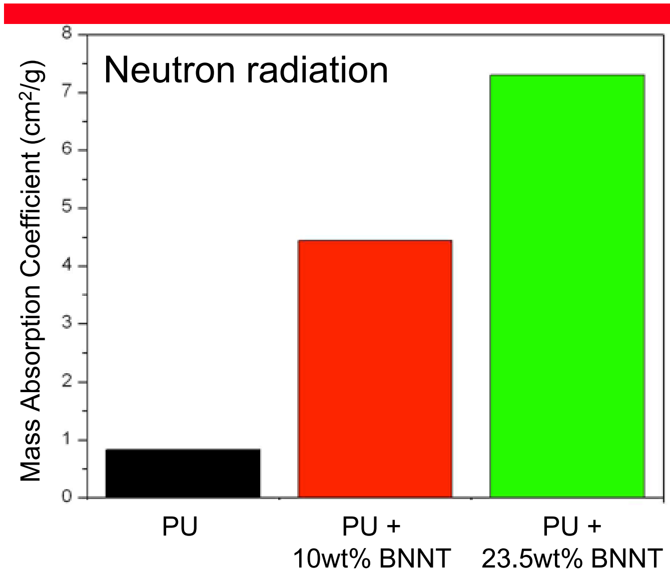
Geiger-Mueller Tube

Modeling
- OLTARIS

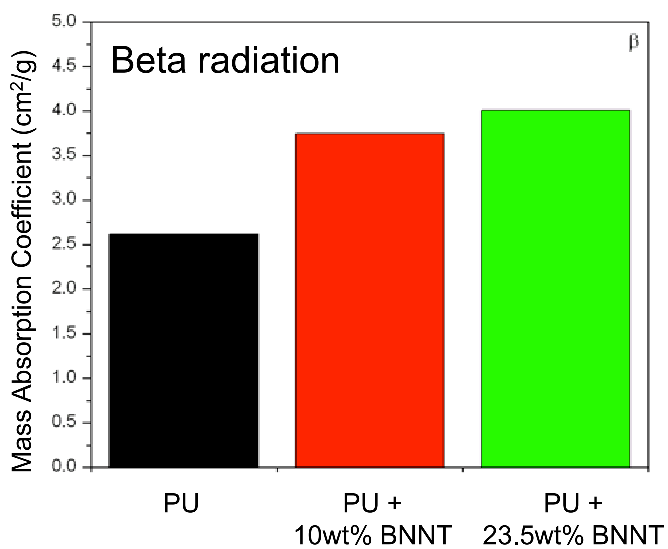
http://www.inp.nsk.su/bnct/introduction/introduction.en.shtml

All images credit: NASA

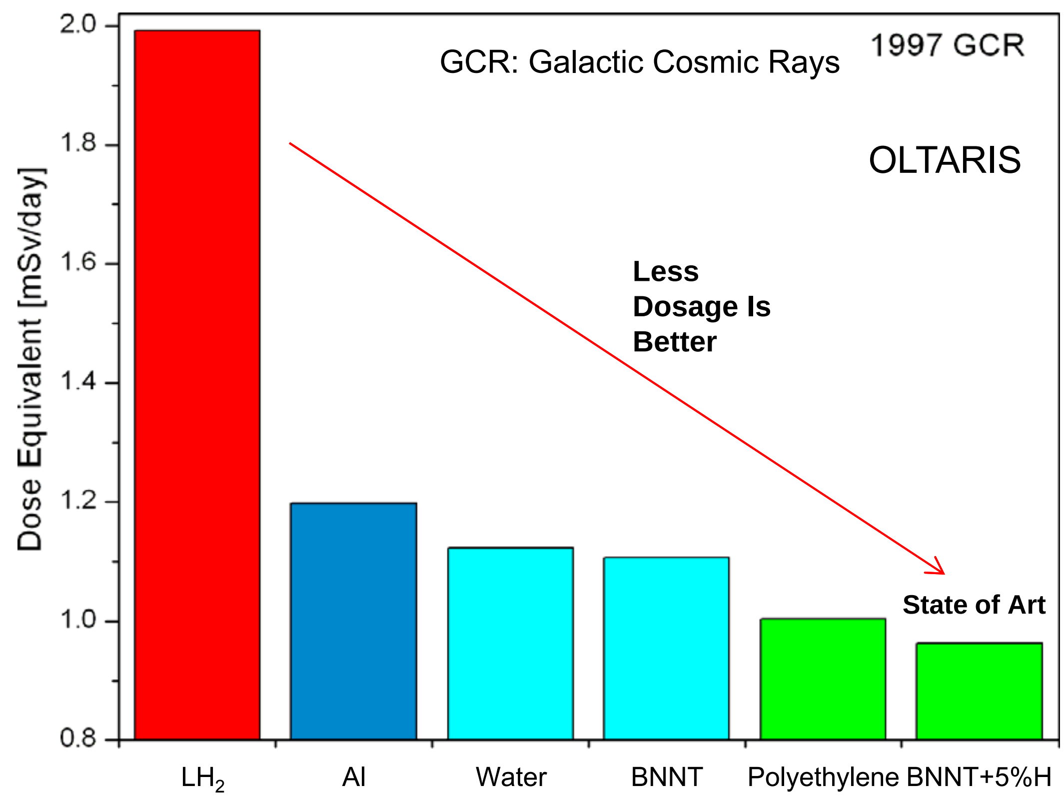
Radiation Shielding Effectiveness of BNNT Composites



PU: Polyurethane



PU: Polyurethane



All images credit: NASA

Summary

- High Temperature-Pressure BNNT synthesis method was introduced.
- BNNT dispersion was successfully achieved by thermodynamic approach using Hansen solubility parameters for single and co-solvent systems.
- Interfacial shear strength and fracture energy of BNNT with polymers were superior to those of CNT.
- BNNT exhibited excellent thermal stability under a simulated planetary entry environment along with flame resistance and retardation properties
- BNNT polymer composites exhibited excellent piezoelectricity as well as electrostrictive behavior even without poling.
- BNNT exhibited excellent neutron and beta radiation shielding effectiveness and hydrogen containing BNNT showed superb shielding effectiveness against GCR and SPE.

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