



Nanomaterials Development for Aerospace Applications

Dr. Diana Santiago de Jesús

NASA Glenn Research Center

Cleveland, Ohio, USA

With Contribution from GRC: Dr. Maricela Lizcano and Dr. Marisabel Kelly

University of Puerto Rico, Río Piedras – November 17, 2021



Background and Expertise

✓ Bachelor in Science, Chemistry

- University of Puerto Rico, Cayey

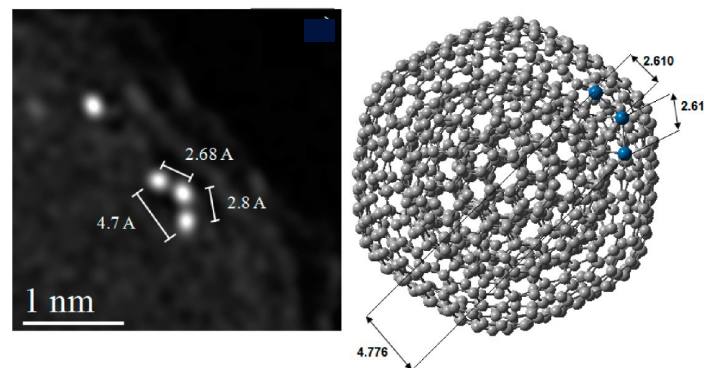
✓ Doctorate Degree, Chemistry

- University of Puerto Rico, Río Piedras
- Thesis on electrochemical preparation of nanomaterials for Fuel Cell application
- Advisor: Prof. Carlos Cabrera



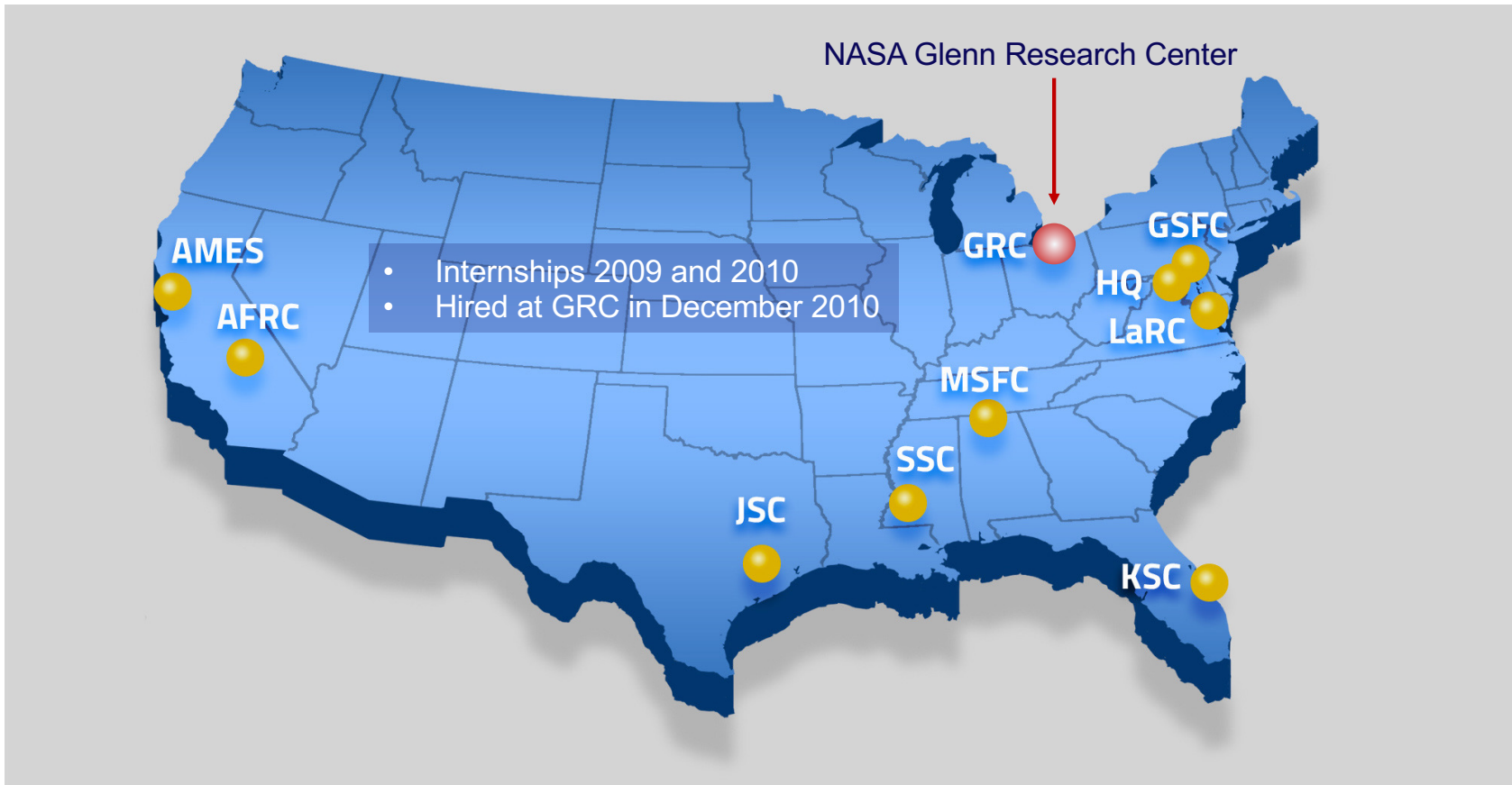
Expertise developed at UPR

- ✓ Surface analysis characterization techniques
- ✓ Electrochemical techniques
- ✓ Preparation of nanomaterials
- ✓ Catalyst preparation for Fuel Cell application





NASA Centers

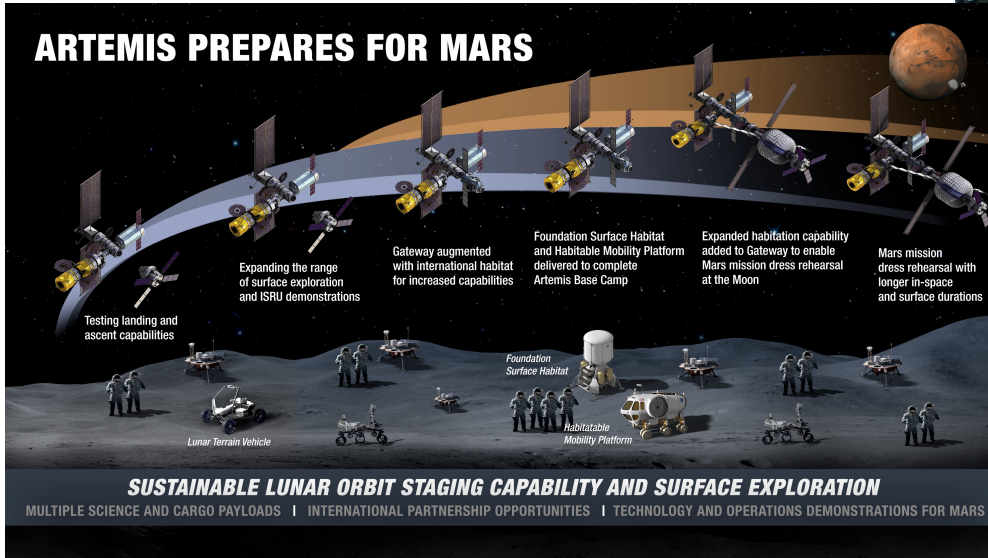


More Recent Applications of my Research at NASA

✓ Next generation of airplane

- Hybrid or Full Electric Aircraft
- High-Voltage and High-Power Transmission

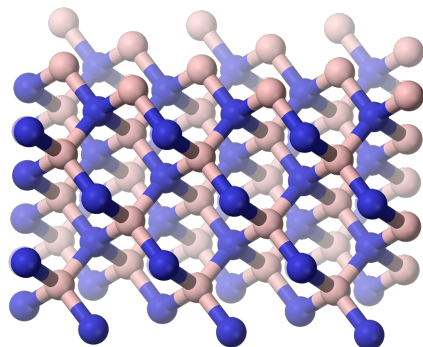
✓ From Moon Habitat to Mars





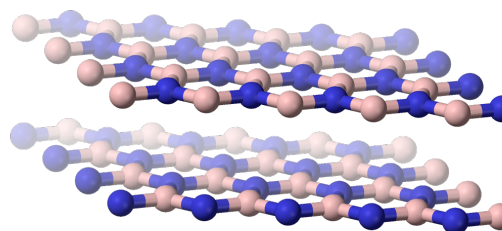
Boron Nitride (BN) Structures

Cubic BN (c-BN)



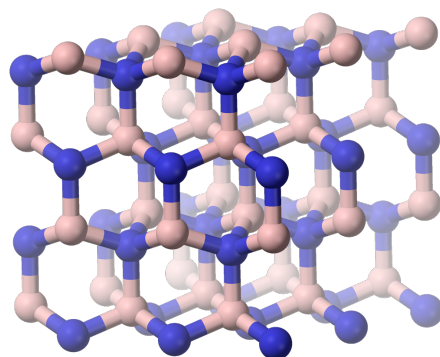
- ✓ Diamond like structure
- ✓ Density: 3.45 g/cm^3

Hexagonal BN (h-BN)



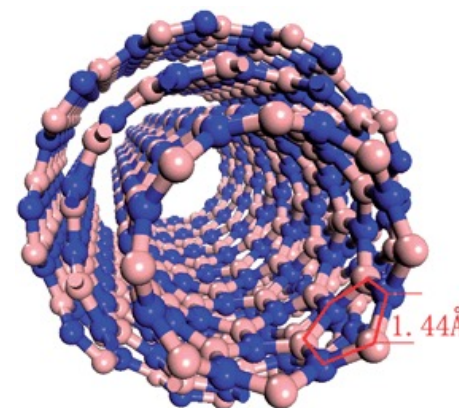
- ✓ Graphite like structure
- ✓ Density: $\sim 2.1 \text{ g/cm}^3$

BN Wurzite (w-BN)



- ✓ B and N are grouped into 6-membered rings
- ✓ Density: 3.49 g/cm^3

Boron Nitride Nanotube (BNNT)



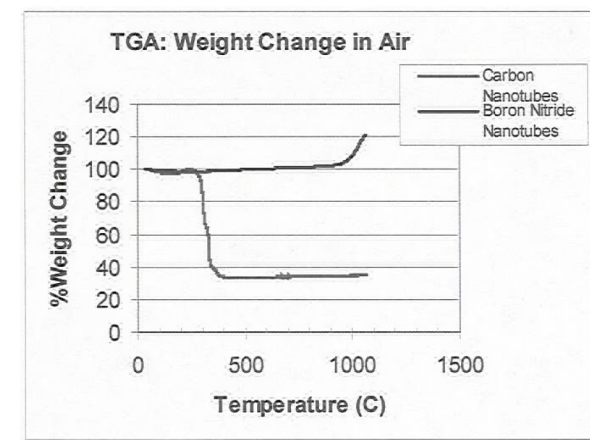
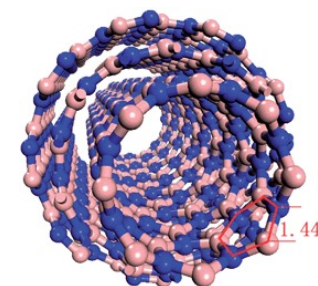
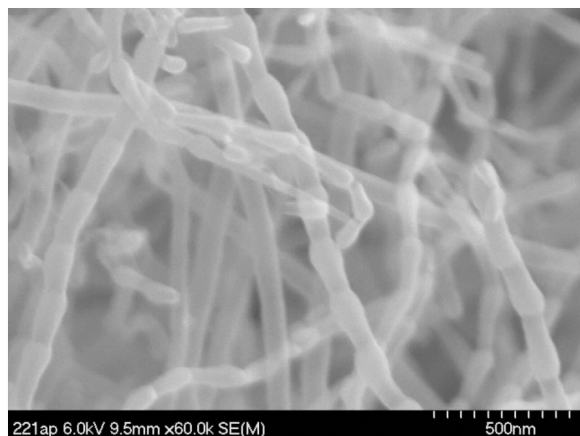
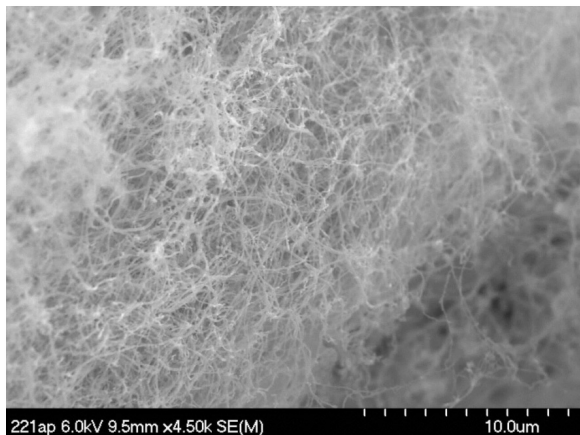
- ✓ Analog of carbon nanotube (CNT)
- ✓ Density (varied): $2 - 2.5 \text{ g/cm}^3$



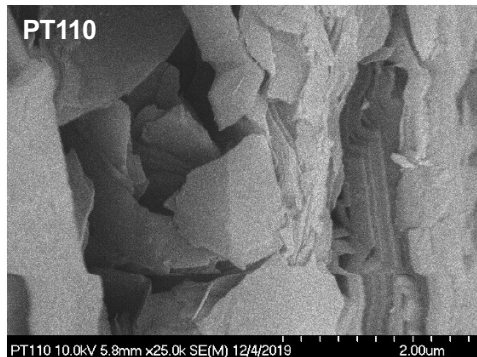
GRC's Synthesis of BNNT for Engineering Applications

GRC developed a modified Chemical Vapor Deposition methodology to successfully and reproducibly synthesize BNNTs

- ✓ 1-2 gram batches are being synthesized per day; however, the process is scalable to much larger batch sizes
- ✓ Synthesis has evolved over the years to prepare different structures to target different applications
- ✓ A preponderance of bamboo structured nanotubes could be achieved by careful additions of catalyst materials and control of processing conditions

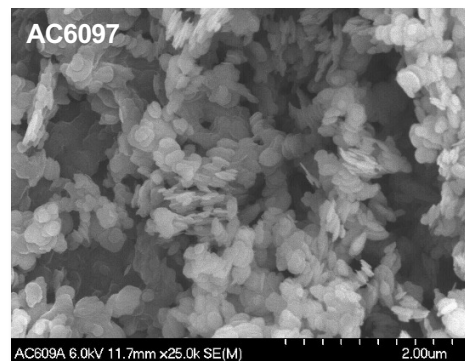


Exfoliation of Commercial hBN Developed at GRC



Momentive PT110:

- Particle size: $\sim 45 \mu\text{m}$
- Surface area: $0.6 \text{ m}^2/\text{g}$

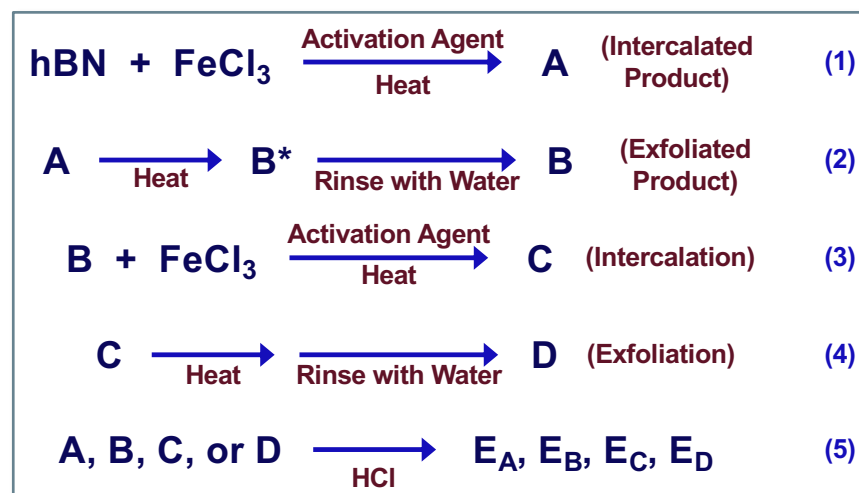
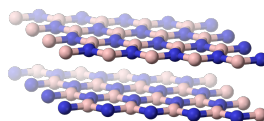


Momentive AC6097:

- Particle size: $\sim 0.50 \mu\text{m}$
- Surface area: $31 \text{ m}^2/\text{g}$

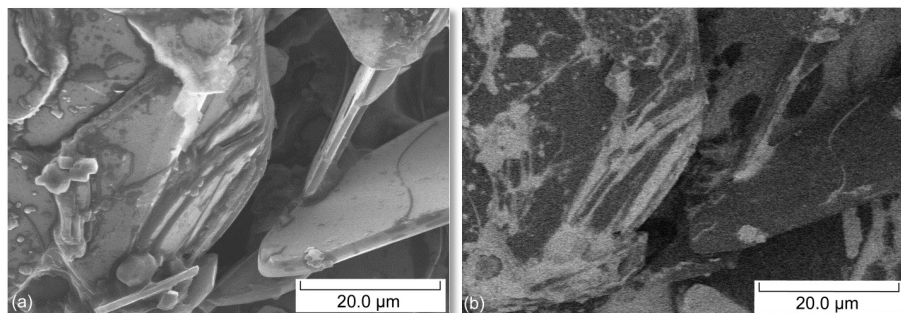
Methodology Process: Iron Chloride Intercalation

- ✓ Activation agent: NaF
- ✓ Intercalation and exfoliation happen on reactions (1) and (2), respectively
- ✓ Repeating these reactions were examined to see if the additional effort cause further exfoliation
- ✓ Further chemical treatment with HCl was done to remove impurities and intercalates



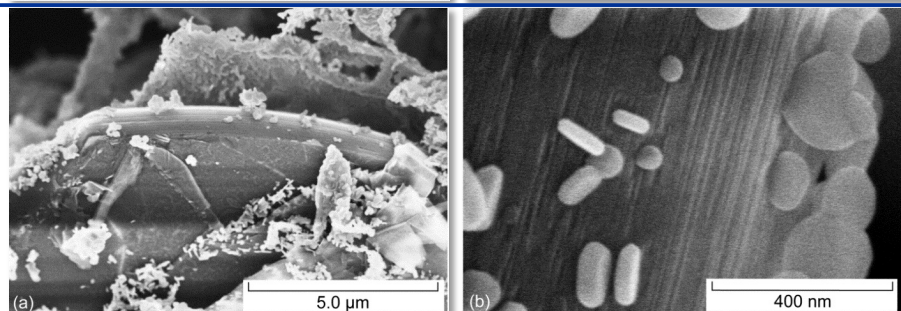
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hBN Exfoliation via Iron Chloride Intercalation



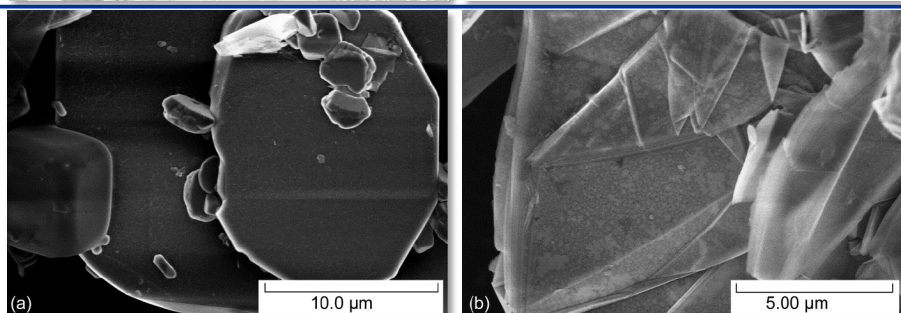
hBN particles intercalated with FeCl_3

- ✓ (a) SED shows the image of hBN
- ✓ (b) BSD highlights the location of the heavy element (Fe) at the edges and sides



Intercalated sample slowly oxidized by oxygen in air produced Fe_2O_3 nanoparticles

- ✓ (a) Nanoparticles arranged in sheets formed alternating layers with hBN
- ✓ (b) Side view of an hBN layer indicates it split into layers about 20 to 30 nm thick



Intercalated sample quickly oxidized

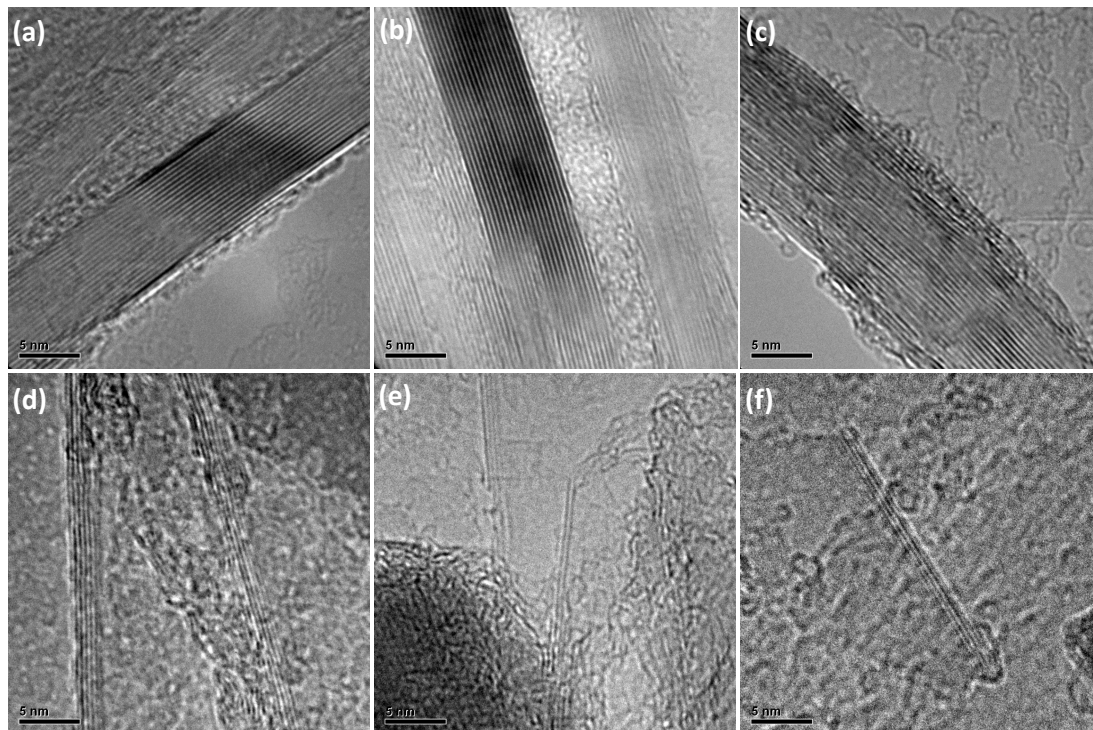
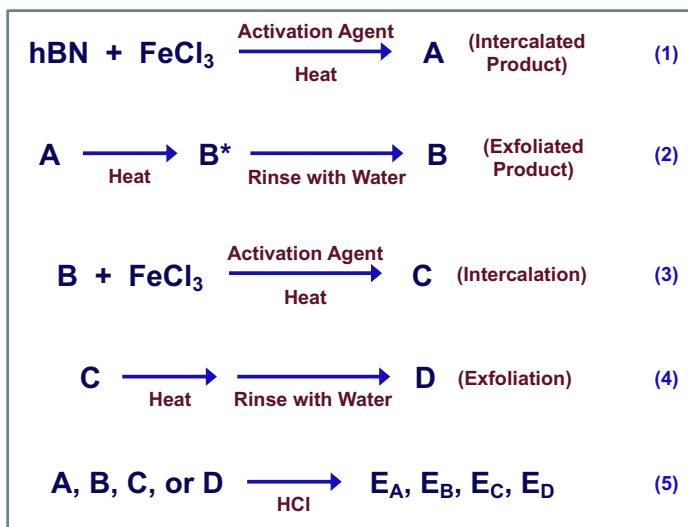
- ✓ (a) Intercalates moved out of the lattice and then oxidized to form micron-sized Fe_2O_3 particles
- ✓ (b) After HCl rinsing, the resulting pure hBN shows exfoliation

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hBN Exfoliation via Iron Chloride Intercalation

BNNS –Boron Nitride Nano Sheets

For “stand alone” hBN sheet, this process need to be repeated several times:



TEM micrographs of BN nanosheets from a sample obtained by intercalation and exfoliation of the large commercial hBN platelets four times. Nanosheets as thin as 1 to 5 layers are rare in original reactant hBN (a) to (c) but are commonly found in exfoliated product (d) to (f).



Hexagonal Boron Nitride and Nanotubes

NASA Glenn Research Center (GRC) has 2 decades of expertise synthesizing BNNTs and other BN nanomaterials for different Aerospace applications due to their multifunctionality

BN Applications:

- ✓ Aerospace structures and components
- ✓ Radiation Shielding
- ✓ Electric propulsion components
- ✓ Energy Storage
- ✓ Tribology
- ✓ Thermoelectric
- ✓ Cosmetics

□ Good Insulation Properties

- ✓ Constant wide band gap above 5.2 eV

□ Good Mechanical Strength

□ High Thermal Conductivity

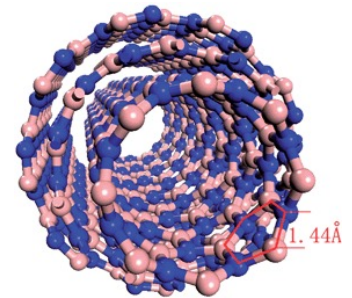
- ✓ Thermal Conductivity (W/(m·K)): BNNT > 600, hBN in plane > 100, hBN through plane ~ 30

- ✓ Ability to dissipate heat in nanoelectrics

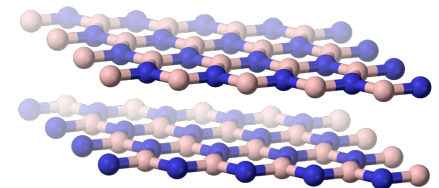
- ✓ Promising results in thermal shock experiments

□ Chemically and Thermally Stable

- ✓ Hydrophobic
- ✓ Chemical stability
- ✓ Oxidation in air above 1100 °C



BNNT

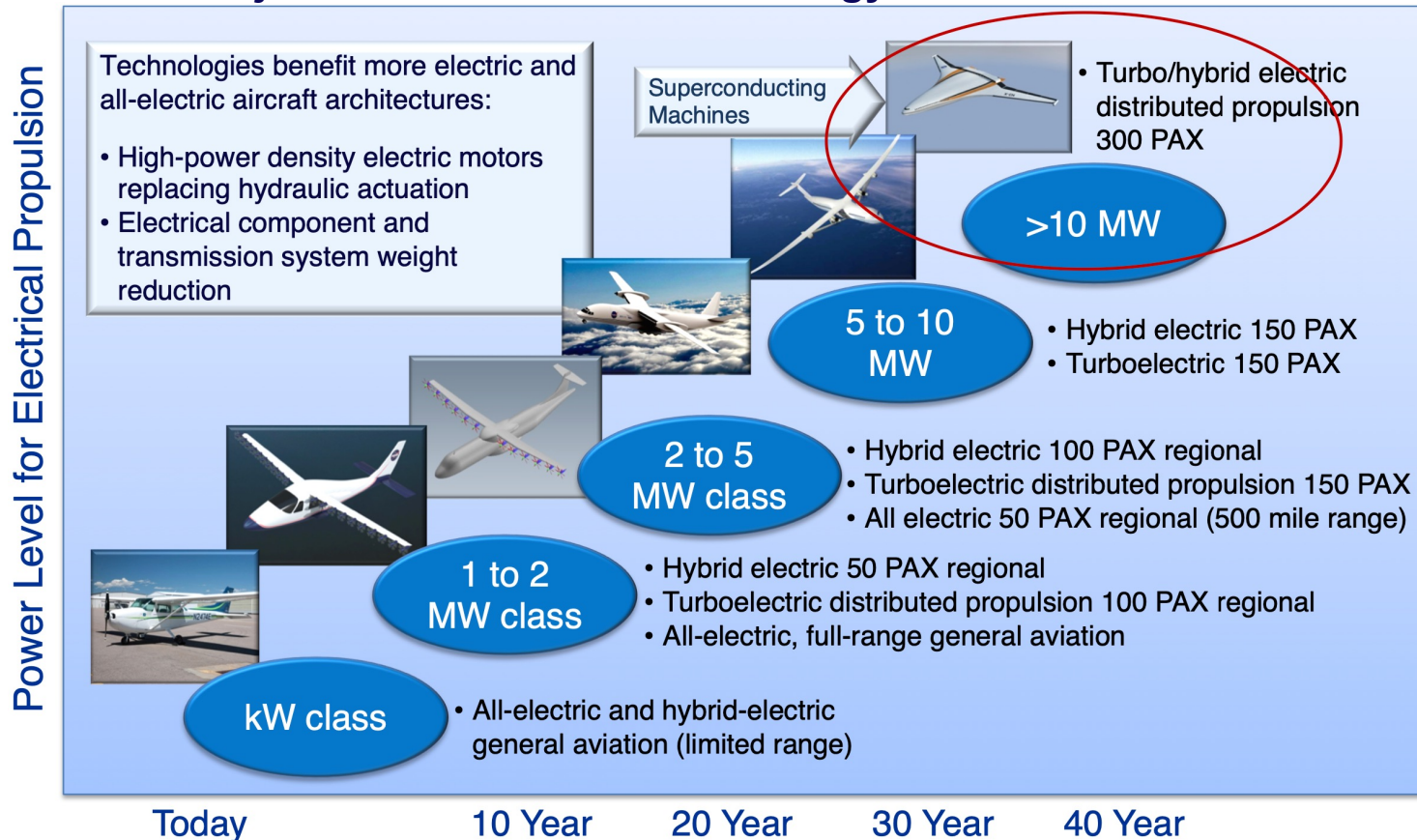


h-BN



Electric Propulsion for Aeronautics

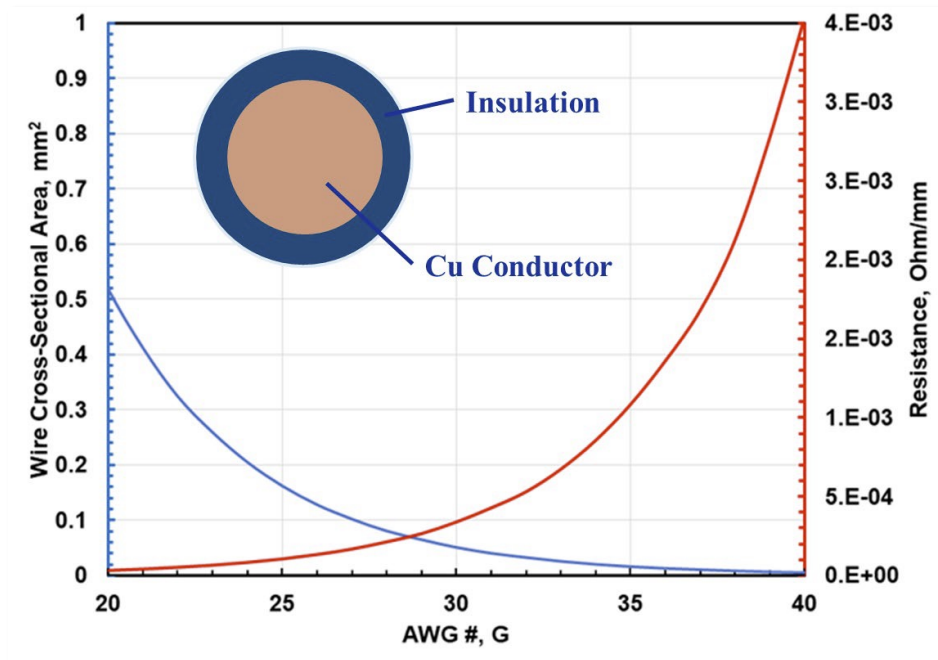
Projected Timeframe to Technology Readiness Level 6



- ❑ Higher power will need high voltage power transmission cables



Lighter-Weight Conductor Cables are Needed for Aerospace Electrical Propulsion



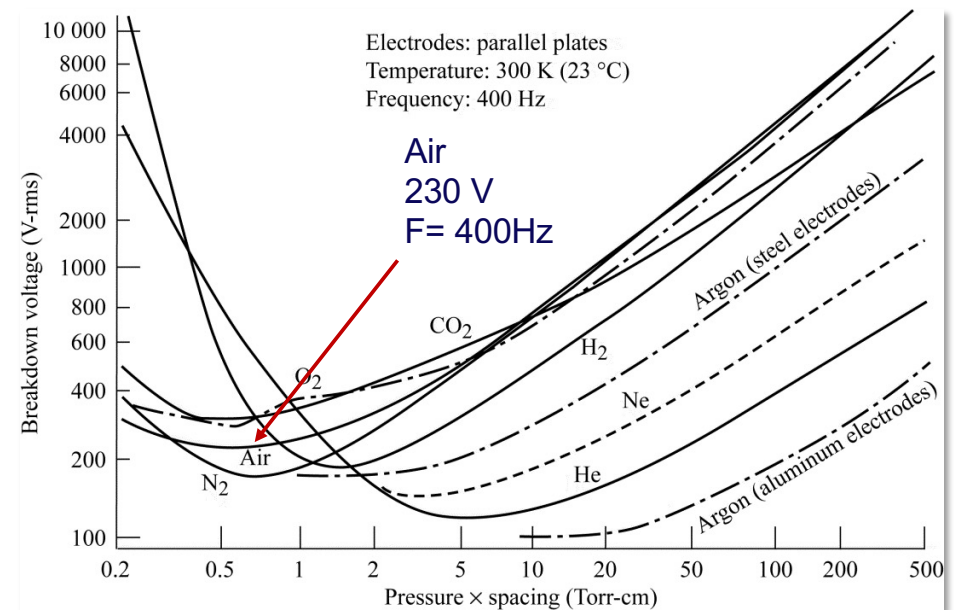
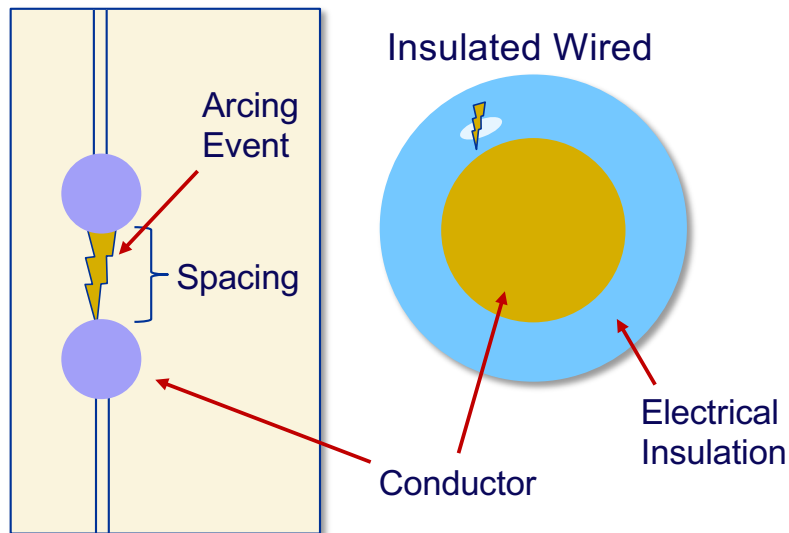
- Electric Propulsion is heavy due all the electric systems
- We can lightweight the conductor by increasing the voltage, V
- $V = I \times R$
- What can go wrong?
 - We need more insulation.

Power $P = I \times V = R \times I^2 = V^2 / R$



Technical Challenges: Partial Discharge and Corona

Partial Discharge in Void



- ✓ The minimum voltage for electrical discharge between two metal conductors at **high altitude** will occur at ~ 327 V.
- ✓ **At 400 Hz the minimum voltage drops to 230 V for breakdown to occur.**
- ✓ Additionally, voids, defects and contaminants in electrical insulation can experience intensified local discharge called partial discharge.

High Voltage Power Transmission: Insulation Materials



High Voltage Insulation Requirements:

- ✓ Thermal conductivity $> 1 \text{ W/m}\cdot\text{K}$
- ✓ Maintain functional operating temperature $> 200^\circ\text{C}$
- ✓ Push temperature $> 260^\circ\text{C}$ if possible
- ✓ Must be compatible with other component materials
- ✓ Retain dielectric strength of state-of-the-art materials ($> 20\text{k V/mm}$ or better)
- ✓ Increased resistance to partial discharge and corona effects



Goal: Development of a material that combines chemical inertness, lightweight and high strength with high electrical resistivity and high thermal conductivity for the insulation component of high voltage power transmission



BN-Epoxy Composite

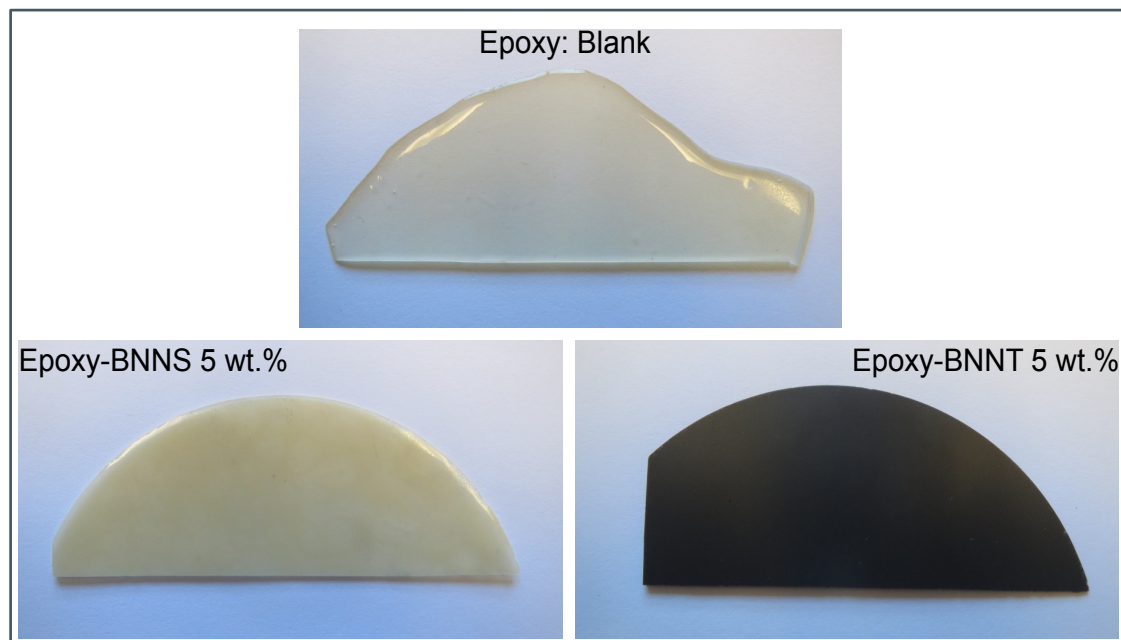
Exploring the use of BNNTs and BNNSs as filler material to develop a custom formulation of epoxy with high thermal conductivity and high electrical resistivity as a moldable nanocomposite

Samples prepared and filler loading:

- ✓ Epoxy/BNNT composite: Between 1.5 and 10.0 wt. %
- ✓ Epoxy/BNNS composite: 1.3 and 5.0 wt. %

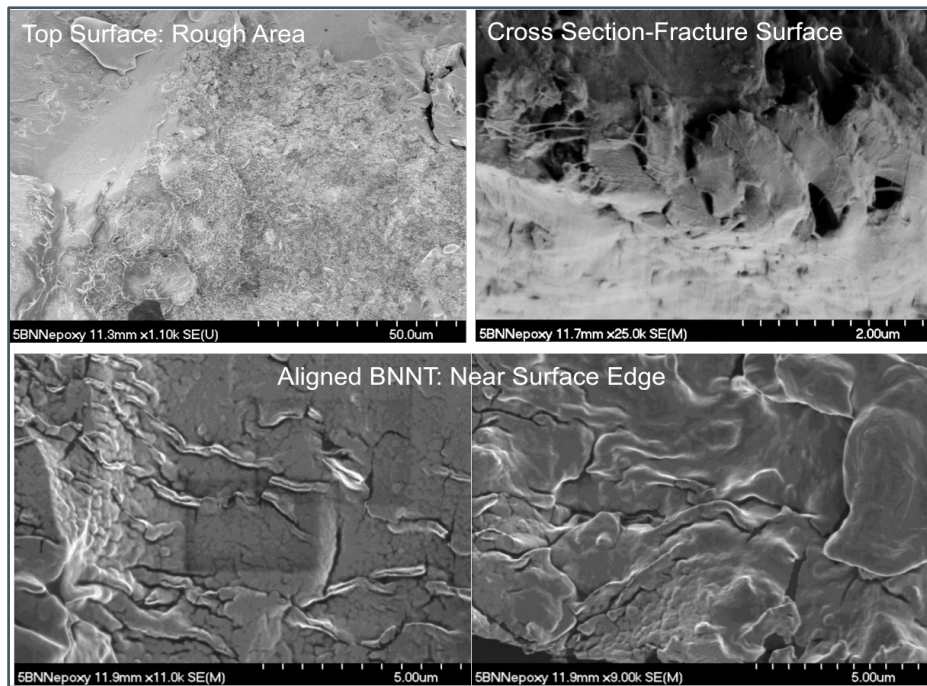
Epoxy used:

- ✓ Low viscosity Epoxy resin: araldite CY 184
- ✓ Epoxy hardener: Aradur HT 907 US
- ✓ Accelerator: DY 183



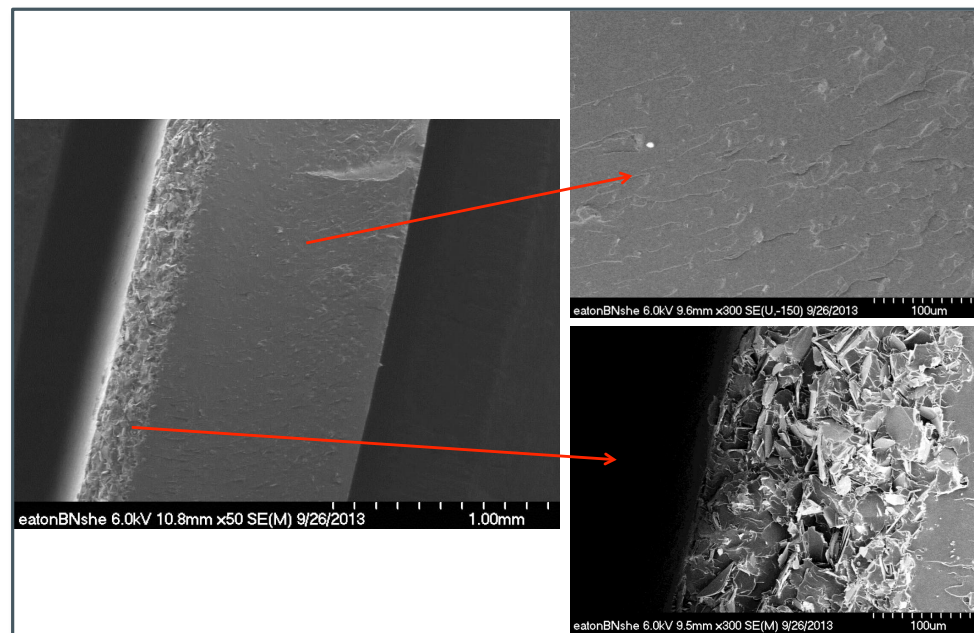


BN-Epoxy Composite



Epoxy/BNNT 5 wt. %

- ✓ Rough appearing areas on the top surface contain BNNT agglomerates
- ✓ Polymer infiltrates agglomerates well

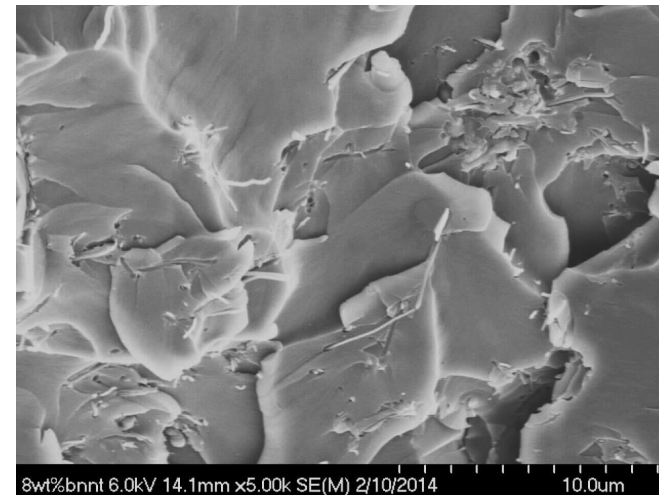
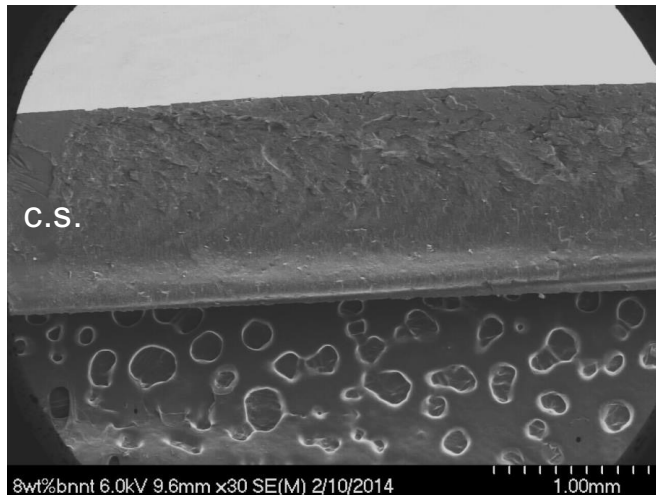


Epoxy/BNNS 5 wt. %

- ✓ BNNS were not well mixed in Epoxy, settling to the lower surface
- ✓ Two layers composites can be study for some applications



BN-Epoxy Composite

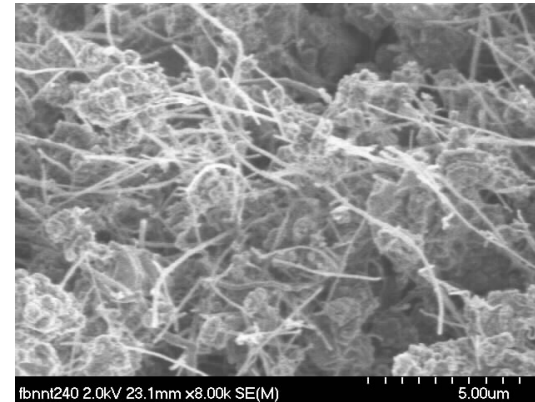


- ✓ **Epoxy-BNNT/BNNS 5 wt% (3:2)**
- ✓ Rough appearance seems to corresponds to BNNT – smaller in this sample than samples with higher BNNT concentrations.
- ✓ No evidence of settling of BNNS as found in BNNS alone
- ✓ Better dispersion of BNNT and BNNS than either alone



Functionalization of BN

- ✓ BN is chemically inert and has problem mixing on composites with polymers
- ✓ Functionalization of BN helps their dispersion in composites



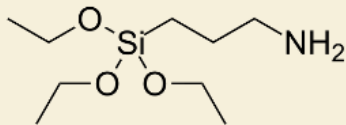
Functionalized BNNT

✓ Acid Treatment

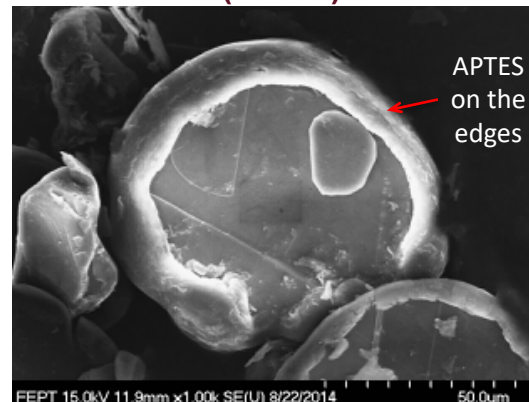
- Nitric acid adds OH on the BN surface

✓ “Silanizing”

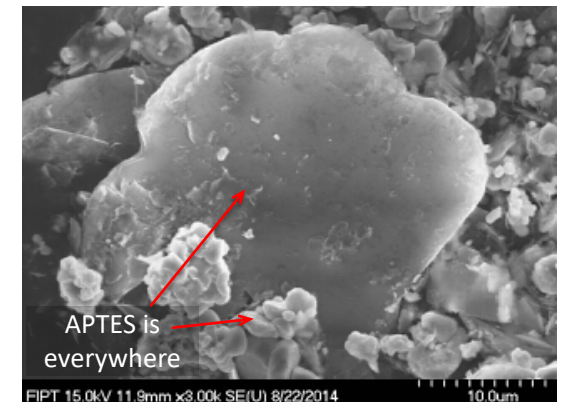
- Functionalization with 3-aminopropyltriethoxysilane (APTES)



Functionalized Exfoliated hBN (PT110)



Functionalized hBN (PT110) Intercalated with Iron Oxide

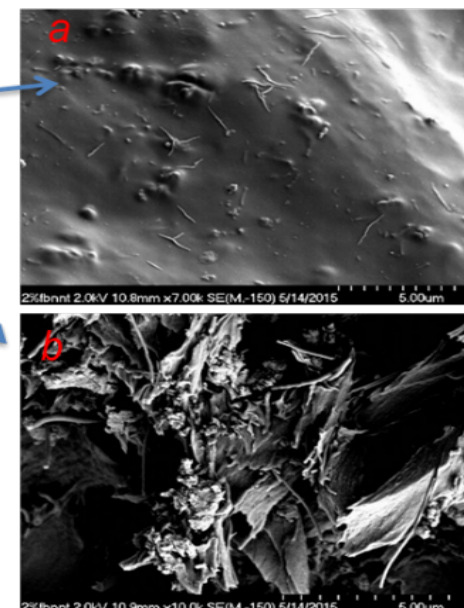


Thermal Conductivity Test of Other Polymer Composites

Matrix	Max. Use Temp. (°C)	Filler, wt. %	TC (W/m-K)
Ultem 1000 (Polyetherimide)	215	0	0.12
		BNNT, 5	0.18
		BNNT, 8	0.22
		BNNT, 10	0.23
		f-BNNT, 5	0.30
TPI-265 (Thermoplastic polyimide)	215	0	0.50
		hBN (800 nm), 25	0.53
Kapton (Thermoplastic polyimide)	240	0	0.12
		hBN (~80-100 μm), 12	0.11
		f-BNNT, 10	0.79
		f-BNNT, 12	0.58
		f-BNNT, 17	0.93
		f-BNNT, 20	1.59
		f-BNNS, 10	0.30
		f-BNNT/f-BNNS, 10/10	0.29
RTM-370 (Thermoset polyimide)	250	0	0.16
		BNNT, 10	0.28



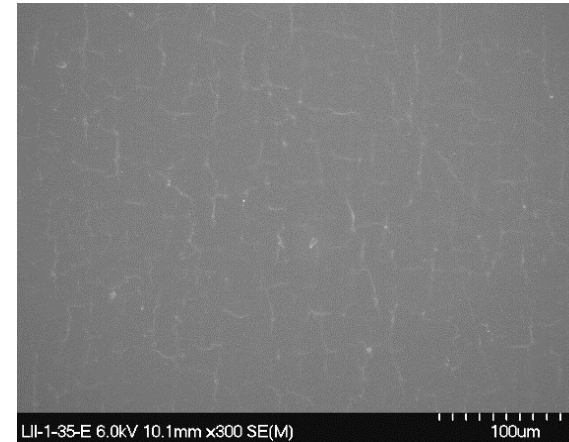
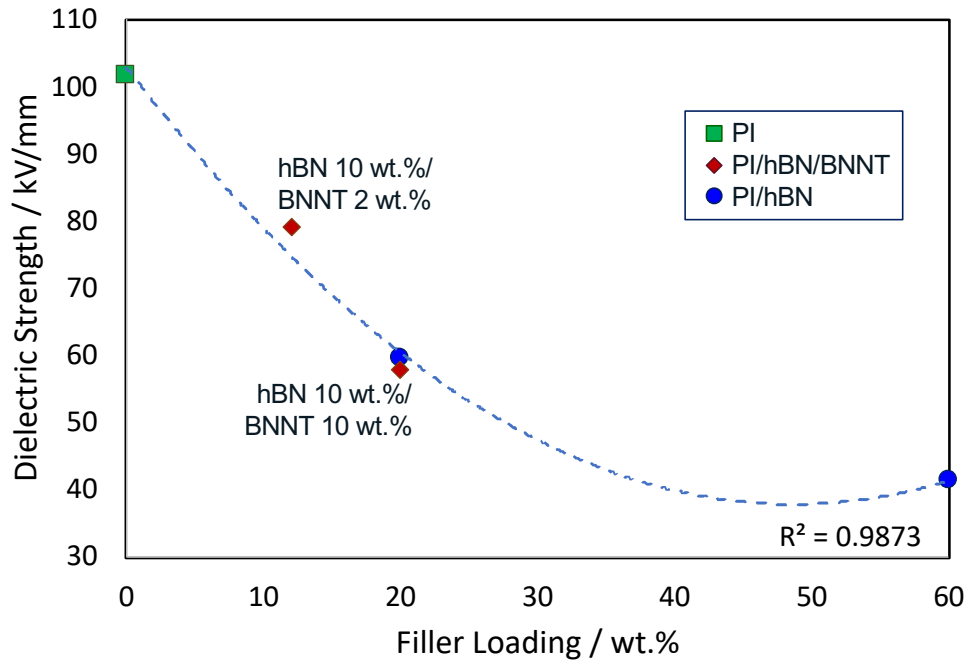
PI/f-BNNT 12 wt. %



SEM: a) surface, b) cross section

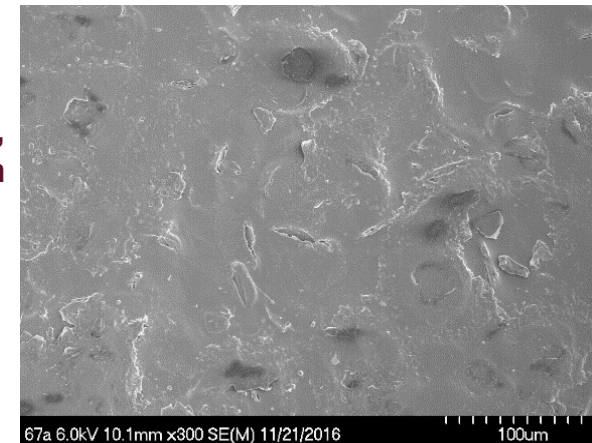
Functionalized BNNTs disperse better in the polymeric matrix than as synthesized BNNTs

Dielectric Strength Test of Polyimide Composites



PI, DS: 101 kV/mm

**PI/h-BN (60 wt.%),
DS: 41.6 kV/mm**



- ✓ Dielectric strength decreases as filler loading increases, as expected
- ✓ Sample with 60 wt.% loading of hBN still has dielectric strength above 40 kV/mm



Ceramic Composite

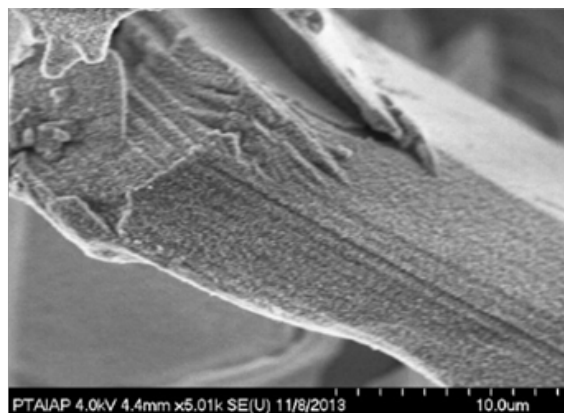
Challenge of using only hBN

- ✓ h-BN sinters at 2000 °C
- ✓ The resulting ceramic splits easily due to flake structure



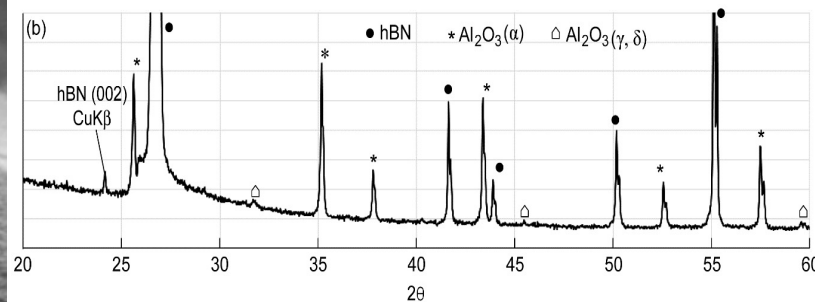
Adding Alumina to hBN for Ceramic Composite

- ✓ Alumina properties:
 - Chemical and physical stability
 - Thermal conductivity: 30 W/m·K
 - High heat resistance
 - High strength and hardness
- ✓ Alumina can help decrease the hot press temperature needed to make a ceramic composite with h-BN



Preparation of hBN/Alumina via Intercalation of hBN with Aluminum Chloride

- ✓ Aluminum chloride (AlCl_3) could also react with h-BN similarly in the presence of NaF, producing an h-BN- Al_2O_3 mixture where nanosized Al_2O_3 particles are inside the h-BN platelets
- ✓ Alumina coating on h-BN can act as a functionalized BN to improve the interaction with other materials



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hBN-Alumina Composite

h-BN/Alumina Hot Press at 1950 °C and 69 Mpa



h-BN/Alumina Composite



Composition:

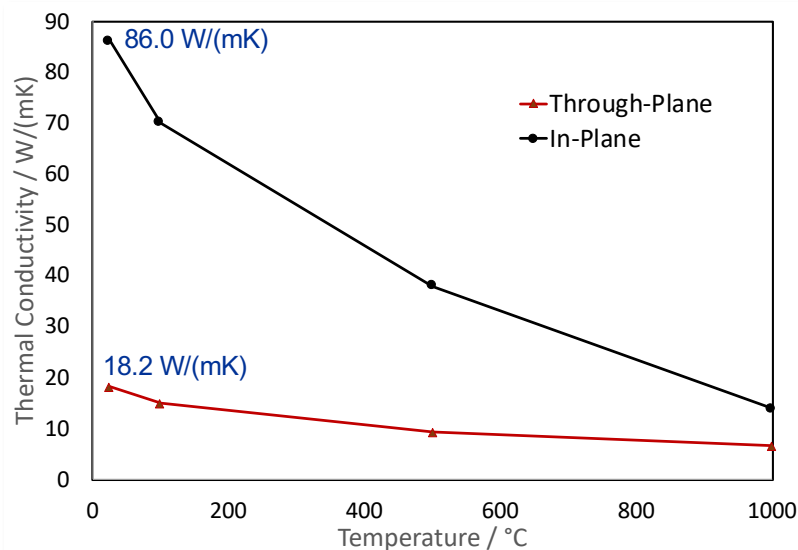
- ✓ 90% h-BN
- ✓ 10% alumina

Density:

- ✓ h-BN: 2.10 g/cm³
- ✓ Alumina: 3.95 g/cm³
- ✓ **This composite:** 2.25 g/cm³

Thermal Conductivity Tests:

- ✓ hBN/Alumina composite of 60 wt.% hBN and 40 wt.% alumina with a density of 2.45 g/cm³
- ✓ Thermal conductivity data was obtained by Netzsch
- ✓ Tests indicate an in-plane thermal conductivity value much higher than the through-plane value, as expected



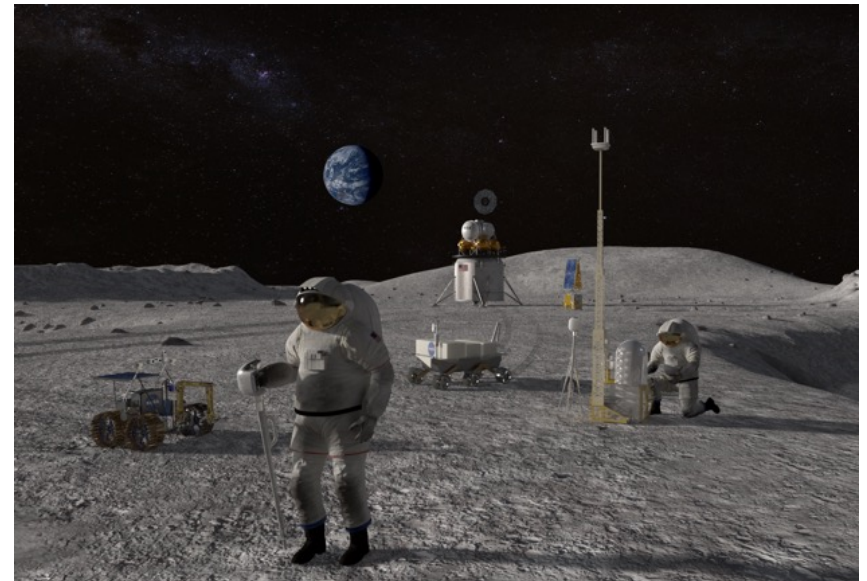
Thermal Conductivity Related properties of Fabricated Exfoliated h-BN/Alumina Composites

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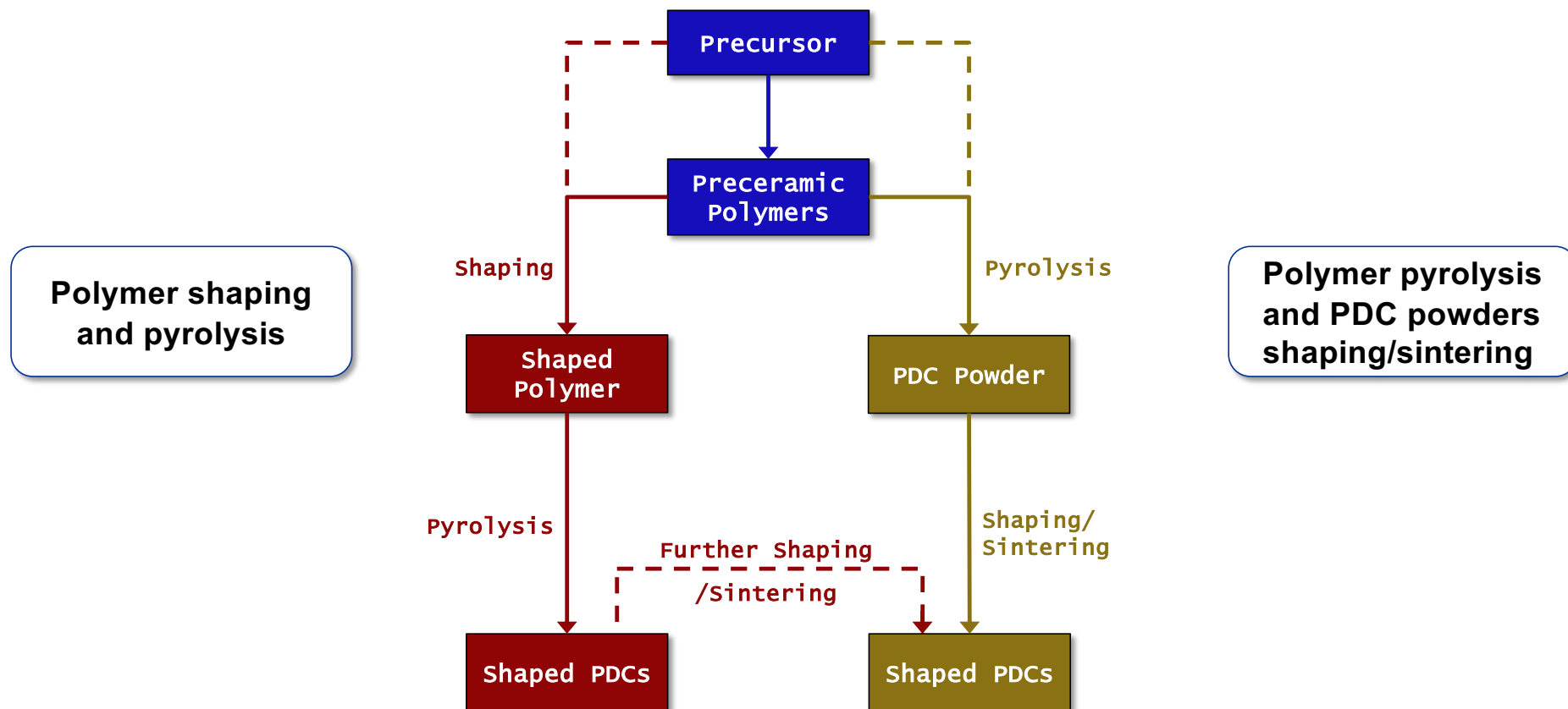
BN Fibers Development

- Develop a polymer derived ceramic procedure to fabricate h-BN fibers that is easy, fast, and has high yield with minimum chemical wastes
- The development of long h-BN fibers will bring continuity of multifunctional properties in a composite including chemical inertness, lightweight and high strength with high electrical resistivity and high thermal conductivity
- BN nanofibers will enhance material development for electric propulsion and other space applications:
 - Electrical insulation for high voltage components
 - Re-entry shielding
 - Radiation shielding
 - Space structures





Polymer Derived Ceramic Process





Forcespinning Machine

- High-yield fiber preparation
- Fibers fabricated by centrifugally spinning a polymeric solution into continuous fibers
- Fiber diameters can be tailored between ≈ 200 nm to $5\text{ }\mu\text{m}$
- Diameters depend on precursor properties (like molecular weight, solution viscosities, and spinning speeds)
- Fibers can be up to 6 ft in length

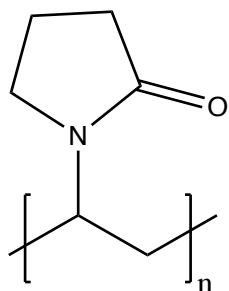


collection rods

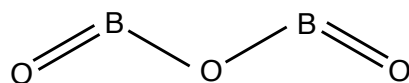
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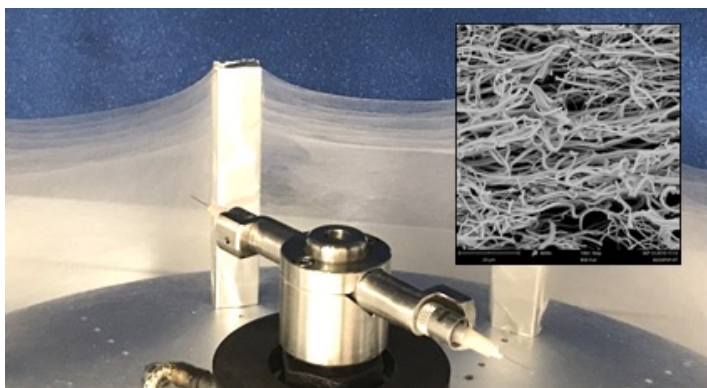
Shaping Fibers



**Polyvinylpyrrolidone
(PVP), C₆H₉NO**



**Boron Oxide,
(Borea) B₂O₃**



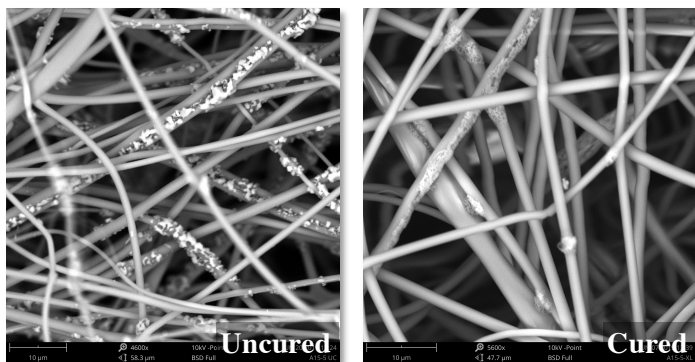
- ✓Fibers were spun in just 3 minutes
- ✓PVP/B₂O₃ fibers were very dry and fluffy



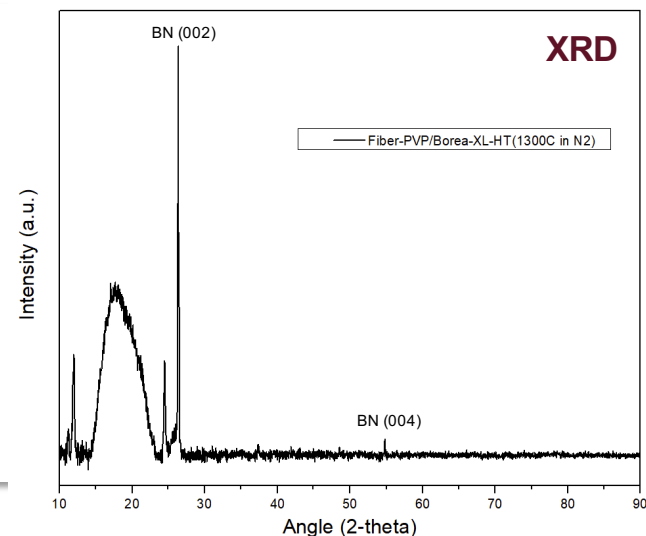
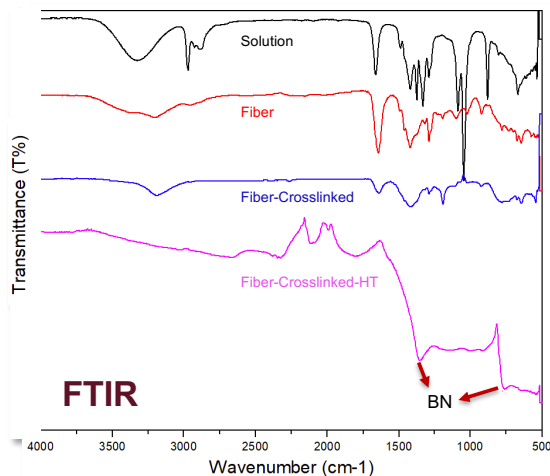
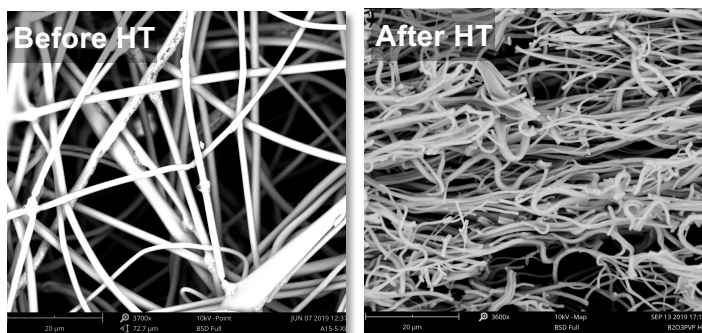


Polymer to Ceramic Conversion

PVP/B₂O₃ Fibers



Before and after Heat treatment



After Heat Treatment Process:

- ✓ Dark gray in color
- ✓ Mechanically strong at touch
- ✓ On SEM they look shorter or like being cut

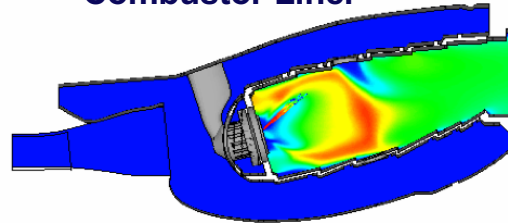
- ✓ FTIR and XRD confirmed heat-treatment process produced BN
- ✓ Proved feasibility

Fuzzy Fibers for Ceramic Matrix Composites (CMC)

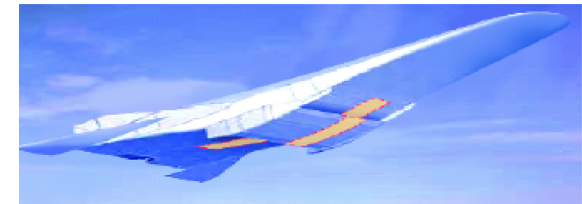
General Objective:

- ✓ High Temperature Advanced Fibers/Interface Composed of Boron Nitride Nanotubes Grown on SiC for Improved Interlaminar Properties
- ✓ Improve interlaminar strength of SiC/SiC CMCs
- ✓ Fuzzy Fibers of carbon nanotubes on carbon fiber with a resultant 69% improvement in interlaminar shear strength
- ✓ BNNT on SiC is suitable for high temperature
- ✓ Planar layers of boron nitride are used in SOA materials for crack deflection
- ✓ BNNT can act as a crack deflection mechanism within the composite and create more tortuous crack deflection paths thereby increasing the amount of energy required to cause fracture

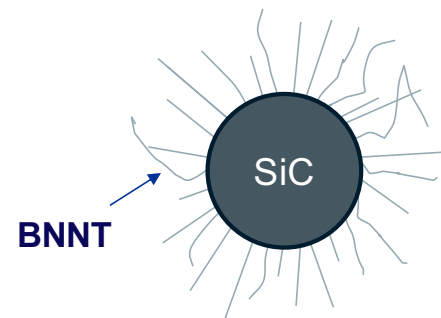
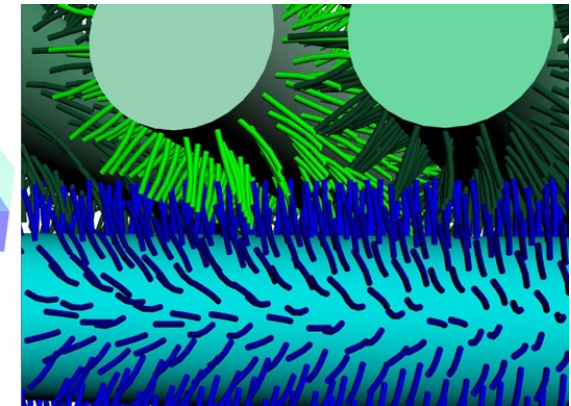
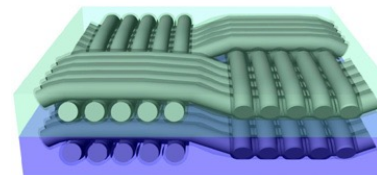
Combustor Liner



Hypersonic Airframe Components

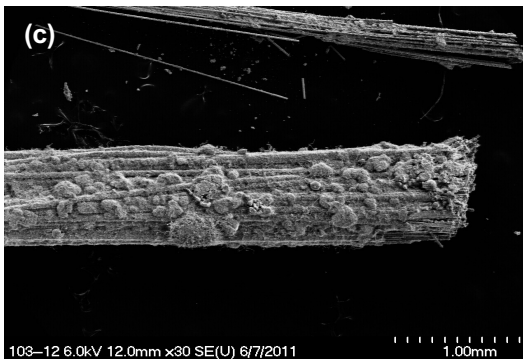
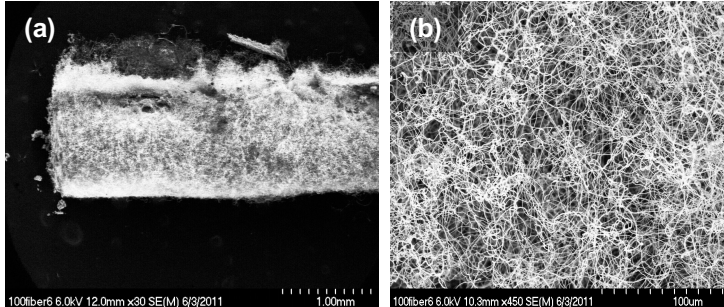


Interply Interface

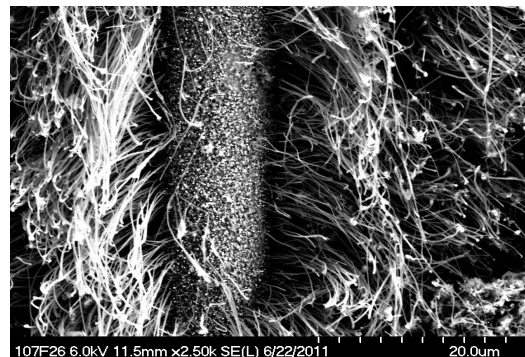




Fuzzy Fibers

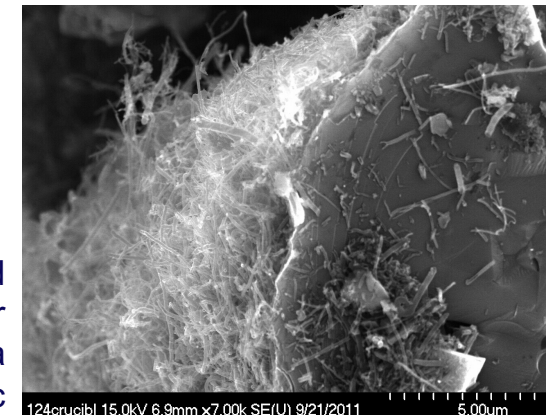


BNNT coating abundantly the SiC Tows of (a) Sylramic and (b) Hi-Nicalon. BNNT coating on (c) Hi-Nic-S Tow was less



Individual fibers are coated within tows

BNNT coated interior fiber surface within a fabric

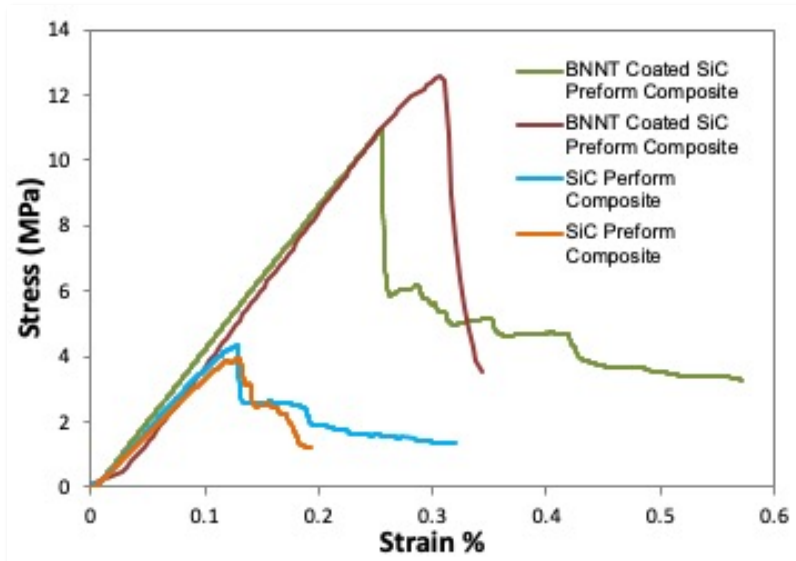


- ✓ SiC tows used as substrate for deposition: Sylramic, Hi-Nicalon, Hi-Nicalon-S
- ✓ In-house Modified-CVD method was used for the deposition of BNNT.
- ✓ BNNT fuzzy fibers were deposited in all three SiC tows types, being Sylramic the one that has the most abundant deposition
- ✓ Individual tow tensile strength of tows coated with BNNT decreased just slightly compared to bare tows

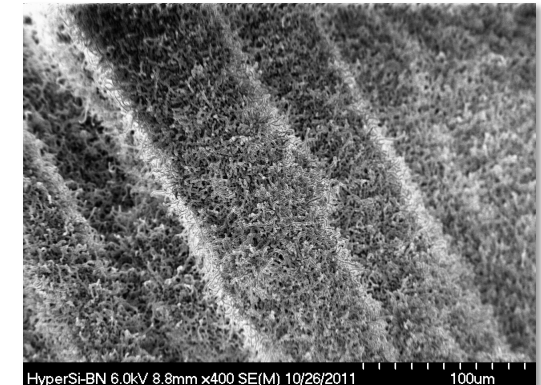


Mechanical Strength of Fuzzy Fibers

Comparison of Tensile Behavior of Hot Pressed SiC Preform Composites - with and without in-situ BNNTs



BNNT survived
hot pressing of
composite
coupon and
composite failure



BNNT/SiC composite sample
demonstrated graceful composite failure

- ✓ In-situ growth of BNNT throughout several SiC preform was accomplished with Hi-Nicalon preforms
- ✓ A 2-3x improvement in tensile strength was observed
- ✓ No damage was observed on the BNNT



The Boron Nitride Team

GRC's Boron Nitride Research Team:

- Dr. Diana Santiago de Jesús
- Ms. Janet Hurst (retired)
- Dr. Ching-cheh Hung (retired)
- Dr. Maricela Lizcano
- Dr. Marisabel Kelly
- Dr. Tiffany Williams
- Dr. Baochau Nguyen
- Dr. Eugene Shin
- Dr. Kathy Chuang
- Dr. Andy Woodworth
- Dr. Kristina Vailonis (new employee)
- Dr. Angel Morales (Summer Faculty 2020 & 2021)

Postdoctoral Position Open!

- Chemistry
- Material Science Engineer
- Chemical Engineer
- Polymer Chemistry
- Ceramic Engineer

Contact email: diana.santiago@nasa.gov



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