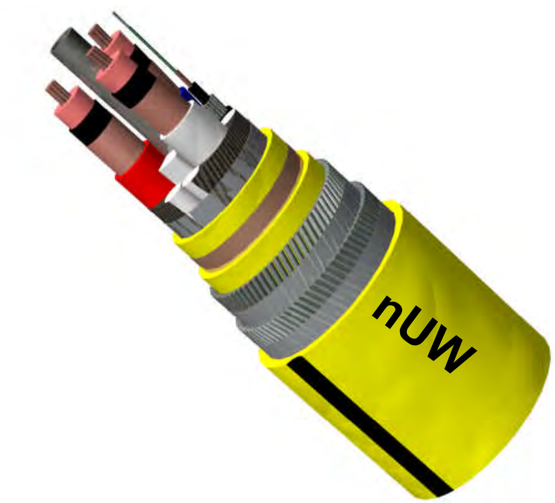

nanoUmbilical Workshop

Ultra-High Conductivity Umbilicals

Enrique V. Barrera

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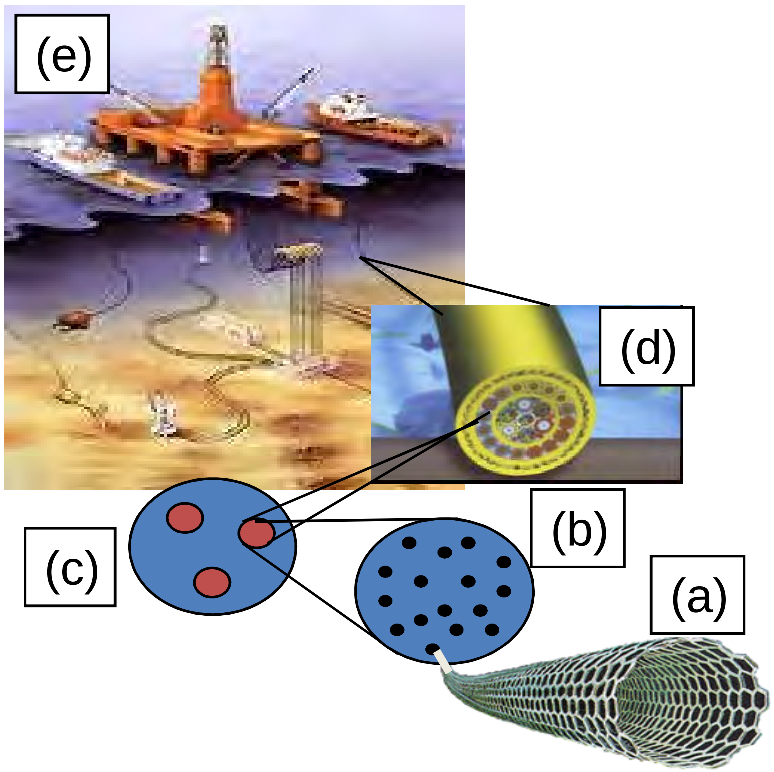
Outline

- Program Goals
- Background on Conduction via carbon nanotubes
- Program tasks and timeline
- Program team
- Outcomes

Program Goals: Reasons for Using SWNTs

Candidate Conductor	Material Availability	Degree of Electrical Conductivity	Processability	Costs	Time to Technology Maturation	Weight Saving Potential
SWNTs	Medium	High	High	High	3 years	High
MWCNT	Medium	Low	High	Medium	3 years	Medium
Nanowire	Low	Low	Med-High	High	5 Years	Low
Quantum Wire	Low	High	Low	High	10 years	High
Bucky Paper	Medium	Medium	Medium	High	3 years	Low

Program Goals: Polymer Nanotube Umbilical



Nanotechnology: From the bottom up!

The PNU is a polymer-nanotube wire that can carry high power to the sea floor.

(a) A SWNT as the conducting species for the conductor wiring.
(b) Cross-section of a Polymer Nanotube Umbilical (PNU) where nanotubes are dispersed in a polymer
(c) Cross-section for a three phase power cable,
(d) The umbilical cable that provides power lines to the seafloor, and
(e) The offshore platform and subsea system.

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Program Goals: Deliverables

(1) Bridge the gap between engineering science and manufacturing technology to produce a piece of wire.

The wire conductor will be a polymer-Nanotube composite that is half the diameter of a Cu conductor that can carry 500 amps at the same voltage used for the Cu conductor.

We will also produce the following:

(2) Report to RPSEA suitable for public release.

(3) A workshop to feature advances in power conductors for oil and gas use.

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Program Goals: Umbilical Parameters

Overall objective is to:

- Design, build and test an engineering prototype of a working ultra-high conductivity “wire”.

- The wire could in later stages be incorporated into an umbilical exceeding 161 km (100 mile in length.

- It would be expected to deliver up to 10 MW at up to 36 kV.

- The operating envelop would range from -1 to 121ºC (~30 – 250ºF) and pressure from 0 to 31.03 MPa (0 – 4500 psi).

Program Goals: Conductor Size

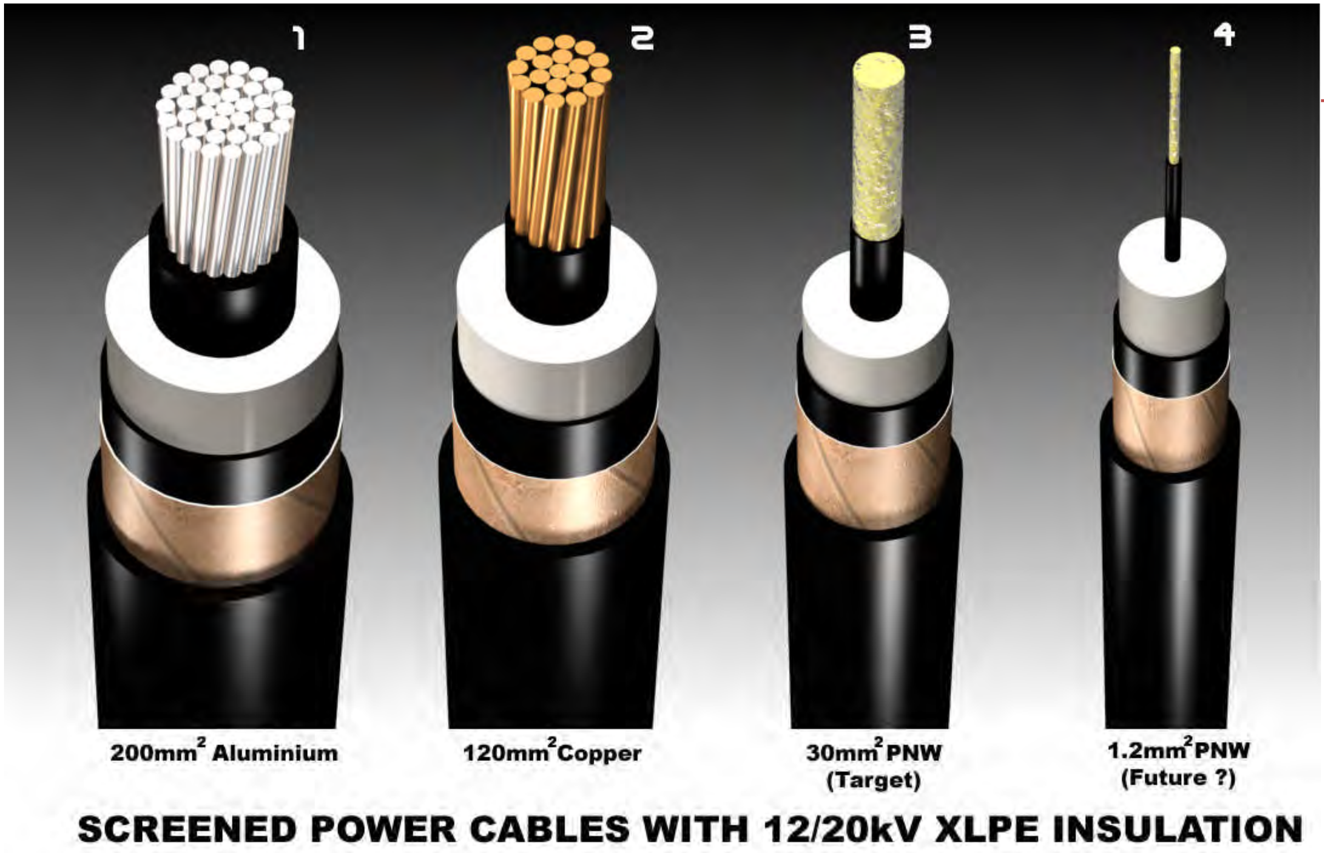


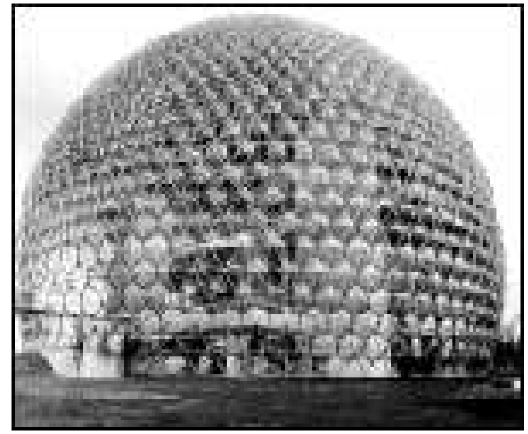
Table D.1.4.1	Cable 1	Cable 2	Cable 3	Cable 4
Cable (area) (mm^2)	200 (Al)	120 (Cu)	30 (PNU)	1.2 (PNU)
Mass in air (kg/m)	1.45	1.82	0.54	0.33
Diameter (m)	0.038	0.0327	0.0253	0.0195
Mass of displaced water (kg/m)	1.16	0.86	0.52	0.31
Weight in water (N/m)	2.820	9.406	0.242	0.234
Or (kg/m)	0.288	0.959	0.025	0.024

Picture compliments of Dave Madden

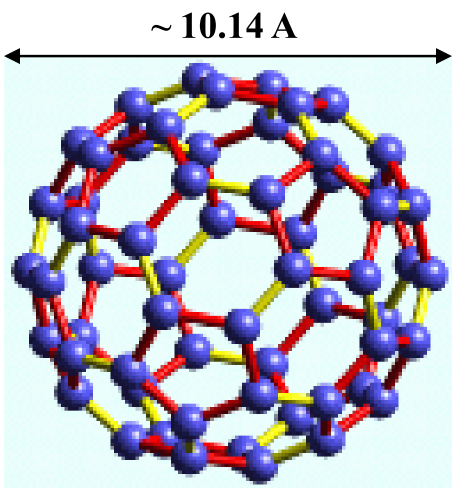
The Third Form of Carbon: Fullerenes

A soccer ball

Geodesic ball



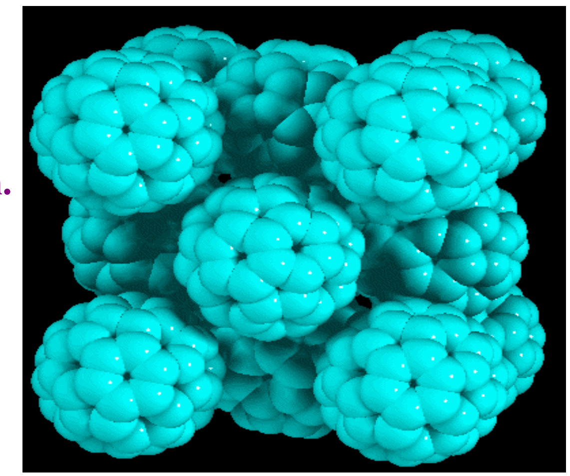
Geodesic Dome



C-C bond in C_{60}

When I am working on a problem,
I never think about beauty.
I think only of how to solve the problem.
But when I have finished,
if the solution is not beautiful,
I know it is wrong.

--------R. Buckminster Fuller



FCC solid C_{60}

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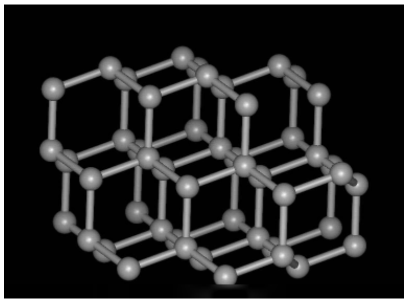
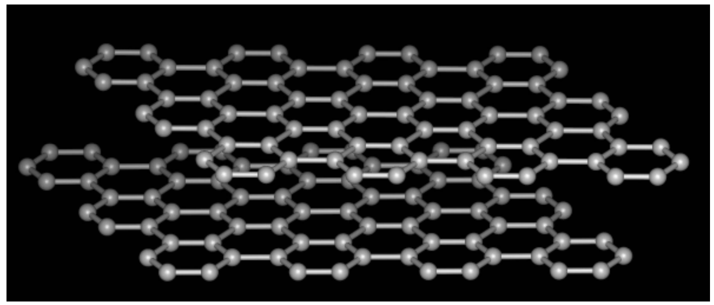
Fullerenes and Nanotubes

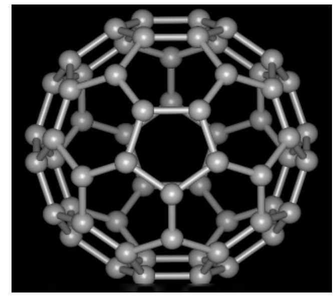
C60 was discovered in 1985.
Nanotubes were discovered in 1991.
Led to Nobel Prize in Chemistry in 1996.



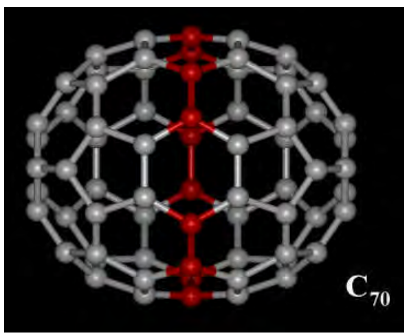
Diamond



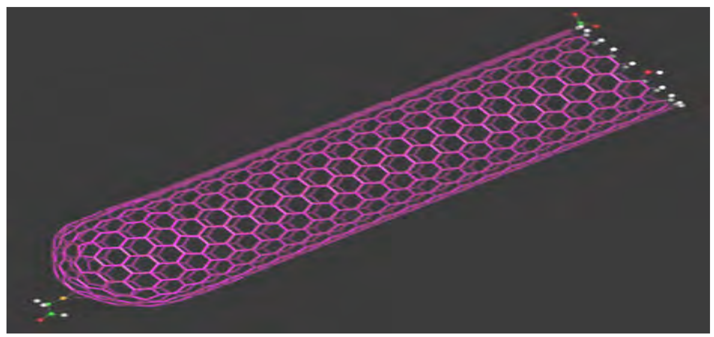
Graphite



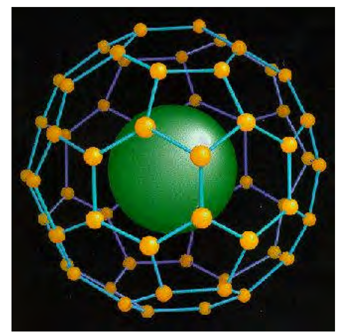
C_{60}



C_{70}

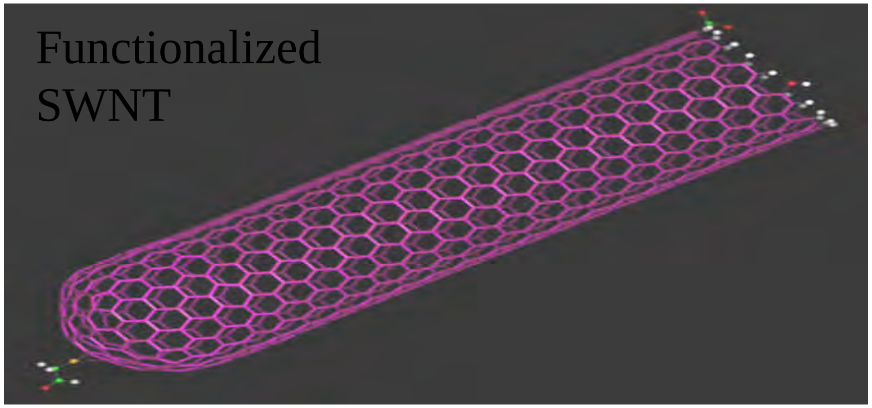


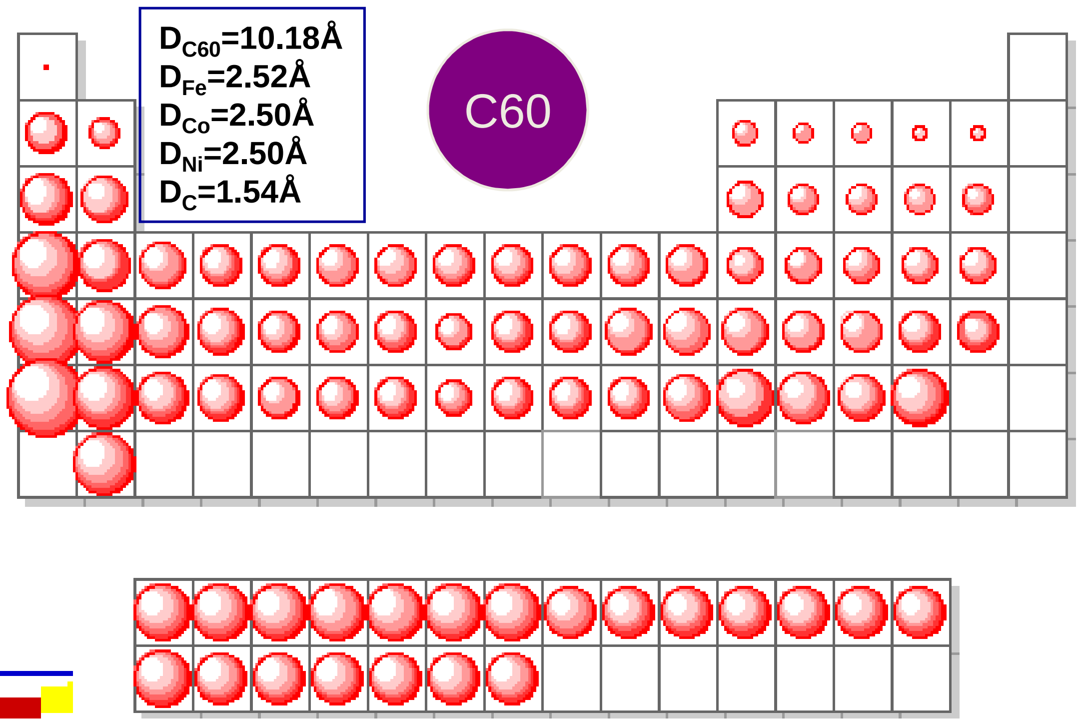
Nanotube

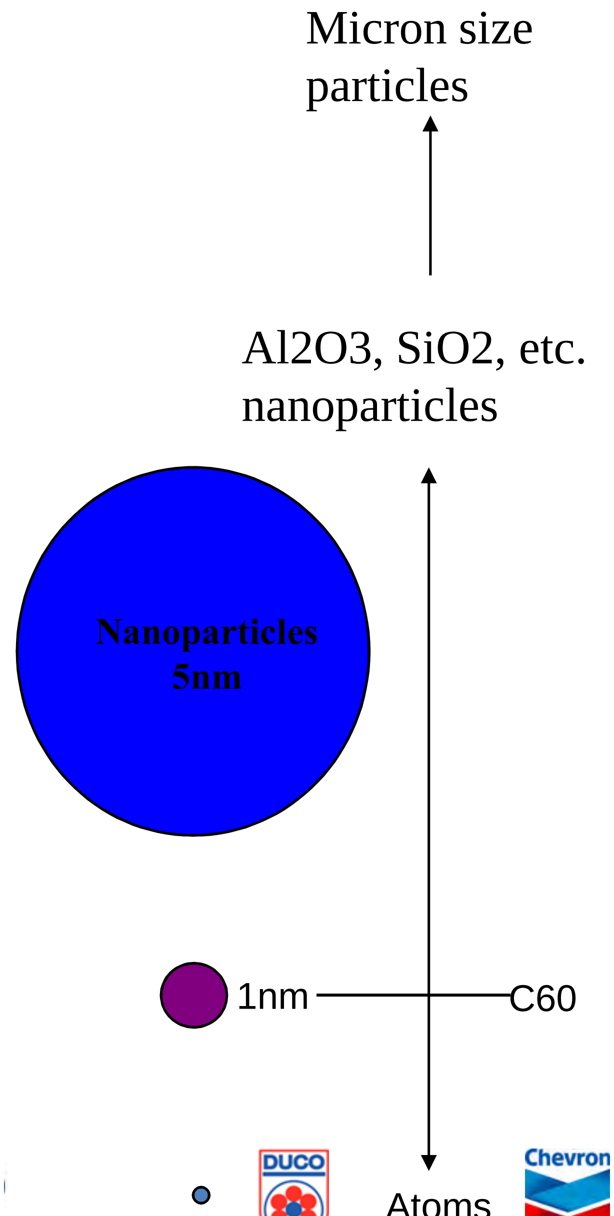


Endohedral C_{60}

Size Comparison of Single C_{60} , Nanotube to Basic Elemental Atoms and Nanoparticles







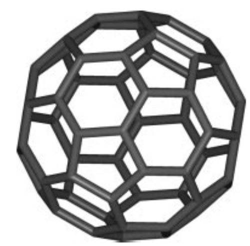
Nanotubes: Data Sheet Engineer's Perspective: Broad Property Range

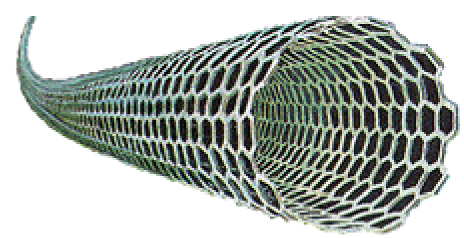
Fullerenes (C_{60})

- **Low thermal conductivity** (0.4 W/m•K)
- **Point scatterer** (~ 1 nm spherical particle)
- **Grain boundary and interfacial effects**

Single Walled Carbon Nanotubes

- Dimensions: 1nm (dia.), 0.3 – 100 μm (length)
- Density: 0.89g/cm^3
- Tensile strength ~50GPa
- Tensile Modulus ~1TPa
- Elongation to failure ~5%
- Electrical Conductivity ~1800-2000 ohms^{-1}
  Semiconducting to conducting like copper
- Thermal conductivity (C_{60}) low in
  transverse direction and high (diamond)
  along tube axis (~2500 W/m•K)
- Nanoscale scattering defects
  - Tubes intact or removed in situ (nanovoids)
- Bonding by van der Waals or by functionalization





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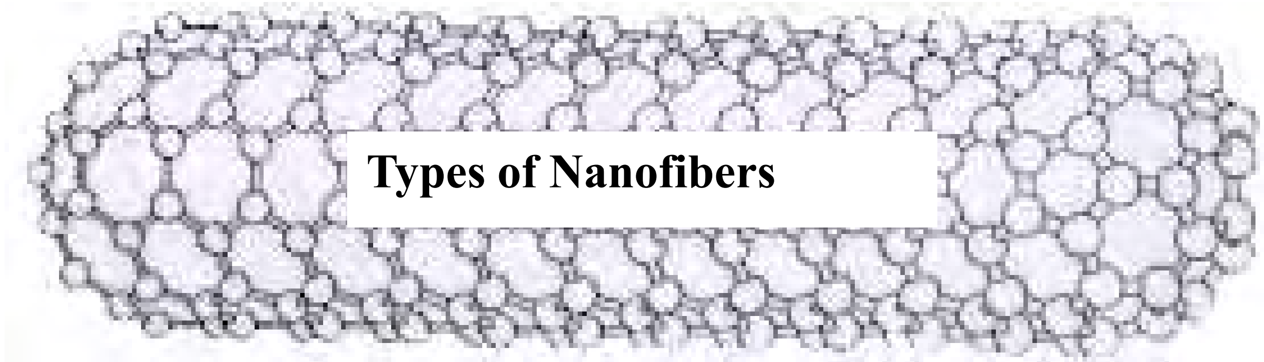
Types of Nanofibers



End capped single wall nanotube

Which nanofibers/nanotubes are of significance to future nanocomposite materials?

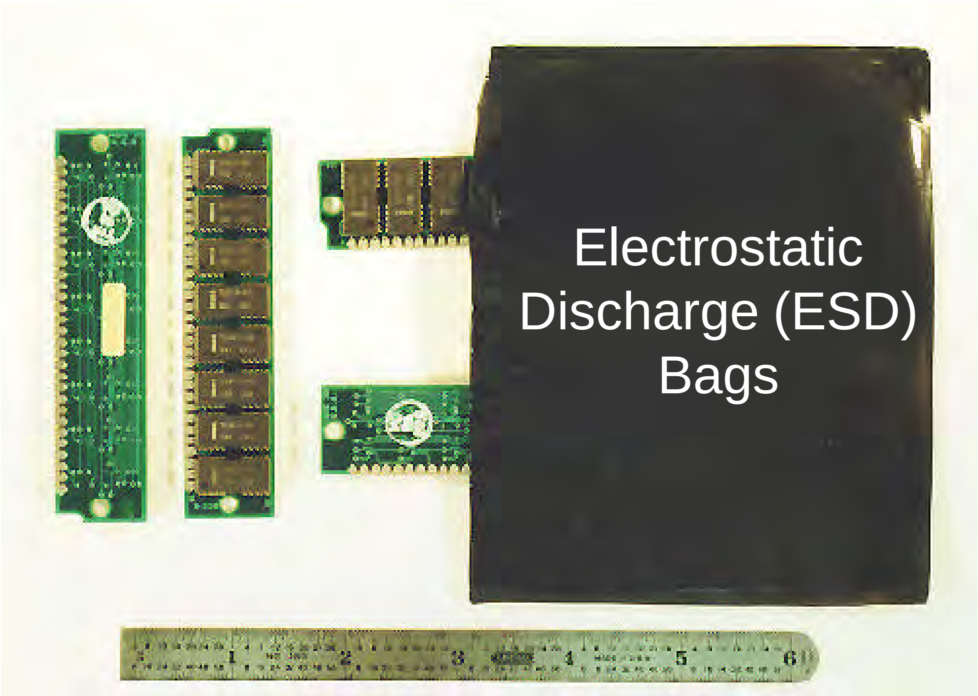
Carbon Fibers:	Type III	Type II	Type I
Nanofibers:	VGCFs	MWNTs	SWNTs
	Useful $0.10/g	Moderate ~$50/g	High Strength & Modulus $500/g (as low as $1/gram)

VGCFs have defects and have large diameters (100 nm)
MWNTs are defected and not as optimal in some cases.
SWNTs are the Holy Grail! No defects, high strength and stiffness.
All have useful anisotropic thermal and electrical properties.

Background on Conduction: Polymer Nanotube Conductors: Pathway to a High Conductor

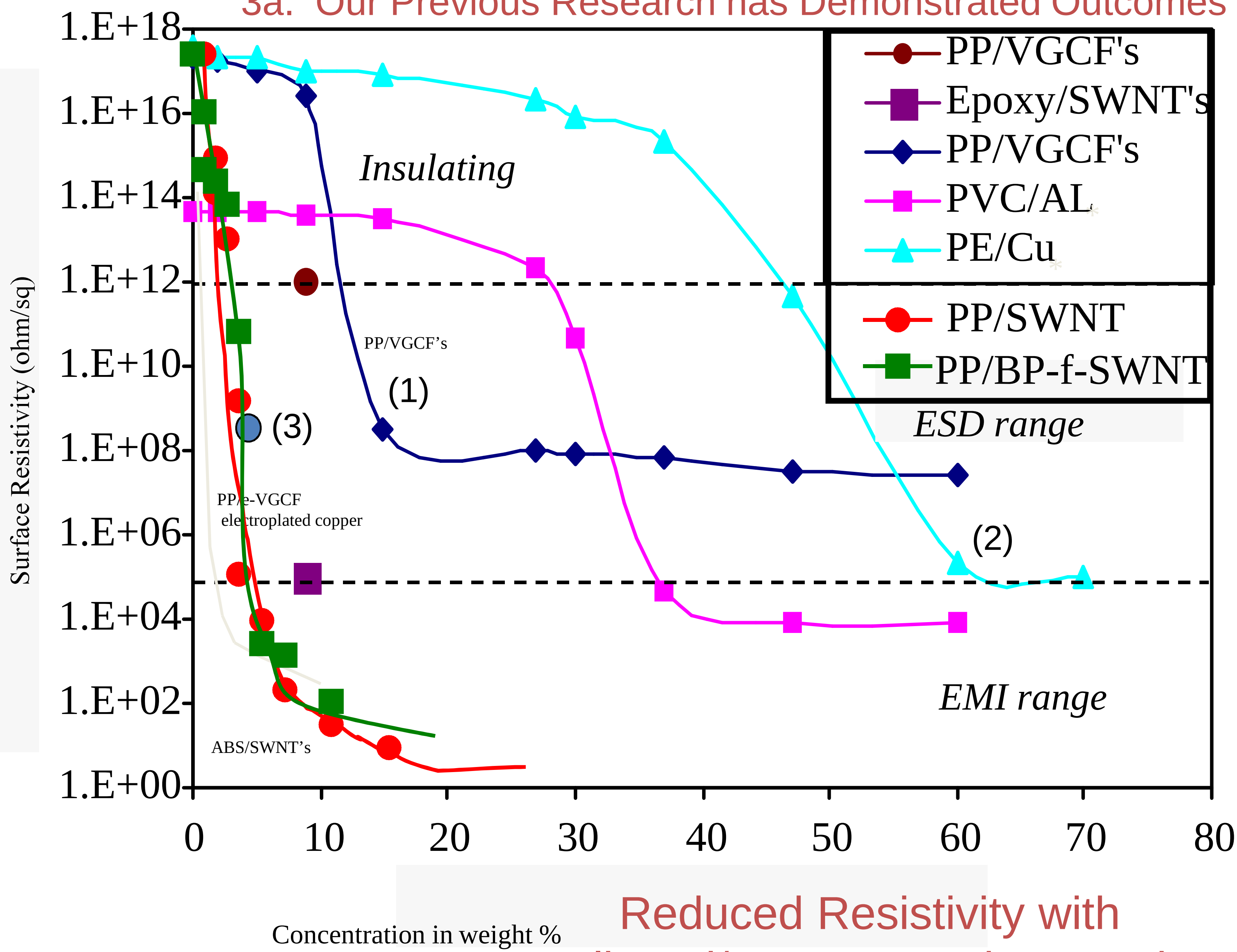
1996-1999: 13 to 14 orders of decrease in electrical resistivity.
1997-1999: Produced Electrostatic Discharge (ESD) materials.
2000: Produce multifunctional Nanotube Continuous Fibers (NCFs).
2002: Produced Electromagnetic Interference (EMI) Materials.
2005: Produced conducting wire.
2007: Produced Lightning strike protection.
2009: First Polymer Nanotube Umbilical (1 ft *Demonstration Sample*).

2009: 19 orders of magnitude decrease in electrical resistivity.



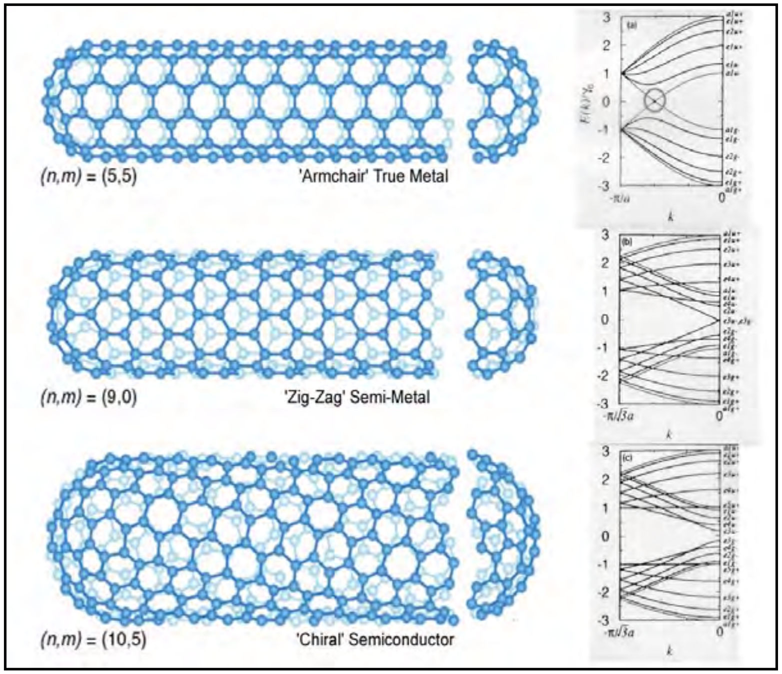
Demonstration Sample in 1999 showing an ESD bag that will hold computer parts. Bag showed rapid discharge in a range of relative humidities.

3a. Our Previous Research has Demonstrated Outcomes

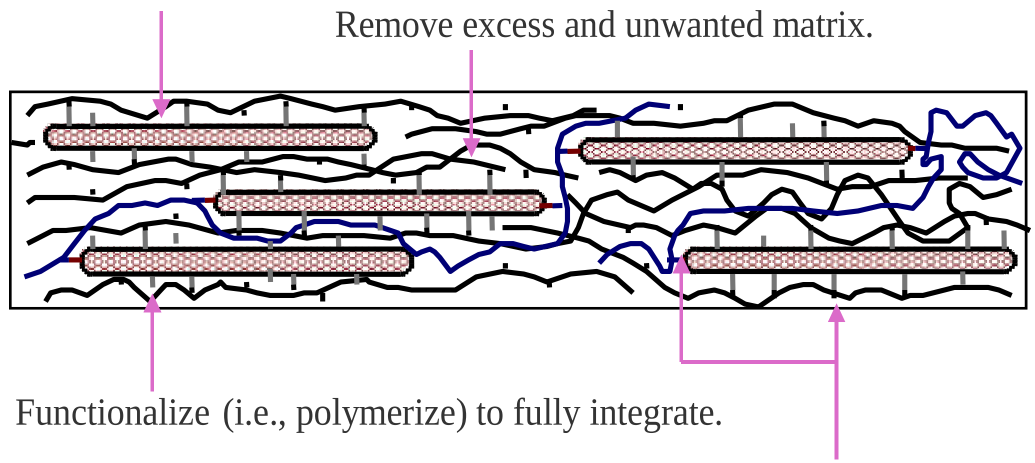


Reduced Resistivity with Unaligned/Unseparated Nanotubes

Background: Nanotechnology Basis for the PNU



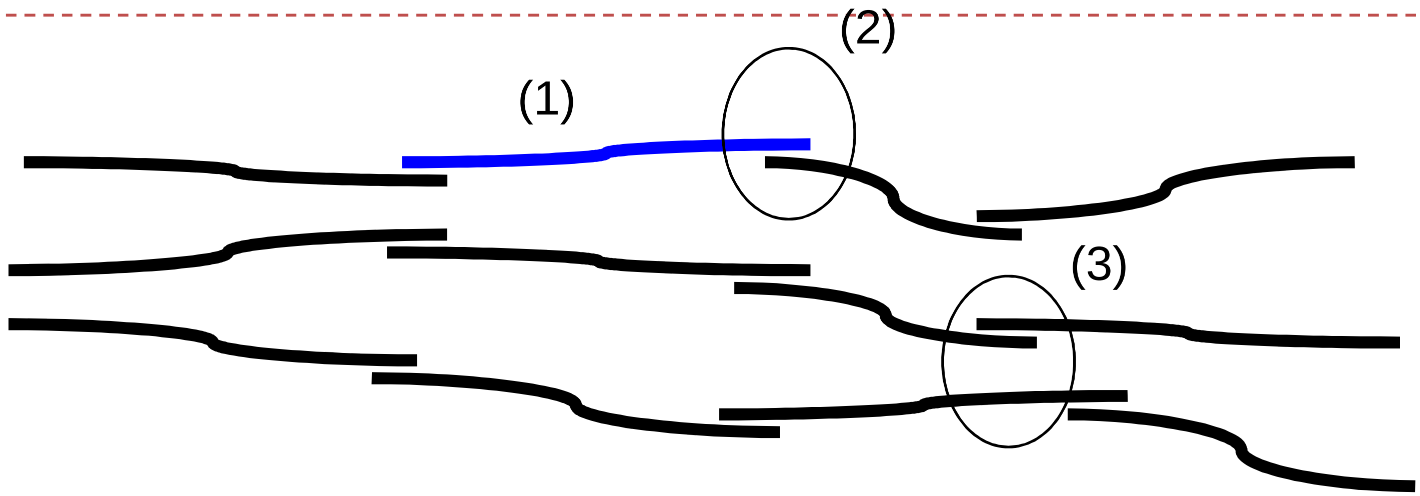
Fully Integrated Nanotube Composites to Achieve Cold Forming



Of the dozens of known nanotube types, one third are metallic; the rest are direct band-gap semiconductors. The metals, especially the ‘armchair’ tubes, have been shown to conduct electricity at least as well as copper, and perhaps some ten times better.

A PNU consist of aligned SWNTs in a polymer matrix such that misalignment assures electrical contact while providing for robust mechanical strength. Use of metallic SWNTs ensures high electrical conduction. Optimizing the concentration of the SWNTs ensures costs control and near term use.

Background: Directed Nanotube Network (DNN)



A schematic depicting a network of (1) m-SWCNTs that are arranged to promote maximum electrical conduction. The network is made up of (2) connected nanotubes that provide for *ballistic transport* along the nanotube length and *resonant quantum tunneling* from one nanotube to the other. Gap distances between the various chains prevent electron hopping from one pathway to the next. m-SWCNTs may vary in length but the (3) connections will be optimized for low contact resistance.

Nanotubes are nanometers (1.4nm) in diameter and microns in length.
Electrical conduction is as high or better than copper.
Mechanical properties include: UTS: ~50-150GPa/Elastic Modulus: 1 TPa

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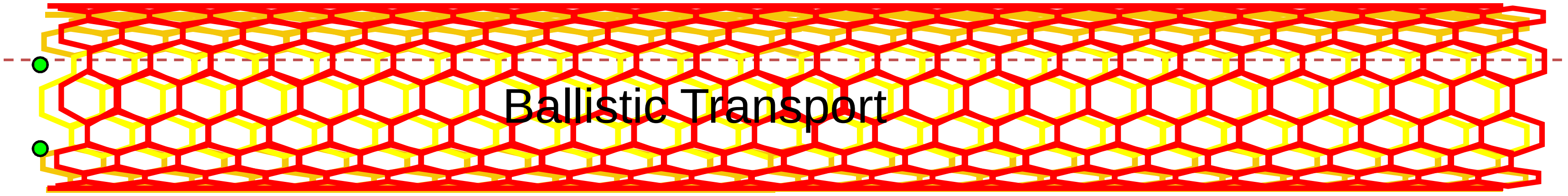
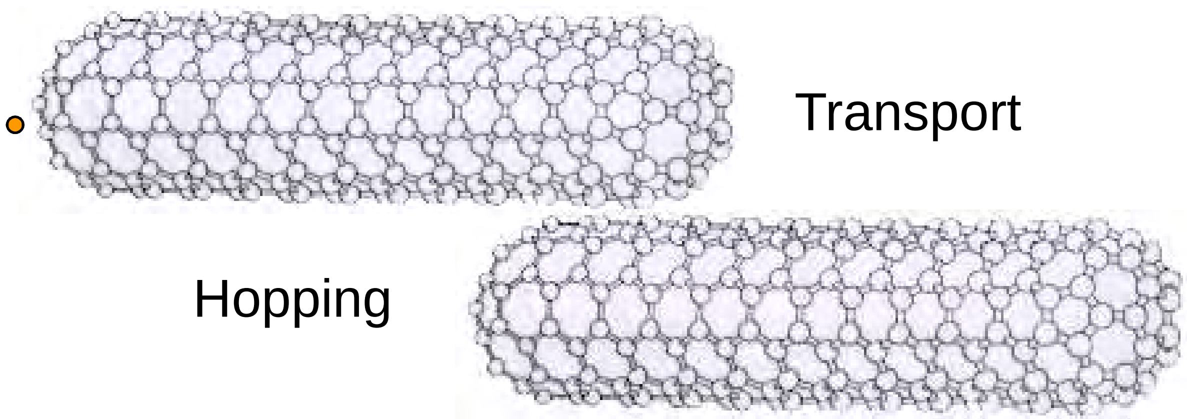
Background: Electron Transport Mechanisms



Ballistic conduction allows electrons to flow through the material without collisions. The collisions cause the electrons to slow down, and cause the material to heat, effectively creating resistance in the material.



Hopping conduction allows electrons to jump from one nanotube to another. Short contact lengths limit electrons from jumping back and forth.

To maximize conduction, Metallic Nanotubes are needed.

Alper Buldum and Jian Ping Lu, Phys. Rev. B 63, 161403 R (2001).

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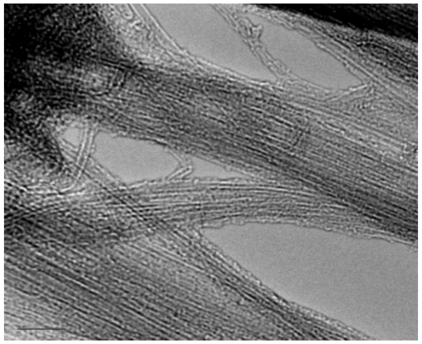
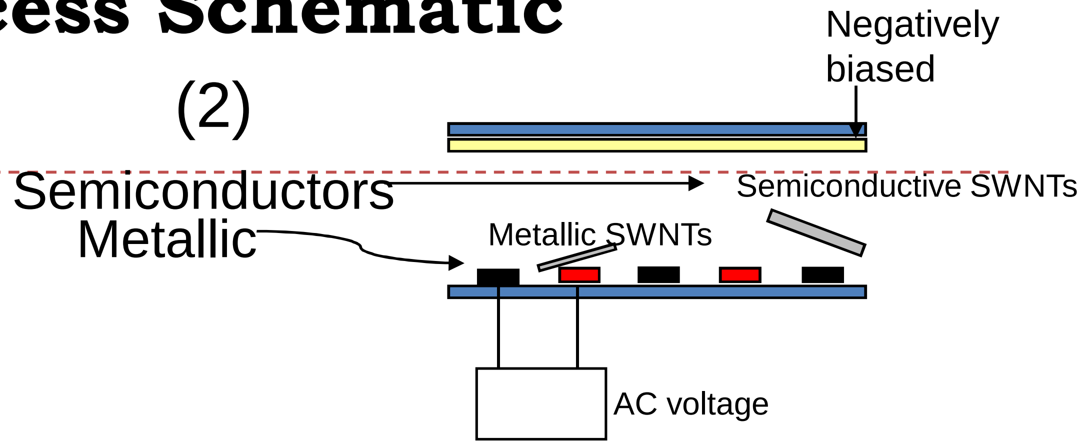
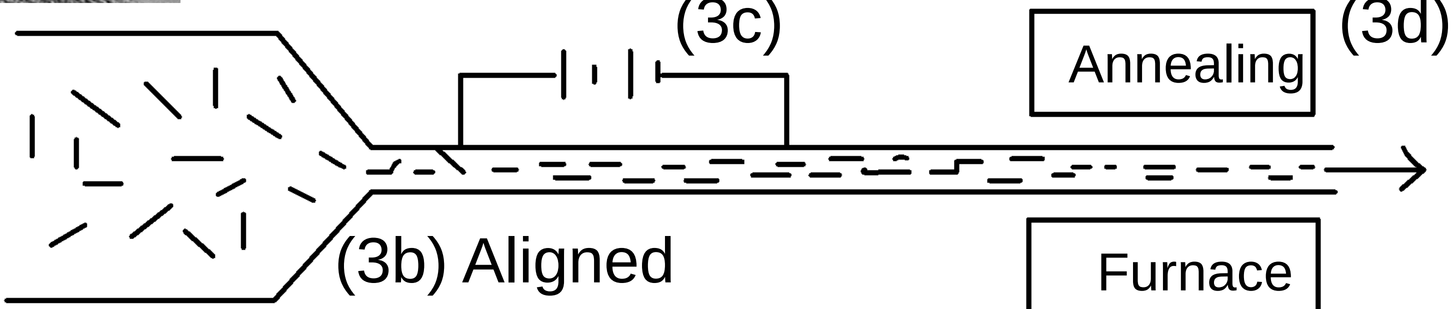
Background: Process Schematic

(1)

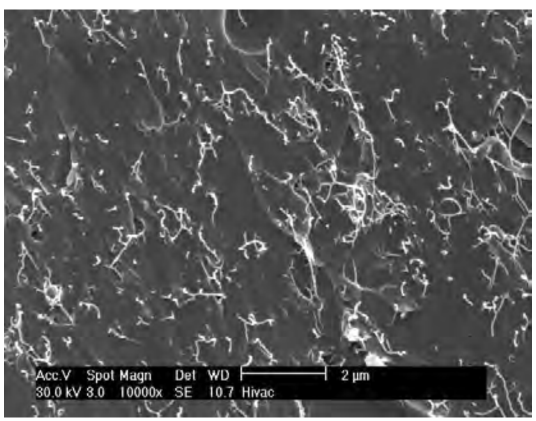


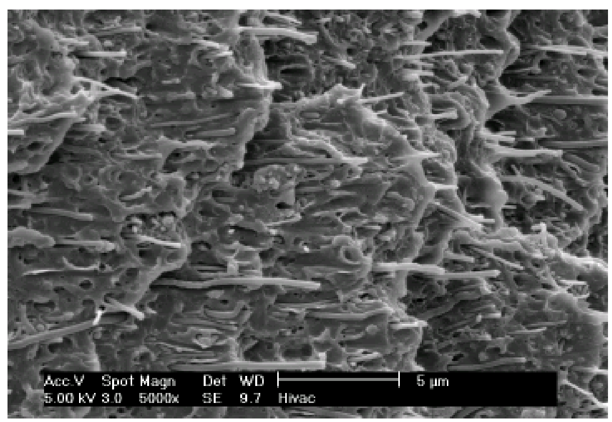
(2)

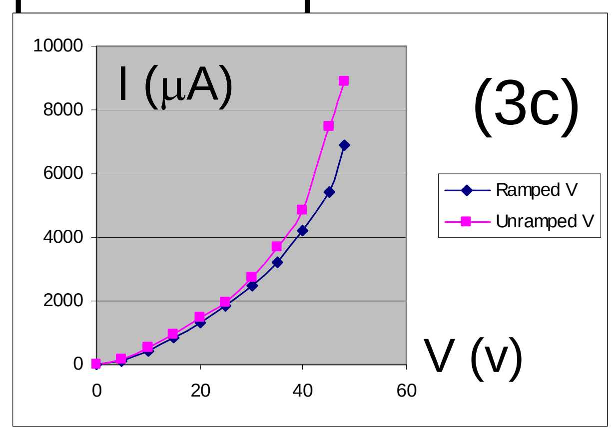




(3a)







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Tasks and Goals for the PNU Program

Technical Tasks (Monthly)	J	F	M	A	M	J	J	A	S	O	N	D
a. Obtain SWNTs & m-SWCNTs	a	a	a	d	d							
b. Process wires w/polymer 1 & 2	b	b	b	c								
c. Test properties of 1 & 2 wire		c	c	c								
d. Characterize m-SWNTs		d	d	d	d							
e. Conduct NT-NT study		e	e	e	e	e	f	f	f			
f. Improve NT-NT conduction		f	f	f	f	f	f	f	f			
g. Disperse SWNTs in 1 & 2	g	g	g	g								
h. Disperse m-SWNTs in 1 & 2			h	h	h	h	h	h	h	h		
i. Implement Electric Fields				i	i	i	i	i	i	i	i	
j. Characterize NT filled wires				j	j	j	j	j	j	j	j	j
k. Conduct physical tests				k	k	k	k	k	k	k	k	k
l. Connection study	l	l	l	l	l	l	l	l	l	l	l	l
m. Reporting			m			m			m			m
Milestones	**J**	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**
1. Obtain m-SWCNTs			X									
2. Produce first 1 ft wire						X						
3. Evaluate for umbilical									X			
4. Evaluation & optimization									X			
5. Optimize and prototype test												X
6. Final Report												X
7. nano-Umbilicals Workshop												X

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Status of Tasks and Goals as of December 10, 2009

Technical Tasks (Monthly)	Completion Date	Status
a. Obtain SWNTs & m-SWCNTs	May	Completed
b. Process wires w/polymer 1 & 2	April	Completed
c. Test properties of 1 & 2 wire	April	Completed
d. Characterize m-SWNTs	May	Completed
e. Conduct NT-NT study	September	In progress
f. Improve NT-NT conduction	September	Completed
g. Disperse SWNTs in 1 & 2	April	Completed
h. Disperse m-SWNTs in 1 & 2	October	Completed
i. Implement Electric Fields	November	Completed
j. Characterize NT filled wires	December	Completed
k. Conduct physical tests	December	In progress
l. Connection study	December	Completed
m. Reporting	Monthly	Completed
Milestones		
1. Obtain m-SWCNTs	March	Completed
2. Produce first 1 ft wire	June	Completed
3. Evaluate for umbilical	September	Completed
4. Evaluation & optimization	September	Completed
5. Optimize and prototype test	December	In progress
6. Final Report	December	Pending
7. nano-Umbilicals Workshop	December	In Progress

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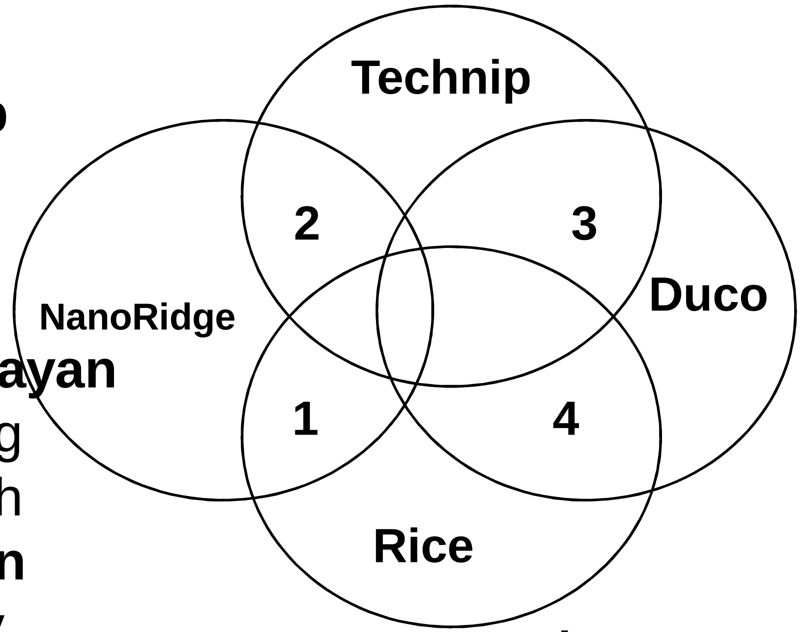
Program Team

NanoRidge Materials, Inc.
Program Lead Organization
Dean Hulsey, Lori Jacob
A nanotechnology company specializing in research to engineering applications"

Rice University
Enrique Barrera, Pulickel Ajayan
Highly recognized institution for conducting carbon nanotube nanotechnology research

Technip, USA **Jim Dailey, Kerri Dawson**
An engineering and construction company in the oil and gas services sector

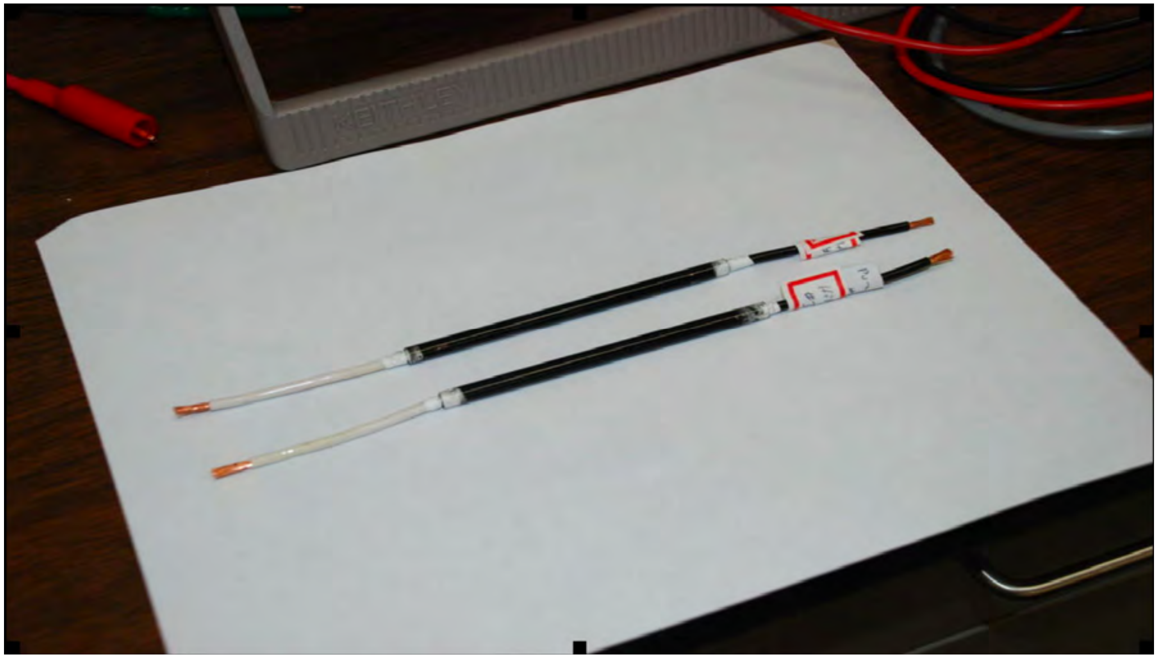
DUCO, Inc. **Dave Madden**
An umbilical designer, manufacturer and supplier for the oil and gas industry



1 – PNU Processing
2 – Process Specification
3 – Umbilical Specification
4 – Connector Study

Outcomes: Polymer Nanotube Umbilical

A PNU Test sample configuration where a number of the processing conditions are used.



<u>Processing Tasks</u>

h: Dispersion
i: Electric Fields
b: Annealing

A Dymex polymer (thermoset) is shown here.

A method to produce the test sample to a one foot length has been identified and is currently being considered (Proprietary).

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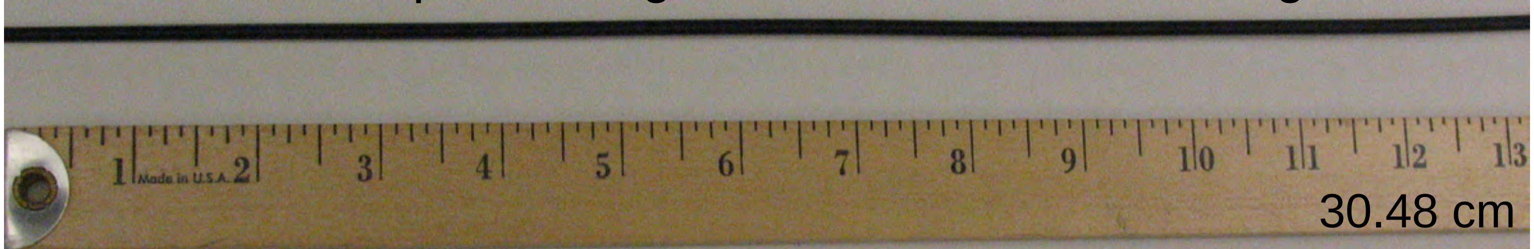
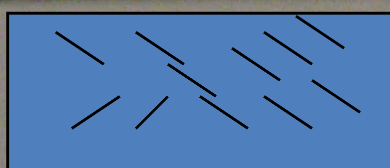
Outcomes: Produce 1st One Foot Wire

PE w/10 wt% SWNTs/Processed by melt spinning.
Various diameters have been produced with smaller diameters being more optimal at this time.

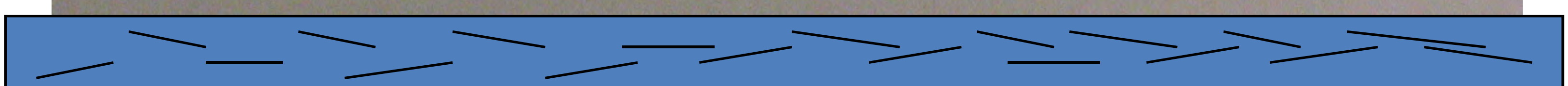
A PNU wire is shown below which exceeds one foot in length.
A number of the processing tasks were used: a, b, f, g, h, i, and l.





Explanation for thinner wire, better conductivity

Keep the same volume, 1/2 diameter, ¼ cross section area, 4 x length



Better alignment in uniaxial direction

Samples for Resistivity Testing

Sample	Resistivity (ohm.cm)	Diameter (cm)	X-section area (cm^2)
Polyethylene (HDPE)	10^{17}	0.394 (~0.4)	0.12
10 wt% CG / MDPE	~ $1*10^3$ – $1.5*10^3$	0.394	0.12
10 wt% CG / MDPE (application of electric field) at room temperature.	~ $5*10^{-1}$ – 10	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field) at room temperature.	~ $2*10^{-1}$ – 5	0.394	0.12
10 wt% CG / MDPE (application of electric field) at high temperatures)	~ $4*10^{-2}$ – $6*10^{-2}$	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field) at high temperature.	~ $2*10^{-2}$ – $6*10^{-2}$	0.394	0.12

Sample	Resistivity	Diameter	X-section area
10 wt% p-Hipco, w/ single core lead	~ $7*10^{-2}$ - $9*10^{-2}$	0.394	0.12
10 wt% p-Hipco w/ smaller diameter	~ $4.5*10^{-1}$ - $8*10^{-1}$	0.2	0.03

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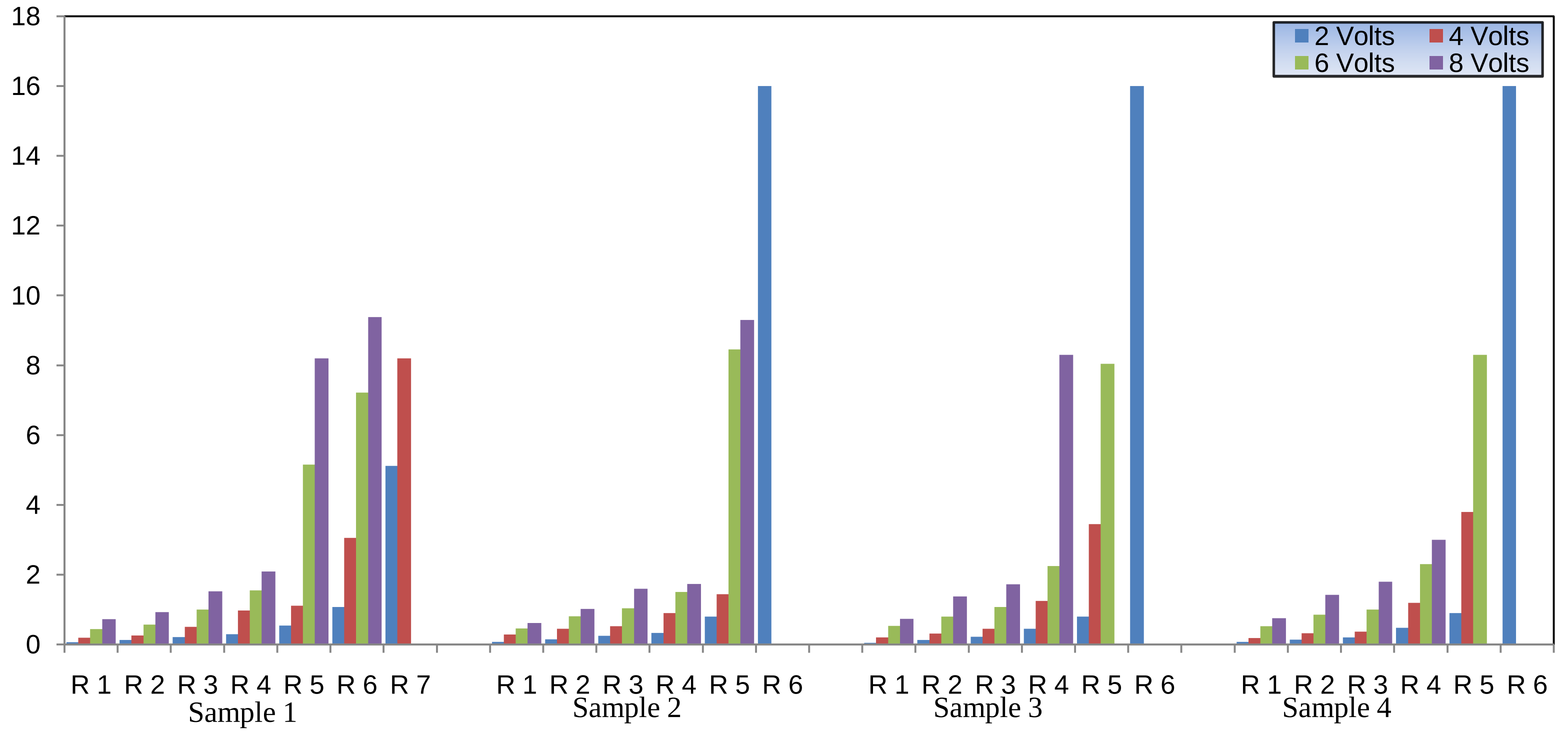
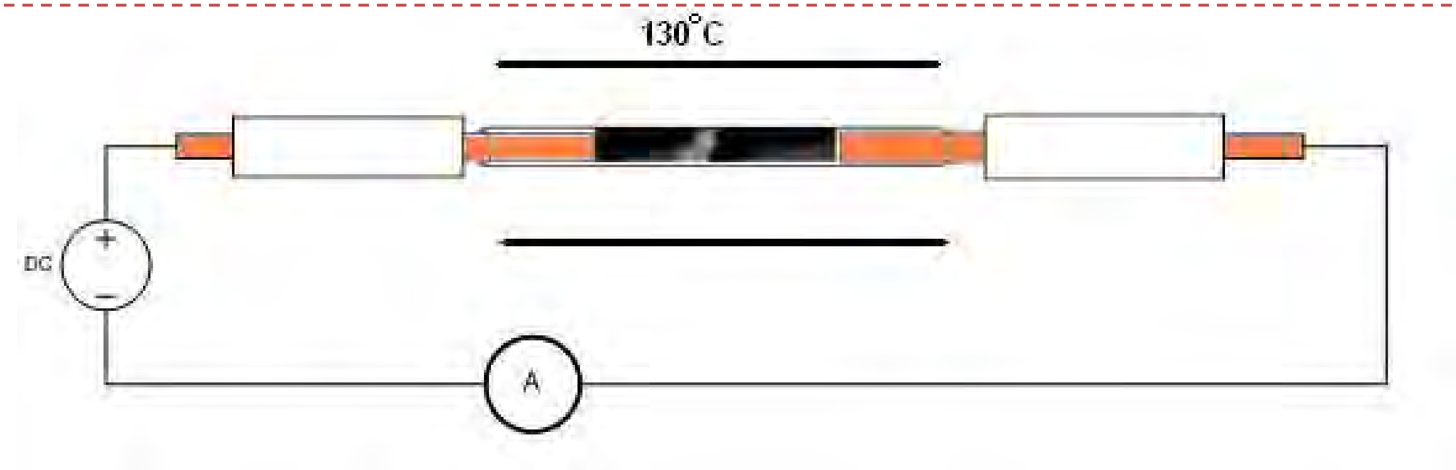
Current Study: Evaluation & Optimization

Target: 500 amps at the same voltage for the copper conductor.
Proposed: (a) Stranded wire (19 strands) or (b) Solid Core wire.
For stranded wire: On average ~26 amps to be carried by each strand.
Current Design and Evaluation: Single strand of SWNTs/PE.



Recent conditions may be limited by available power supply.

Current method for implementing the electric field

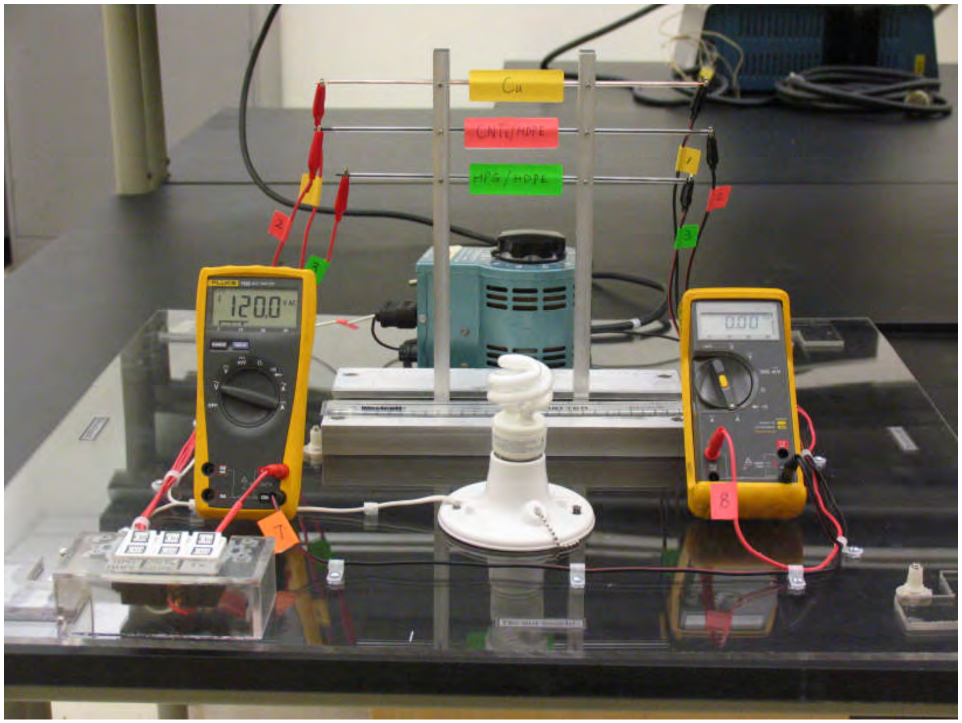


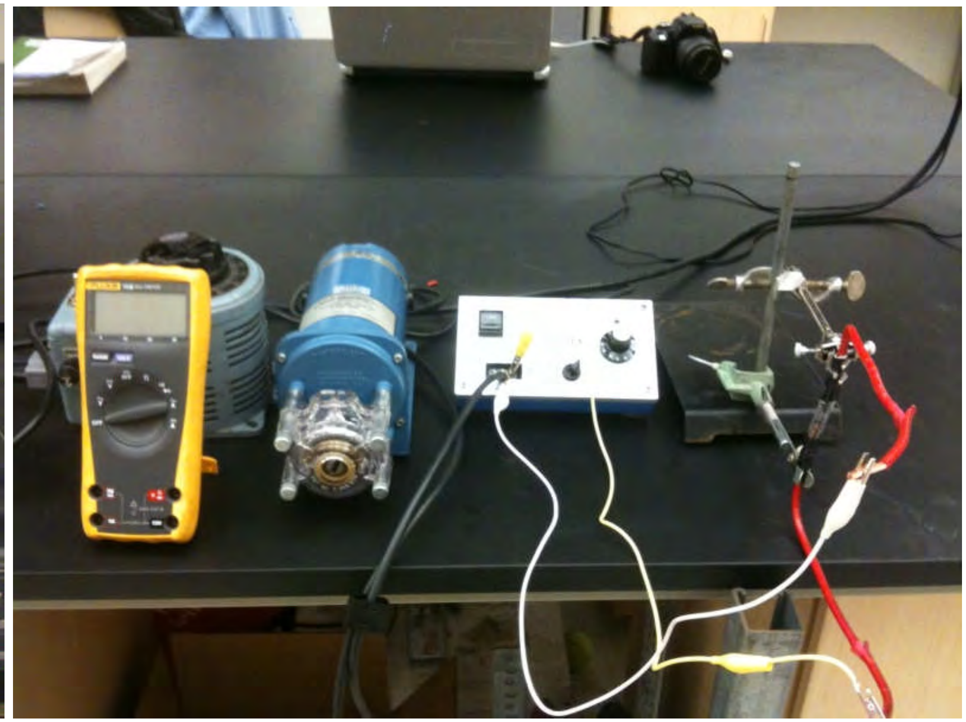
- 4 samples (MDPE + 10 wt% SWNTs) were tested.
- Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.
- Conditioning rounds were reduced with improvements made to the test sample.

- The best samples carried a current of close to 16 amps for 2 V.
- The distance between the leads for the best sample is close to 0.7-7.62 cm.
- Specific resistivity was 2.1 * 10^{-2} ohms / sq cm

Outcomes: Demonstrations

Two demonstration set-ups to show samples produced and conditions tested.





Set-up #1: Demonstration with a light Bulb. Comparisons.

Set-up #2: Demonstration with a Pump. Higher voltage condition.

Outcomes: What was Learned

<u>Partial listing related to conduction (with a low concentration focus):</u>

- Approach: Advance materials properties by adding nanotubes then **lower** concentrations to get even more advancements.
- Dispersing nanotubes in the polymer leads to conduction at **low** concentrations while segragated nanotubes in polymer do not enhance mechanical strength.
- Nanotubes dispersed in a polymer fiber enable handling aligned nanotubes for a range of applications at 0 to 100% concentrations.
- Synergism between various nanoconstituents leads to enhancements at **lower** concentrations than used by the individual additives.
- Nanotubes can act as templates for other nanoconstituents to promote multifunctionality at **low** concentrations.
- A Directed Nanotube Network (DNN) can produce high conduction while **low** concentrations of nanotubes can be used.

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Outcomes: Talking Points

- Produced PNUs with nanotube concentrations up to 90 wt%.
- Polyethylene, Dyamx, and polystyrene were used as the polymers.
- The lowest resistivity value reached was $2*10^{-2}$ Ωcm.
- The highest voltage carried by the PNU was 40V (the limit has not been evaluated).
- The highest current carried by the PNU was 16 A (not fully optimized).
- Several new steps for lowering the resistivity have been identified.)

Outcomes: Supplemental Enhancements

- Enhanced purification
- Microwave heating (proprietary)
- Centrifugation
- Functionalization
- Annealing
- Higher concentrations
- Doping
- Enhanced NT-NT connections
- Retained polymer
- Stretching