



nanoUmbilical Workshop

Outcomes **Enrique V. Barrera**

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Outline

- ▶ Goals
- ▶ Approach
- ▶ Completed Tasks
- ▶ Processing Approach
- ▶ Samples Produced
- ▶ Concerns and Issues
- ▶ Proven Approach
- ▶ Outcomes
- ▶ Demonstrations
- ▶ Closing Comments

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



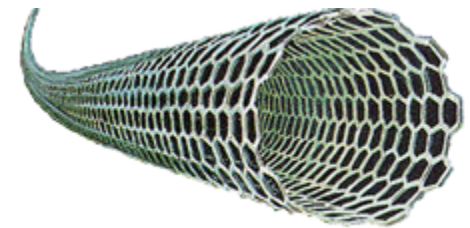
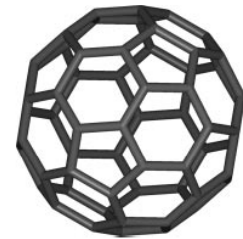
Fullerenes (C₆₀)

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

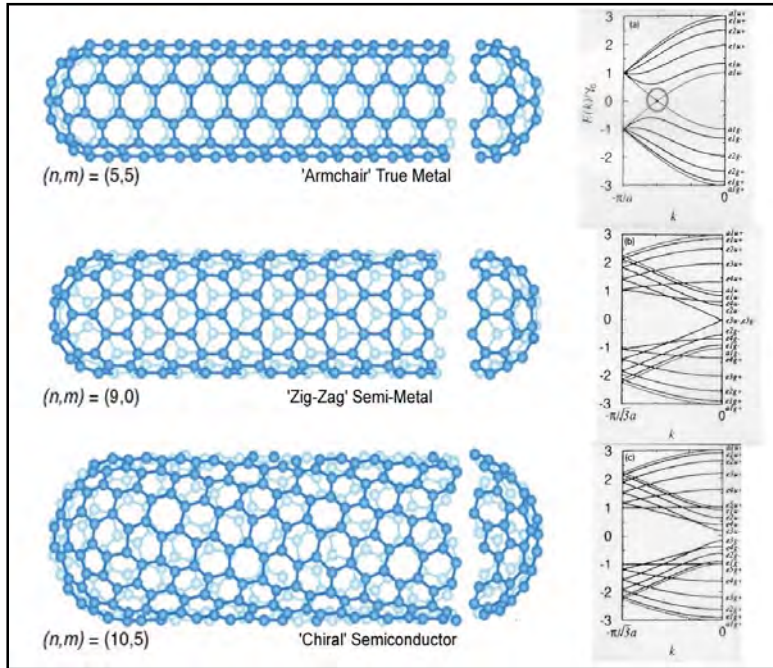
Single Walled Carbon Nanotubes

- Dimensions: 1nm (dia.), 0.3 – 100 μm (length)
- Density: 0.89g/cm³
- Tensile strength ~50GPa
- Tensile Modulus ~1TPa
- Elongation to failure ~5%
- Electrical Conductivity ~1800-2000 ohms⁻¹
Semiconducting to conducting like copper
- Thermal conductivity (C₆₀) 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

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



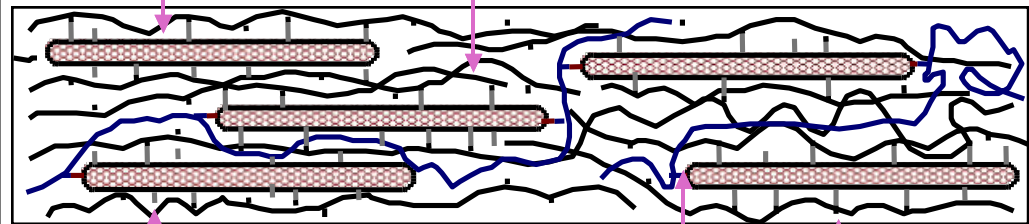
Background: Nanotechnology Basis for the PNU



Fully Integrated Nanotube Composites to Achieve Cold Forming

Align single nanotubes by shear/elongational processing.

Remove excess and unwanted matrix.



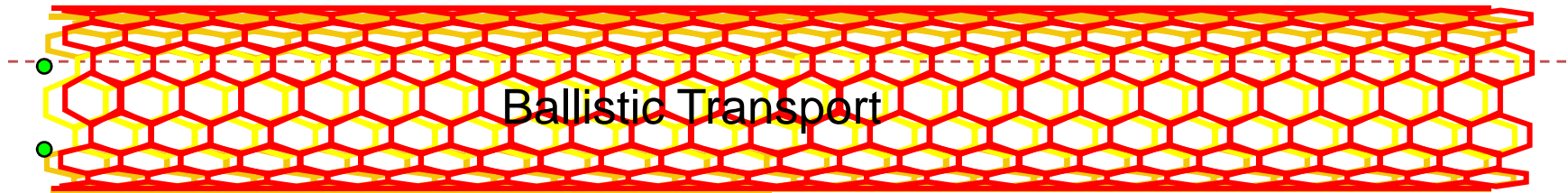
Functionalize (i.e., polymerize) to fully integrate.

Identify appropriate functionalization:
Side wall vs. end attachment.

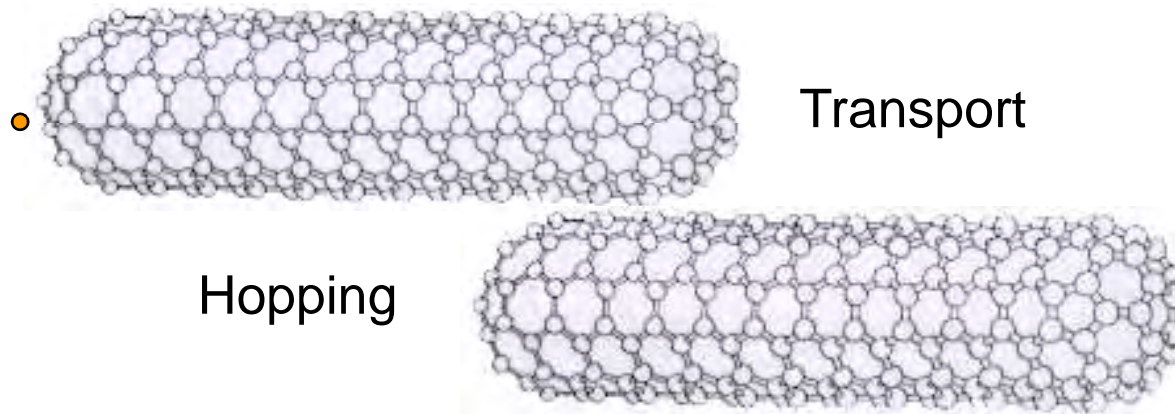
Of the dozens of known nanotube types, one third are metallic; the rest are direct band-gap semiconductors. The metals, especially the ‘armchair’ tubes, have been shown to conduct electricity at least as well as copper, and perhaps some ten times better.

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: 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.

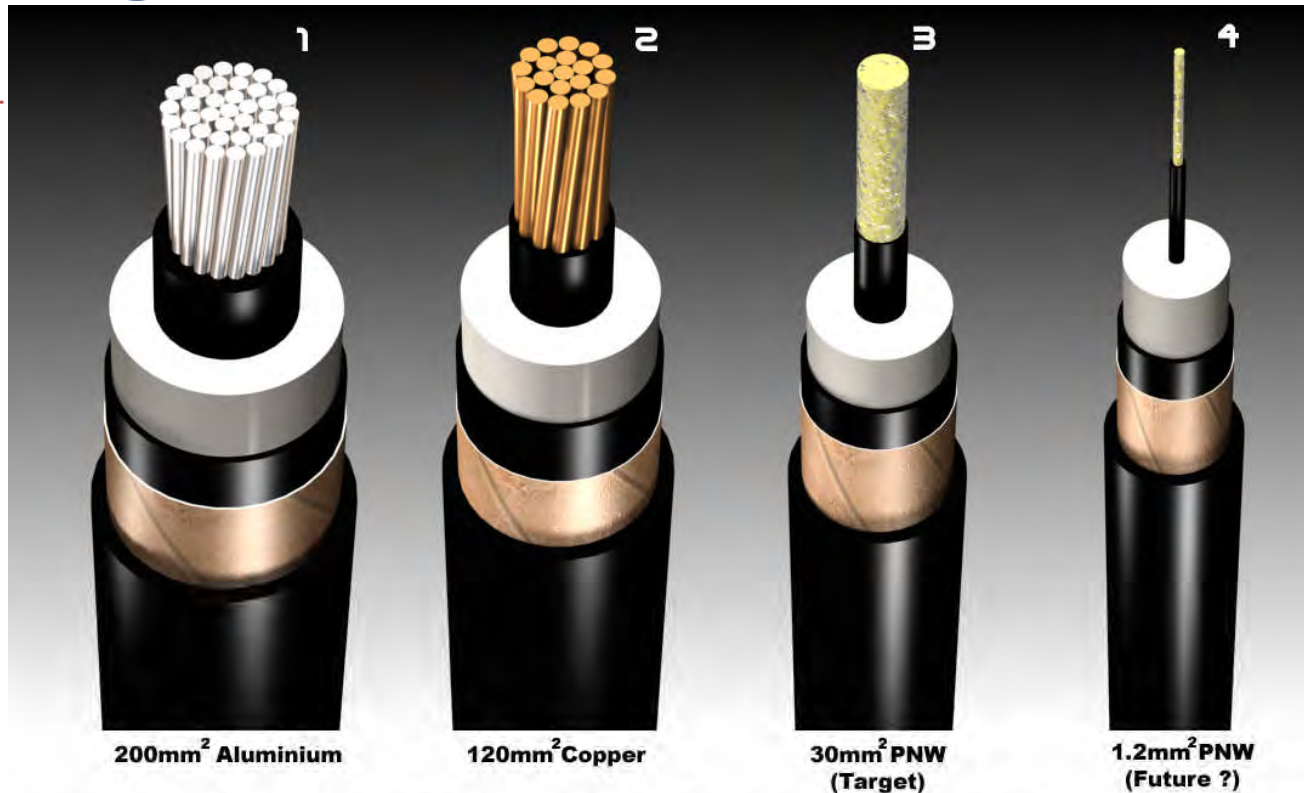


Hopping conduction allows [electrons](#) to jump from one nanotube to another. Short contact lengths limit electrons from jumping back and forth.

To maximize conduction, Metallic Nanotubes are needed.

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

Program Goals: Conductor Size



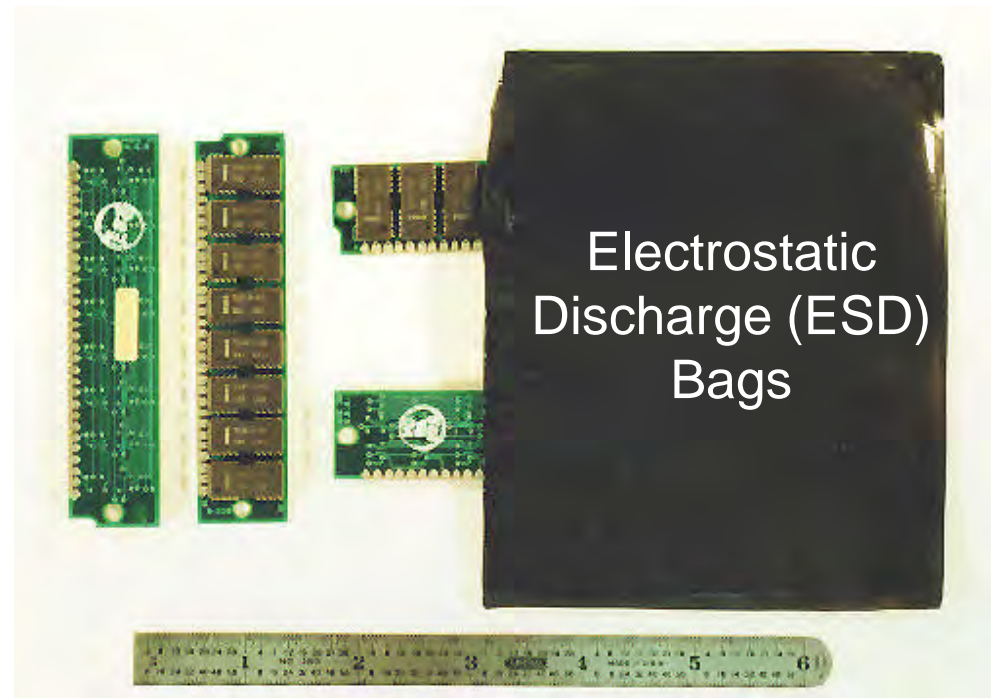
SCREENED POWER CABLES WITH 12/20kV XLPE INSULATION

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

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.



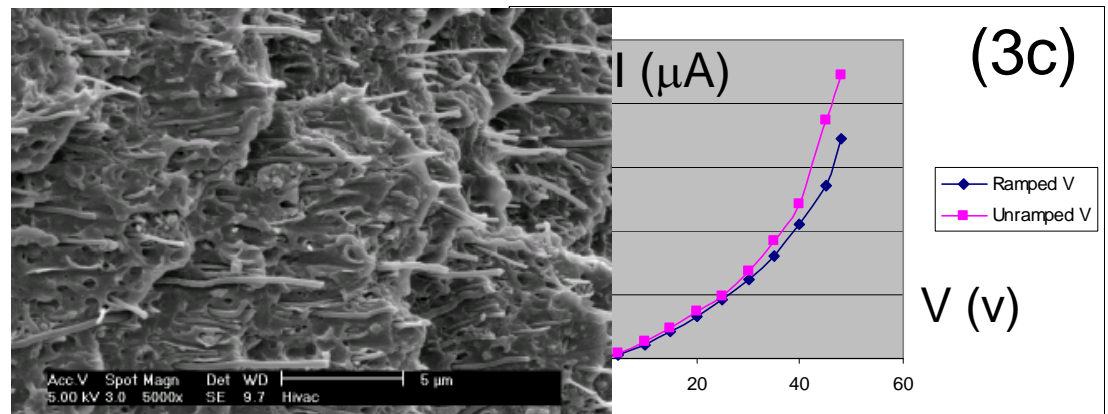
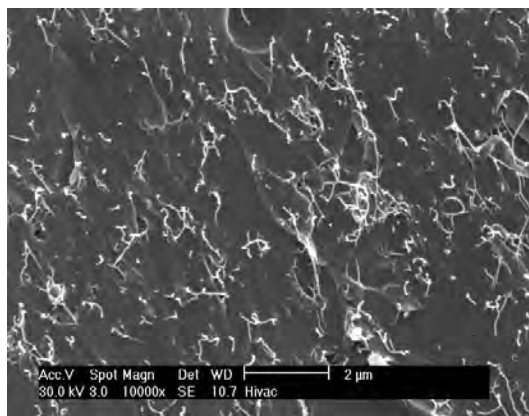
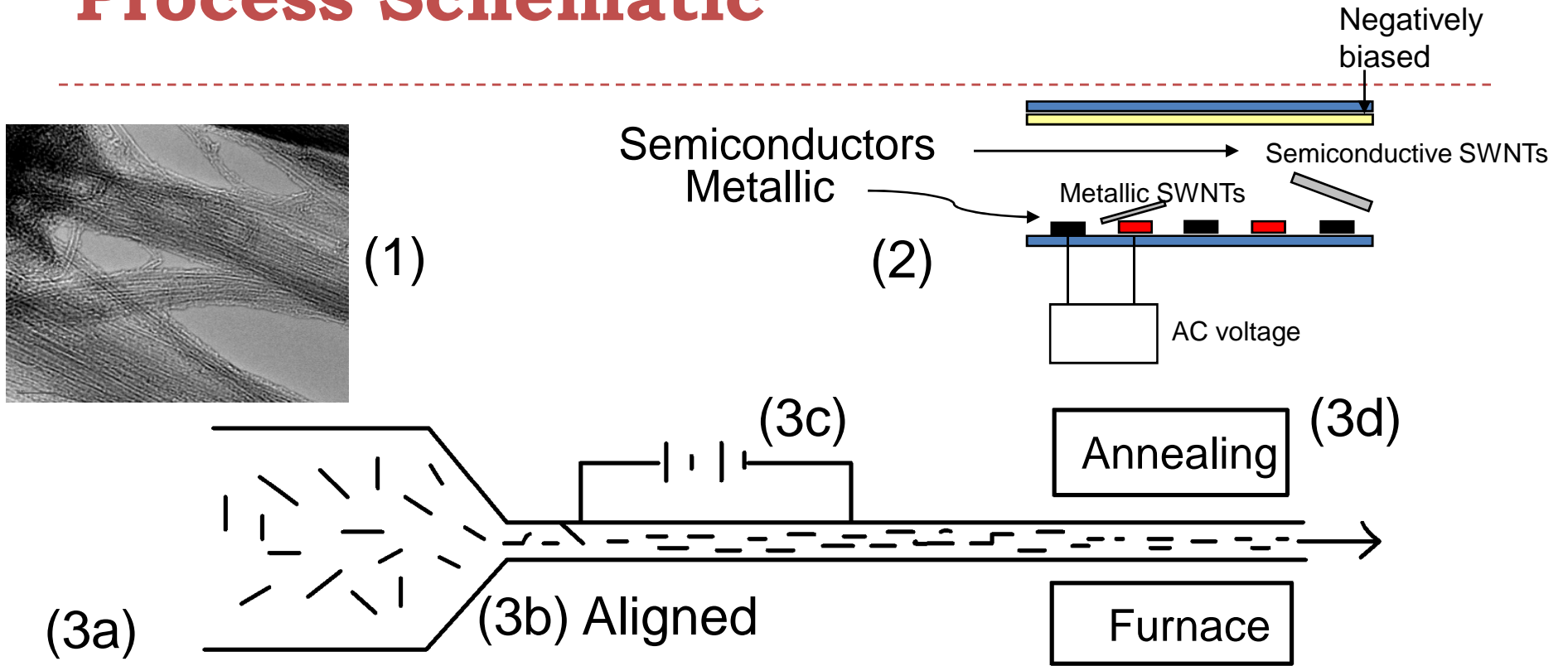
Demonstration Sample in 1999 showing an ESD bag that will hold computer parts. Bag showed rapid discharge in a range of relative humidities.



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

Process Schematic



Our approach to build the proposed product

- (1) Preparation (Purification) of starting nanotube material. ✓ -
Further improved purification of m-SWNTs (two approaches)
- (2) Separation of the metallic SWNTs. ✓ -
Selected SWNTs with enhanced metallics (40% m-SWNTs)
- (3) Processing into a polymer wire or tape. ✓ -
 - (3a) Mixing in a polymer. ✓ -
Increase nanotube content to 90 wt%. Used incipient wetting and the “Winey Method”. Need to implement decanting.
 - (3b) Use of extrusion and/or elongational flow. X +
Still need to further improve alignment.
 - (3c) Use of electric fields. ✓ -
Need to find gap size and to shorten time.
 - (3d) Polymer Annealing. ✓ -
Demonstrated improvement but need optimization process.
 - (3e) Optional: Deposition of metal contacts. ✓ -
Demonstrated improvement but need to move to larger scale.

Advances have been made, next steps will bring more resistivity reduction.



Example Samples Processed to Date

Composites	Wt% of NTs	Processing method
MWNTs/HDPE	5%	Dry mixing + Injection
MWNTs/HDPE	10%	Dry mixing + Injection
MWNTs/HDPE	15%	Dry mixing + Injection
MWNTs/HDPE	20%	Dry mixing + Injection
MWNTs/HDPE	5%	Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Dry mixing + Miniextrusion
MWNTs/HDPE	10%	Dry mixing + Miniextrusion
MWNTs/HDPE	15%	Dry mixing + Miniextrusion
MWNTs/HDPE	20%	Dry mixing + Miniextrusion
MWNTs/HDPE	30%	Dry mixing + Miniextrusion
MWNTs/HDPE	40%	Dry mixing + Miniextrusion
MWNTs/HDPE	50%	Dry mixing + Miniextrusion
MWNTs/HDPE	60%	Dry mixing + Miniextrusion
CG NTs/HDPE	10%	Winney sample + Injection
CG NTs/HDPE	10%	Winnery sample + Miniextrusion
MWNTs/MDPE	5%	Dry mixing + Haake extrusion
MWNTs/MDPE	10%	Dry mixing + Haake extrusion

Three melt processing approaches are being used:

Injection molding
(up to 6 grams)

Mini-extrusion
(10 grams)

Haake extrusion
(100 grams).

Wt%s from 5 to 60 are being processed. Typical concentrations are 10 wt%.



Outcomes: Polymer Nanotube Umbilical

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

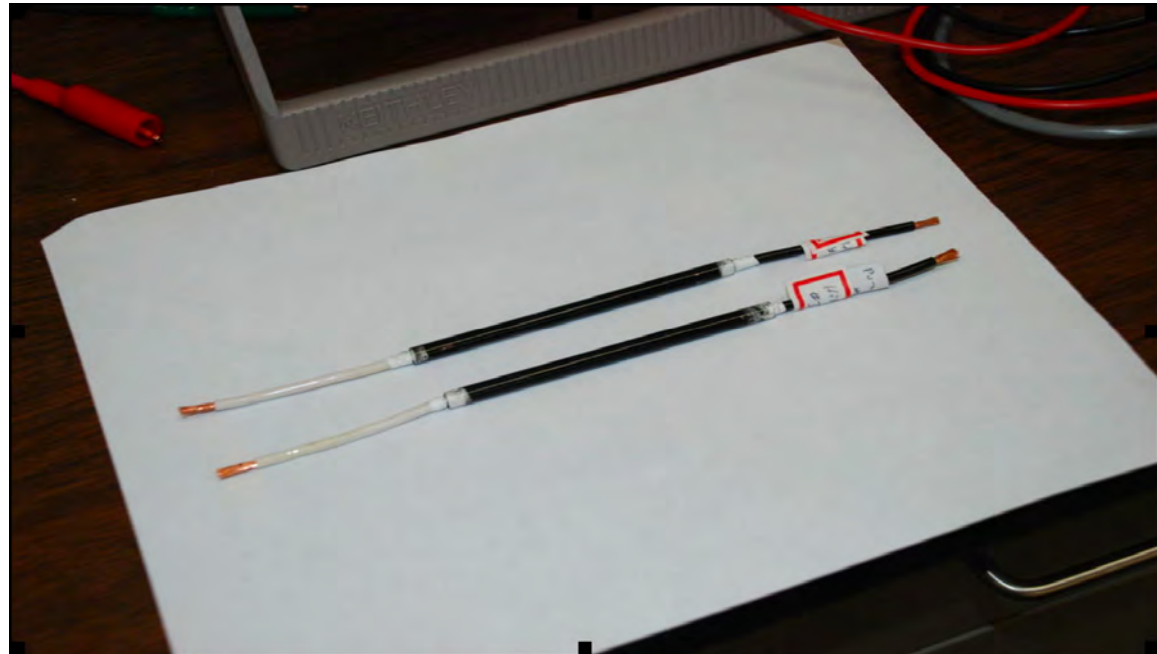
Processing Tasks

h: Dispersion

i: Electric Fields

b: Annealing

A Dymex polymer (thermoset) is shown here.

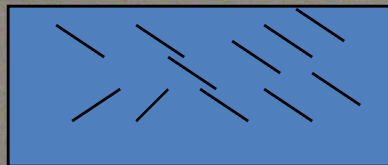
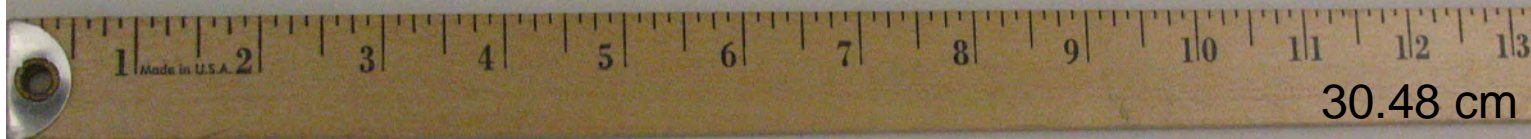


A method to produce the test sample to a one foot length has been identified and is currently being considered (Proprietary).

Outcomes: Produce 1st One Foot Wire

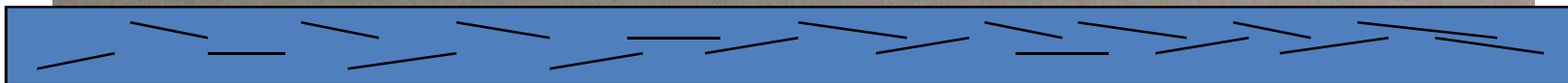
PE w/10 wt% SWNTs/Processed by melt spinning.
Various diameters have been produced with smaller diameters being more optimal at this time.

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

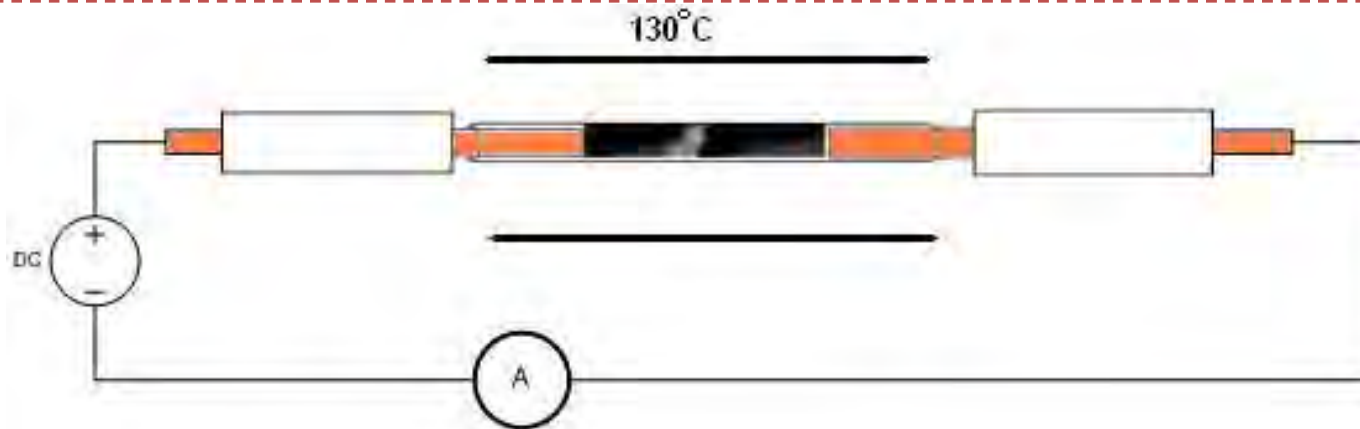
Keep the same volume, 1/2 diameter, 1/4 cross section area, 4 x length



Better alignment in uniaxial direction



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

Nanotube Conductivity

<http://www.nano.gov/html/news/SpecialPapers/Nanotubes%20For%20Power%20Transmission%20Line%20MaterialsA.htm>.

This reference cites the following:

“This high conductivity derives from the highly efficient transmission of electrons down the individual tubes acting as quantum wave guides in one direction, and the efficient resonant quantum tunneling of the electrons from tube to tube as the current passes down the fiber.”

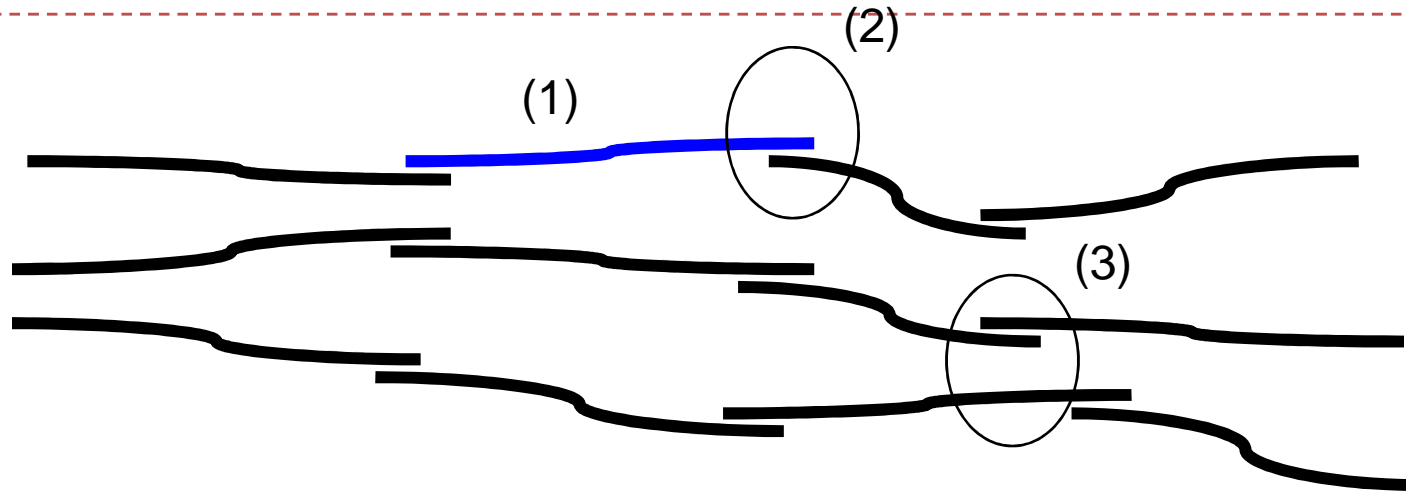
Several researchers have demonstrated that one single wall carbon nanotube can carry currents up to **20 microamperes**.



Concerns

1. Starting purity plays a role.
2. Obtaining separated nanotubes.
3. Level of disentanglement plays a role.
4. Nanotube type is important for two reasons.
 - Probability of metallic to metallic plays a role.
 - Nanotube to Nanotube contact is important.
(S to M (10^0), S to S (10^1), M to M (10^3))
5. Properties produced in the laboratory are not what can be produced in manufacturing.
 - Ropes vs. single nanotubes plays a role.
 - Polymer between the nanotubes plays a role.
 - Wire diameter plays a role.
5. Conditions of the electric fields play a role.
6. Final annealing plays a role.

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.

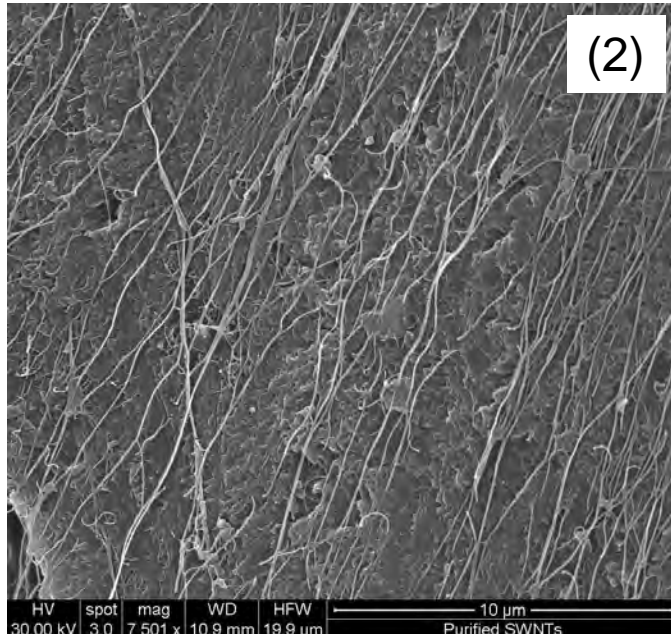
Mechanical properties include: UTS: ~50-150GPa/Elastic Modulus: 1 TPa

Disperse m-SWNTs

The Winey method for dispersion:

A version of the Incipient Wetting method where the following is used:

- 1) SWNTs are dispersed in Dichlorobenzene and sonicated.
- 2) After 3 hours, the temperature of the SWNT + DCB is raised to 110C. In a different beaker MDPE is dissolved in DCB at 110C. 3) The DCB + MDPE solution is added to the SWNT dispersion. 4) The mixture is placed in a ice bath and sonicated till the temperature reached below 70C. 5) The mixture is then vacuum filtered and dried.



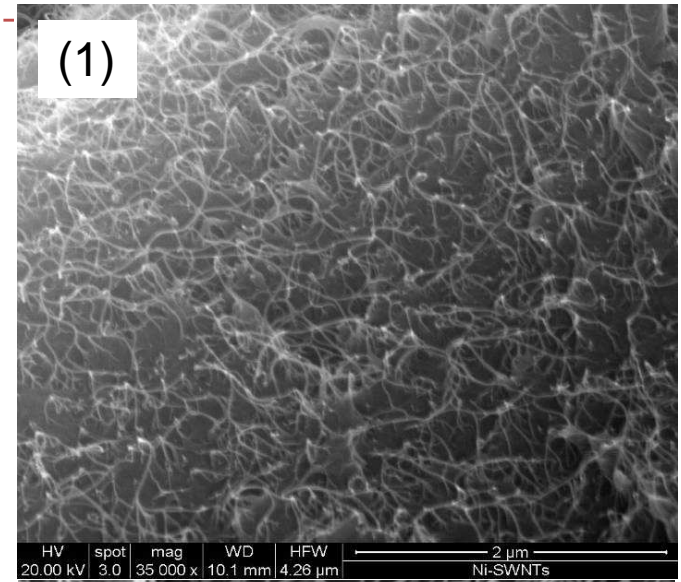
(1) After Winey Method.

(2) After electric Field applied.

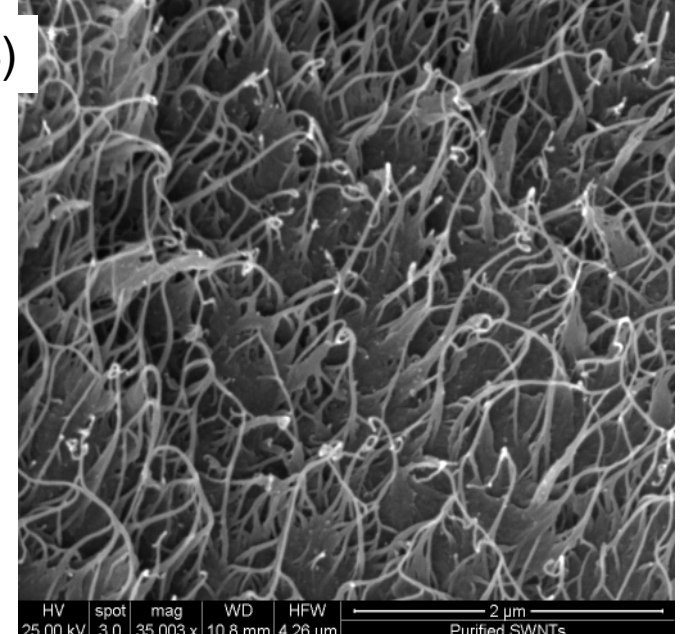
(3) After electric Field applied.

CE
SITY

Technip



(3)



Improving Percentage of Metallic Nanotubes

(2) Higher percentage m-SWNTs ensures similar type NT-NT contacts. Current nanotube compositions have some metallic to semiconductor contacts (not optimal contacts).

With unseparated nanotubes:

First nanotube is metallic (1/3 chance is metallic)
Second nanotube is metallic (1/3 chance is metallic)
Chance of metallic to metallic: (1/9)

With current sorted nanotubes:

First nanotube is metallic (2/3 chance is metallic)
Second nanotube is metallic (2/3 chance is metallic)
Chance of metallic (4/9 chance, improved by 2)

With proposed enhancement:

First nanotube is metallic (8/9 chance is metallic)
Second nanotube is metallic (8/9 chance is metallic)
Chance of metallic (64/81 chance, improved by 7)



The Role of Concentration and Shear

High Mechanical Performance Composite Conductor: Multi-Walled Carbon Nanotube Sheet/Bismaleimide Nanocomposites By Qunfeng Cheng, Jianwen Bao, JinGyu Park, Zhiyong Liang,* Chuck Zhang, and Ben Wang, Adv. Funct. Mater. 2009, 19, 1–7.

“Applying mechanical stretching and prepregging (pre-resin impregnation) on initially randomly dispersed, commercially available sheets of millimeter-long MWNTs leads to substantial alignment enhancement, good dispersion, and high packing density of nanotubes”.

“The nanocomposites demonstrate high electrical conductivity of $5\ 500\ \text{S cm}^{-1}$ along the alignment direction”. Concentration of nanotubes was 60 wt% MWNTs.

High concentrations and shear can enhance conduction conditions.



Electric Field Specifications

A review and analysis of electrical percolation in carbon nanotube polymer composites Wolfgang Bauhofer, Josef Z. Kovacs, Composite Science and Technology, 69 (2009) 1486-1498.

Review of 121 papers on electrical properties.

Results from the review: (1) Dispersion is very important.

times (2) Entanglements reduce conductivity (up to 50 (MWNTs))

(3) Electric fields align nanotubes and enhance attractive forces between nanotubes.

400 x 10⁻⁶m (0.4 mm) separation between electrodes for electric field use.



Electric Field Alignment

Electric-field assisted assembly and alignment of metallic nanowires
Peter A. Smith, Christopher D. Nordquist, Thomas N. Jackson, and
Theresa S. Mayera, *Benjamin R. Martin, Jeremiah Mbindyo, and*
Thomas E. Mallouk

“This letter describes an electric-field assisted assembly technique used to position individual nanowires suspended in a dielectric medium between two electrodes defined lithographically on a SiO₂ substrate. During the assembly process, the forces that induce alignment are a result of nanowire polarization in the applied alternating electric field. This alignment approach has facilitated rapid electrical characterization of 350- and 70-nm-diameter Au nanowires, which had room-temperature resistivities of approximately 2.9 and 4.5 x 10⁻⁶ ohm cm”.

(5 micron wide electrodes)

<http://research.chem.psu.edu/mallouk/articles/APL01399.pdf>



Electric Field Alignment

Aligned Single-Wall Carbon Nanotube Polymer Composites Using an Electric Field
CHEOL PARK, JOHN WILKINSON, SUMANTH BANDA, ZOUBEIDA OUNAIES,
KRISTOPHER E. WISE, GODFREY SAUTI, PETER T. LILLEHEI, JOYCELYN S.
HARRISON, Journal of Polymer Science: Part B: Polymer Physics, 44 (2006) 1751-
1762.

Use of electric fields 0.03 wt% Hipco.

**Electrodes placed at a separation distance of
2.3 mm. In the electric field for 10 minutes. 10^{-6} S/cm**

**Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their
Alignment and Deposition as a Film in a dc Field Prashant V. Kamat, K.
George Thomas, Said Barazzouk, G. Girishkumar, K. Vinodgopal, and Dan
Meiselt.**

5 mm apart.

“When a dc voltage of ~ 40 V was applied, we observed a slow movement of carbon nanotubes from the suspension toward the positive electrode”.



Tunneling

Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube–based composites Chunyu Li, Erik T. Thostenson, and Tsu-Wei Chou,
Applied Physics Lett. 91 (2007) 223114-1 to 223114-3.

Maximum tunneling distance is found to be 1.8 nm.

“Electrical conductivities of composites with in plane random distributions of carbon nanotubes follow the scaling law and the critical exponent depends on the level of contact resistance”.

“It is also noted that the extrapolation of the EC of CNT networks without insulating layers at 100% content gives about $7.2 \cdot 10^5$ S / m, which is very close to the conductivity of 10^6 S / m of individual CNTs we used”.



Conduct NT-NT Study/Improve NT-NT Connection

- Three Approaches:
- (1) Zyvex manipulation
 - (2) Ames Interdigitized Sample
 - (3) Use of Focused Ion Beam Equipment
 - (4) Doping

Use of Focused Ion Beam Equipment

IPICyT in San Luis Potoci, Mexico has equipment for conducting high sensitivity nanotube manipulation.

With this equipment we can imagine at the nanoscale, move nanotubes around, and create contact conditions for measuring electrical conductivity (NT-NT contact).

Experiments are being conducted to achieve samples of several nanotube conditions.



Conductivity of SWNT Networks

Electrical Conductivity of Single-Walled Carbon Nanotube Networks

P. N. Nirmalraj, P. E. Lyons, S. De, J. N. Coleman, and J. J. Boland, Nano Lett (2009) 3890-3895.

“Transport in single-walled carbon nanotube networks is shown to be dominated by resistance at network junctions which scale with the size of the interconnecting bundles”.

“Acid treatments that dope the individual nanotubes produce a dramatic reduction in junction resistance.

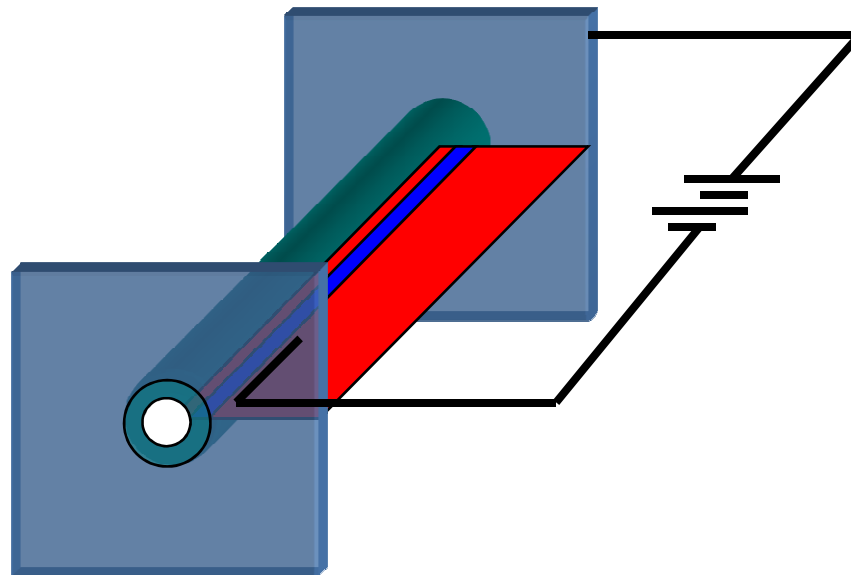
Smallest resistances occurs between individual nanotubes.



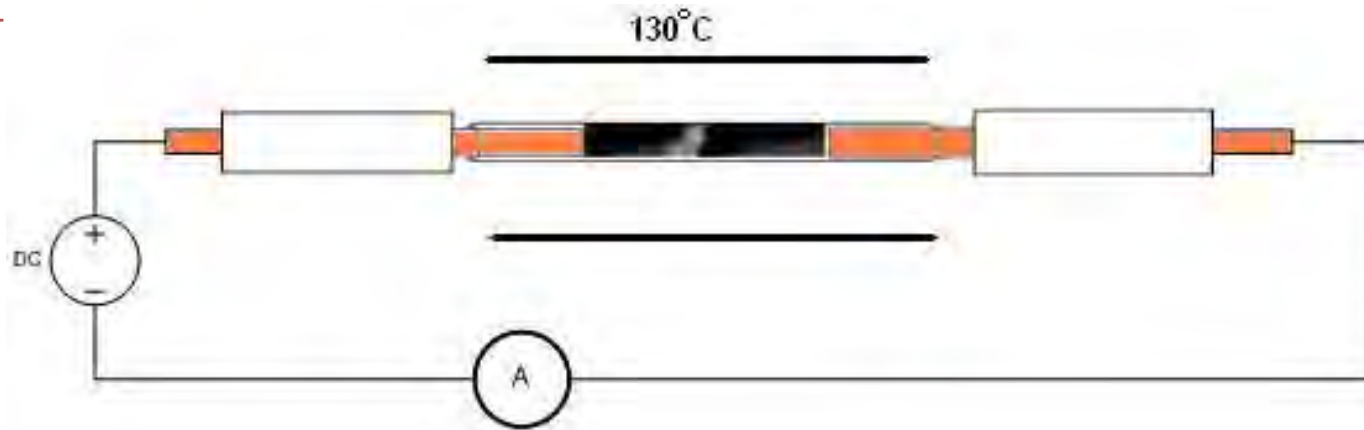
Implement Electric Fields

Design of an Electric Field Fixture:

1. Separated parallel plates with a hole in the middle so the PNU can go through.
2. A tube is placed in the holes so that a heating element can be put around the wire.



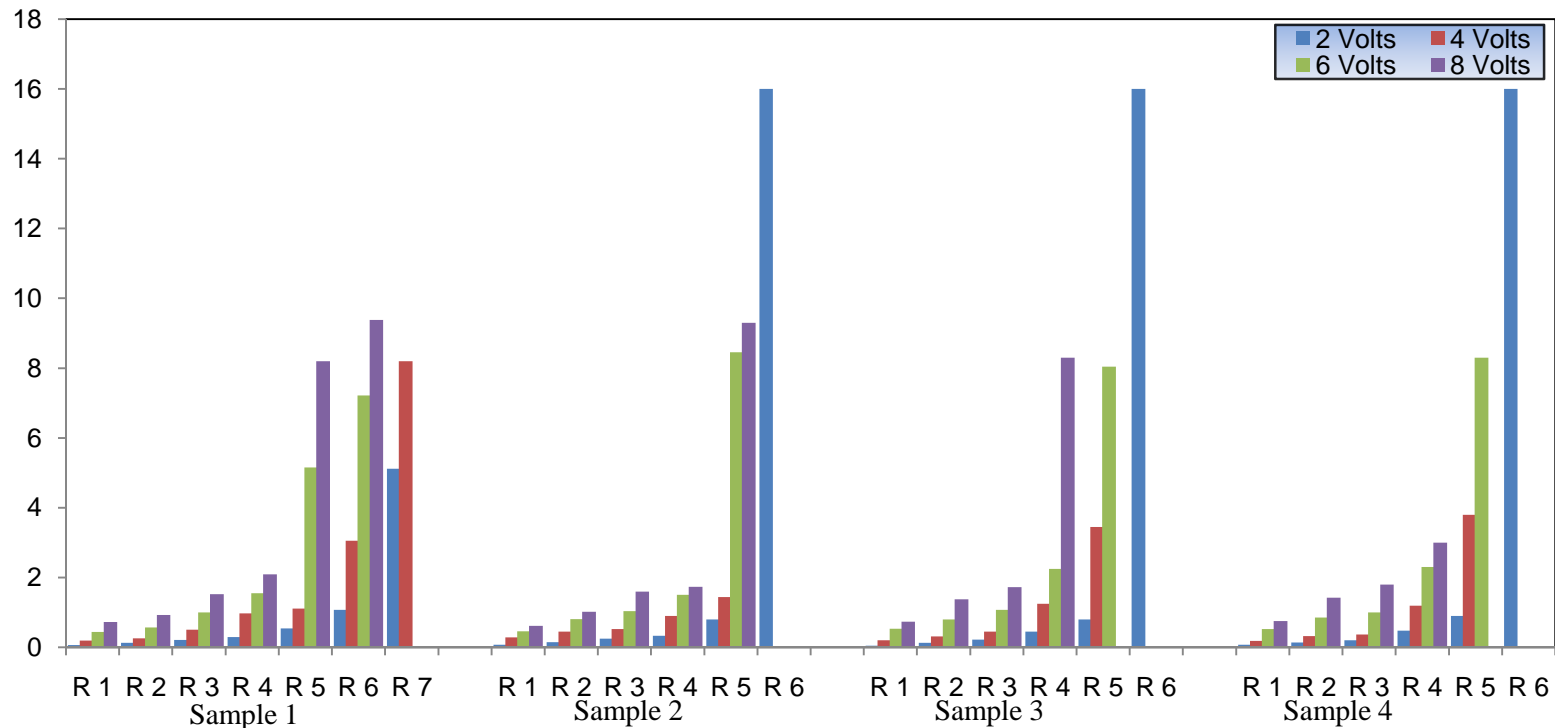
Current method for implementing the electric field



- 4 samples (MDPE + 10 wt% SWeNTs) were tested.
- Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.
- 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 cm.
- Specific resistivity was $2.1 * 10^{-2}$ ohms / sq.cm
- Current samples require conditioning (more than one melting pass).

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.

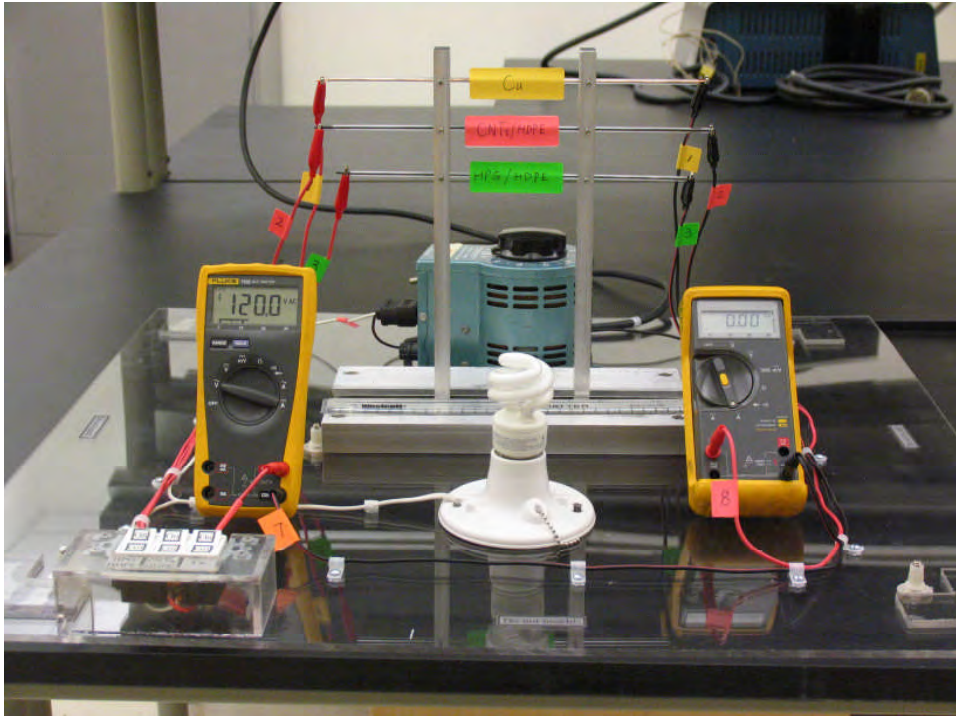
Samples for Resistivity Testing

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

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

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

Partial listing related to conduction (with a low concentration focus):

- ▶ 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 segregated 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.

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 $2 \cdot 10^{-2} \Omega\text{cm}$.
- ▶ 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 (improved dispersion)
- ▶ Functionalization
- ▶ Annealing (proven improvements)
- ▶ Higher concentrations
- ▶ Doping Up to 100% improvement (Synergism)
- ▶ Enhanced NT-NT connections
- ▶ Retained polymer
- ▶ Stretching

Program Outcomes

1. One foot wire conductor produced.
2. High dispersion has been achieved by the “Winey” Method.
3. We have used electric fields and designed a fixture for process manufacturing.
4. We have produced a number of samples using the Dymax sample configuration. Early samples were produced with styrene. A number of samples have been processed by melt spinning.
5. A current carrying capability of 16 amps has been produced
6. where 26 A is needed..
The sample was limited by the power supply used.
More optimization is planned.
6. The workshop is being held on Ultra-High Conductivity Conductors.
7. The test wire is being demonstrated at the workshop.

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