



nanoUmbilical Workshop

Steps to Achieving Conduction

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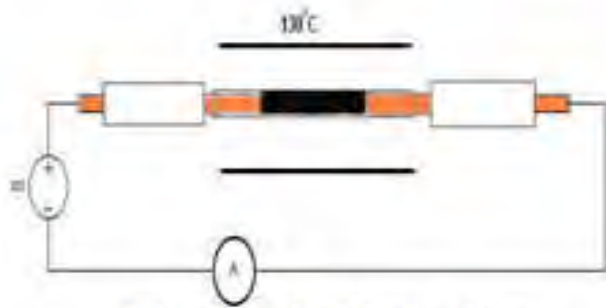


Outline

- Dispersion of carbon nanotubes (CNTs).
- Decanting the CNTs – solvent suspensions.
- Processing CNTs – medium density polyethylene composites (MDPE).
- Electric field studies on CNT – MDPE composites.
- Outcomes.



Process



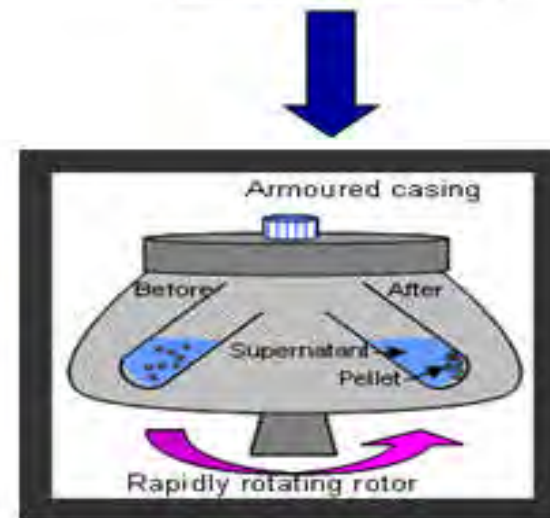
Electric field studies



Dispersion of CG-SWNTs in dichlorobenzene



Composite Processing



Decanting process

Dispersion of Carbon Nanotubes

- Carbon nanotubes tend to agglomerate due to the strong Van der Waal's attraction .
- In order to effectively use their properties, good dispersion of CNTs in the solvent / polymer is very essential.
- Good dispersions can be achieved by using suitable solvents and surfactants, sonication, homogenizing etc.

Macroscopic Dispersion behavior in solvents



Precipitation /unstable

Separates into two phases : a precipitant and a clear liquid



Stable / No precipitation

A homogeneous black stable suspension with no visual precipitation



- Common solvents used to disperse CNTs are N-methylpyrrolidone, dimethylformamide, tetrahydrofuran and dichlorobenzene.
- In our studies we used dichlorobenzene to disperse the CNTs and the concentration was maintained at 0.2 mg / ml.
- The CNT – dichlorobenzene suspensions were sonicated for 3 hours using a probe sonicator.

Use of a good solvent and sonication aided in stable dispersions of CNTs

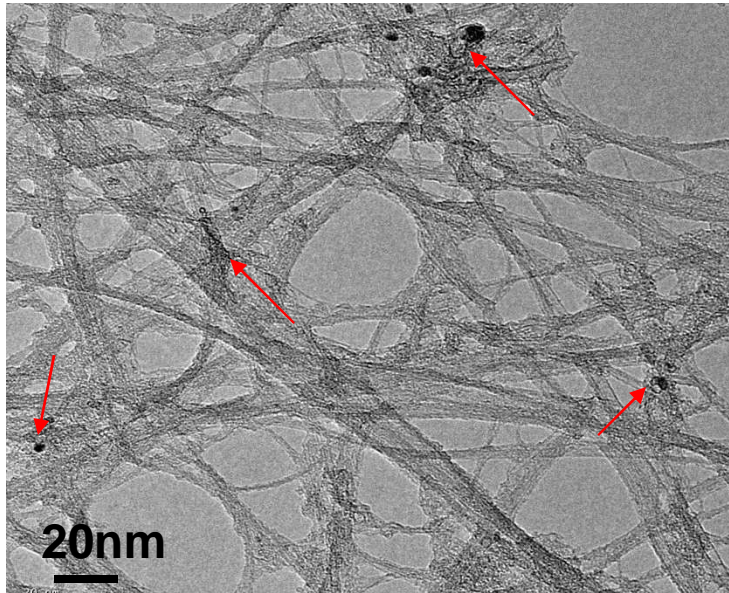


Decanting Studies

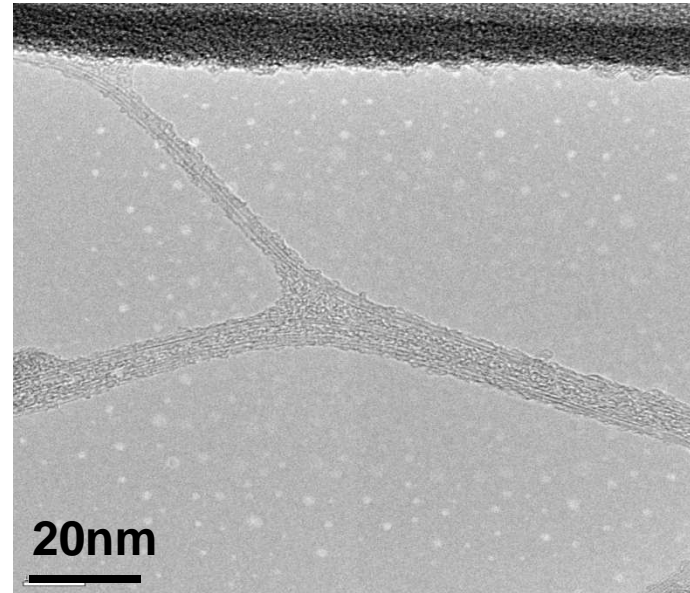
- Centrifuging the CNTs removes the heavier catalyst particles, large agglomerates and amorphous carbon from the nanotube suspensions leaving behind non-agglomerated, well dispersed CNTs.
- CNT / dichlorobenzene suspensions were divided into 50 ml aliquots for decanting studies.
- Samples were centrifuged at various g's (15000, 50000, 85000) for different time intervals (15 , 30 and 45 minutes).
- Our studies revealed that the heavier particles fall out of the suspension only at the highest g force when centrifuged for 45 minutes.



Characterization of decants



Before Decanting



After Decanting (85000 g for 15 minutes)

- A weight analysis on the pellet showed that 30% of the original sample sedimented out of the solution.
- Clean non-agglomerated CNTs and smaller diameter bundles of CNTs were obtained.

- De-agglomeration is the synergy between decanting and dispersion of CNTs.
- In our studies we successfully dispersed the CNTs in dichlorobenzene
- Decanting process removed the amorphous carbon, heavy catalyst particles and, heavy agglomerates leaving behind clean, smaller diameter bundles and single CNTs.

Deagglomerated CNTs can be used in processing of polymer composites because their excellent electrical , mechanical and thermal properties can be efficiently utilized.



Composite Processing (Winey Method)

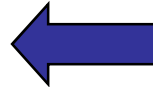
Further the composite was vacuum filtered to remove the DCB and dried at 100 °C

Sonicated 10 wt% CG SWNTs or HiPco SWNTs (0.2 mg/ml) in dichlorobenzene (DCB) for 3 hours



CG-SWNTs or Hipco SWNTs in DCB were then cooled to below 70 °C while simultaneously sonicating the mixture.

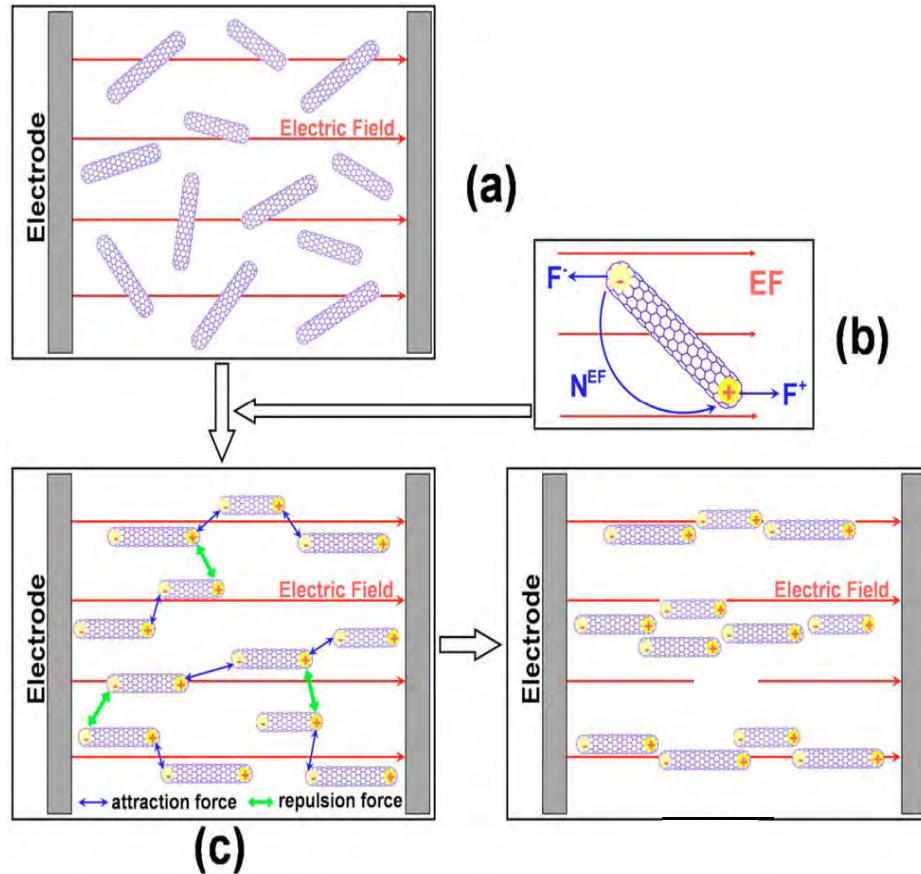
Heated the above dispersion to 110 °C and added MDPE dissolved in DCB at 110 °C .



Haggenmueller.R *et al* , *Macromolecules* 40, 2417-2421,2007.



Alignment of Carbon Nanotubes in a medium under the effect of electric field



- Polarization of SWNTs.
- The electric field induces a dipole moment on the nanotubes.
- Rotational forces makes them align in the direction of the field.

Zhu *et al*, Journal of Applied Physics, **105**, 054319 (2009).

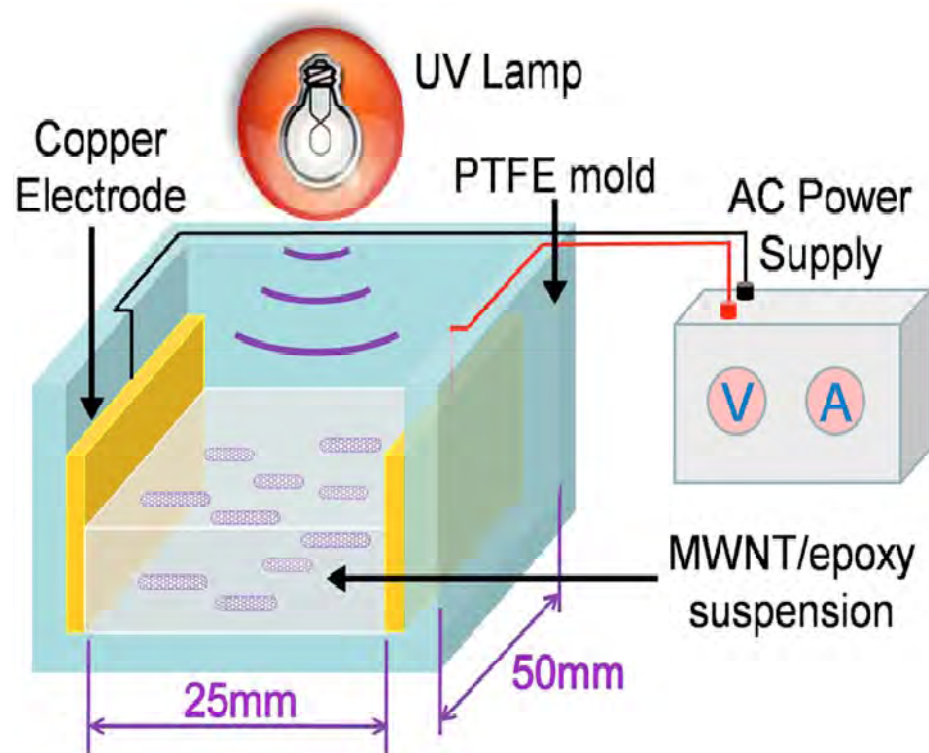
Illustration of CNT alignment in an electric field

- Functionalized CNTs suspended in THF were used.
- At low DC field (<100 V) the nanotubes moved from the suspension towards the electrode and deposited on the electrode.
- At high DC field (>100 V) the nanotube bundles begin to align perpendicular to the electrode surface.

Kamat.P.V *et al*, J. Am. Chem. Soc. **126**, 10757 2004.



Alignment of CNTs in polymer composites



Zhu *et al*, Journal of Applied Physics, **105**, 054319 (2009).

- MWNTs nanotubes in epoxy suspension were used.
- AC voltage of 2000 V and 2000 Hz peak to peak was applied for 10 minutes to study the alignment.
- UV light was used to irradiate the samples to polymerize the suspension.
- The resistivity of the composite reduced from 10^{15} ohm.cm to 10^{10} ohm.cm by addition of 0.5 wt% MWNTs

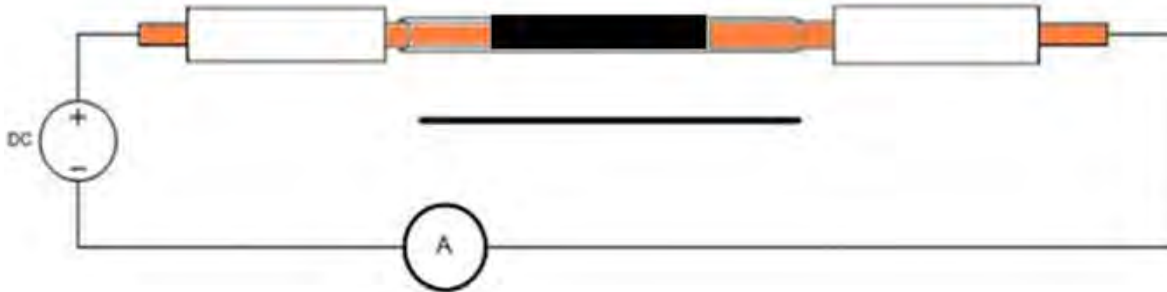
Effect of DC electric field on medium density polyethylene / CG-SWNT composites

- Using the previously discussed studies, we incorporated the principles of CNT alignment under the effect of electric field within our CNT / MDPE composites.
- 10 wt% CG-SWNTs, 10 wt% Purified HiPco SWNTs in MDPE were used.
- AWG 8 multistranded copper wire (18 strands) and silver soldered single core wires were used in our study.



Process

145°C



- Samples were heated to 145 °C for 30 minutes before the electric field was applied.
- Before applying the electric field, the distance between the copper leads was maintained at 1.5 cm.
- Low DC electric field was applied and the voltage was increased from 1 to 8 volts.
- Samples had to be conditioned a minimum of three times to be able to carry high currents.

Challenges and Solutions towards Optimizing the Process

	<u>Challenge</u>	<u>Solution</u>
1	<p>For CNTs to effectively align in the polymer, the polymer has to have low viscosity.</p> <p>Resistivity (~ 200 ohm.cm)</p>	<p>Our composites were heated to 145 °C to allow the nanotubes to align and form a network.</p> <p>Resistivity (~ 2.5 ohm.cm)</p>
2	<p>For the electric field to be effective, there should be a solid contact between the copper leads and the sample.</p> <p>Resistivity (~ 2000 ohm.cm)</p>	<p>The sample was compacted between the leads by applying pressure and the leads were clamped in place.</p> <p>Resistivity (~ 60 – 100 ohm.cm)</p>
3	<p>Unlike all previous studies where the polymers are either photo curable and UV curable, PE is not UV curable or photo curable</p> <p>Resistivity (~ 50 – 100 ohm.cm)</p>	<p>A low voltage electric field was applied when polymer was allowed to harden after alignment tests</p> <p>Resistivity (~ 0.5 ohm.cm – 10 ohm.cm)</p>

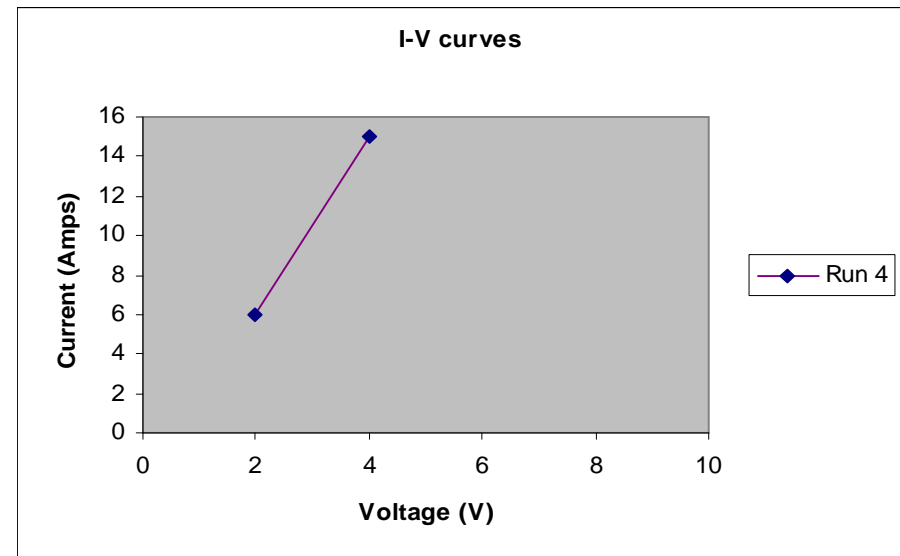
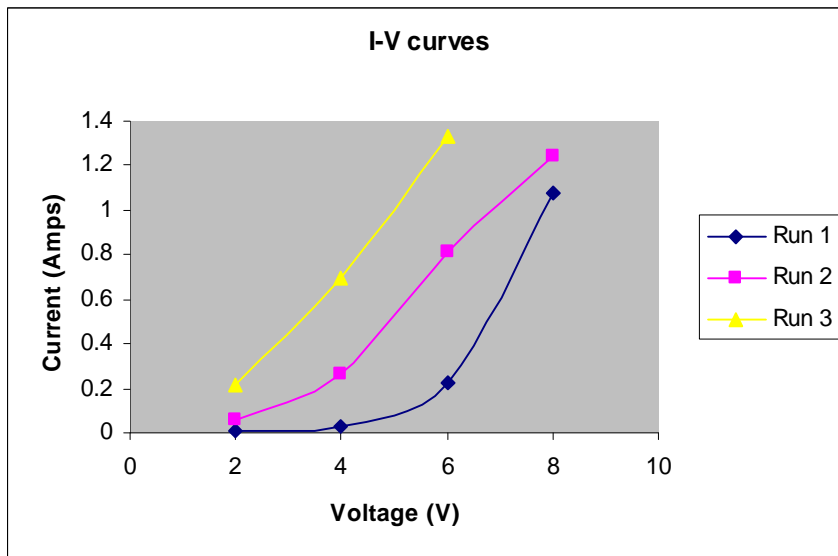


	<u>Challenge</u>	<u>Solution</u>
4	Void formation which will prevent a continuous network for electron flow. Resistivity at 145°C (~ 2.5 – 5 ohm.cm)	Samples were conditioned and after each conditioning run the leads were pushed in further to eliminate the voids. Resistivity at 145°C (~ 0.02 – 0.09 ohm.cm)
5	Upon applying force on the copper leads, the polymer flows on the exterior of the leads due to a minor difference between the inner diameter of quartz tube and the copper leads. This decreases the amount of polymer between the leads.	Sealing the area between the copper lead and inner diameter of the quartz with Teflon and holding the copper in place using a insulating tape and clamp reduced the polymer flow.

A unique process of electrically conditioning the MDPE / CNT composites was developed.



Example of current – voltage characteristics for MDPE / 10 wt % purified HiPco samples



- After each run, the composite was able to carry higher currents at the same voltage indicating a decreasing in the resistivity of the composite.
- The **sample was able to carry 16 amps of current** at 145 °C because of a very good network formation of CNTs.



Electrical Resistivity of MDPE / Carbon nanotube composites

<u>Sample</u> AWG 8 – 18 strand copper wire as <u>leads</u>	<u>Resistivity</u> (ohm.cm)	<u>Diameter</u> (cm)	<u>Surface area</u> (cm ²)
Polyethylene (MDPE)	10^{15}	0.394	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 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
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



<u>Sample</u>	<u>Resistivity</u> (ohm.cm)	<u>Diameter</u> (cm)	<u>Surface area</u> (cm ²)
10 wt% purified Hipco / MDPE (application of electric field at high temperature) (Single core copper lead)	$\sim 7 * 10^{-2} - 9 * 10^{-2}$	0.394	0.12
10 wt% purified Hipco / MDPE (application of electric field at high temperature)	$\sim 4.5 * 10^{-1} - 8 * 10^{-1}$	0.2	0.031

- To ensure repeatability of the process 10 to 15 samples were tested in each category described in the table.
- Initially it required 5 to 6 runs for the sample carry high currents at low voltages, but with process optimization the number of runs reduced to 4.
- With use of single core wire , it required 3 to 4 runs to condition the sample and the time required for conditioning was reduced by 30 minutes.

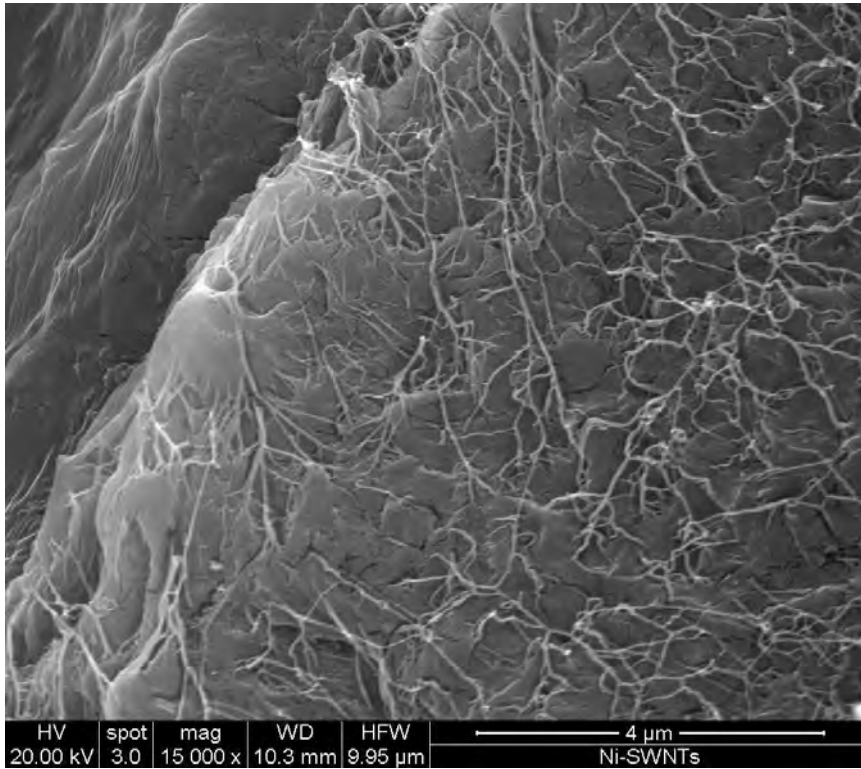


- Composites with 10 wt % CNT (CG – SWNTs / HiPco) showed the best resistivity at elevated temperatures.
- After the application of electric field : five order decrease in the resistivity at elevated temperatures and four decrease at room temperature was obtained for CNT / MDPE composites.
- The optimal distance between the leads was found to be 0.7 to 0.8 cm for the best conducting samples.
- A reduction in resistivity can be due to two reasons :
 - At high temperatures, when the polymer melts, the nanotubes tend to align to form a network because they are free to rotate under the influence of electric field.
 - Also, in areas which are polymer rich, resistive heating of the polymer due to high current would bridge the gap between nanotubes and this in turn will lead to a continuous network formation.

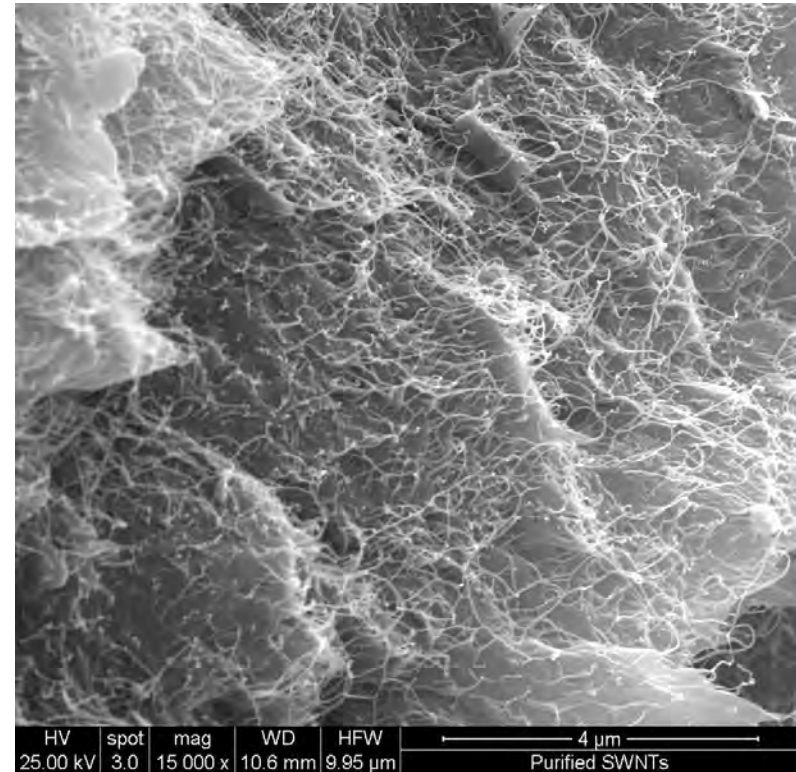
De-agglomeration , continuous network formation and alignment, proper contact, reduction in void formation are some of the important factors that reduced the resistivity of the composite.



Characterization of MDPE / SWNT composites

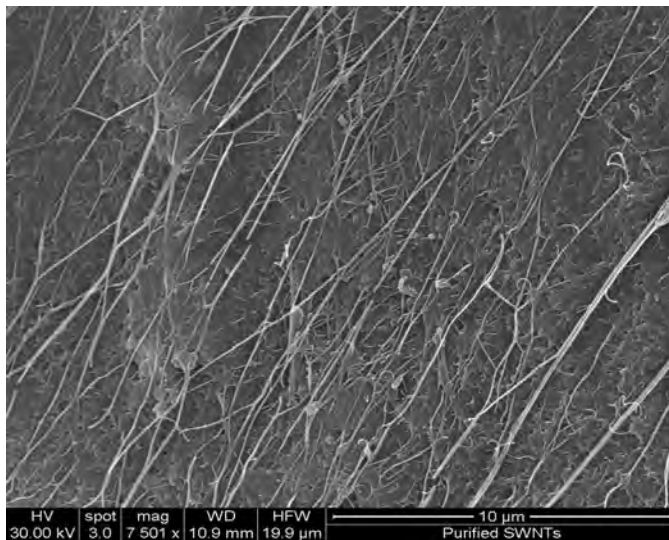
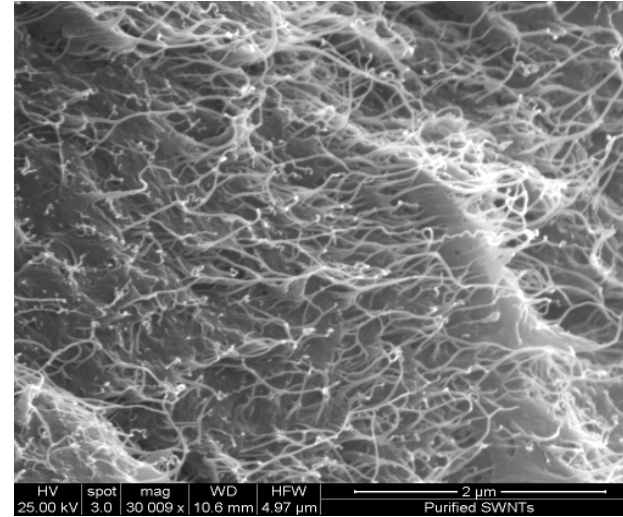
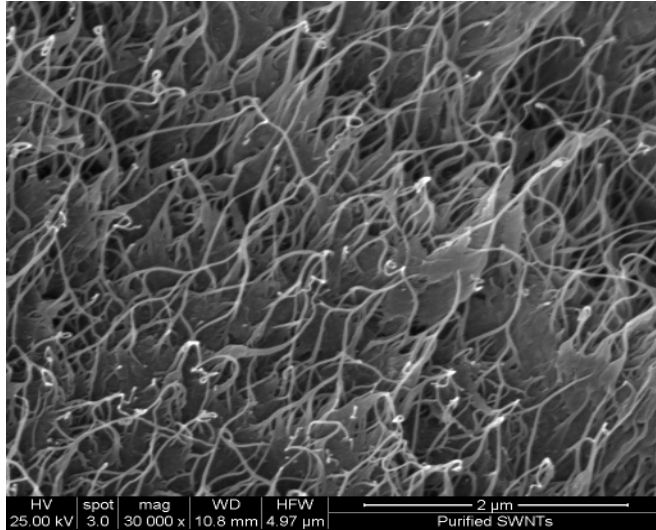


Before Electric Field



After Electric Field





Due to electric field:

- a) In some areas, alignment of CNTs was observed.
- b) In most areas, a net alignment and a better network of CNTs was observed.



Outcomes

- Efficient dispersion and decanting of CNTs.
- A unique process to condition the MDPE / CNT composites was developed.
- Continuous network formation by bridging gaps under the influence of electric field, aided in improving the conduction in MDPE / CNT composites.

Resistivity of the composite decreased by 17 orders of magnitude as compared to neat medium density polyethylene composite.

