The Need for Purification in Nanocomposite Synthesis

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The Need for Purification

- Nanotube Composite Systems
- Nanotube Stability
- Dispersion in Fluids
- Dispersion in Thermoplastics
- Dispersion in Thermosets
- Functionalization
- Property Development

Nanomaterials Research

Matrix of Understanding

Nanotubes in fluids and heat transfer nanofluids	Banbury mixing using high shear and elongational flow	Nanocomposites with functionalized nanotubes	Conducting polymers, radiation protection, and multifunctional materials
High temperature stability of nanotubes	Mimicking polymeric properties of nanotubes	Epoxy and epoxy composites development	Polymerization for hybrid formation
Metal matrix nanocomposites & metal-nanotube reactions	Nanotube interactions with various matrices	Mimicking nanotubes to higher scales	New polymeric architectures for mimicking Nanotubes
Ceramic matrix nanocomposites	Molecular to microscopic arrangements to enhance properties	Alignment and tangle manipulation	Adaptive, sensing, self-healing smart materials (FINCs)

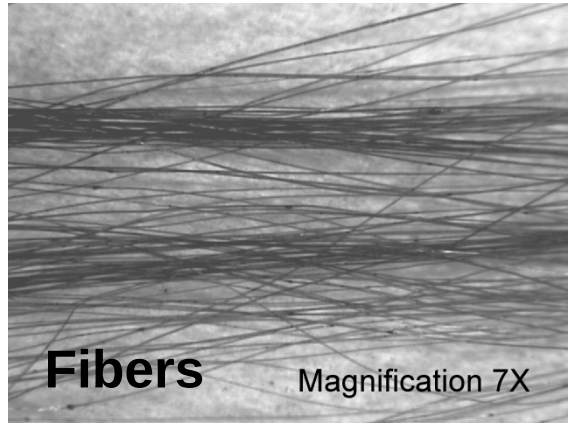
Synthesis Protocol

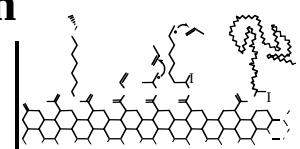
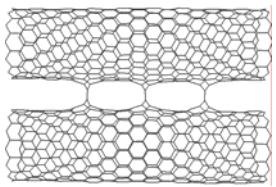
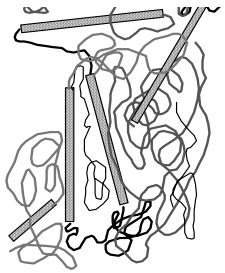
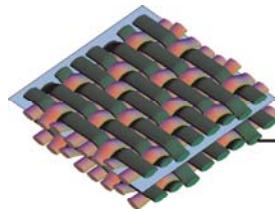
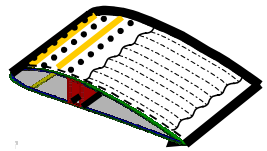
Calculations indicate that conventional composite materials development will not fully utilize the full potential of carbon nanotubes.

A prime objective but hard to achieve.	We don't have the nanotubes that we really need.	Functionalization is necessary but must be done with care.	Certainly the near term opportunity since high strength has not occurred.	Our Holy Grail, A method of fuller use of nanotube properties.
Ultra High Strength Nanotube Material	Processing w/VGCFs, SWNT Ropes, SWNTs	Need for Functionalization and how to process	Arrive at Multi-Functional applications	Nanotube Hybrid Material

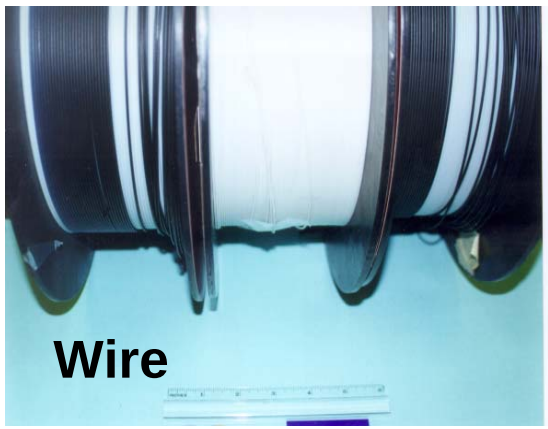
Current Status

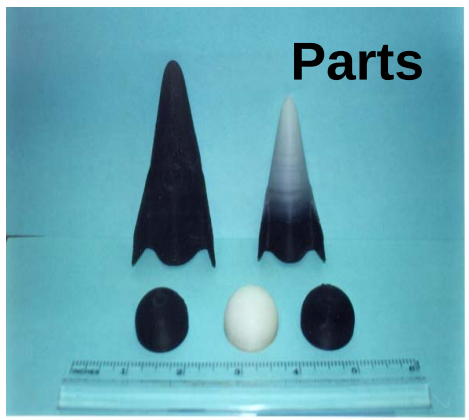
50-100% Increases in strength w/good elongation.	Low cost ESD materials	F-SWNT in Vinyl ester-Glass fiber composite	Several composites for mech./elect., mech./thermal, thermal coatings, mech./impact.	Hybrid nylon, PE, and epoxy.



	Functionalized Single Walled Carbon Nanotubes	Single Wall Crosslinked Nanotubes	Functionalized Nanotube Composite	Multifunctional Structural Supercapacitor	Multifunctional Aerospace Vehicle	
Approach						Products

10^{-10}m ⟷ 10^{0}m

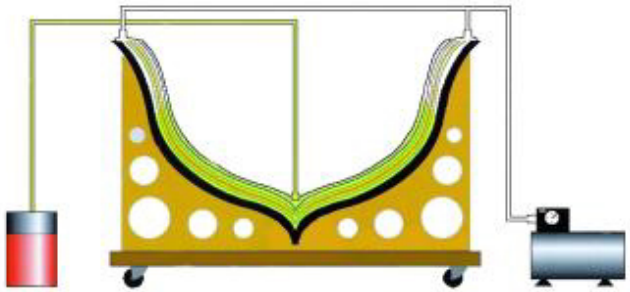




Composite Systems Studied

EMI

Epoxy Composites



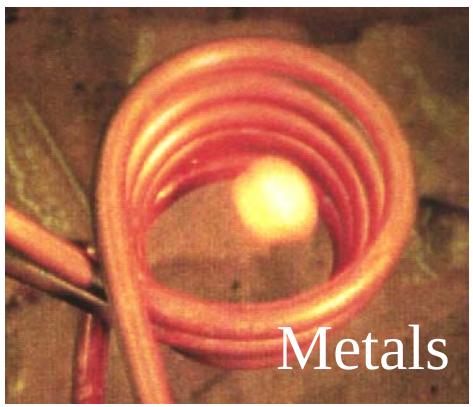
VARTM

Functionalizations

epoxy-, amino-, allyl, fluoro-, silano, Cl-silano-, bromol-, vinyl-, hydroxylated-, bisphenol-SWNT

Composite Systems

VGCF/ ABS, ASA, Acetal, PE, PET, PP
VGCF/ Cu, Al
VGCF/ Si3N4, ZrO2, Y2O3 Stablized ZrO2
MWNT/Oil and SWNT/Oil
SWNT/ ABS, PE, PP, styrene
SWNT/ Epoxy, Vinyl Ester
SWNT/ Cu, Al, Ni
SWNT/ Si3N4, ZrO2, Y2O3 Stablized ZrO2



Metals

Ceramics

A NanoSword

SWNT Purification Protocol

Oxidation / Annealing

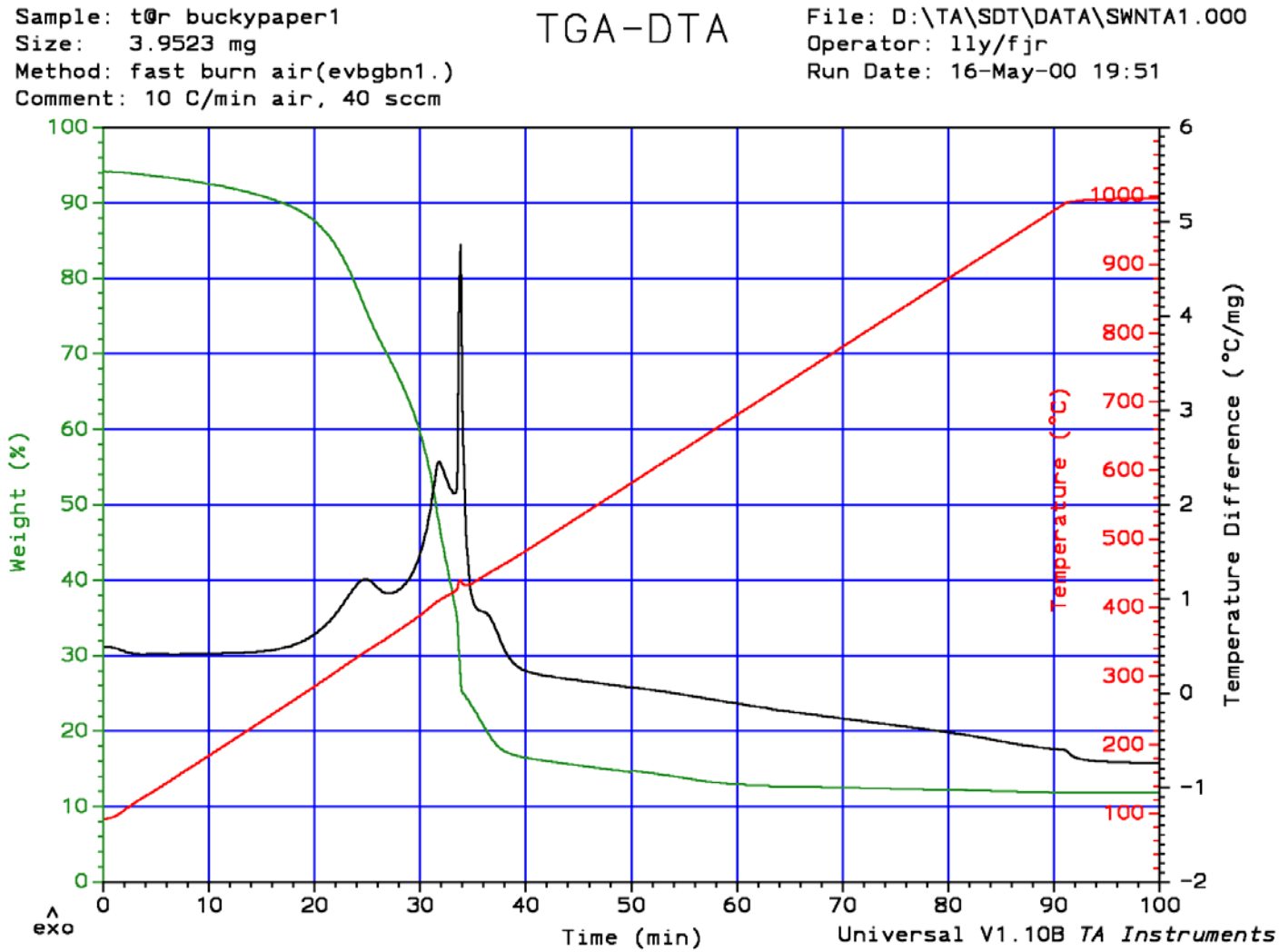
Take 200 mg of raw tubes and place into glass gas tube, Place gas tube in larger glass tube and put in furnace
Turn on Argon (80cc) and Oxygen (20cc)
Hook up gas line to gas tube
Close furnace and turn program on with 1 hour ramp time to 225 C and 22 hrs annealing tim
After 23 hrs turn off program, off gas and allow apparatus to cool down

2. **HCl wash**

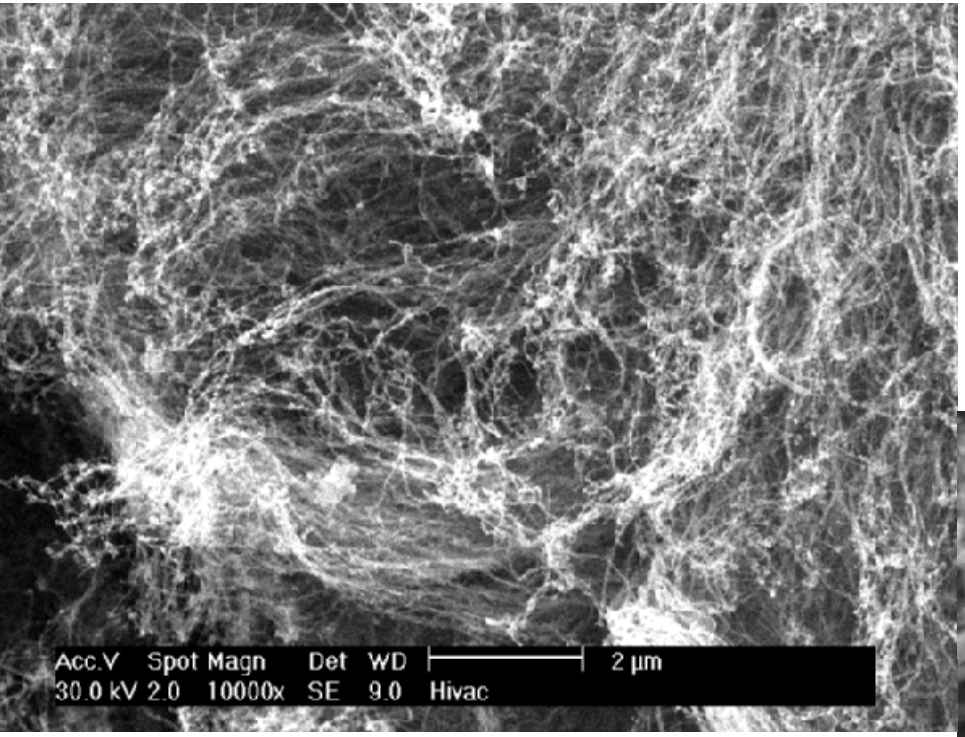
Take annealed tubes, and put in glass jar. Fill halfway with 12M HCl
Sonicate glass jar in bath sonicator for 4 hrs
Neutralize the HCl with at least an equal volume of DI water.
Filtrate with 47 mm Teflon filter with smooth side up, Wash with a large amount of water and EtOH.
Put oven to try at 70 C overnight

Unannealed SWNTs with Mass Loss at ~400C

L. Yowell



MWNTs by Rao

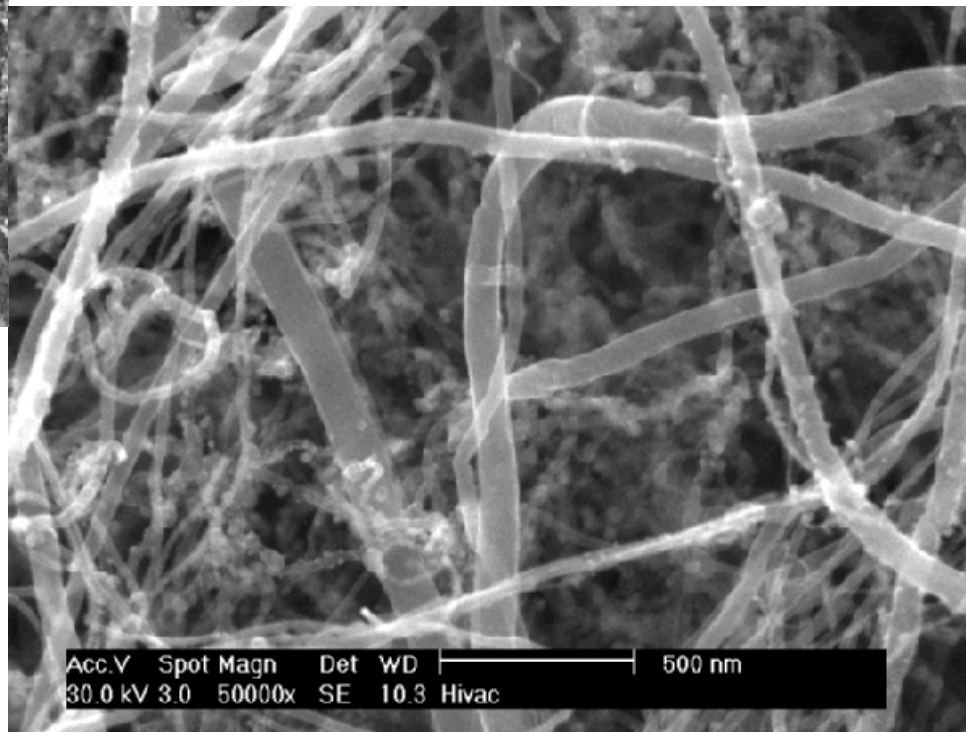


Substrate MWNTs

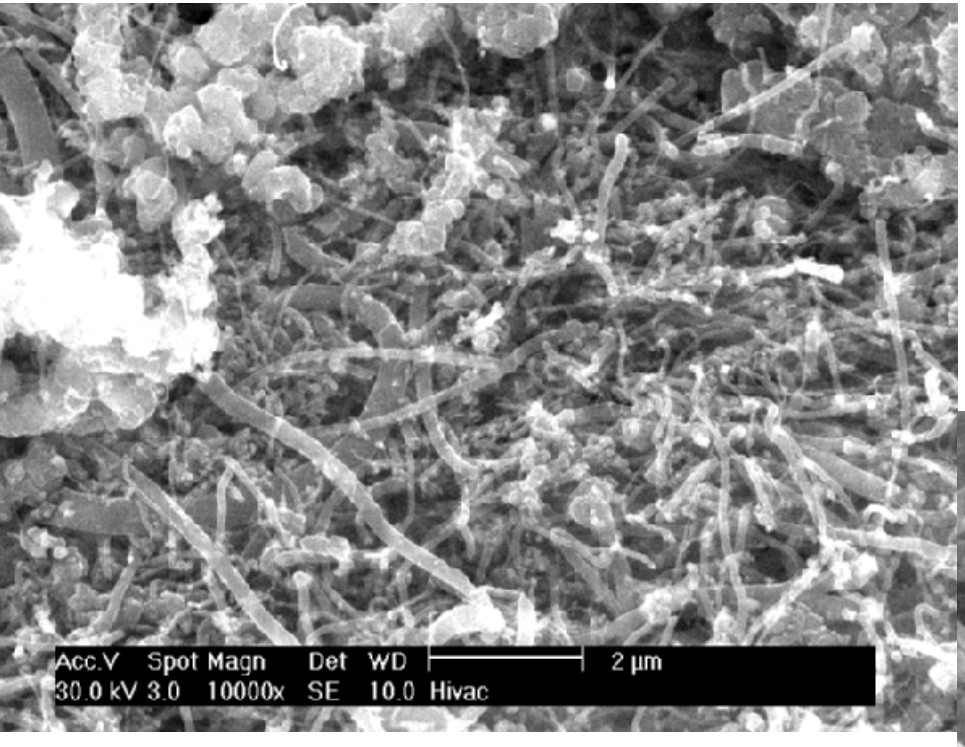
Used in Heat Transfer Nanofluids

See the Nested Highly entangled Nanofiber mass.

See the non nanotube material

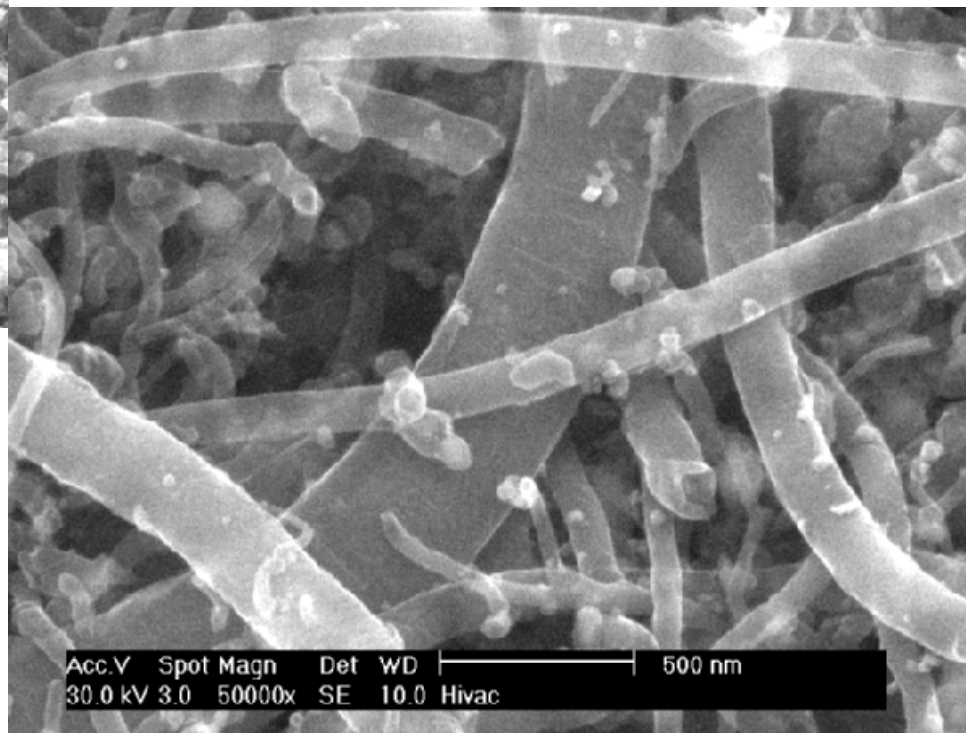


MWNTs by Rao



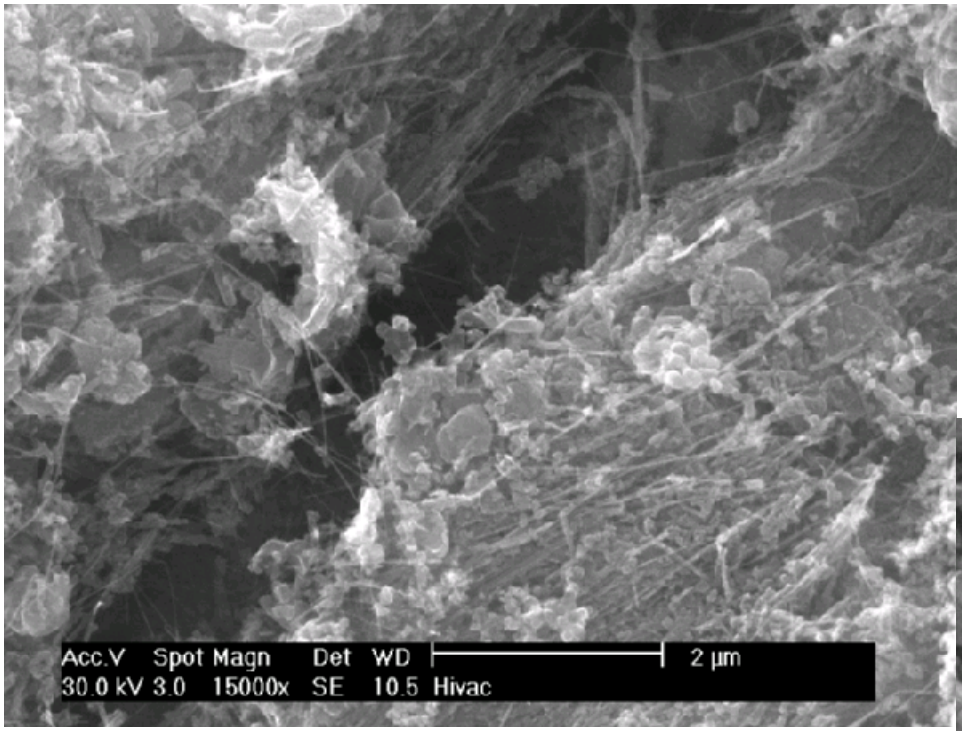
Used in Heat Transfer Nanofluids

Note the non nanotube material



Wall MWNTs

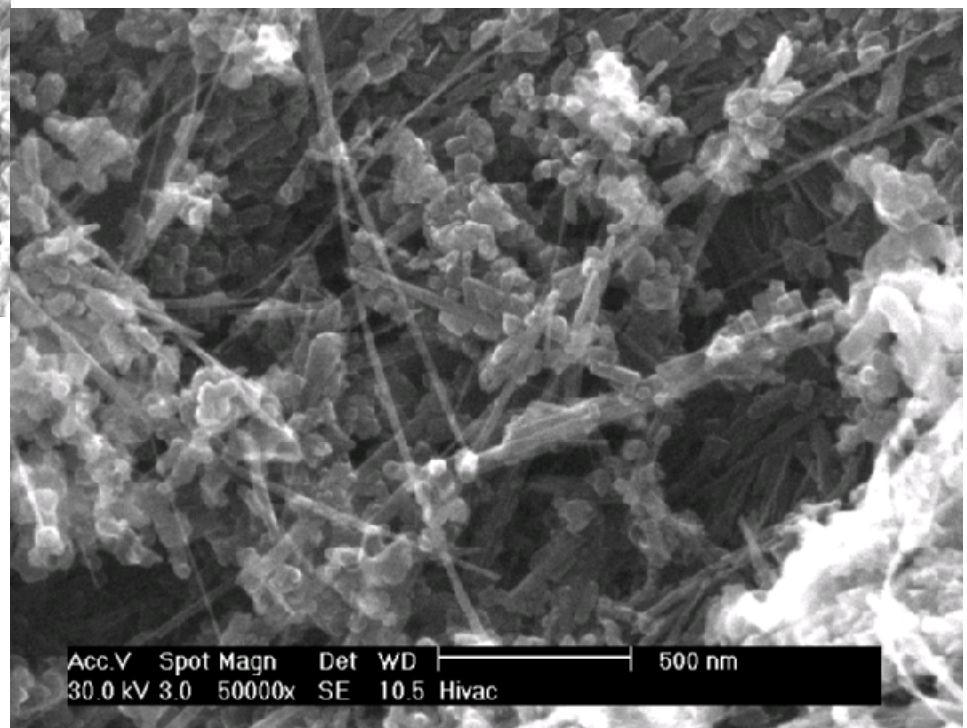
MWNTs by NanoTex



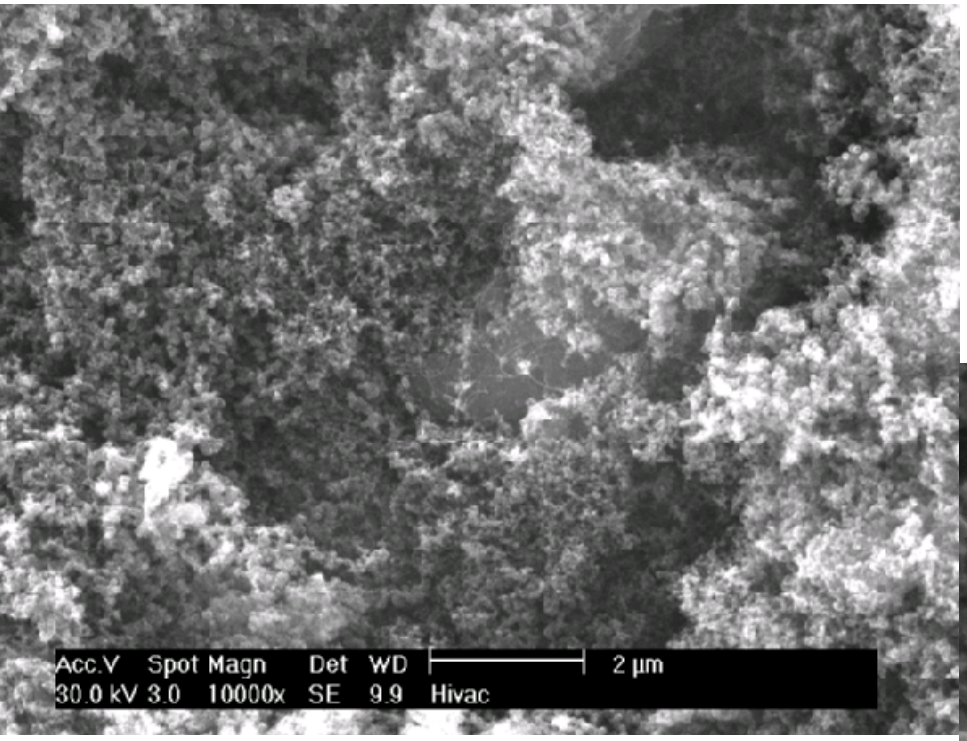
A large amount on non nanotube material

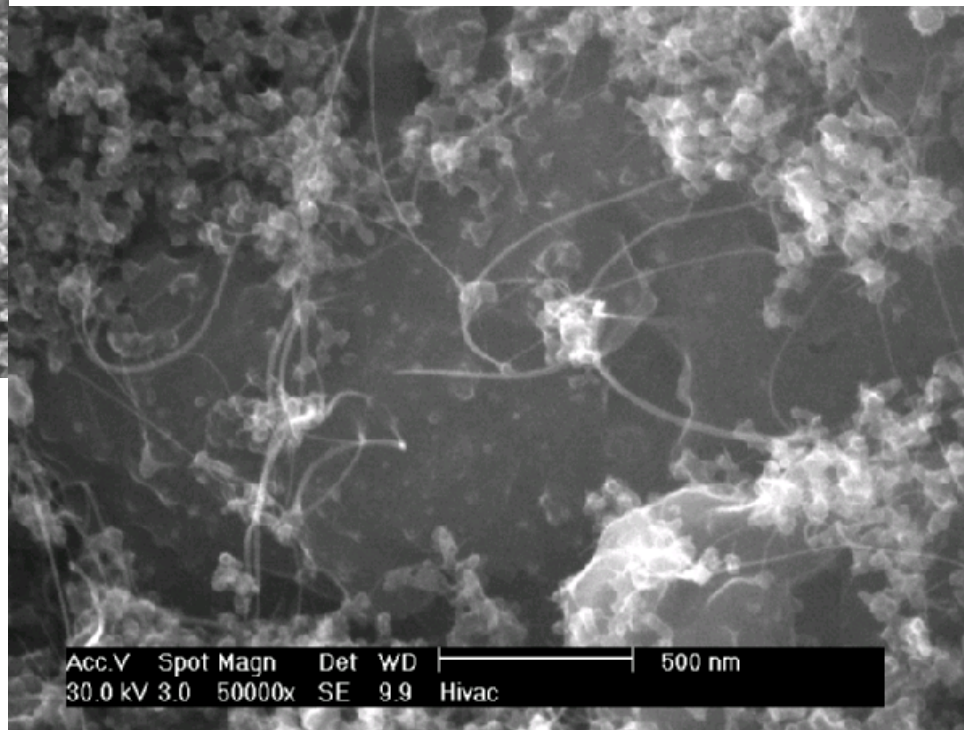
Non nanotube material limits dispersion

Non nanotube material limits stability

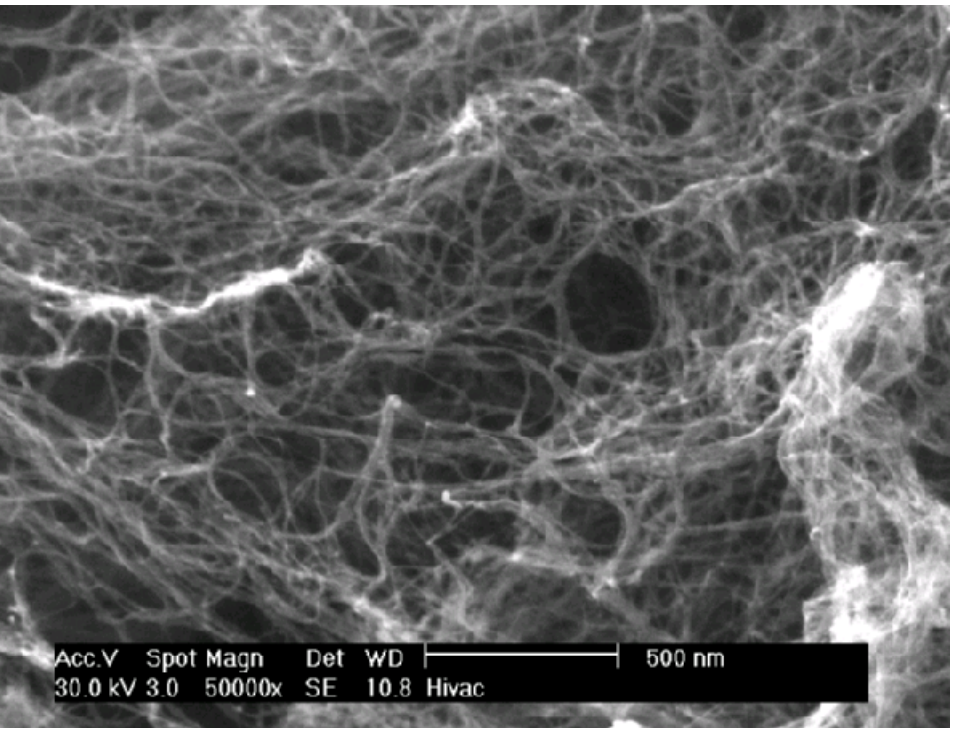


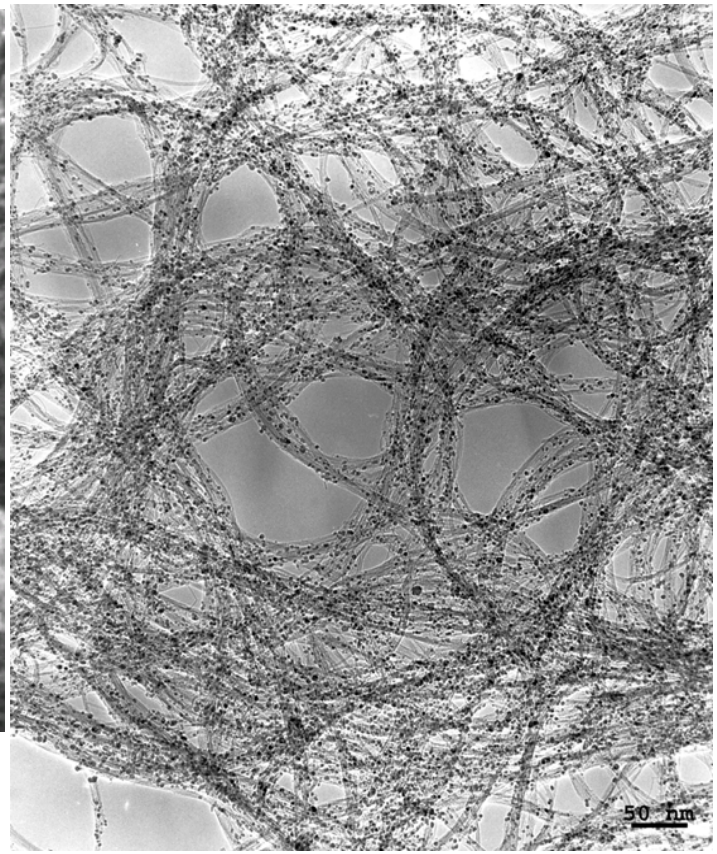
SWNTs by NanoTex





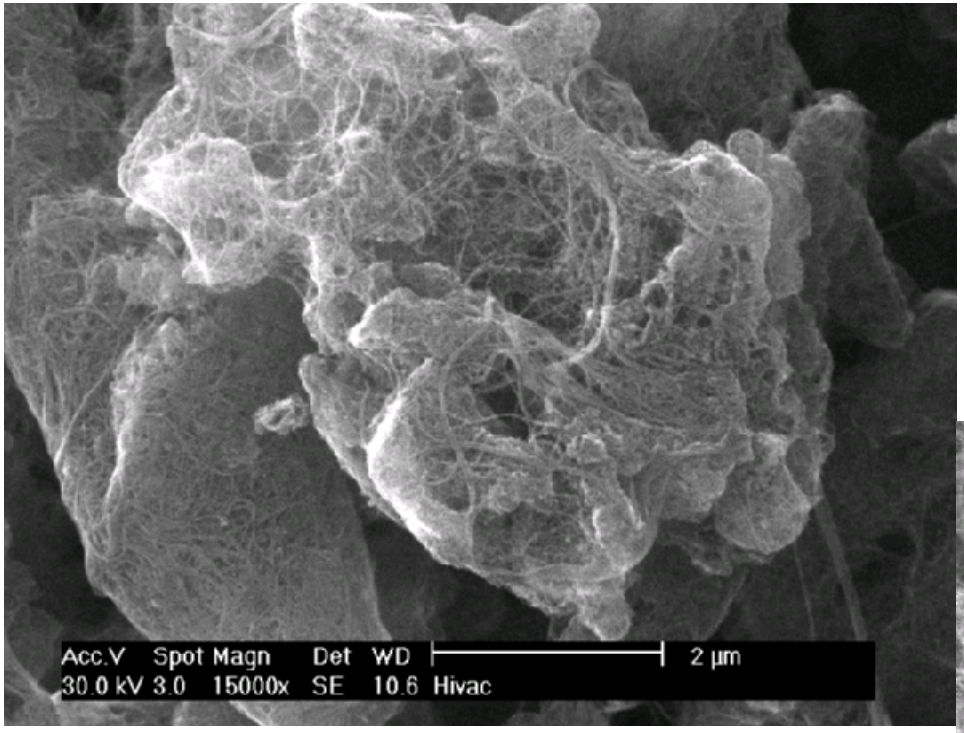
SWNT Fluff from Smalley

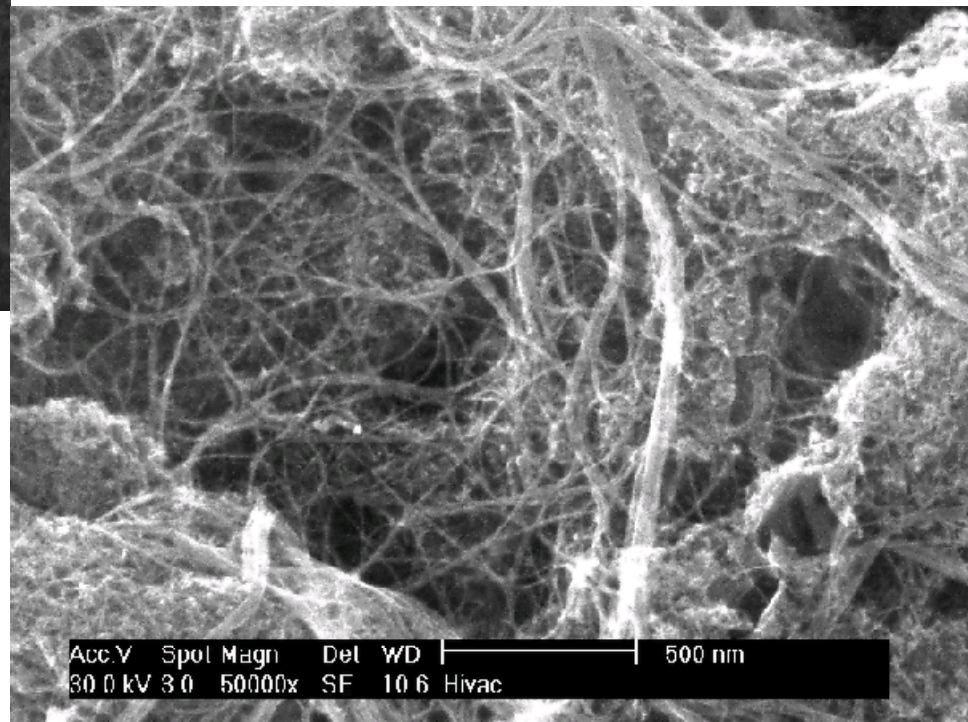




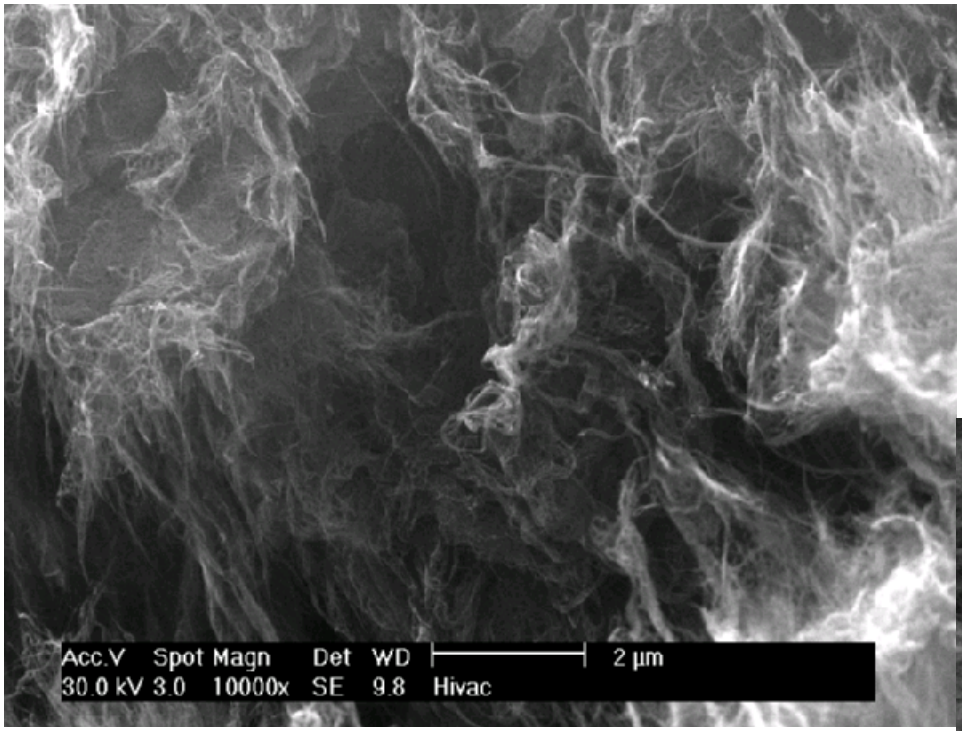
A Figure of a TEM micrograph of HiPco SWNTs. The ropes are relatively small and there is 7.2 wt.% metal impurities dispersed with the nanotubes.

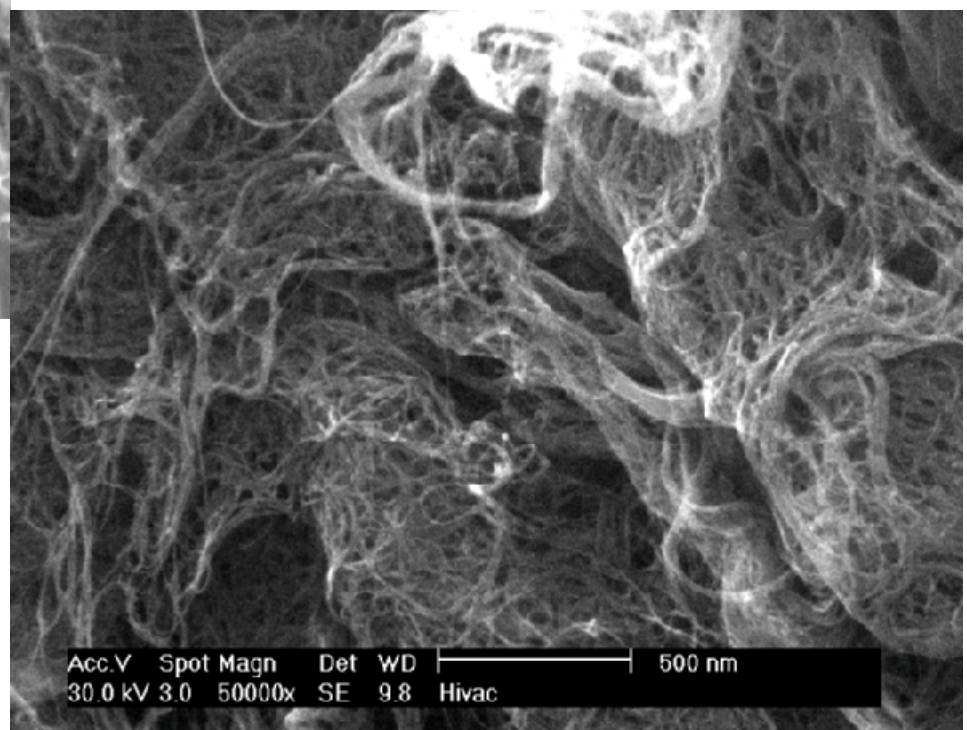
SWNT Powder from CNI





SWNT Pearls from CNI

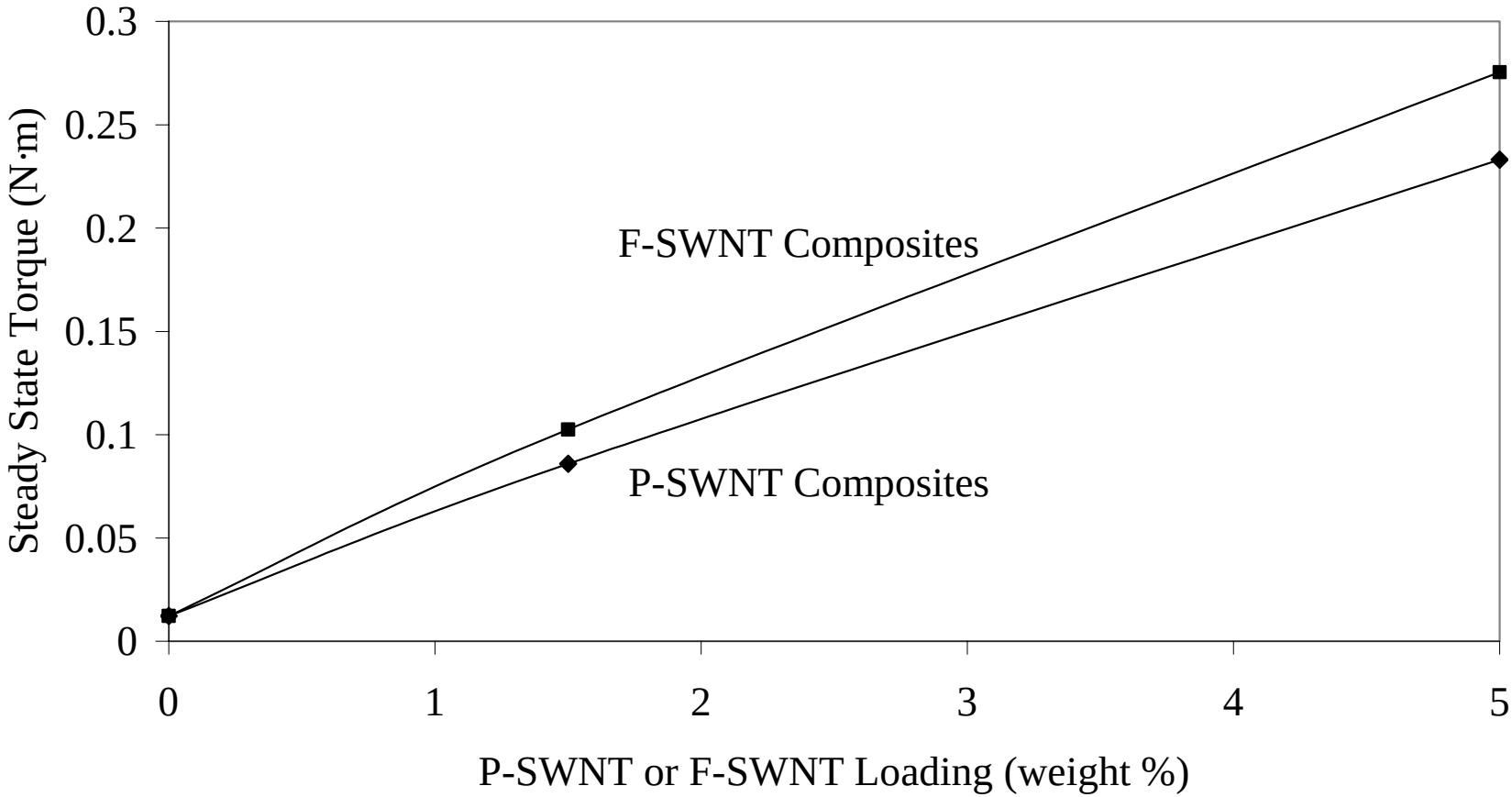




Methodologies for Creating Nanotube Composites

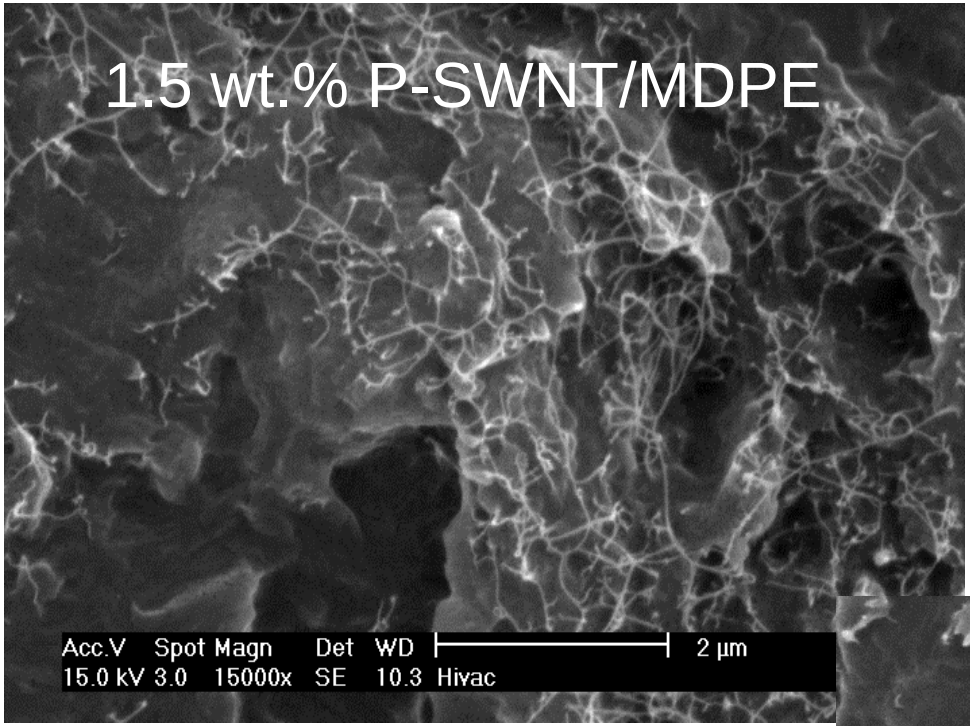
Column 1	Column 2	Column 3	Column 4
Starting nanotubes	Dispersion	Interface	Alignment
As-received	**Spreading**	**Polymer selection**	**High shear mixing**
Purified	Bench mixing	**Tangle reduction**	Extrusion
Functionalized	Homogenization	Dispersion	Elongational flow
Substrate grown	Sonication	**Alignment**	Fiber spinning
Dry aggregate	High shear	**Unroping**	Magnets
Pearls	Stretching/Drying	Purification	Stretching/Drying
Powder	Ball milling	**Unwrapping**	Dip/Spin coating
In water	Polymerization	**Polymerization**	Gel/Wet spinning
In solvents	In situ	**In situ**	SFF
Wrapped	Incipient wetting	**Stabilizing for T**	Tape casting
Masterbatched	Extrusion	Functionalization	Substrate grown

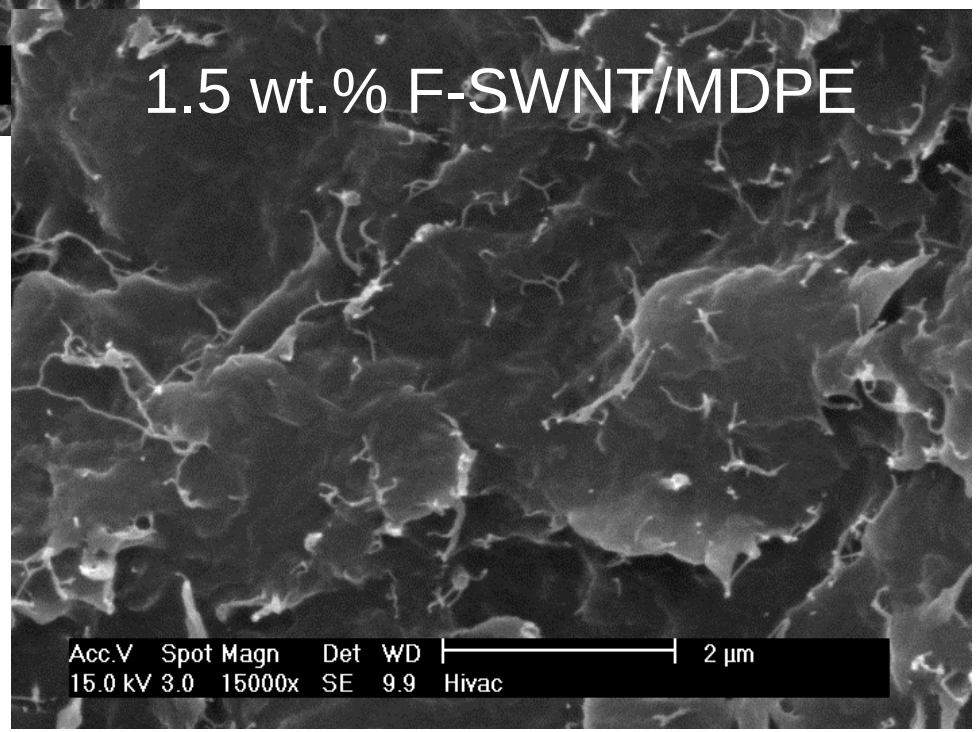
High Shear Mixing: Functionalization Study



Greater torque increases observed with the same concentration of F-SWNTs

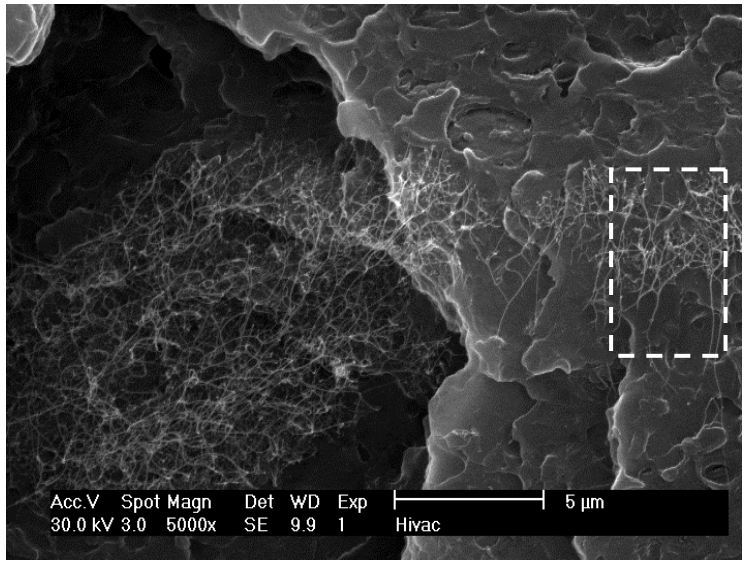
P-SWNT vs. F-SWNT Dispersion



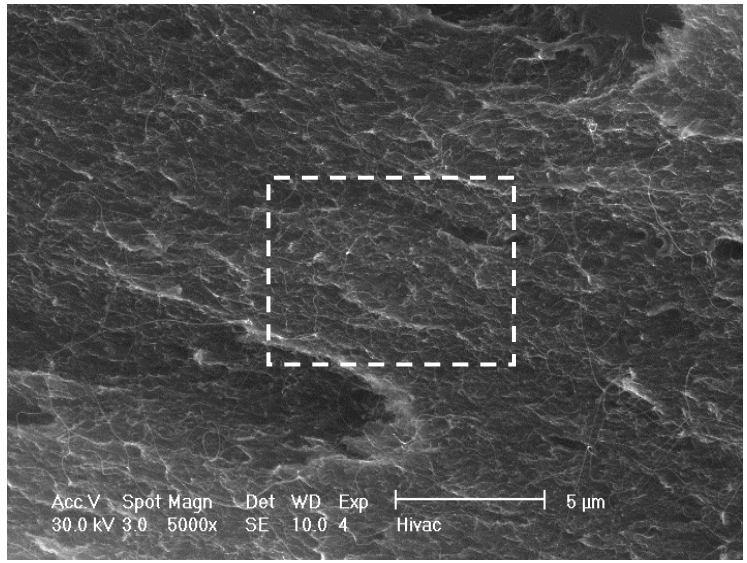


F-SWNTs dispersed more evenly at the same processing conditions as compared to P-SWNTs

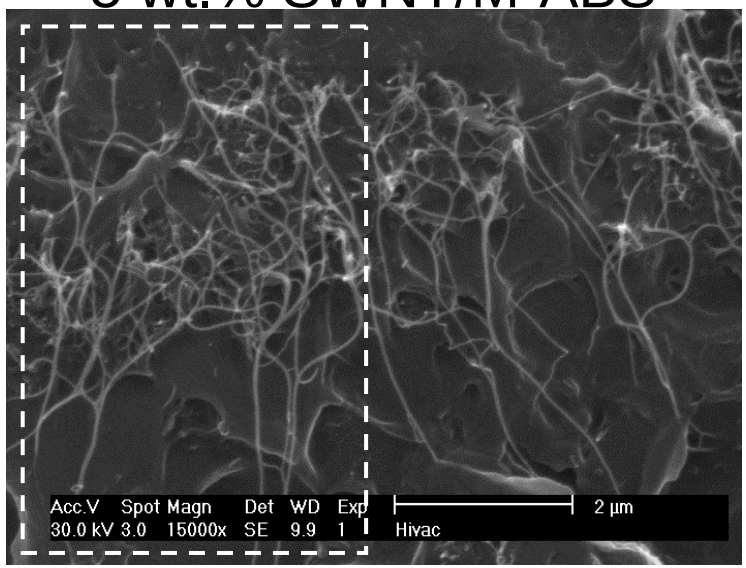
SWNT Dispersion

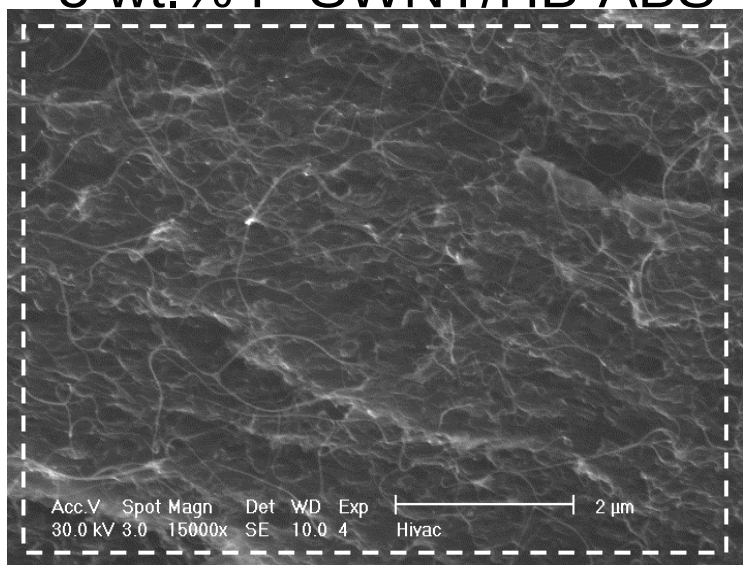


5 wt.% SWNT/M-ABS



5 wt.% P-SWNT/HB-ABS





Choices for Producing Nanotube Composites

Column 1	Column 2	Column 3	Column 4
Starting nanotubes	**Dispersion**	**Interface**	**Alignment**
As-received	**Spreading**	**Polymer selection**	**High shear mixing**
Purified	**Bench mixing**	**Tangle reduction**	**Extrusion**
Functionalized	**Homogenization**	**Dispersion**	**Elongational flow**
Substrate grown	**Sonication**	**Alignment**	**Fiber spinning**
Dry aggregate	**High shear**	**Unroping**	**Magnetic fields**
Pearls	**Stretching/Drying**	**Purification**	**Stretching/Drying**
Powder	**Ball milling**	**Unwrapping**	**Dip/Spin coating**
In water	**Polymerization**	**Polymerization**	**Gel/Wet spinning**
In solvents	**In situ**	**In situ**	**SFF**
Wrapped	**Incipient wetting**	**Stabilizing for T**	**Tape casting**
Masterbatched	**Extrusion**	**Functionalization**	**Substrate grown**

The Green highlighted choices show a path for an Epoxy composite

Challenges to Development of Nanotubes Composites

- Very low solubility in most organic solvents like acetone, toluene, chloroform, dichloromethane, dichlorobenzene, DMF, THF, etc (typically < 1 mg/mL).

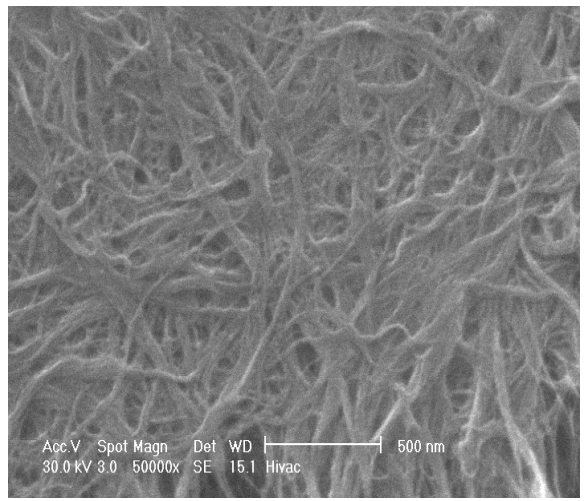
- Typically SWNTs are highly entangled in the form of bundles and ropes

- Poor dispersion in polymer matrices

- Limited interfacial interaction and bonding

- Significant viscosity increases

- Many applications prefer unroped nanotubes that are hard to achieve in a final composite system



Highly entangled roped SWNTs

Strategies for Developing Nanotubes Reinforced Polymeric Composites

Obtaining high dispersion in polymer composites in multistep processes

-Starting nanotube conditions are critical

-Physical approaches – solvents and surfactants, ultrasonication, high shear mixing, homogenization, polymer wrapping

- **Alignment - shear mixing, extrusion, drawing, magnetic**

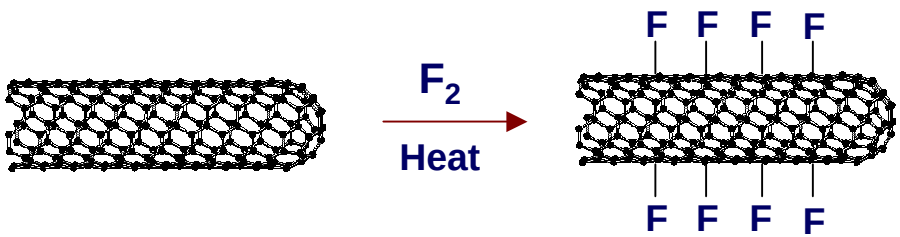
-Chemical approaches - surface modification by functionalization

- **Improving interaction and load transfer by functionalization**

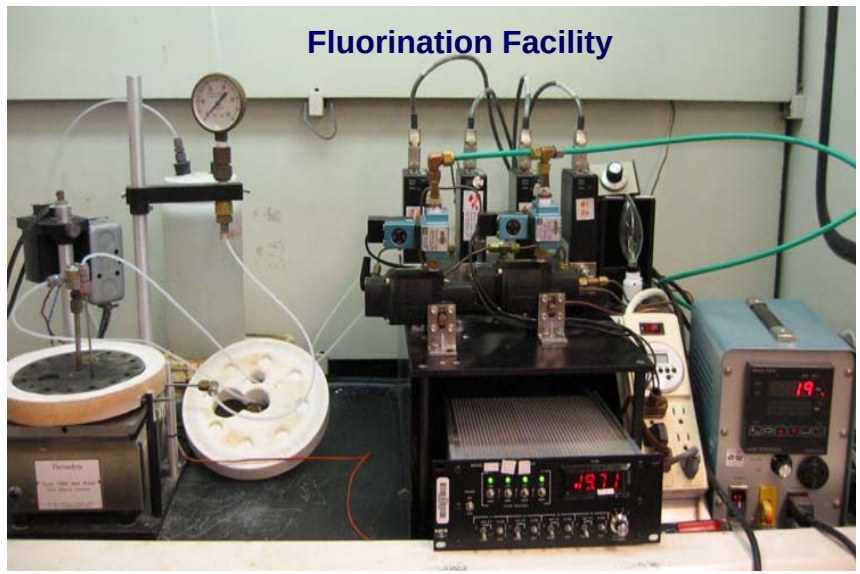
Covalent Chemical Fuctionalization of SWNTs

- Oxidation to produce end functionalization (COOH).
- Covalent bonding via F (Margrave approach)
- C-N, C-C, C-O covalent Bonding (Tour, Billips, Khabashesku)
- Flurotubes as precursors (Barrera)
- Peroxide method (Khabashesku, Billips, Margrave)

Fluorination

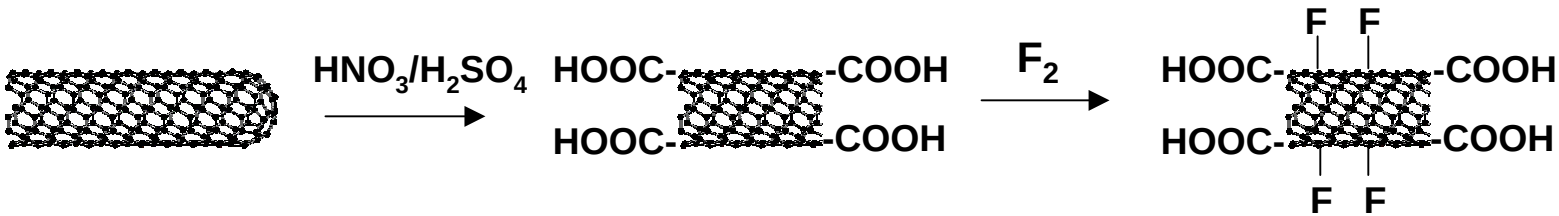


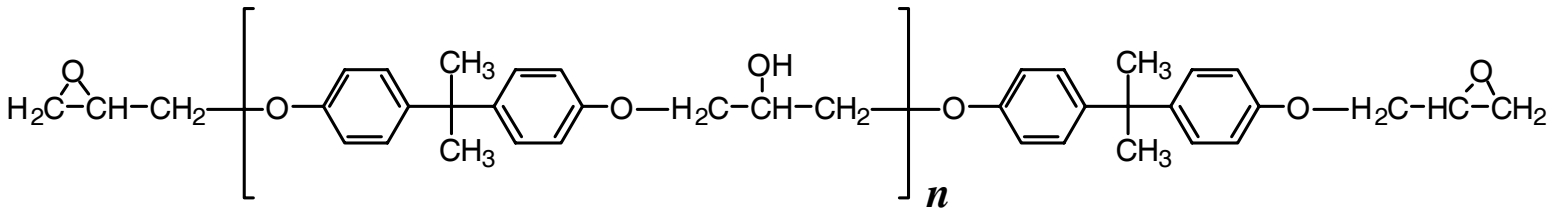
Currently a good intermediate step to achieve unroped unentangled nanotubes

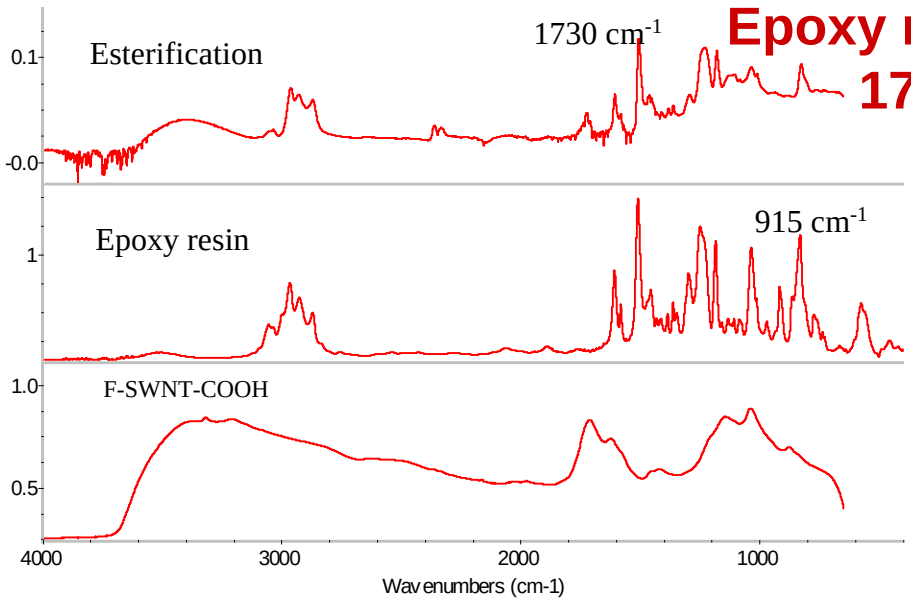


V. N. Khabashesku, Chemistry, Rice University

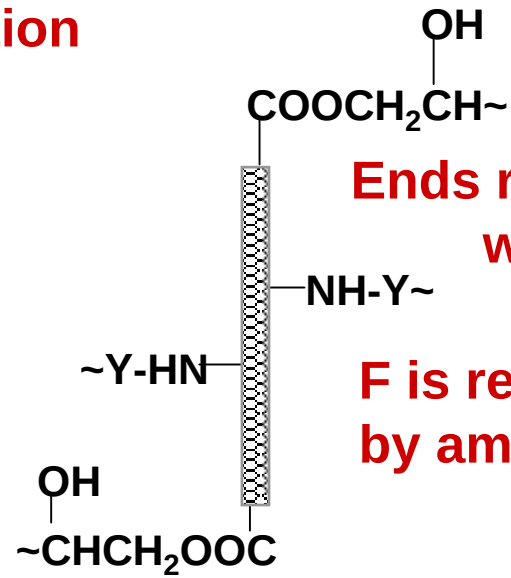
Single-walled Nanotubes/ Epoxy Composites (I)







Epoxy reaction 170C



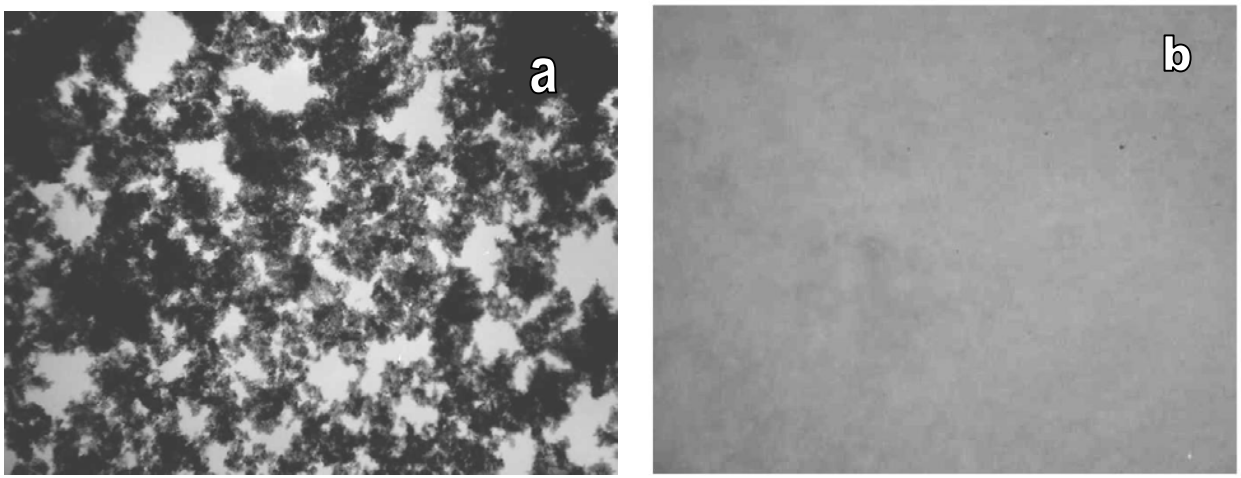
Ends react w/epoxy

F is replaced by amine

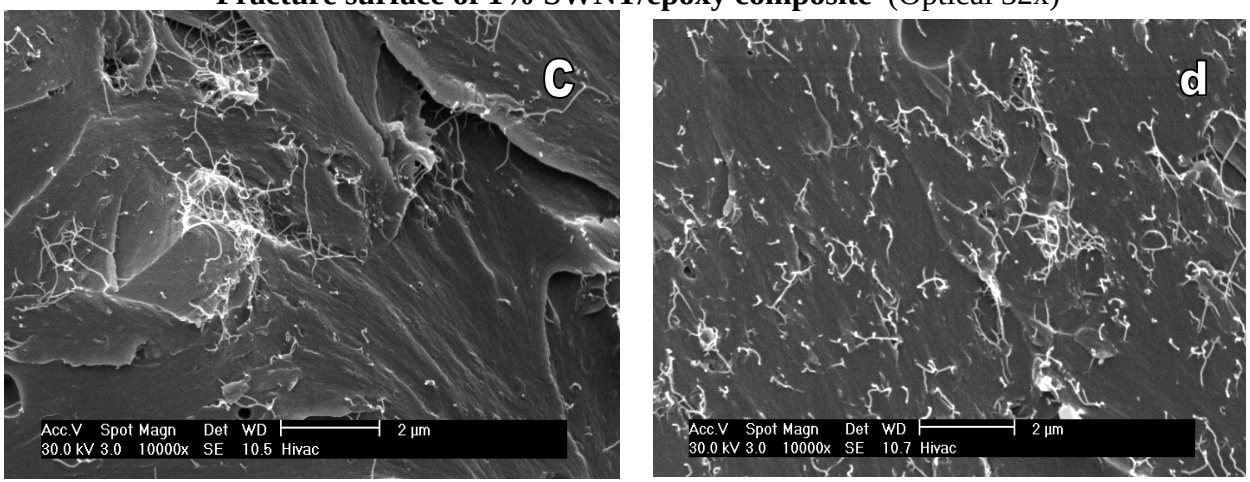
J. Zhu et al.,"Improving the Dispersion and Integration of Single-Walled Carbon Nanotubes in Epoxy Composites Through Functionalization" *NanoLetter*, 2003, Vol. 3. No. 8, 1107-1113

Single-walled Nanotubes/ Epoxy Composites (I)

Dispersion in solvent (DMF)



Fracture surface of 1% SWNT/epoxy composite (Optical 32x)



(a)(c) Buckpearl SWNT

(b)(d) F-SWNT-COOH

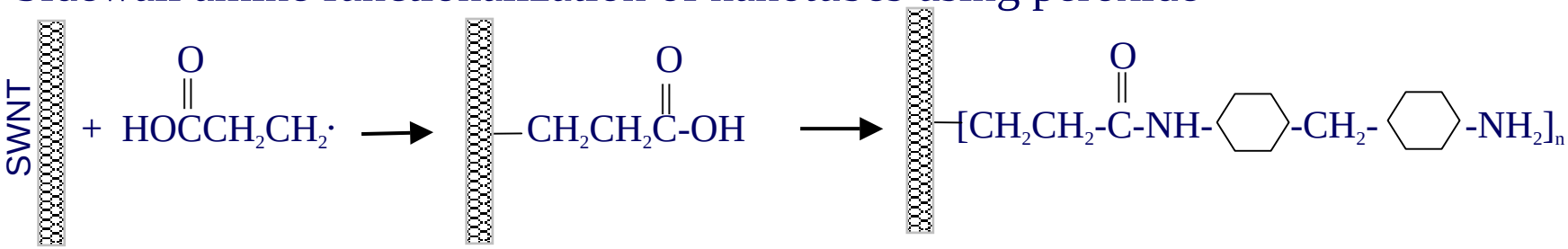
Unfunctionalized roped nanotubes stay heavily agglomerated.

Functionalized nanotubes have smaller to no ropes and can more easily be untangled.

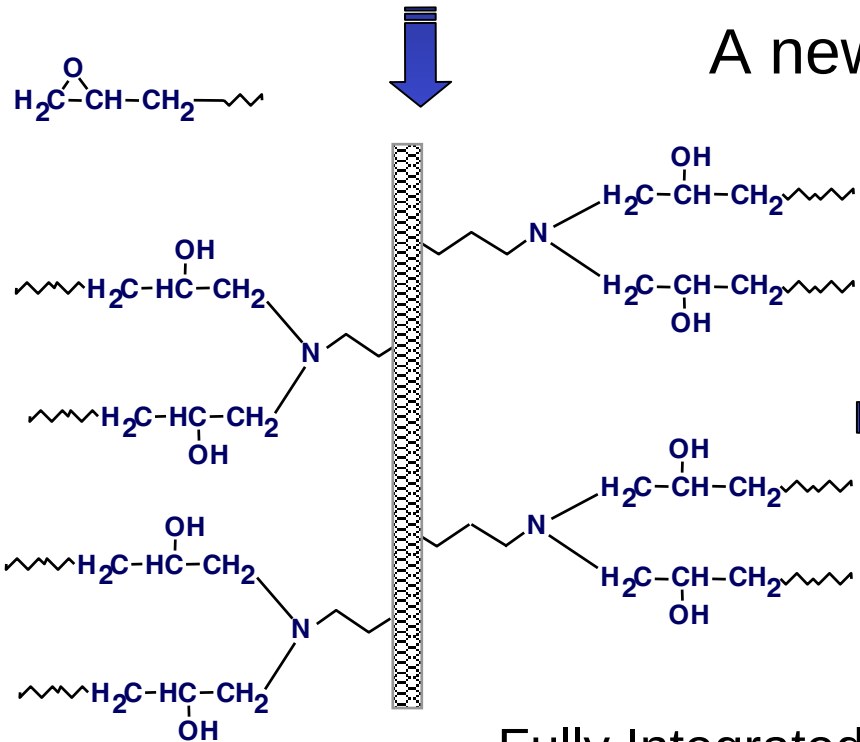
Functionalized nanotubes stay untangled.

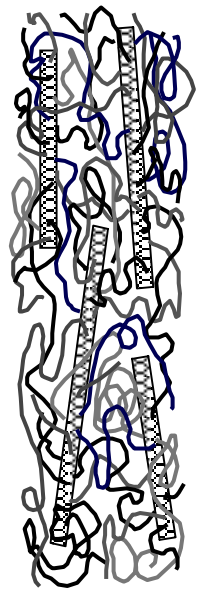
Single-walled Nanotubes/ Epoxy Composites (II)

Sidewall amine functionalization of nanotubes using peroxide



A new curing agent





Nanotubes become Integral to the epoxy.

The epoxy is (reformulated).

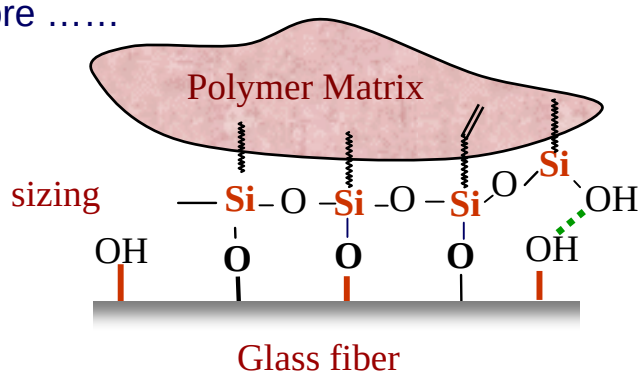
Fully Integrated Nanotube Composite

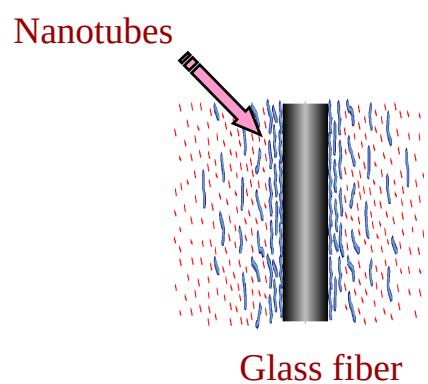
Tailoring the Interface of Vinyl Ester Composites

- Z-axis properties dominated by fiber/matrix interphase (0-100nm)
- Conventional organosilanes are used to size the glass fibers.
- Functionalized nanotubes can be integrated in a number of ways

Polymer	Silanes
Epoxy	amino/epoxy/anhydride functional silanes
Vinyl ester / Polyester	acrylated/methacrylated/vinyl/olefin silane
Polystyrene	acylated/dipodal functional silanes
Polyethylene	amine/vinyl/olefin functional silanes
Polypropylene	acrylate/azide/vinyl/olefin functional silanes

And many more ……

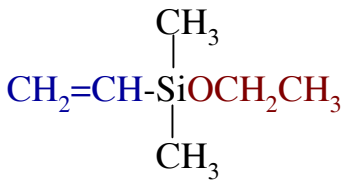




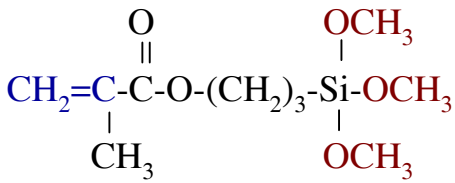
- Bond in matrix
- Bond to fibers
- Functionally grade the fiber/matrix interface

Tailoring the Interface with Organosilane

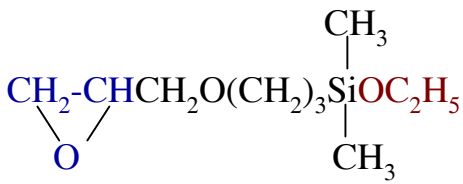
Vinyldimethylethoxysilane



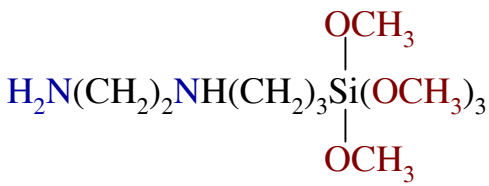
Methacryloxypropyltrimethoxysilane



(3-Glycidoxypropyl)dimethoxylethoxy-silane



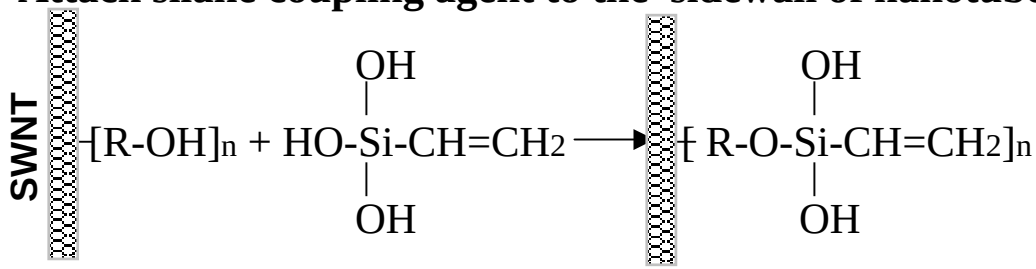
N-(2-Aminoethyl)-3-Aminopropyltrimethoxysilane



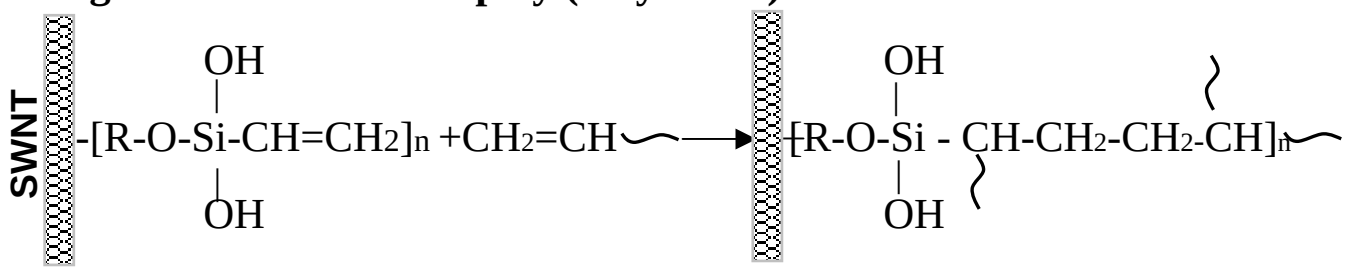
- We have silane functionalized nanotubes
- We have attached to glass fibers
- We have removed silane from glass fibers and resized with silano-SWNTs
- We are working on a functionally graded silano matrix/fiber interface

Sidewall Functionalization of Nanotubes Using Organosilane

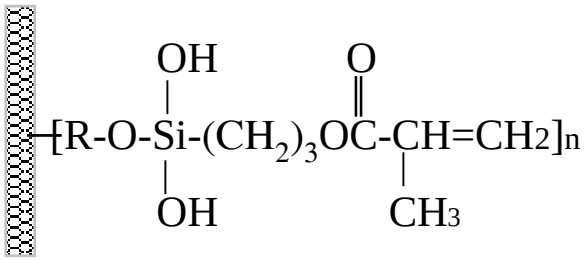
- **Attach silane coupling agent to the sidewall of nanotubes**

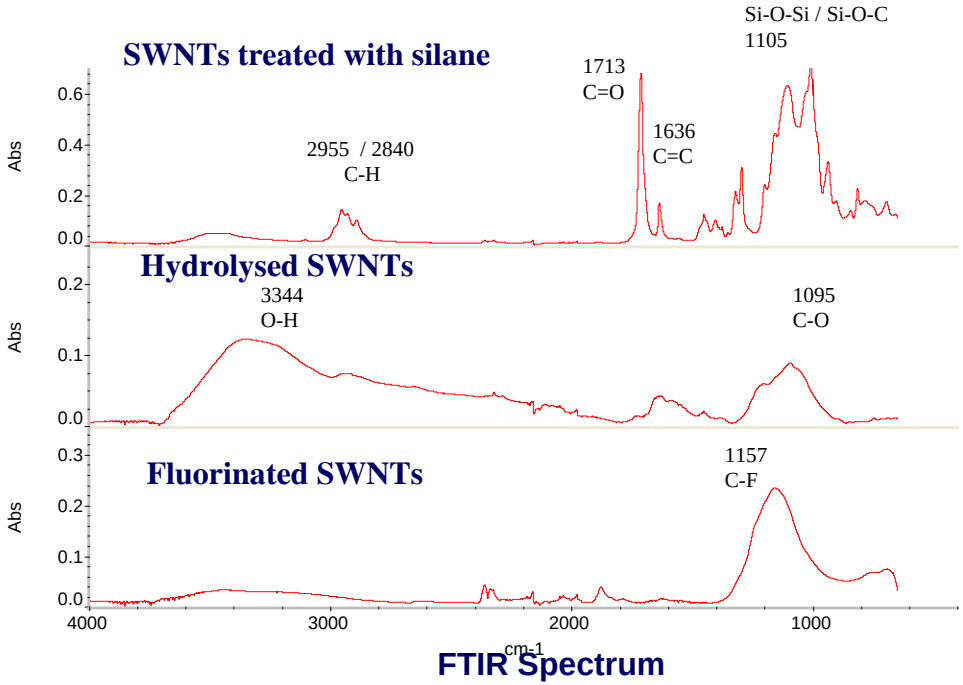


- **Integrate nanotubes into poly (vinyl ester) resin**

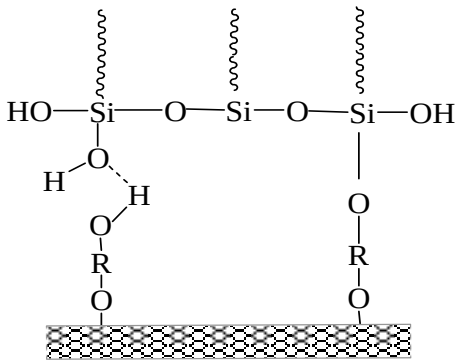


Sidewall Functionalization of Nanotubes Using Organosilane

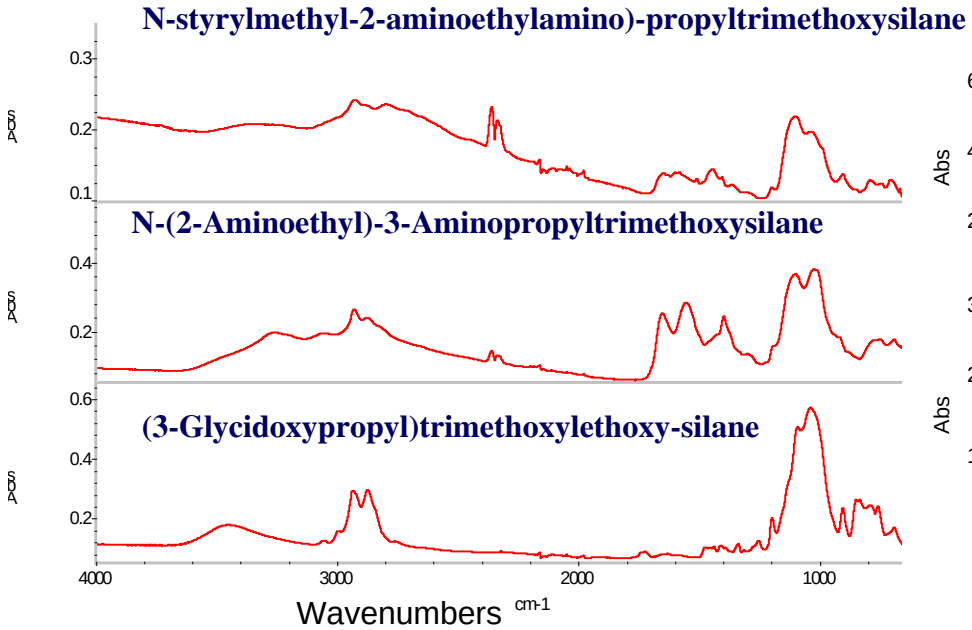




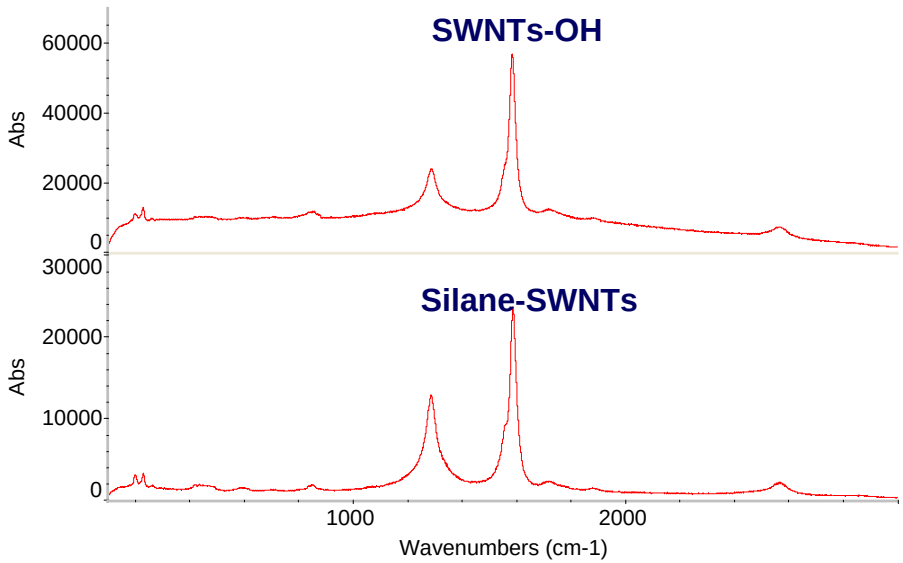
FTIR Spectrum



FTIR and Raman Characterization of Functionalized SWNTs



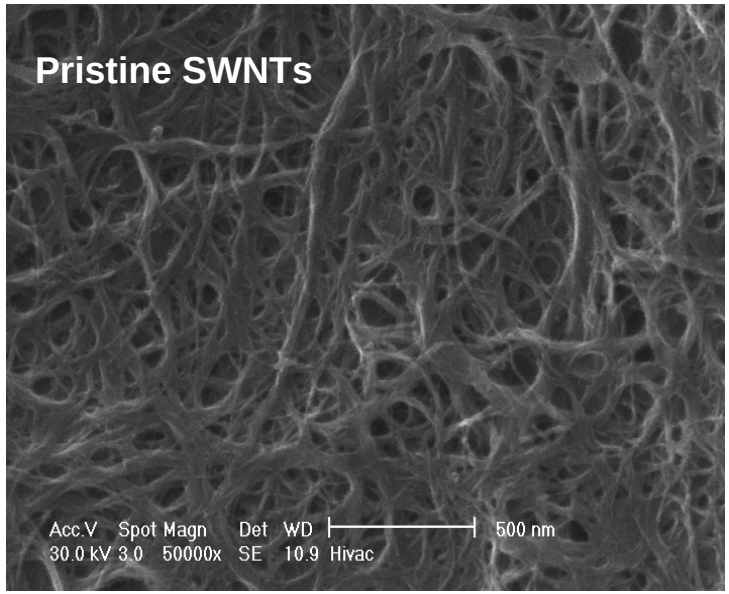
IR spectrum of several Silane-SWNTs

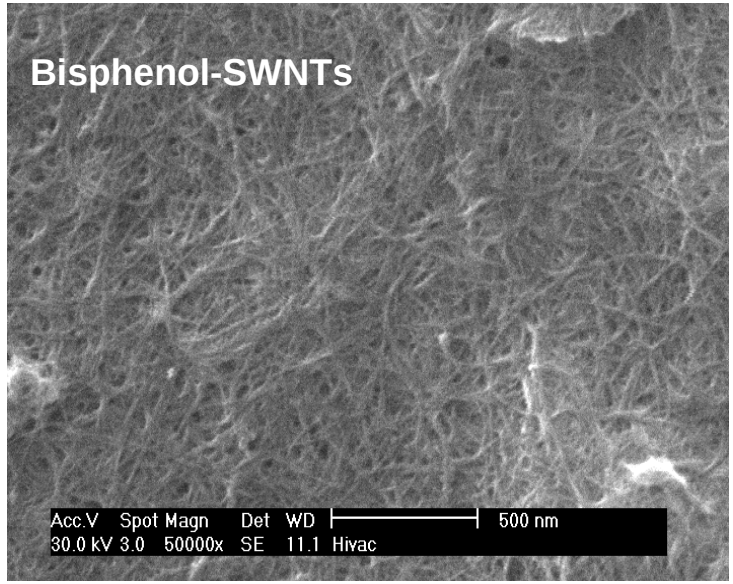


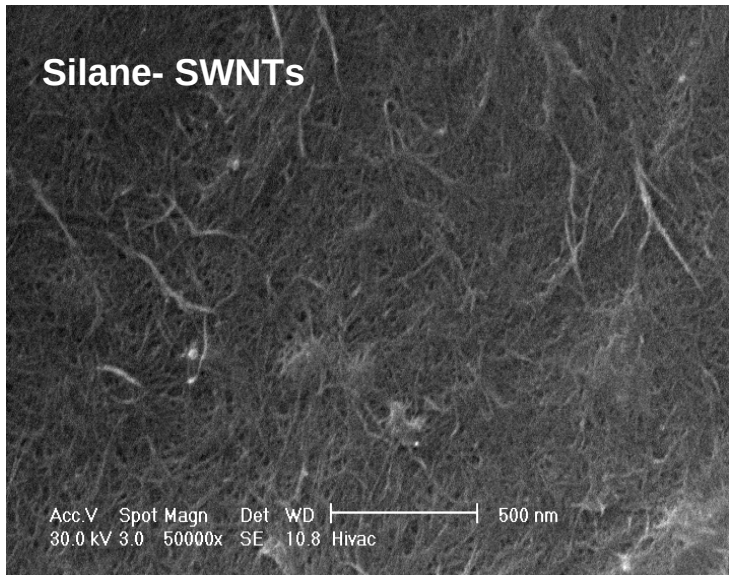
Raman Spectrum

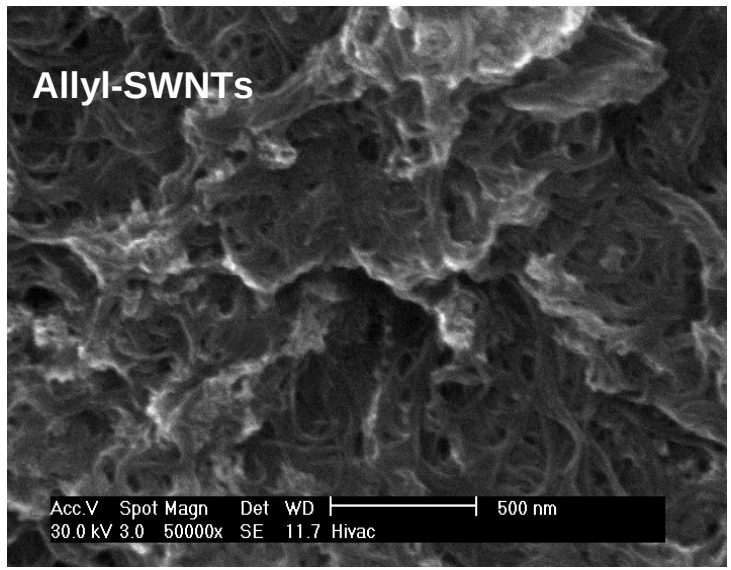
IR, Raman, TEM, TGA, uv-Vis as characterization methods

SEM Characterization of SWNTs

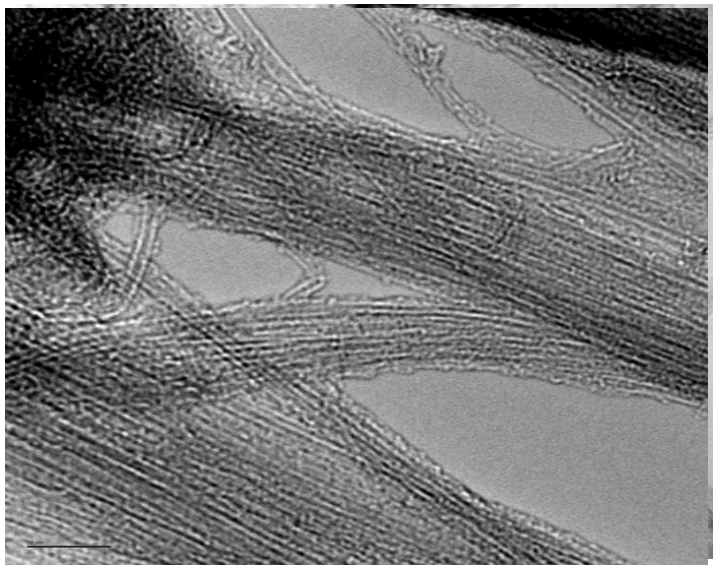


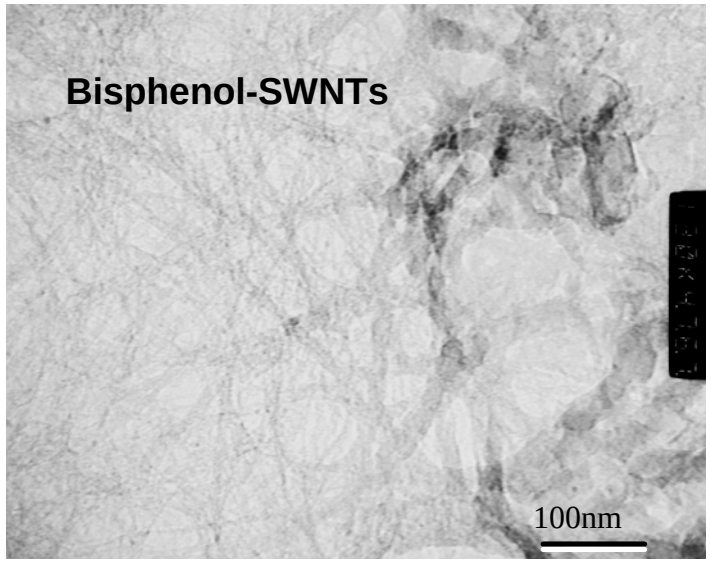


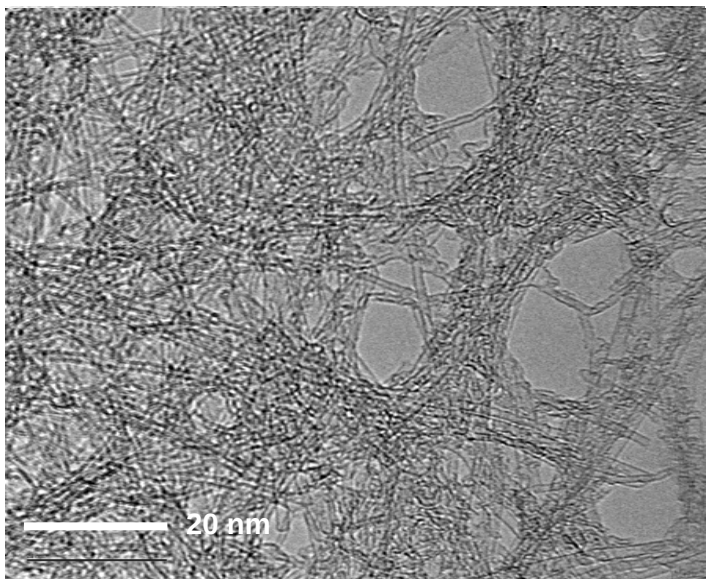


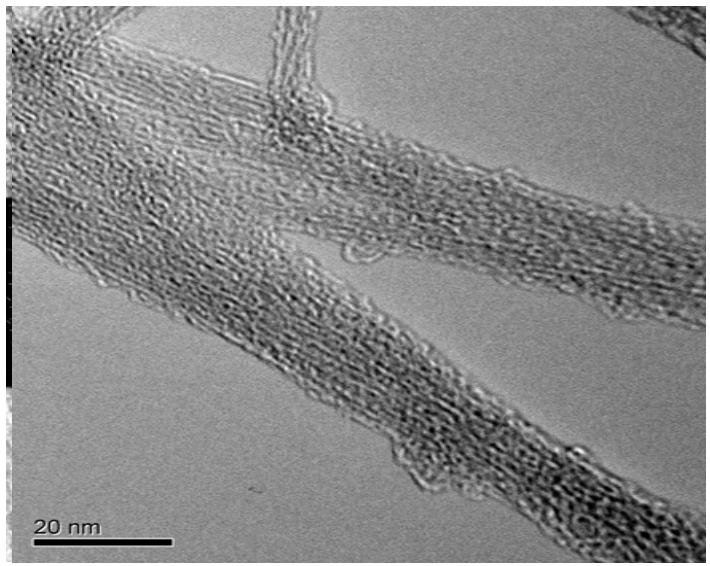


TEM Characterization of SWNTs









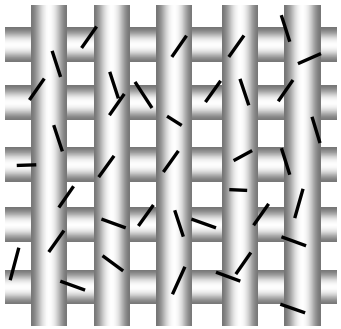
Pathway: Key Steps for an Epoxy Composite (Matrix Enhancement)

- Select purified nanotubes in best starting condition (pearls)
- Oxidation to cut and open entangled form
- Fluorinate to achieve unroped and smaller rope forms
- Amino functionalize to remove fluorine and to produce reactive unroped and unentangled nanotubes (nanotubes stay unroped)
- Integrate in epoxy using solvents, sonication, etc.
- Solvent removal (limit bubble formation)
- Process into parts with consideration to viscosity changes

Results: Compared to unfunctionalized nanotubes the F-SWNTs provide higher dispersion and less entanglement

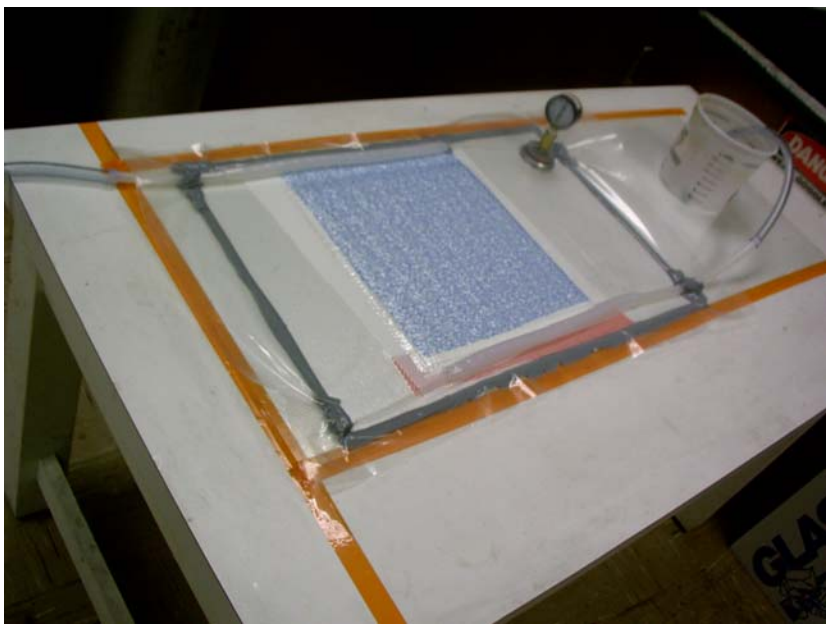
Concerns: Solvent insertion is not ideal so use incipient wetting.

Fabrication of Nanotube Reinforced Composites by VARTM (Vacuum-Assisted Resin Transfer Molding) Processing

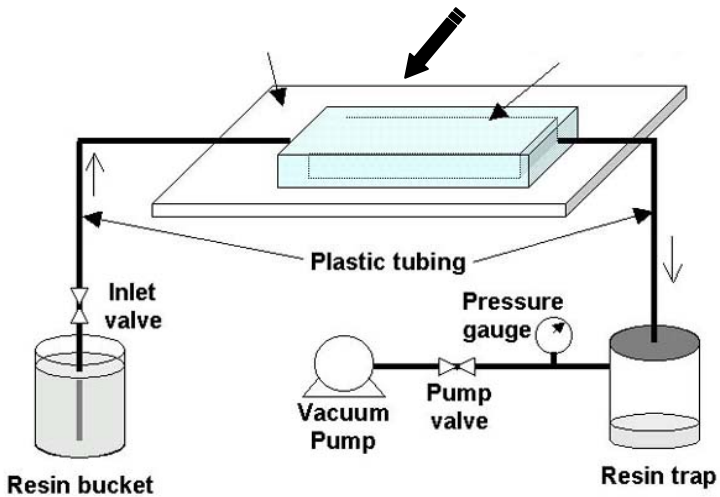


Functionalized nanotubes will bridge the matrix and glass fiber via multiple functional groups

- Vacuum bagging
- Tacky tape - vacuum seal
- Release film
- Disperse film
- Wrap pipes - Inlets/Outlet
- Woven fibers
- Mold

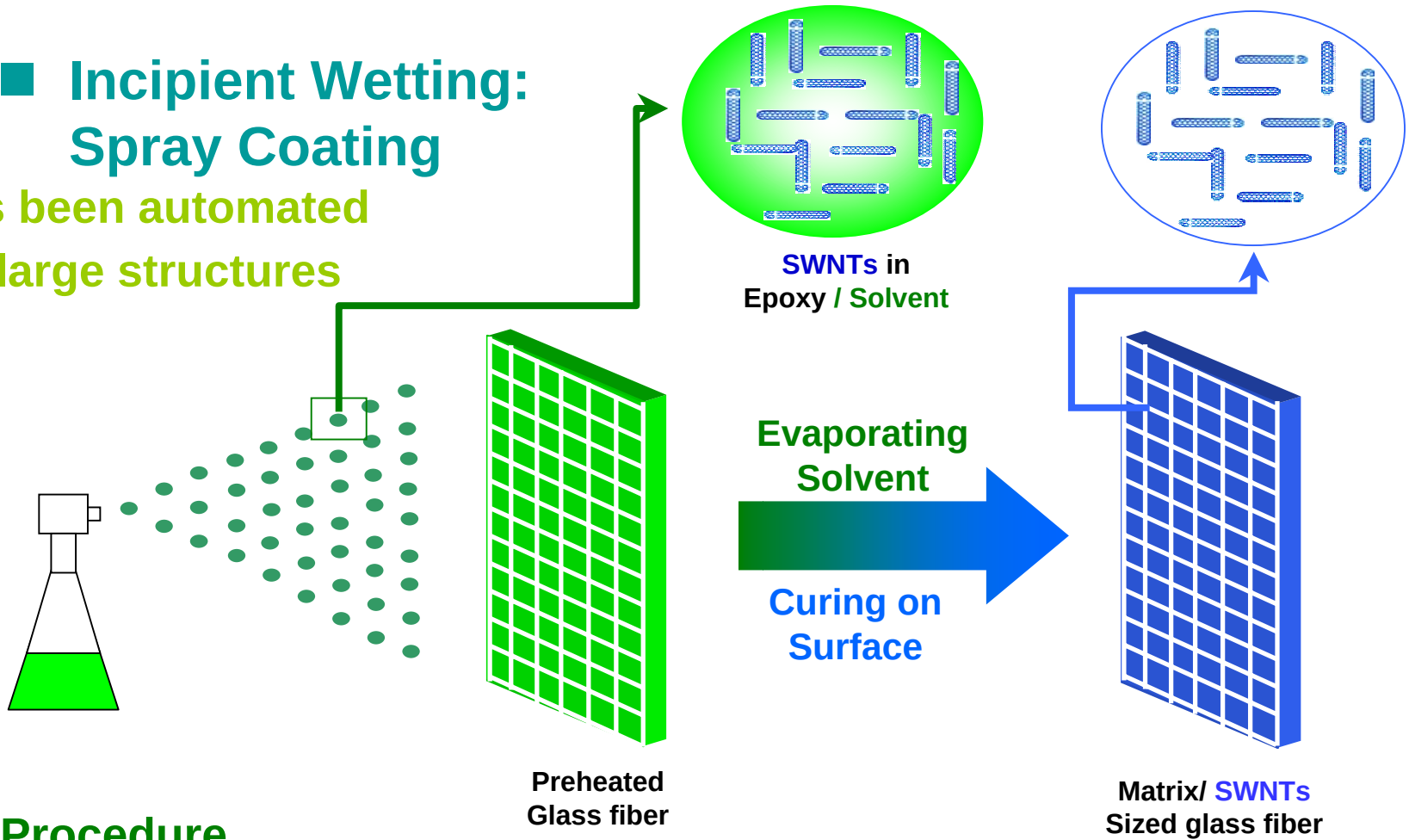


Vacuum bagging lay up



SWNTs Sized Glass Fibers

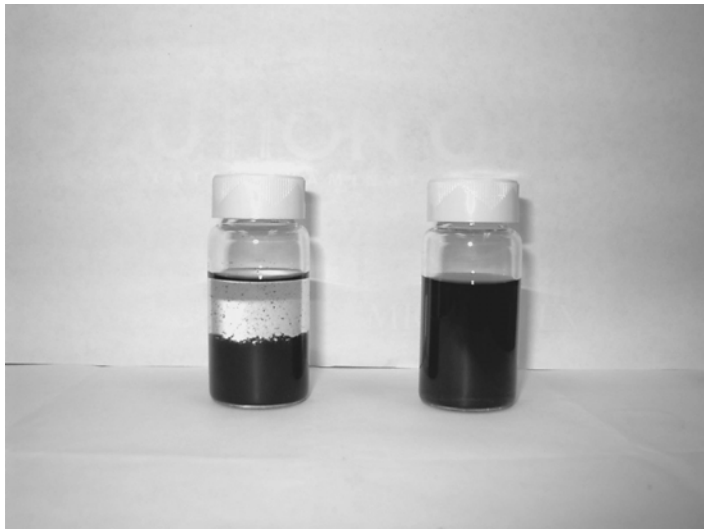
- **Incipient Wetting: Spray Coating**
- **Has been automated for large structures**



- **Procedure**
  1. **Solvent / SWNTs / Matrix.**
  2. **Spray on Fiber Reinforcements.**
  3. **Immediate Curing Epoxy with SWNTs & Solvent at one time.**

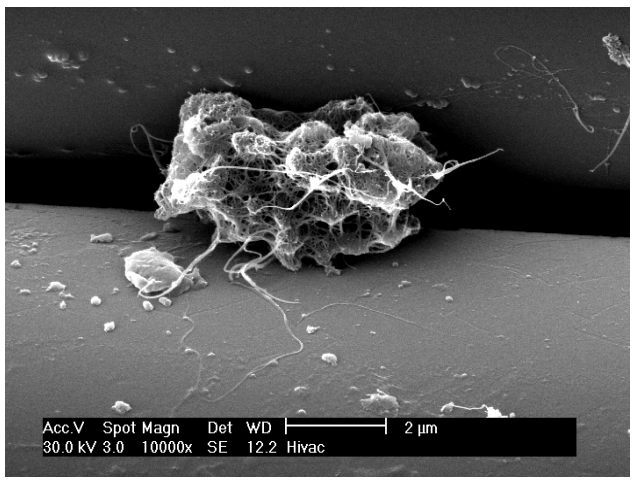
Making Fiberglass Reinforced Vinyl Ester Composite with Highly Dispersed Nanotubes

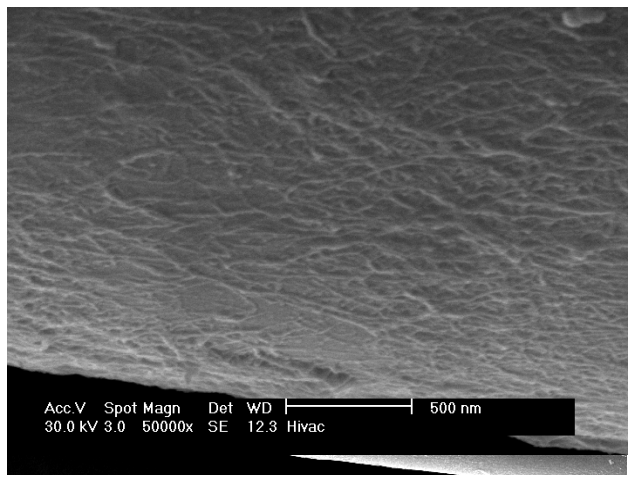
P-SWNTs



F-SWNTs

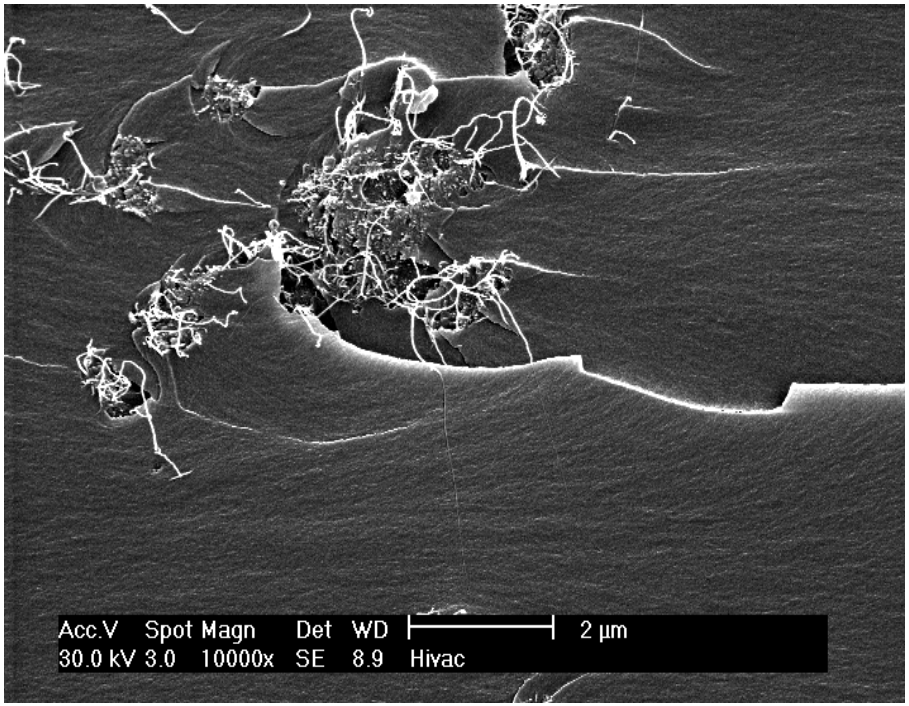
P- and F- nanotube dispersion in alcohol solvent





Glass fiber weave overcoated with pristine and Functionalized nanotube

Fracture Surface of SWNTs/Vinyl Ester Composites

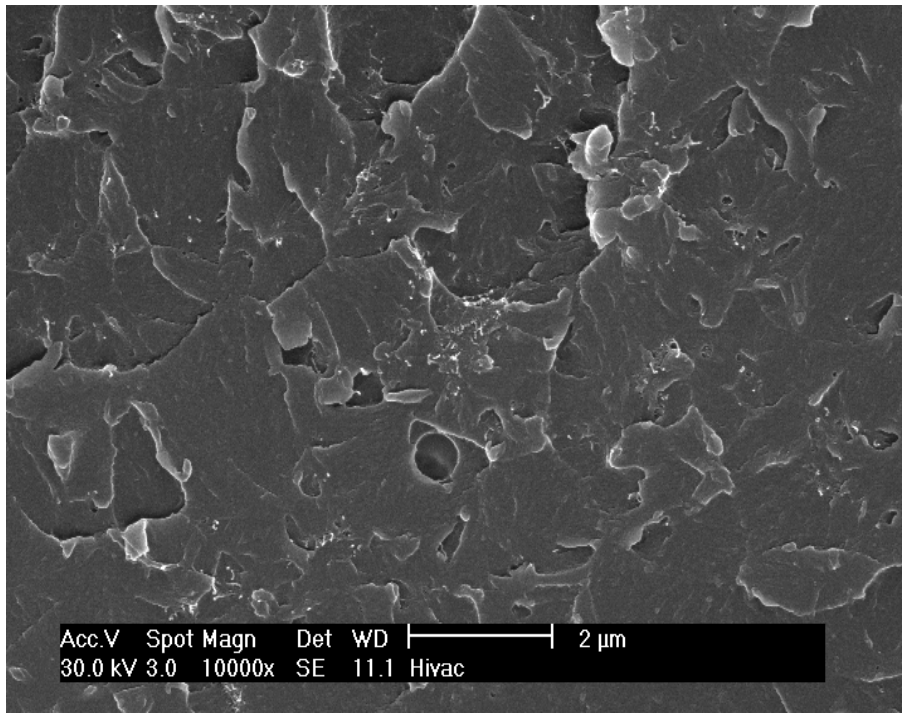


1wt% pristine SWNTs

- With P-SWNTs dispersion is poor and shows agglomerates

- With silano-SWNTs the nanotubes are well dispersed and unentangled
- Not easily seen since highly unroped

1wt% Functionalized SWNTs



Multi-functional Nanocomposite Materials with High Temperature Polymer Resin Matrices

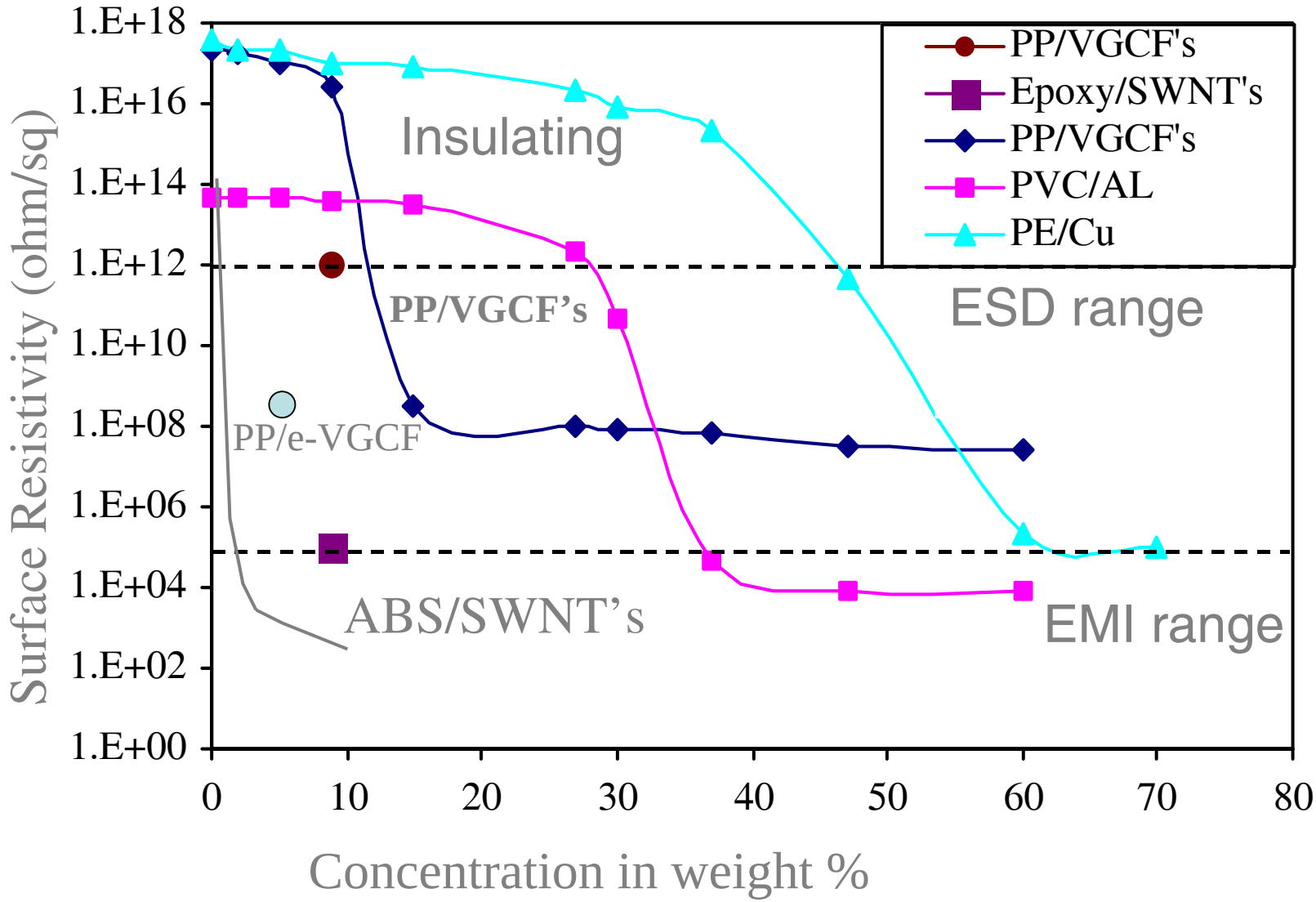
Carbon Fiber/ Bismaleimide (BMI) Composite with Nanotubes

- Elevated temperature VARTM
  - Infusion between 200-230°F, cured at 350°F for 6 hrs, post-cure at 440°F for 6 hrs
  - Specimens fabricated for tensile, SBS and DCB
    - 8 layer samples for tensile
    - 16 layers for DCB and SBS

VARTM with nanotubes in the resin (achieved 8-9 layer samples
VARTM with incipient wetting of nanotubes (no layer limit)

14 orders of magnitude
Change in electrical resistivity

Impurities influence network formation, the percolation threshold, and the electrical conduction



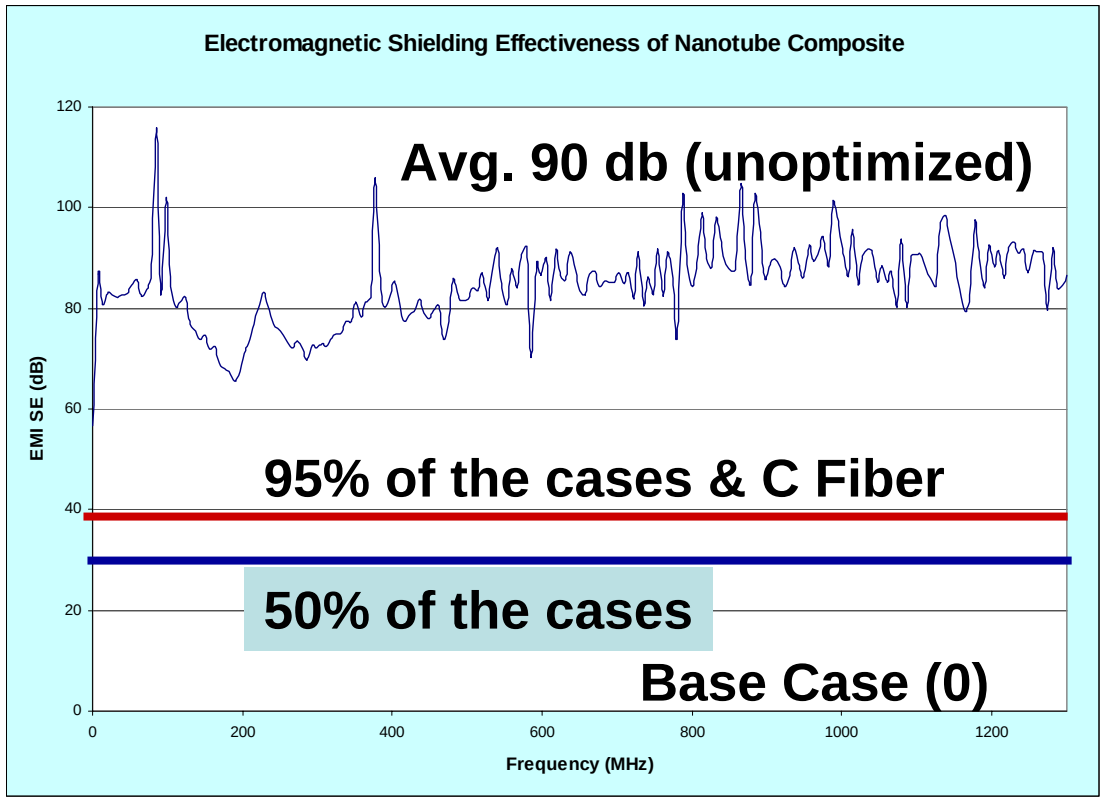
SOME EMI RELATED RESULTS

<u>Mechanisms for EMI attenuation</u>:
Reflection, absorption, and multiple reflection.

$$SE = 50 + 10\log_{10}(\rho \cdot f)^{-1} + 1.7t(f/\rho)^{1/2}$$

SE of nanotube reinforced polymer composite with a volume resistivity of 10^10 ohm.cm

SE of 10 = 90% of signal is blocked
20 = 99%
Automotive and computer industries agree that a reduction of signal strength by 30 dB is adequate in 50% of the cases,
and 40 dB fulfills 95% of their requirements



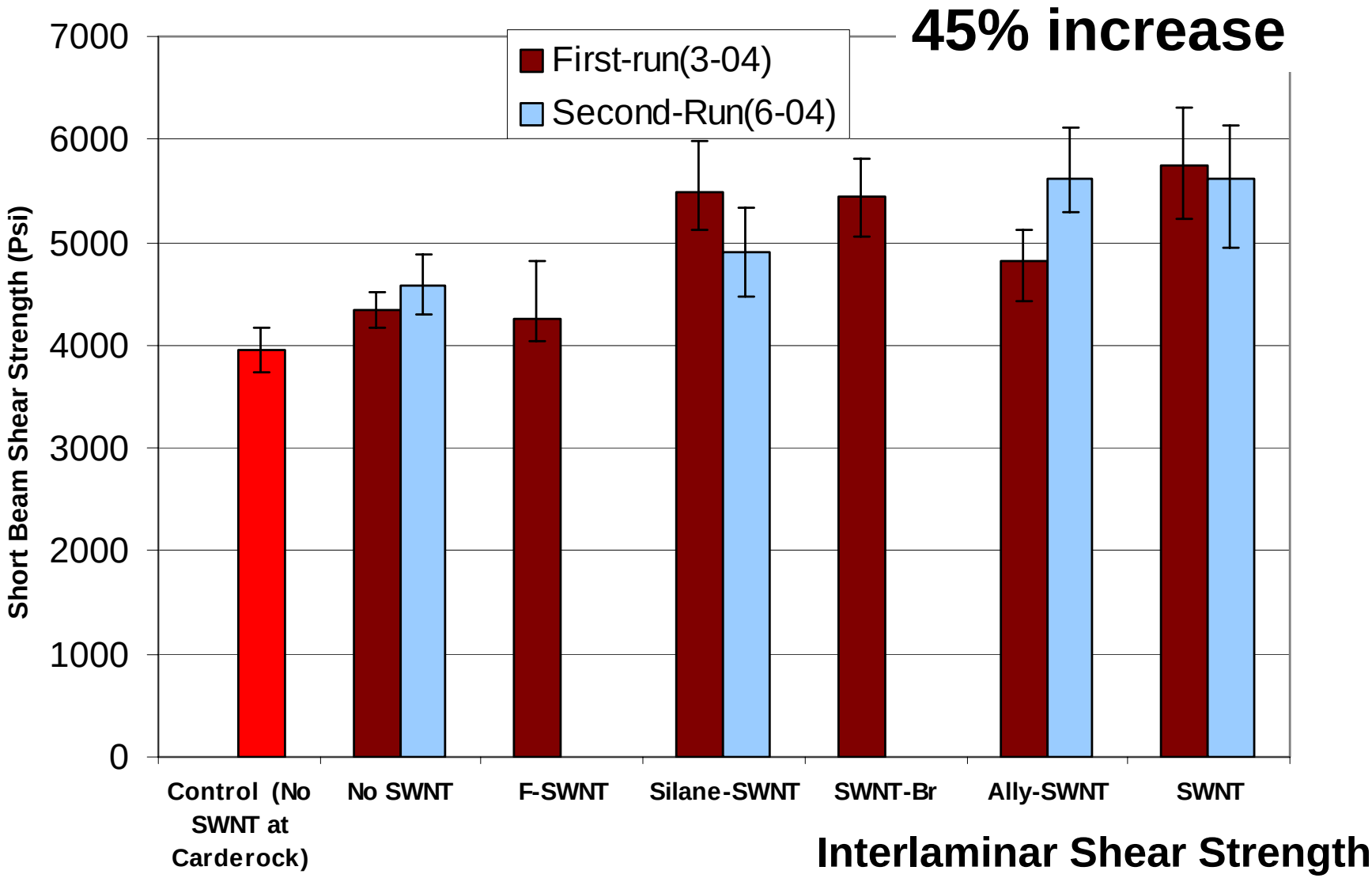
Simon RM, EMI shielding through conductive plastics, Polym.-Plast. Technol. Eng 1981; 17(1):1-10.

Pathway: Key Steps for an Vinyl Ester Composite Z-axis Mechanical Enhancement of a Laminate Structure

- Select purified nanotubes in best starting condition (pearls)
- Oxidation to cut and open entangled form
- Fluorinate to achieve unroped and smaller rope forms
- Silano-functionalize to remove fluorine and to produce reactive unroped and unentangled nanotubes
- Incipient wet on glass fiber plys using controlled spraying
- Vacuum assisted resin transfer molding of a laminate structure
- Use the nanotubes in prescribed locations for property enhancement

- Results: Small nanotube concentrations (0.025 wt.%) show very good enhancements.

Short Beam Shear Strength of Nanotube/Fiberglass Composite



Rice Functionalization Team

James Tour, Director
Enrique Barrera, Co-Director
Valery Khabashesku, Co-Director

Goal: Advance the state of the art of nanotube functionalization and achieve a versatile array of functionalizations for materials advancement.

Nanotube Functionalization Initiative--Workin

				Focus Areas		
Synthesis	**Separation**	**Theory**	**NanoFluids**	**Composites**	**Fibers**	**Bio/Pharm**
bundles	metallics vs. semiconducting	mixing	viscosity modifiers	elastomers	neat	bone/tissue
individuals	-en route to cloning	rheology	heat transfer fluids	epoxies	fiber blends (PBO)	drug delivery
sidewall func.		func/defunc. thermodynamics	lubricants/greases	thermoplastics	thermoplastic blends (PP)	fluorescent markers
end cap func.		nanotribology	high performance additives	ceramics	fiber sizing on glass and carbon fibers	radiolabeled drugs
covalent func.				metals	TWARN/Kevlar	thermoablative (microwave)
noncovalent func.						

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E. Billips, Chemistry
R. Hauge, Chemistry
Valery Khabashesku, Chemistry
M. Pasquali, Chem Engineering
R. Smalley, Chemistry
J. Tour, Chemistry

Bio/Pharm	In Situ Func./Defunc.	Outgrowth	Environmental	Education
bone/tissue	profunctional-ization	design tools	CBEN tie-in	NanoKids tie-in
drug delivery	time release	expert systems	environmental fate	Nano Engineering
fluorescent markers	pressure	master batching	recovery and recycling of nanotubes	Materials Magic
radiolabeled drugs	thermal	drop off technology		
thermoablative (microwave)	radiation (microwave)	enabling platform		
	electron beam processing			

Summary

- A number of nanotube functionalizations have been developed for epoxies and vinyl ester composites. Some are very general.
- Functionalization leads to enhanced dispersion and mechanical properties. Single unroped nanotubes are achieved.
- Incipient wetting leads to good dispersion and can be processed for matrix, matrix/fiber property enhancement. Functionally graded interfaces are possible.
- Mechanical enhancement of polymer composites is demonstrated using functionalized nanotubes and VARTM.
- Multifunctional nanocomposites combine various types of nanotubes with conventional fiber systems for near term use.

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