Metallized Nanotube Polymer Composite (MNPC)

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Materials Research Society, Boston, MA
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Outline

- Motivation
- Approach
- SWCNT-Polymer Composites
- MNPC
- Morphology
- Physical properties
- Summary

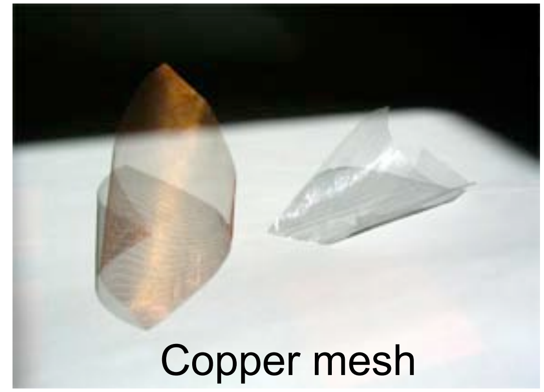
Motivation

Why Nanomaterials in Aerospace Vehicles?

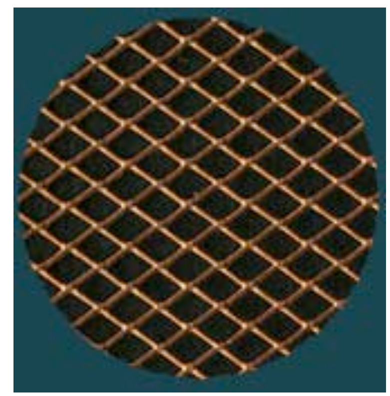
$$\text{Aircraft Range} = \frac{\text{Velocity}}{\text{TSFC}}\left(\frac{\text{Lift}}{\text{Drag}}\right)\ln\left(1 + \frac{W_{fuel}}{W_{PL} + W_{O}}\right)$$

- Engine Fuel Consumption
- Aerodynamics
- Empty Weight

Astrostrike



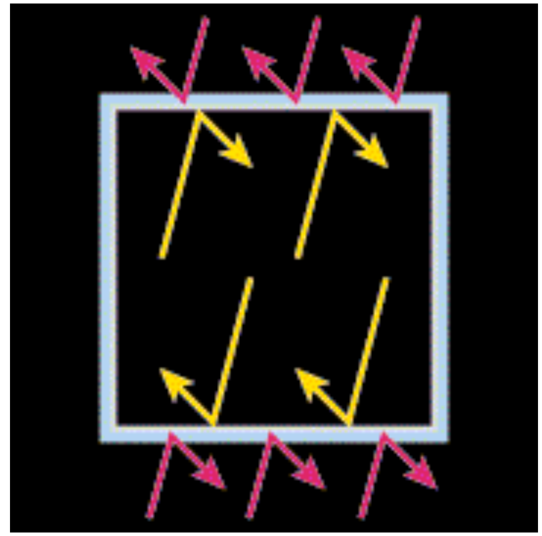
Copper mesh



- Lightweight, multifunctional composite aerospace vehicles
- Lack of Electromagnetic effect (EME) shielding: Lightning, EMI…
- Current methods include flame spraying of conductive coatings, use of conductive paints, woven wire fabrics, metallized cloth or fibers, conductive foils and interwoven wire in carbon fibers, copper mesh…

Copper's density is 8.9 g/cm^3 and CNT's is around 1.3 g/cm^3

Electromagnetic Interference (EMI) Shielding



Metal coating (electroplating…)
Poor adhesion and wear resistance
Different thermal expansion coefficient

Conductive polymer (doped)
Poor mechanical and thermal properties
Poor processibility

Approach

Metallized Nanotube Polymer Composite (MNPC)

1. lightweight, high temperature, high performance polymer matrix
2. highly strong, stiff reinforcing nanotubes
3. nanoparticle inclusions metallized by a SCF infusion method

Metal Coated Carbon Nanotubes: Increased Conductivity

• Y. Zhang, Nathan W. Franklin, Robert J. Chen and Hongjie Dai, “Metal coating on suspended carbon nanotubes and its implication to metal tube interaction,” *Chem. Phys. Lett.*, 24 35-41 (2000)

• Y. Zhang and Hongjie Dai, “Formation of metal nanowires on suspended single-walled carbon nanotubes,” *Appl. Phys. Lett.*, **77** 3015 (2000)

• Y. Feng and H. Yuan, “Electroless plating of carbon nanotubes with silver,” 39 3241 (2004)

• S. Yoshimoto et al, *Jap. J. of Appl. Phys*. Vol. 44, No. 51, 2005, pp. L1563-L1566 ”Electrical Characterization of Metal-Coated Carbon Nanotube Tips”

• C. Yang et al, “Carbon Nanotube/Copper Composites for Via Filling and Thermal Management,” Electronic Components and Technology Conference, 2007. ECTC '07. Proceedings. 57th
Abstract: **…Electrical measurement of the CNT/copper composite vias demonstrates much lower electrical resistance than that of vias with CNT only…**

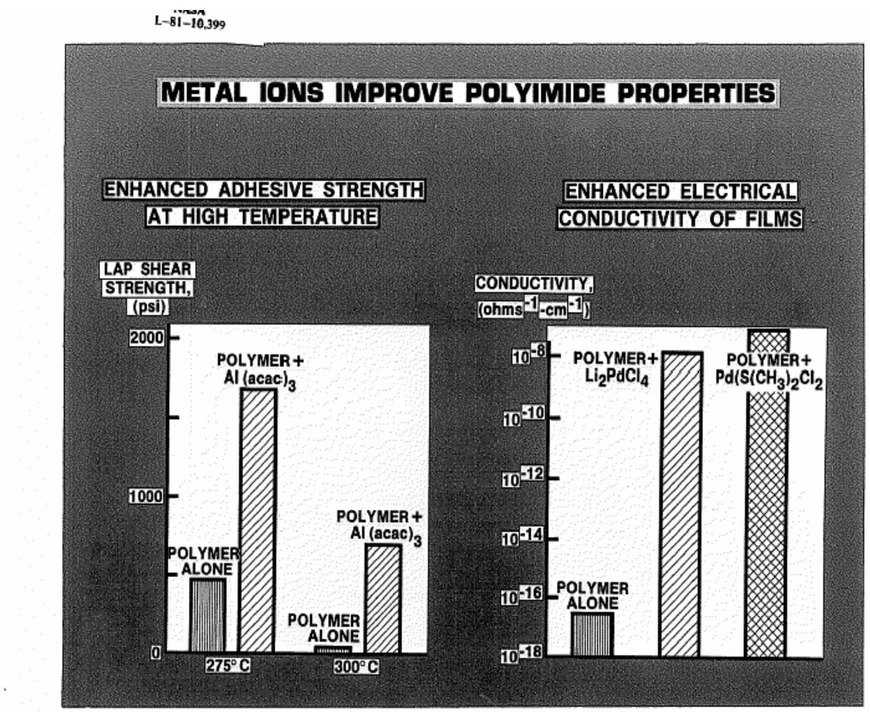
• HH3.73. Carbon Nanotube/Copper Composite Coatings, Fabricated by Cold Spraying. S. Kwon; D. Lee; D. Park; A. Yoon; K. Lee, MRS Fall 2007…Conductivity increased with CNT incorporation…

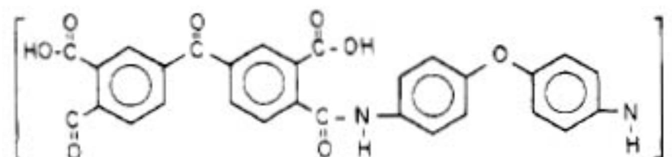
Metal Impregnation into Polymers with Metal Salts

R. J. Angelo and E. I. du Pont de Nemours ***8*** Co., US. Patent 3 073 785 (1959)
St. Clair, Carver, Taylor, Furtsch, *J. Am. Chem. Soc.*, **102** 876 (1980))

Table I. Palladium Containing BTDA-ODA-Polymer Films

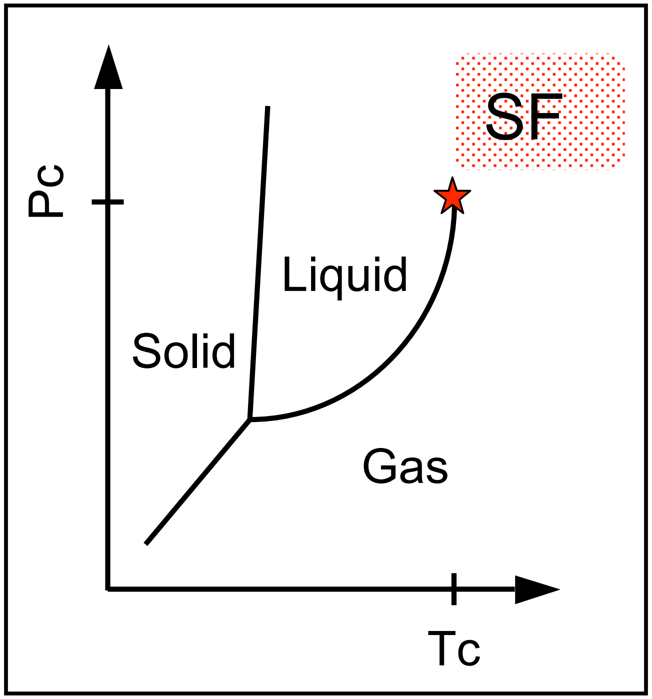
films	volume resistivity, Ω cm	surface resistivity, Ω	metal content, %
polymer + Li_2PdCl_4	6.1×10^{10}	4.5×10^7 (side 1) 8.2×10^{10} (side 2)	0.17 Li 5.33 Pd
polymer + $Pd[S(CH_3)_2]_2Cl_2$	3.3×10^{10}	very low (unmeasurable)	0.23 S 7.02 Pd
polymer + Na_2PdCl_4	2.3×10^{15}	$>10^{16}$	1.36 Na 4.69 Pd
polymer alone	$\sim 1.0 \times 10^{17}$	$\sim 1.0 \times 10^{17}$	





POLYAMIC ACID III

Properties of Supercritical Fluids



- Environmentally safe (no toxic solvent)
- Lower viscosity (low surface energy)
- Higher mass transfer (diffusivity)
- Recyclable: economically beneficial
- Controllable dissolving power

	SF	Liquid
Viscosity [Pa.s]	10^{-4}	10^{-3}
Diffusivity [m^2/s]	10^{-7}-10^{-8}	$< 10^{-9}$

- CO_2 (Tc=31°C, Pc=73bar) is the most used supercritical fluid with a small amount of solvent to increase elutropic strength

Supercritical Impregnation on polymers

First demonstration by A. R. Berens in 1986

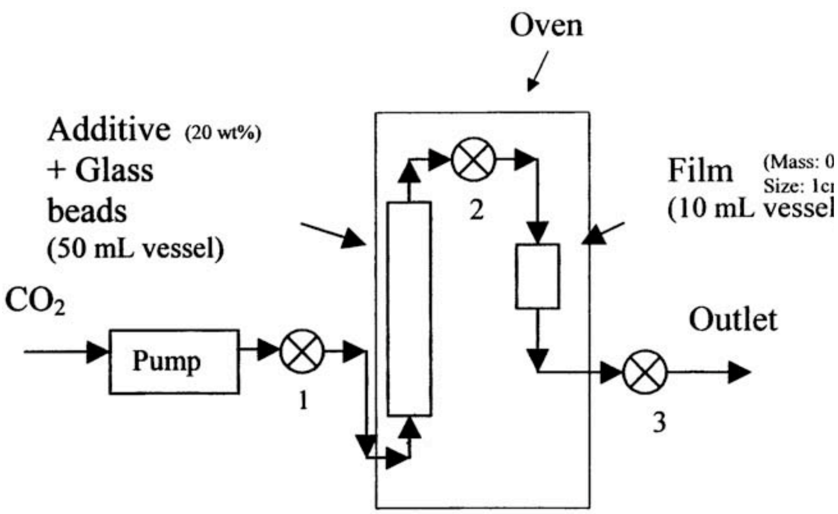
A. R. Berens et al, *J. Appl. Polym. Sci.* **46** 231 (1992)

A. R. Berens et al, (Eds.), Supercritical Fluid Science and Technology, 1989 ACS Symp. Ser. 406, Chapter 14.

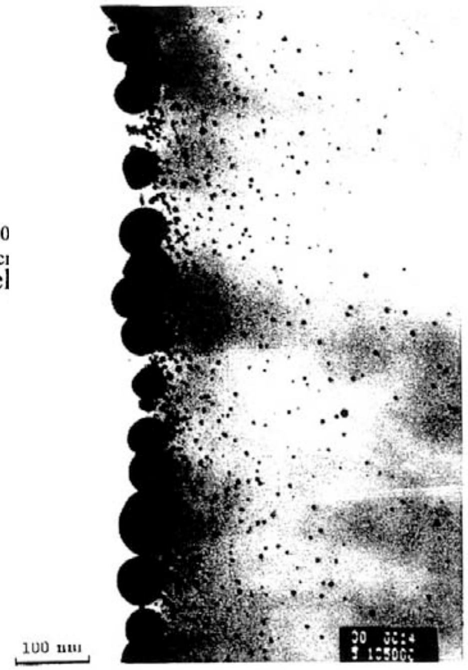
Critical Factors in the Success of Supercritical Fluid Metal Impregnation with a Polymer Substrate

1. Solubility of metal precursor in the SF
2. Diffusion of SF into the polymer
3. Partition of metal precursor between SF and polymer
4. Reduction of metal precursor to the metallic state

Schematic of SCF Infusion process



1. Pressurize additive vessel (15 min): valve 1 open, valve 2 and 3 closed
2. Impregnation step (120 min): valve 1 closed, valve 2 open, valve 3 closed
3. Decompression step: valve 1 and 2 closed, valve 3 open



TEM: Ag-PEEK

TEM: Ag-PS

Nazem, Taylor, Rubira, *J. Supercritical Fluid*, **23** 43 (2002)

Experimental

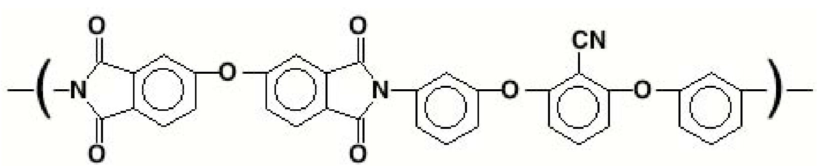
<u>Materials</u>

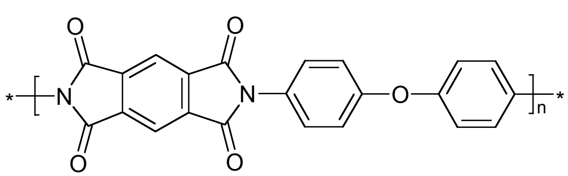
Impregnated films: SWNT/polyimide films
Polyimide: (β-CN)APB-ODPA: (bCN-AO), PMDA-ODA,
SWNT: 0, 0.035, 0.075, 0.1, 0.2, 1, 2, 5, and 10wt% (HiPco, Honda, CSI P2 & P3)

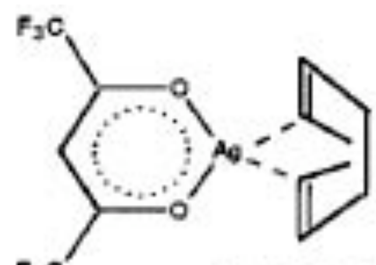
Supercritical fluid (CO_2) impregnation of $[Ag(COD)(HFA)]_2$,
(1,5-cyclooctadien-1,1,1,5,5,-hexafluoroacetylacetonato) silver(I) dimer, followed by thermal reduction of the silver-containing film to silver metal.

<u>Instruments</u>

Applied Separations (Allentown, PA) supercritical fluid system (Spe-ed SFE)
Impregnation condition: 20-90wt% salt and glass beads (1/3 volume of the vessel)
345 atm (5000psi) CO_2 pressure at150˚C for 1hr (345/150/1)
Reduction condition: 250˚C for 1hr (250/1)







Ag(COD)(HFA)

How to disperse CNTs?

1) Kinetic Approach

High shear (stirring, homogenization)
Sonication (cavitational force)
Melt mixing (twin screw mixer, extruder, capillary rheometer, fiber spinning)
In-situ polymerization
In-situ polymerization under sonication & high shear (Park et al, *Chem. Phys. Lett.* **364,** 303 (2002))

2) Thermodynamic Approach

Covalent bonding

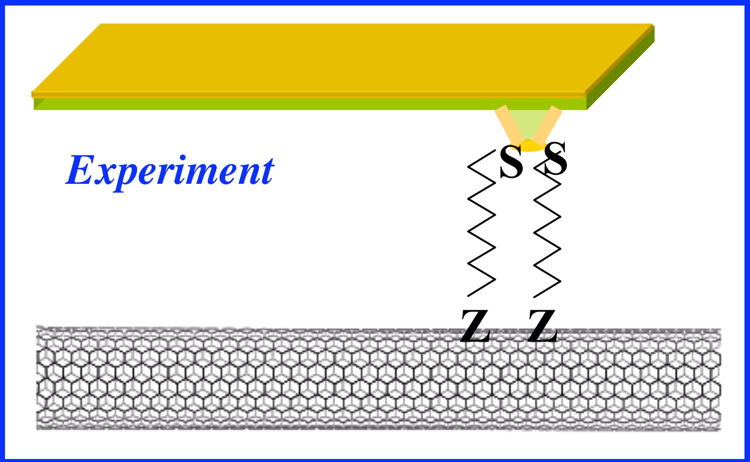
Acid etching
Stirring, reflux, and soxhlet extraction with H_2SO_4, HNO_3, and HCl
Functionalization
Fluorination, reflux with amine, electrochemical (diazonium compound)

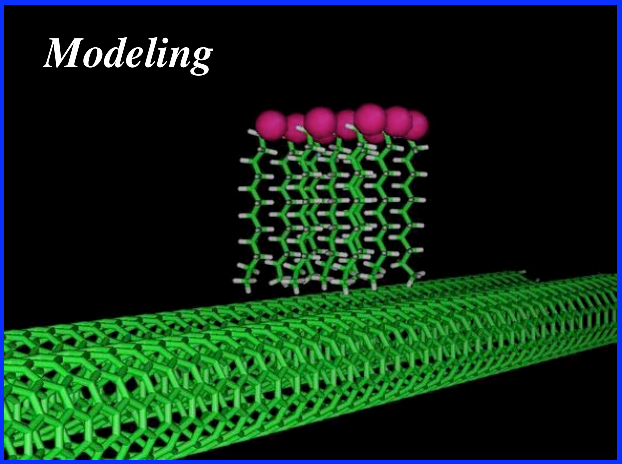
Non-covalent bonding

Amphiphilic (surfactant), hydrophobic interaction: Water soluble polymers
Wrapping: PmPV, Polyvinyl pyrrolidone, Polystyrene sulfonate, PPE
Charge Transfer (Donor-acceptor) (*Chem. Phys. Lett.* **391,** 207 (2004))
Dispersion Interaction
Zwitterion
Complex formation
Nonspecific interaction

Probe Microscopy

- **Using Functionalized AFM tips interaction forces can be directly probed.**





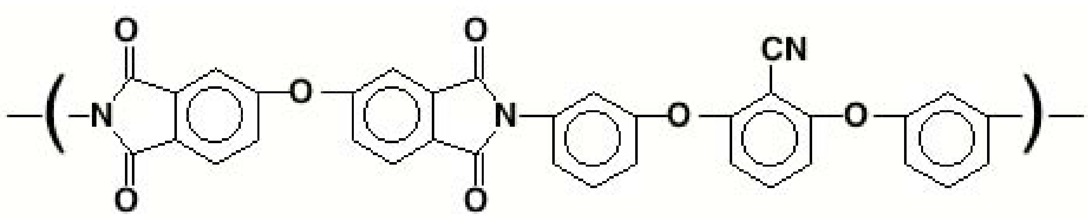
Alkyl-thiol	**Force/molecule (pN)**	
Endgroup	***Experiment***	***Modeling***
-OH	9.6 ± 2	
-perfluoro	8.7 ± 3	
-SH	9.2 ± 3	
$-CH=CH_2$	8.1 ± 2	
$-CH_3$	7.6 ± 2	1.92
-COOH	12.2 ± 3	
$-NH_2$	23.4 ± 4	2.98
	GIT	**K. Wise (NIA)**

Aryl-thiol Thiol	Rupture Force per molecule (pN)	Standard Deviation
4-Methylbenzene	18.94	5.65
4-Nitrobenzene	21.79	5.29
4-Aminebenzene	22.64	4.66
4-Bromobenzene	26.92	3.55
4-Hydroxybenzene	32.00	8.39
4-Fluorobenzene	39.47	8.84
4-Methoxybenzene	41.51	10.9
H-Benzene	46.79	11.79
4-Nitrilebenzene	56.93	15.47

Poggi, Bottomley, Lillehei; *Nano Letters* **2004,** 4(1), 61-64.

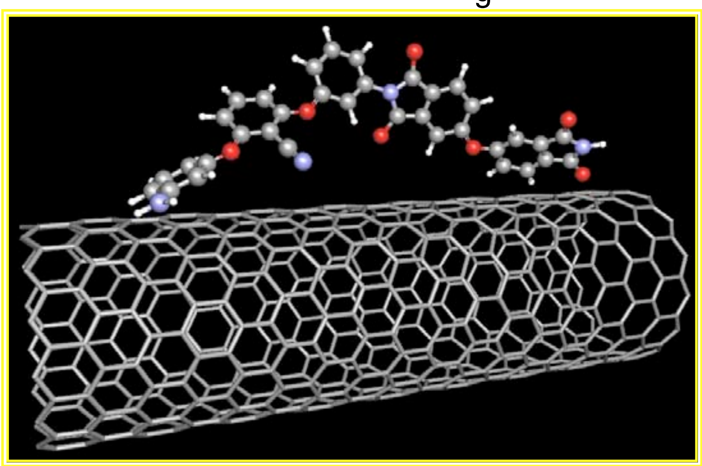
SWNT/Polymer Nanocomposites

Electroactive High Performance Polyimide

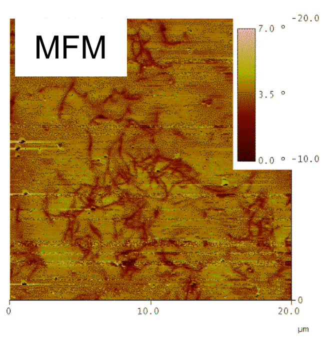


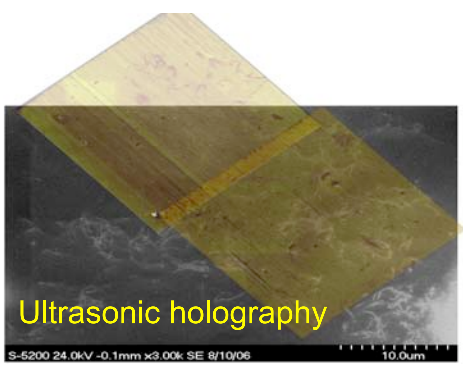
- Dispersion Interaction
- Donor-Acceptor interaction
- In-situ Polymerization under sonication and shear

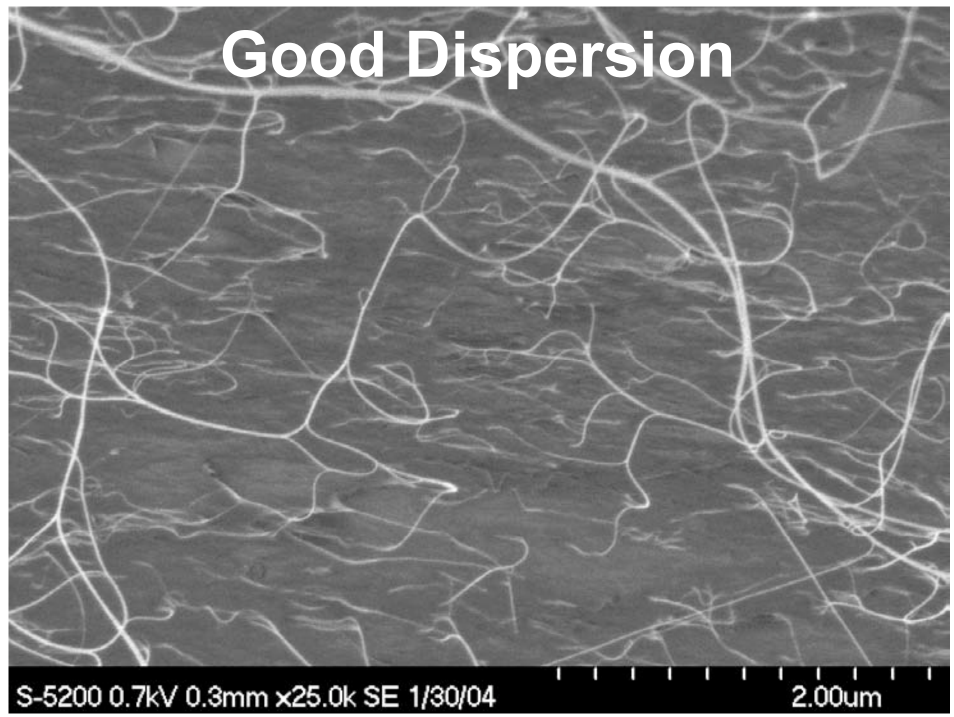
(β-CN)APB/ODPA (T_g = 220°C)



Polyimide + SWNT

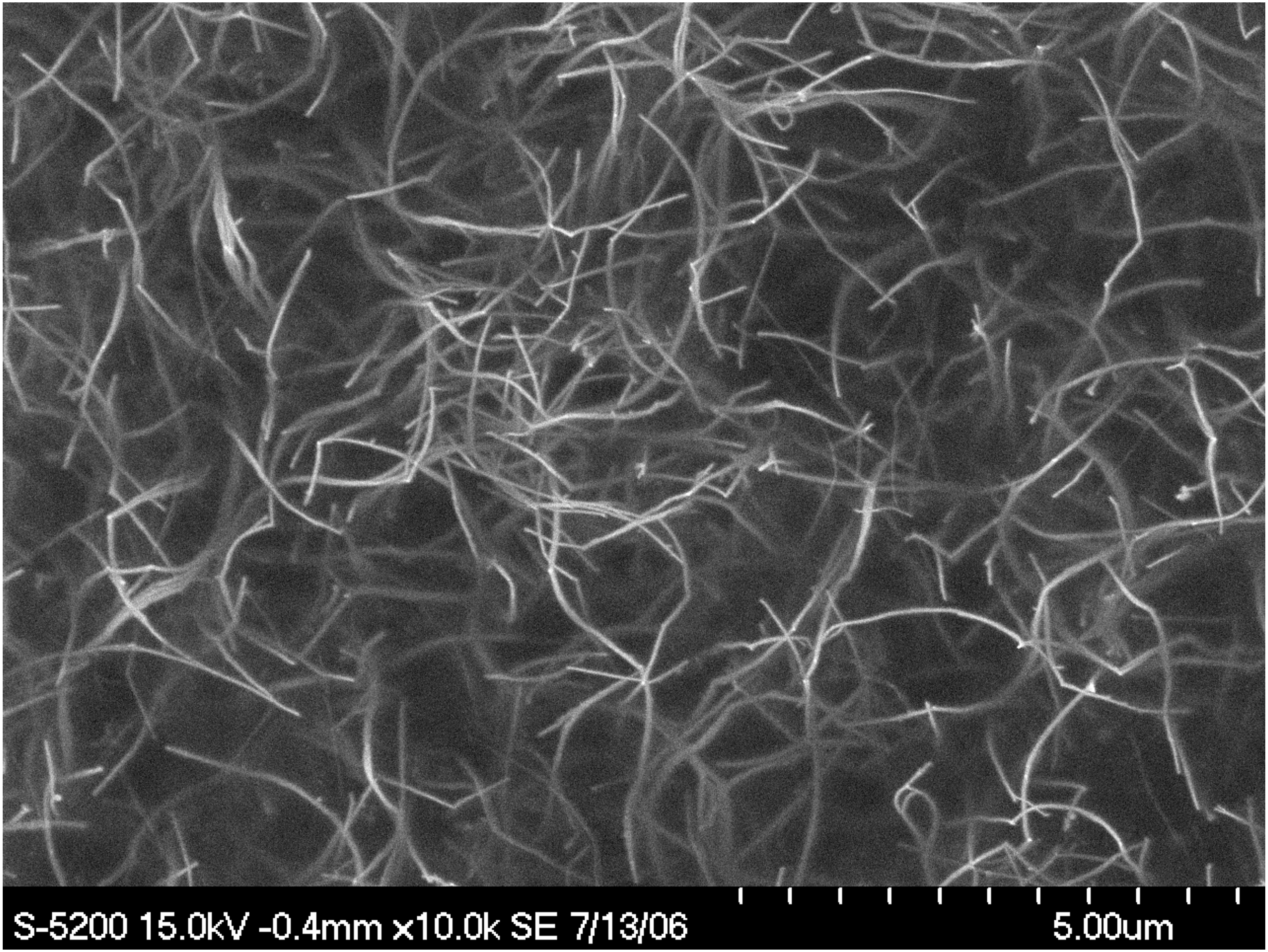




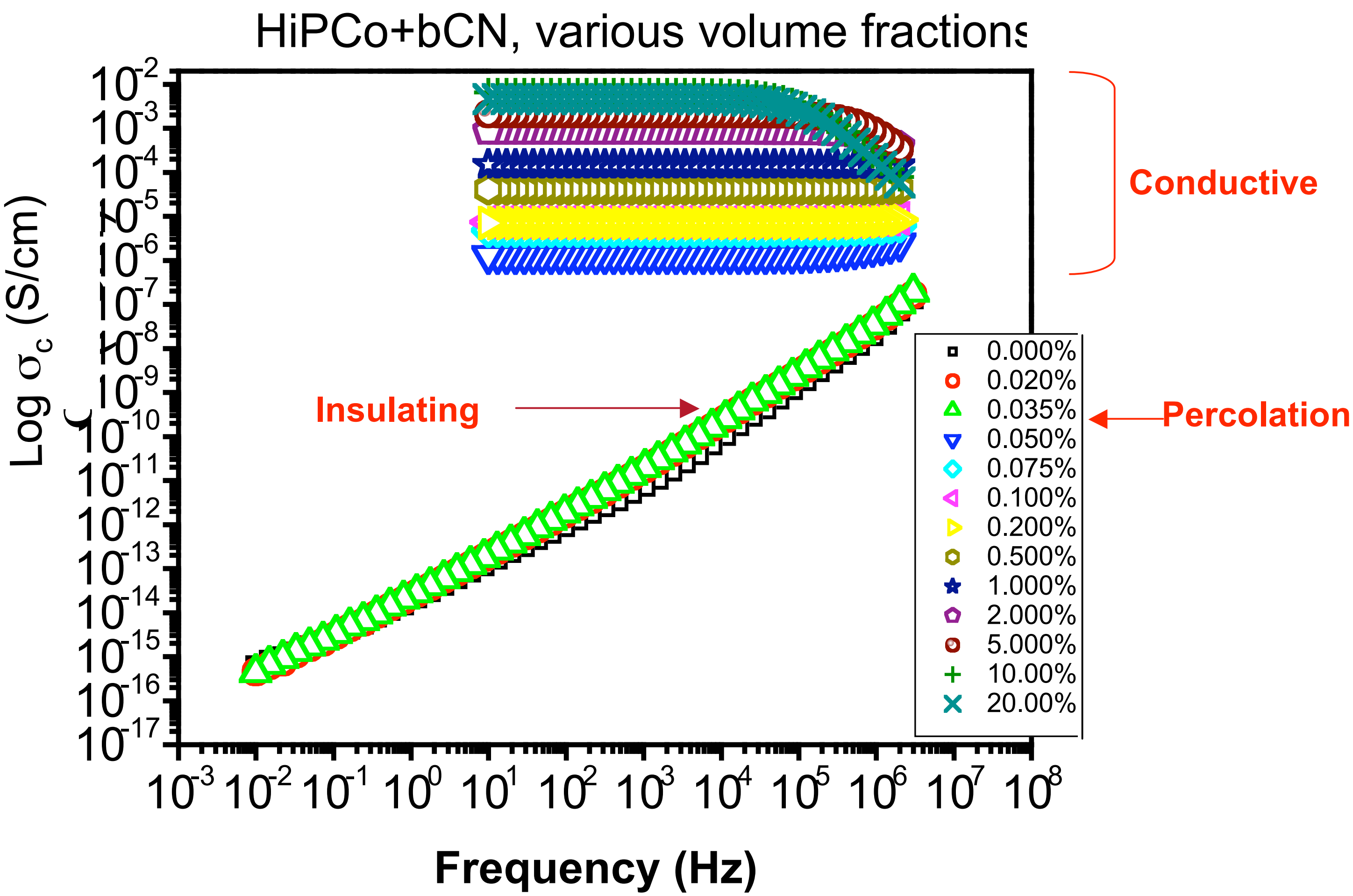


Chem. Phys. Lett., **364** 303 (2002)

Chem. Phys. Lett. **391** 207 (2004)


S-5200 15.0kV -0.4mm x10.0k SE 7/13/06
5.00um

AC Conductivity of SWNT/Polyimide Nanocomposites

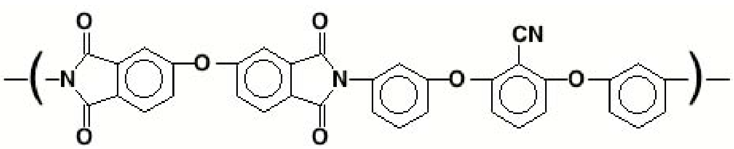


Good dispersion --> Low percolation threshold < 0.05%

J. Poly. Sci.: Poly. Phys. **43** 3273(2005)

NMPC: Silver Infusion Process into SWNT/(β-CN)APB-ODPA Film

SWNT/polyimide film formation:good dispersion



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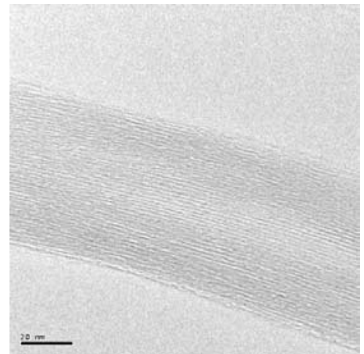

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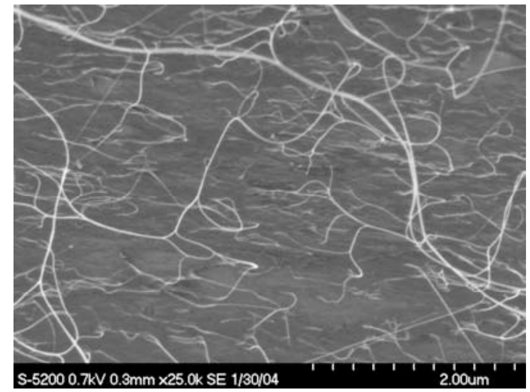
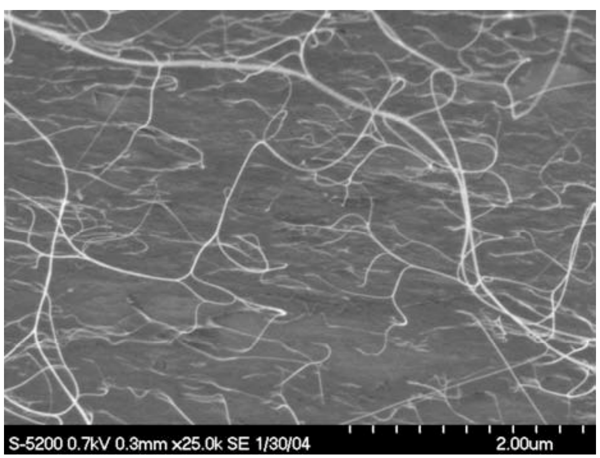


Ag-MNPC (Ag/SWNT/polyimide) film formation: SCF Ag impregnation



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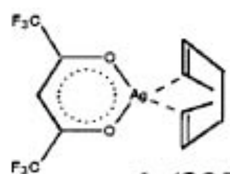
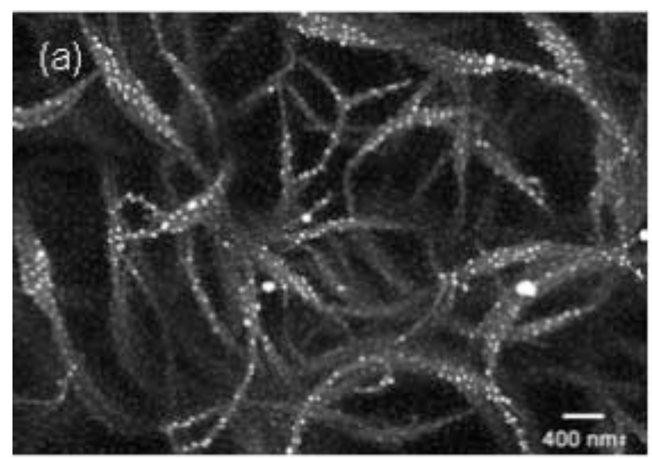


Ag(COD)(HFA)

345atm
150˚C
1hr

→

250˚C
1hr



NASA LaRC LAR 17106-1: Invention disclosure

Ag-MNPC Films with various SWNT Concentration

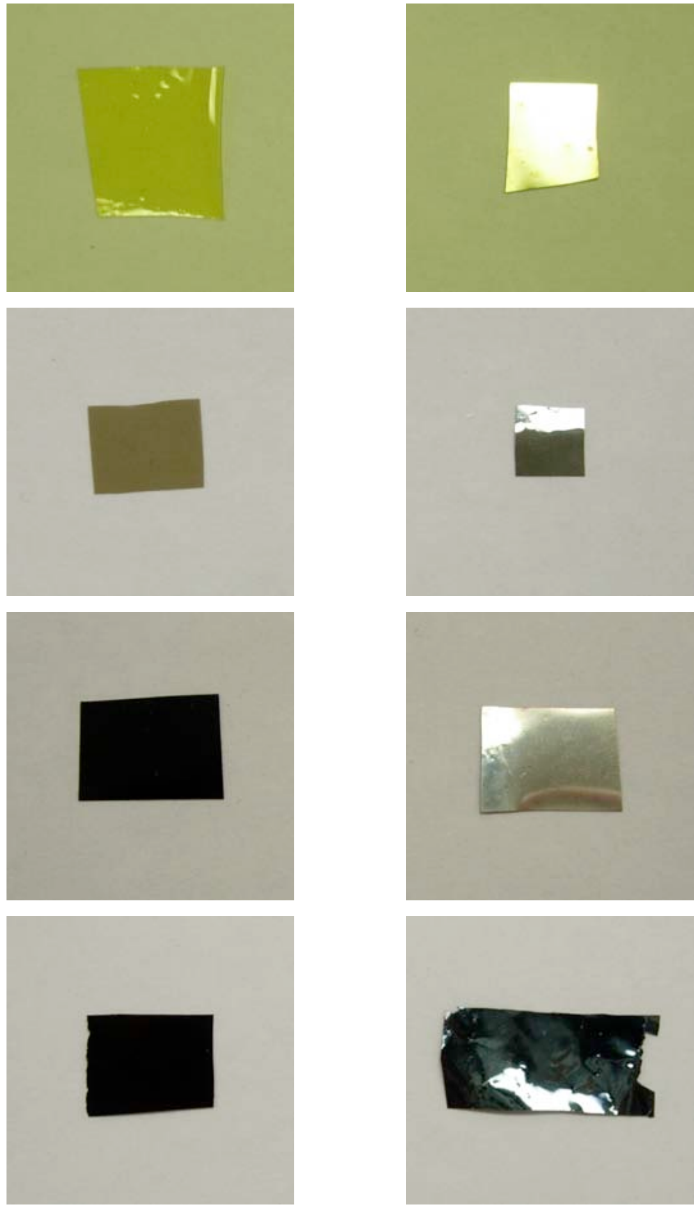
Control | Ag-MNPC

0%SWNT

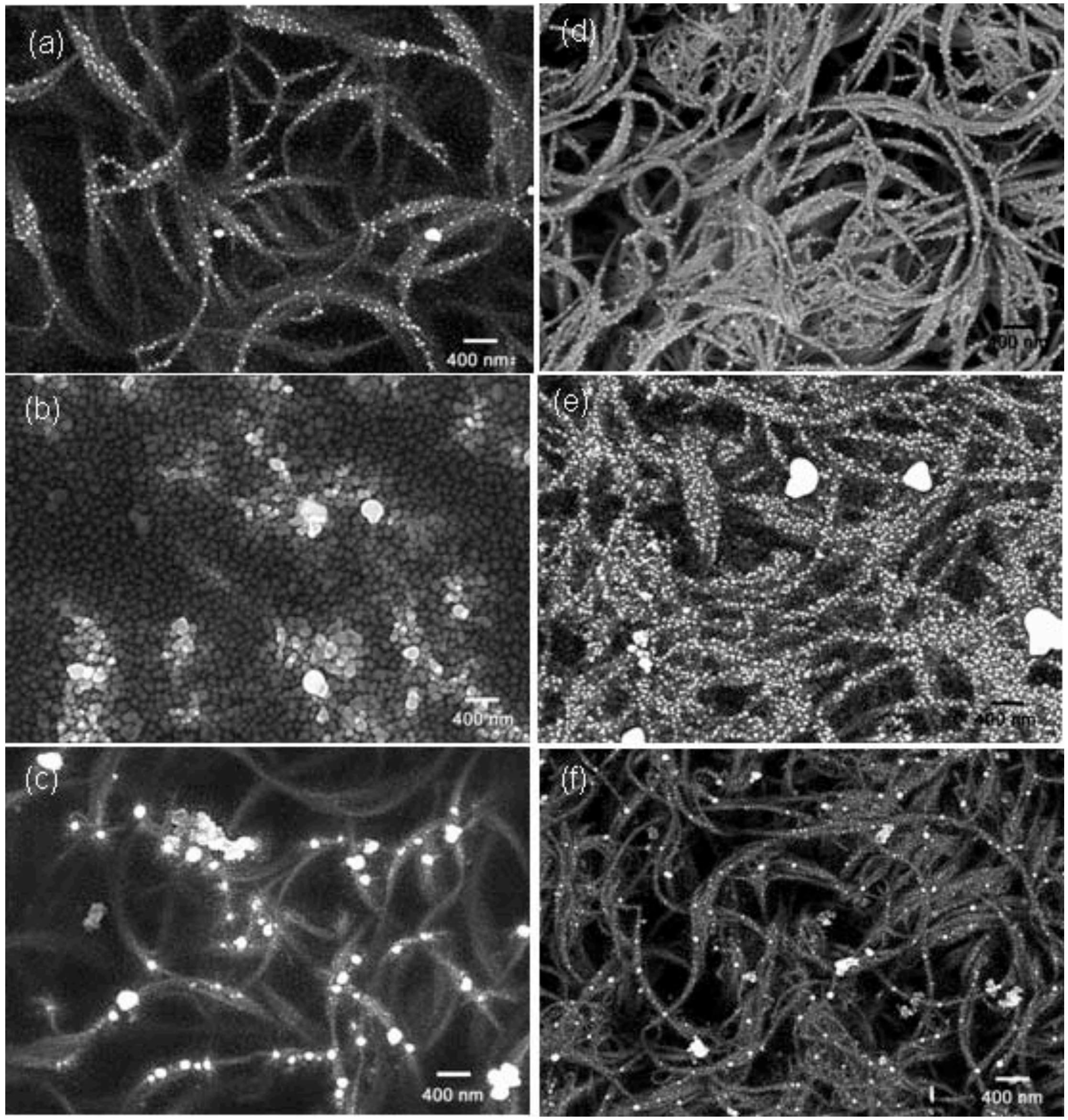
0.1%SWNT

2%SWNT

5%SWNT

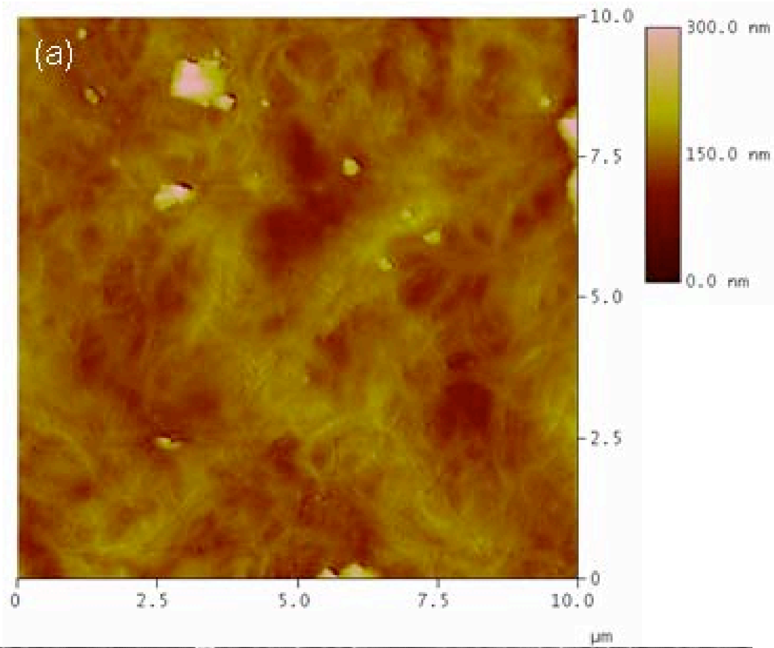


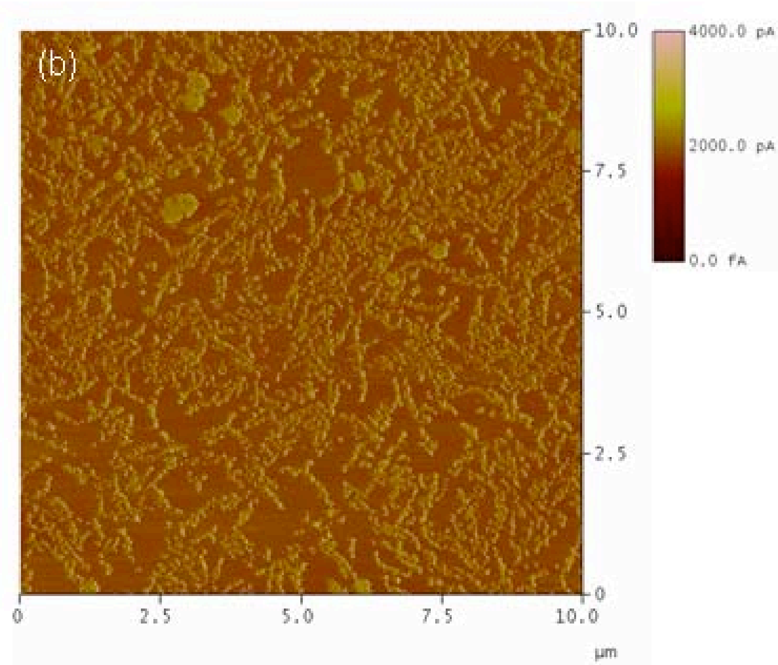
HRSEM: Polytransparency: MNPC: Ag/SWNT/βCN AO



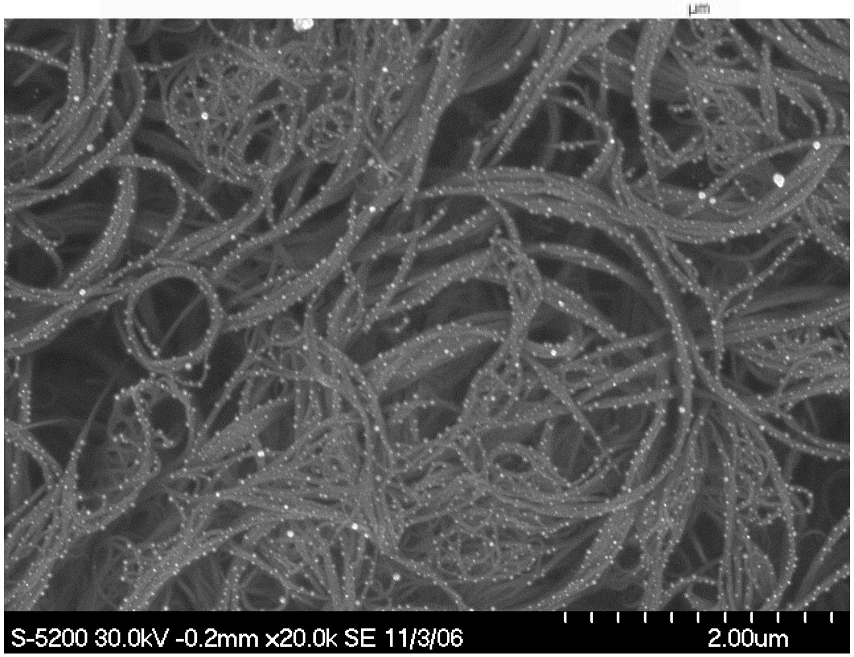
HR-SEM images of MNPCs at a high accelerating voltage: Ag/1 wt% SWNT/b-CN AO prepared by (a) 20 % and (b) 70 % metallization solutions, and Ag/10 wt% SWNT/b-CN AO prepared by (d) 20 % and (e) 70 % metallization solutions after curing. (c), (f) 1 wt% and 10 wt% SWNT/b-CN AO/Ag samples prepared by 70 % metallization solution before curing, respectively.

Tunneling AFM & HRSEM: Ag-MNPC: Ag/10%SWNT/βCN AO



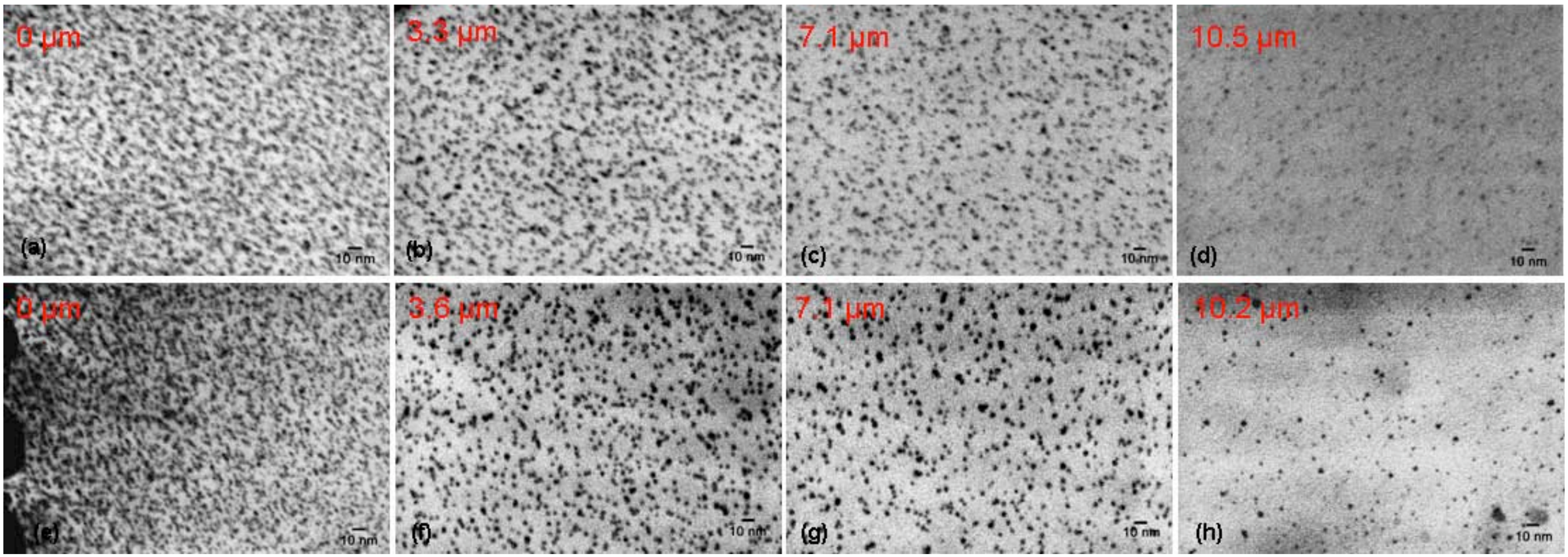


Above: Topograph and tunneling AFM images of 10 wt.% SWNT/b-CN AO/Ag prepared by 20 % metallization solution.



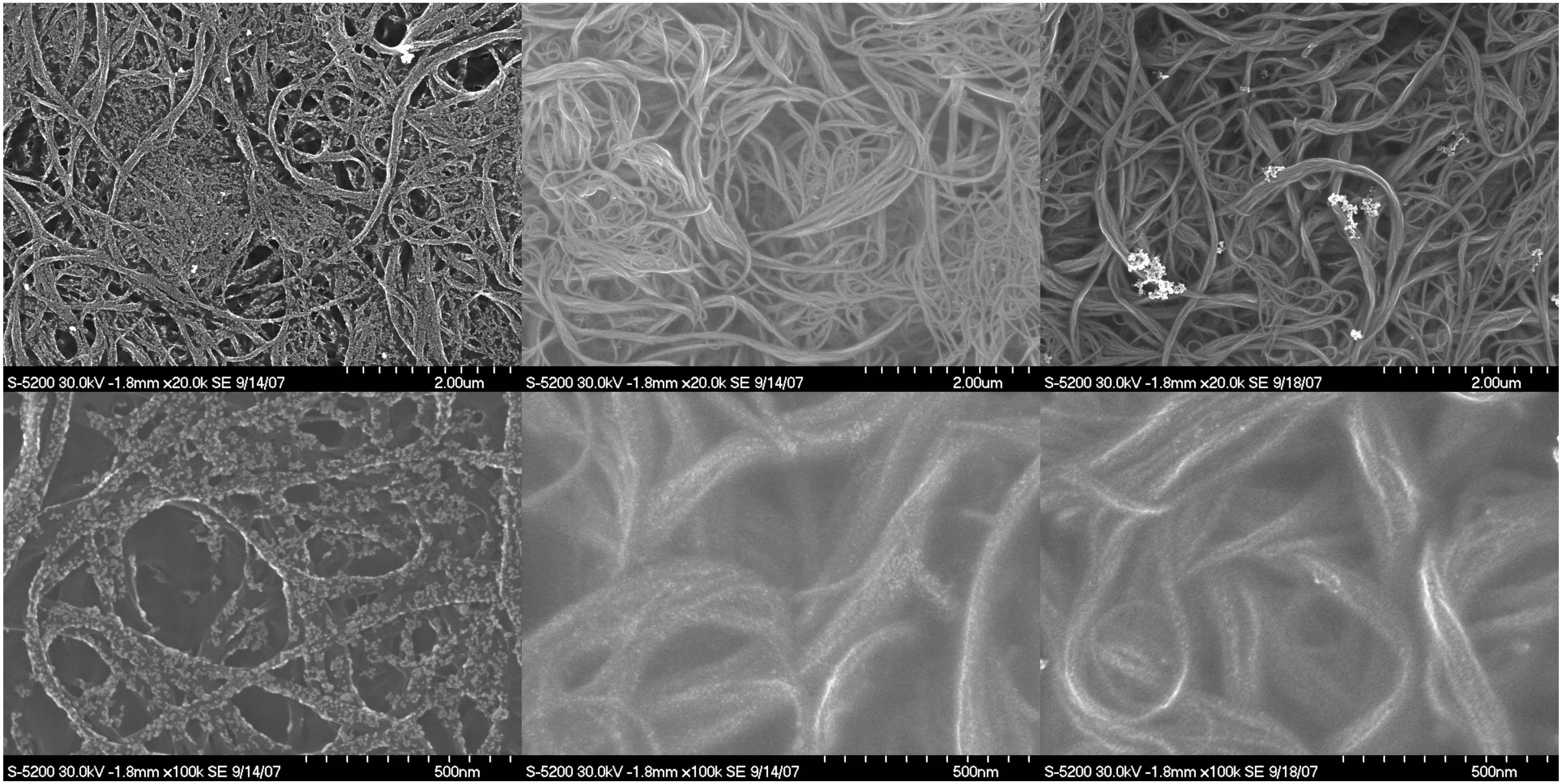
Left: HRSEM micrograph of 10 wt.% SWNT/ b-CN AO/Ag prepared by 20 % metallization solution.

HRSEM: STEM (microtomed) : MNPC: Ag/0.1%SWNT/βCN AO



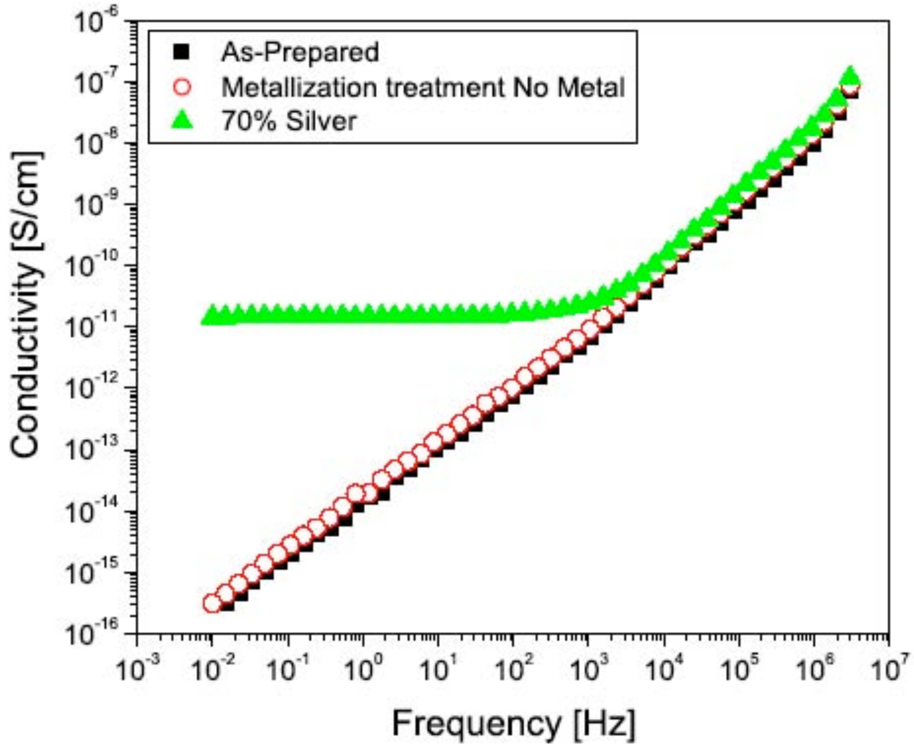
STEM images of b-CN AO/Ag samples taken at specific locations from the surface with 0.1 wt.% SWCNT (e ~ h) and without SWNT (a ~ d). Samples are prepared by the supercritical fluid method with 70 % metallization solution and then microtomed to visible inside morphology.

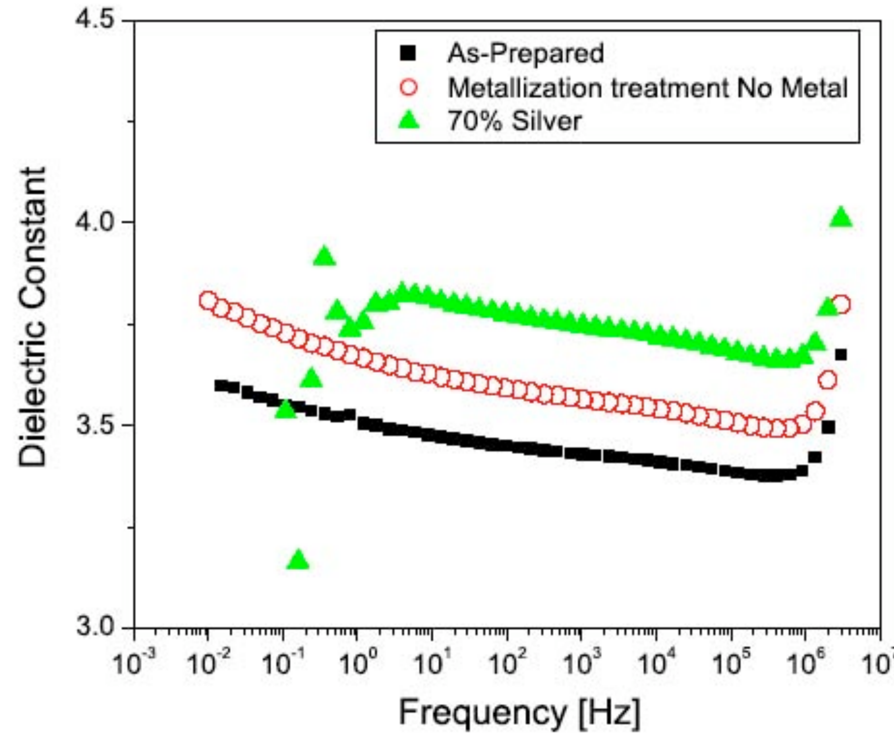
Pt, Ni, Fe-MNPCs



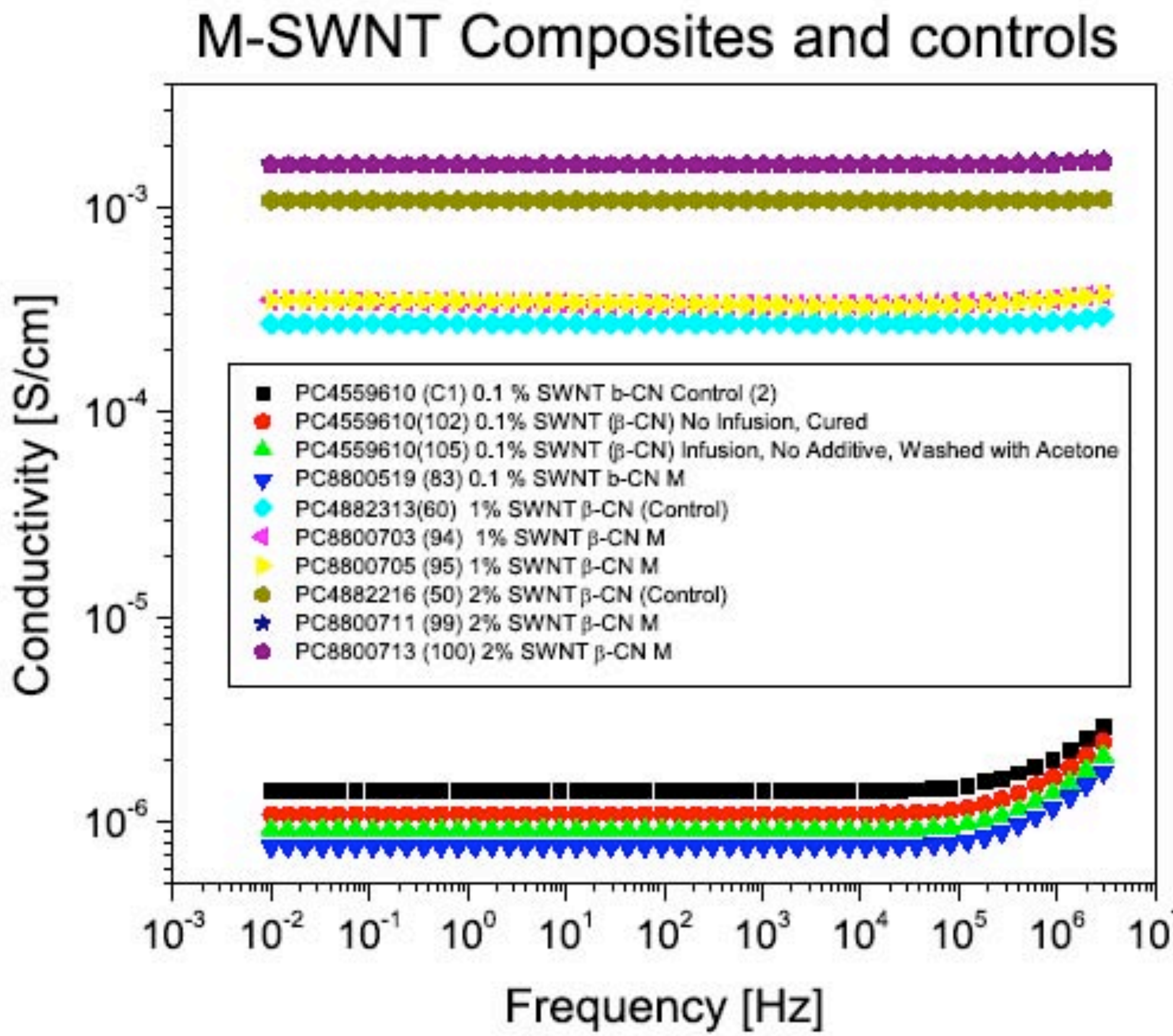
(a) Pt/10%SWNT/βCNAO (b) Ni/10%SWNT/βCNAO (c) Fe/10%SWNT/βCNAO

Ag-MNPC: 0.1%Honda SWNT/Polyimide





NMPC: Nanotube Metallized Polymer Composites



Conductivity of MNPC

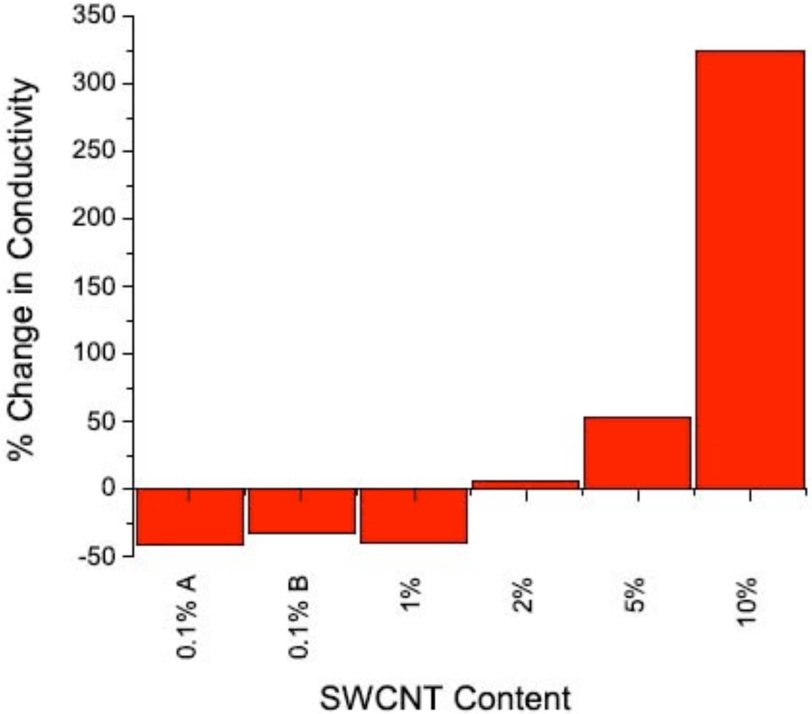


Figure 1: Summary of the change in the low frequency conductivity of metallized samples (70% metal) with different SWCNT content. The changes are calculated relative to unmetallized control samples. Below a 2% SWCNT loading, the increase in the conductivity from the added metal is not enough to overcome the decrease due to processing of the samples. At 2% and above, the conductivity of the metallized samples inreases by as large as 300% at 10% SWCNT.

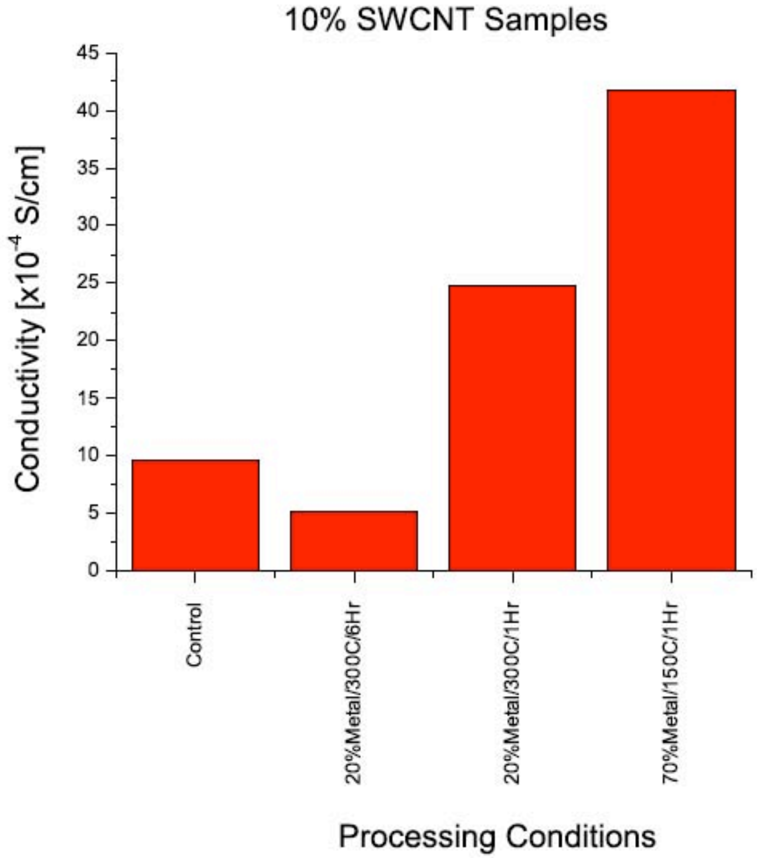
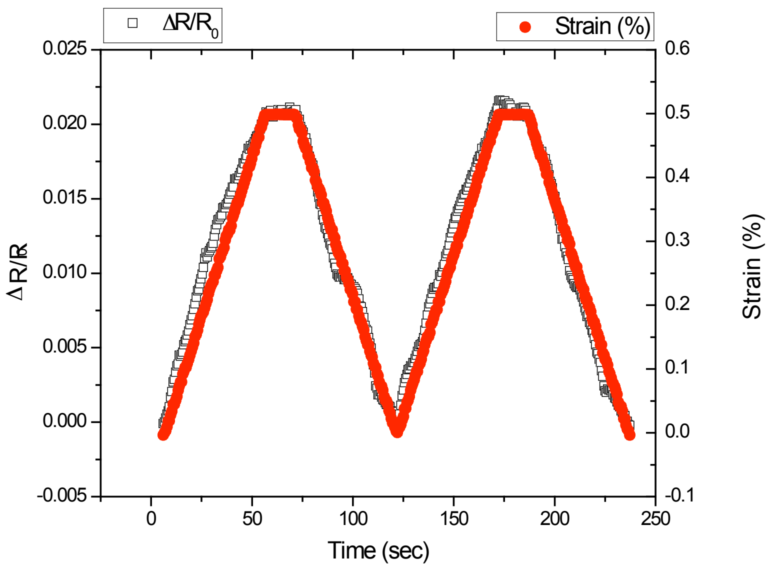
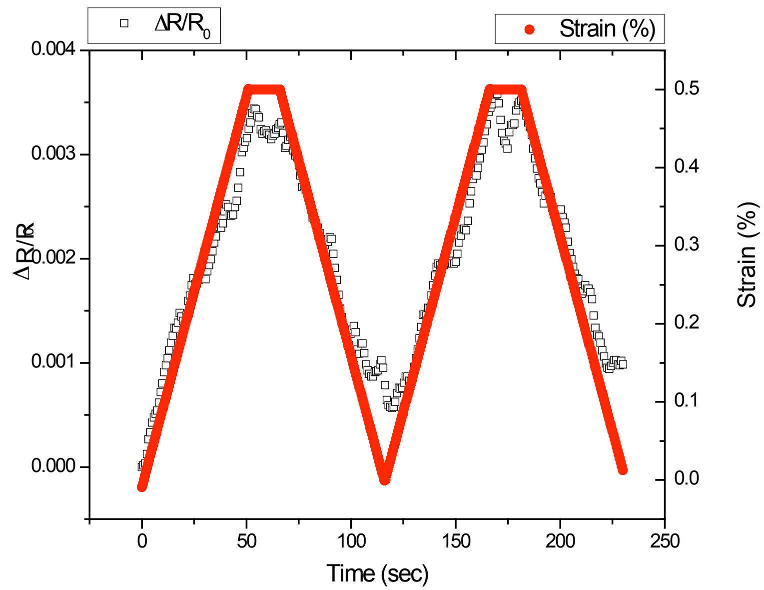


Figure 4: The effects of differernt metal concentration and processing conditions on the low frequency conductivity of samples containing 10% SWCNT

Piezoresistivity Measurement of SWNT/polyimide Film





0.05%SWNT/Polyimide
0.5%strain --> $\Delta R/R_0$ = 0.02

10%SWNT/Polyimide
0.5%strain --> $\Delta R/R_0$ = 0.0035

Summary

- Successful metallization into polyimide and SWNT/polyimide (Ag, Pt, Fe, Ni…)
- Preferential deposition of metal on the nanotube surfaces
- Increased conductivity with metallization
- Surface reflectivity (metallic appearance) increased with metallization
- Increased conductivity with higher metallization concentration
- Conductivity and reflectivity can be controlled by the SCF infusion conditions
- Increased toughness with SCF Infusion Process (with or without metal salts)
- No catalysts or reducing agents are required to reduce metals from the salts on CNTs

Future Research Plan

- Optimization
- Free volume measurement (PALS)
- EMI shielding test
- Lightning test

Acknowledgements

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Nancy Holloway

Advanced Materials and Processing Branch

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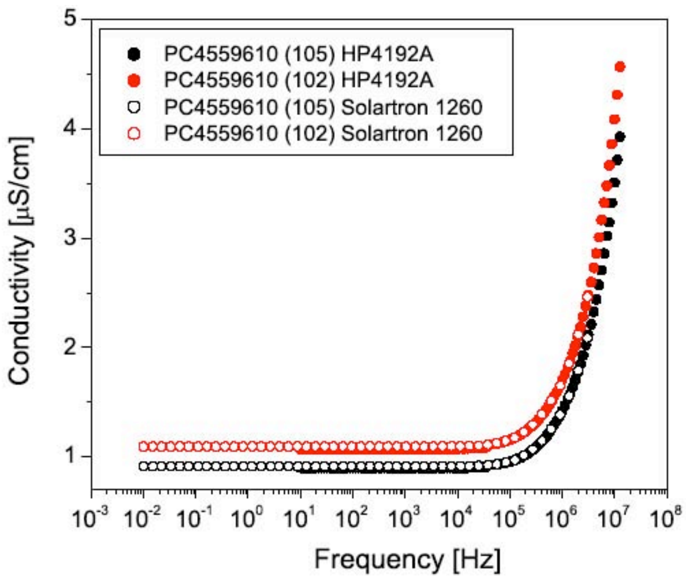
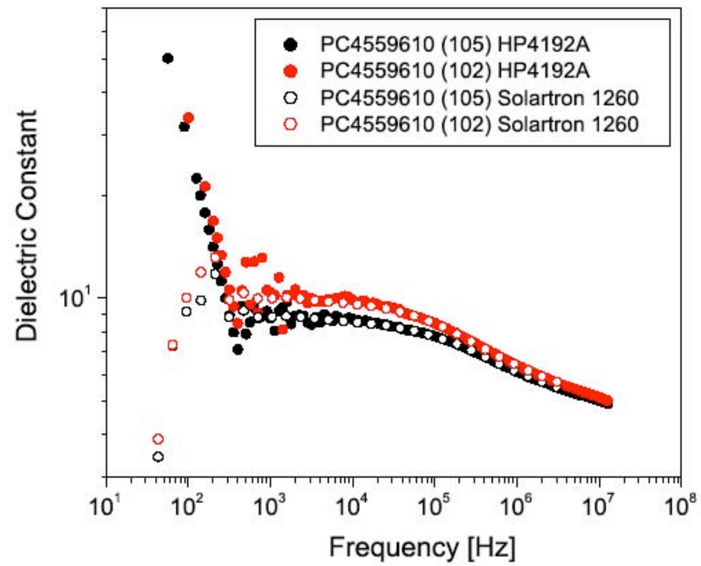
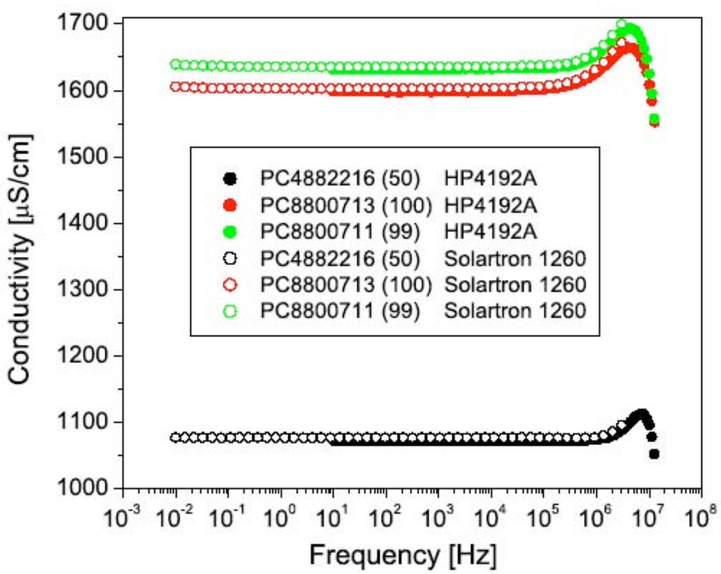
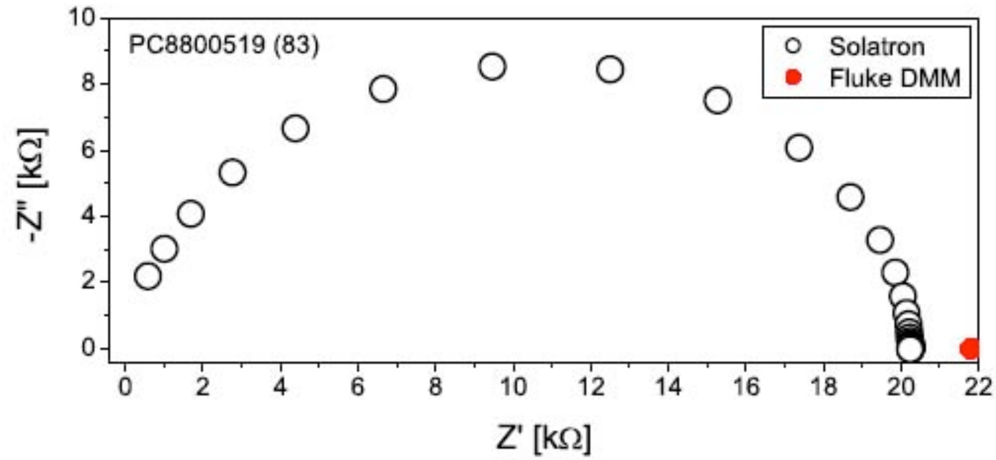
DARPA Revolutionizing Prosthetics
DARPA SkyWalker

Reliable Measurement: HP4192A vs Solatron 1260

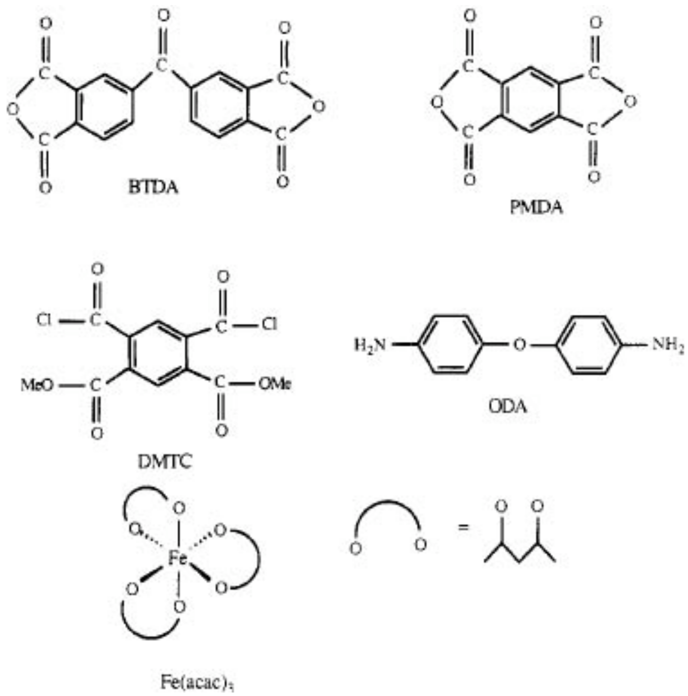








Complex impedance plane plot of the data from a Solartron measurement and a dc measurement on the Fluke DMM. The resistance measurement on the DMM is consistent with the low frequency intercept of the impedance arc. (It is expected for the directly measured dc resistance to be slightly higher than the arc intercept as observed here).



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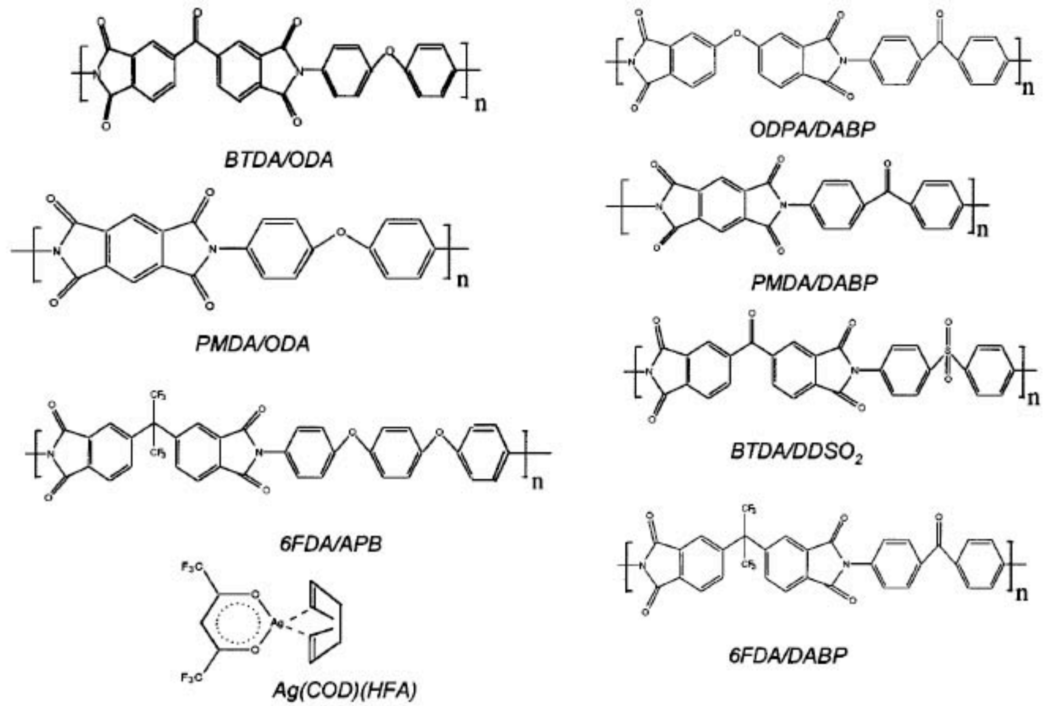

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