Strategies for Improved Properties in Nanotube / Polymer Composites

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SWNTs

- **Aspect Ratio**
- **Purity**
- **Type**

Fabrication

- **Coagulation**
  PMMA
- **Hot-Coagulation**
  LDPE, HDPE
- **Infiltration**
  Epoxy
- **In Situ Polymerization**
  Nylon 66, Nylon 6,10
- **Melt-Mixing**
  PS, HDPE
- **Cellular Network**
  PS

Processing

- **Melt-Fiber Spinning**
- **Extrusion**
- **Hot-Pressing**
- **Nitrogen Gasification**
  PMMA

Morphology

- **SWNT Bundle Size**
  AFM from suspension
- **SWNT Dispersion**
  Raman mapping
- **SWNT Orientation**
  Polarized Raman
  X-ray scattering
- **Matrix Microstructure**
  X-ray scattering
- **SWNT-Matrix Interface**
  FTIR

Properties

- **Mechanical Properties**
- **Melt Rheology**
- **Electrical Conductivity**
- **Thermal Conductivity**
- **Flammability**

#1

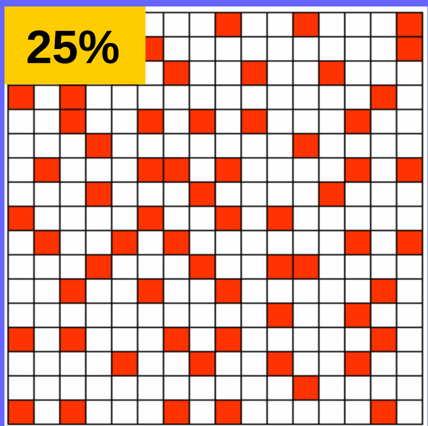
Electrical conductivity as a function of filler orientation and filler aspect ratio.

Fangming Du (UPenn PhD 2005, GE Lighting)
Lai-Ching Chou (UPenn MS 2007)
Sadie White (UPenn)

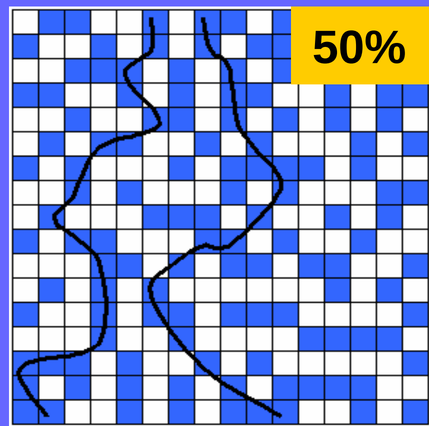
Jack Fischer (UPenn)
Brian Didonna (UCLA)

Percolation and Electrical Conductivity

Aspect Ratio (L/D) = 1

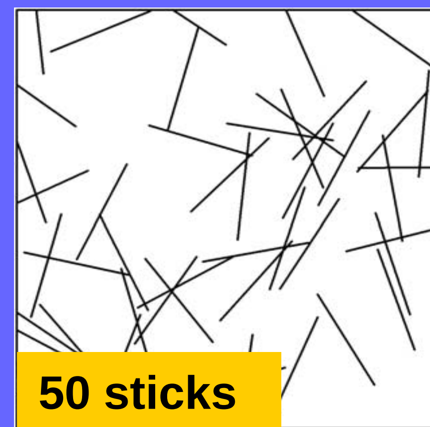


No percolation

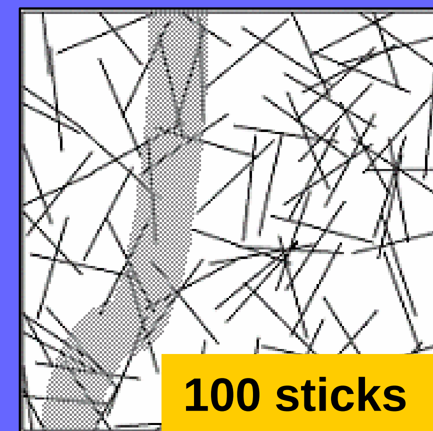


Percolation

Aspect Ratio (L/D) > 10



No percolation



Percolation

Percolation – filler particles form a *cluster of particles* that span the macroscopic sample.

Percolation dominates electrical conductivity in polymer nanocomposites when

(1) the interfacial resistance between fillers is small and

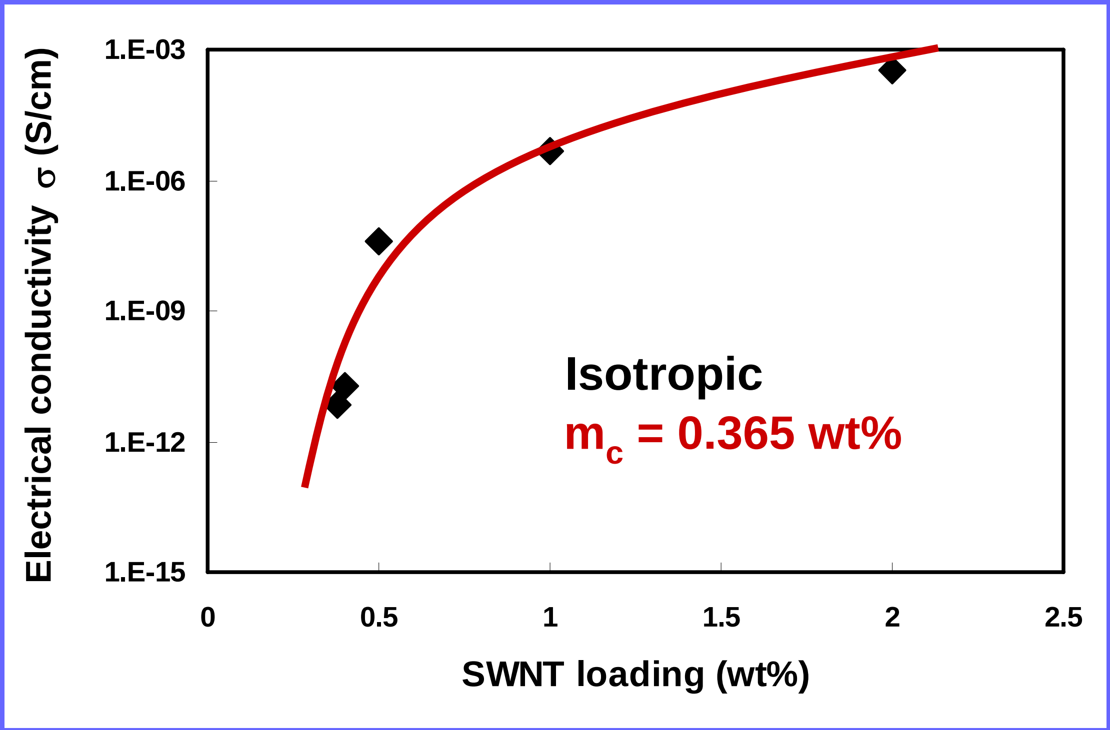
(2) the conductivity of the filler is significantly higher than the matrix polymer.

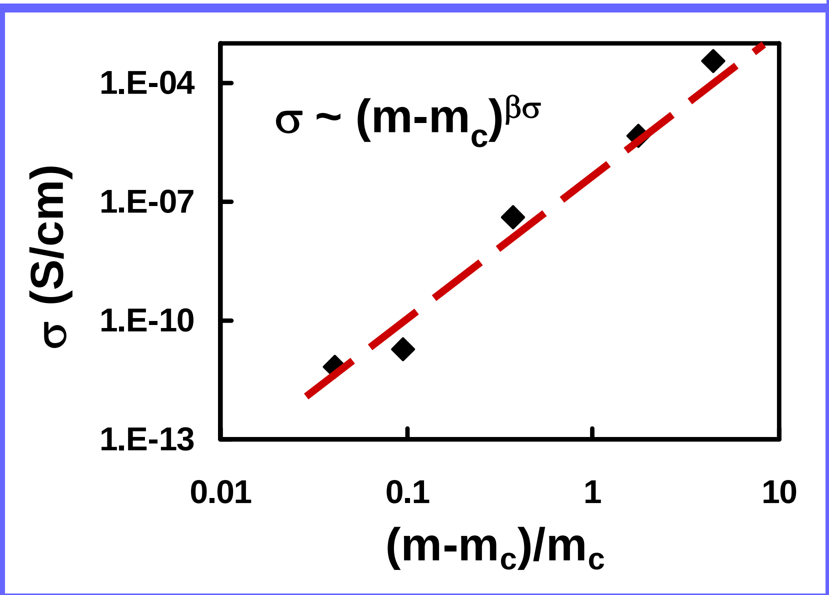
www.cs.colby.edu/.../Images/percolation.gif

Methods for Controlling Electrical Conductivity in Nanotube Composites

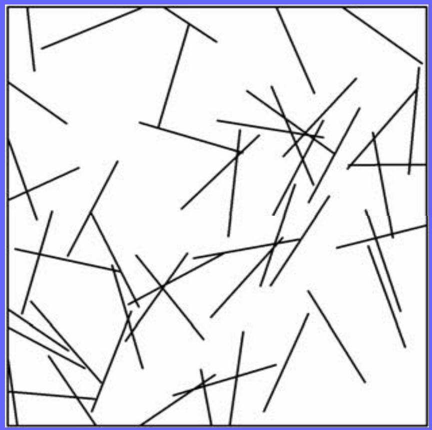
1. **Loading**
2. **Aspect Ratio**
3. **Orientation**
   - Filler is well-dispersed by coagulation method
   - SWNT, MWNT, carbon nanofiber (CNF) in PMMA
   - Simulation
4. **Spatial Distribution and Disperion**
   - Coated particle process (CPP)
   - Continuous, cellular SWNT structure in PS

Electrical Conductivity: SWNT Concentration

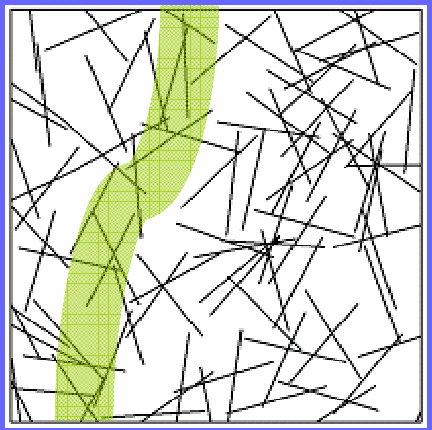




50 sticks, isotropic, insulating



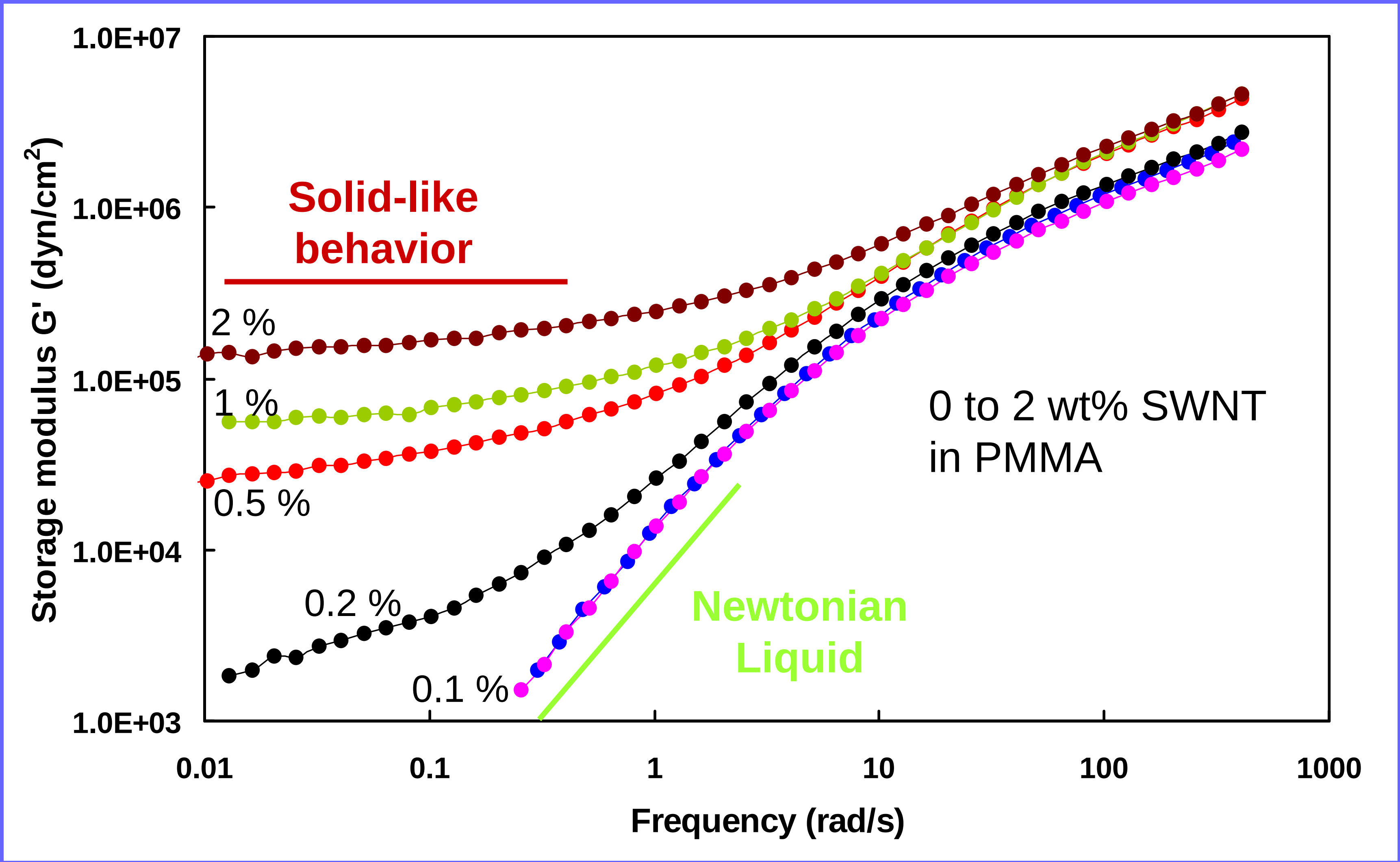
Filler loading



100 sticks, isotropic, conducting

Du, et al. *J. Polym. Sci., Polym. Physics*, 2003.

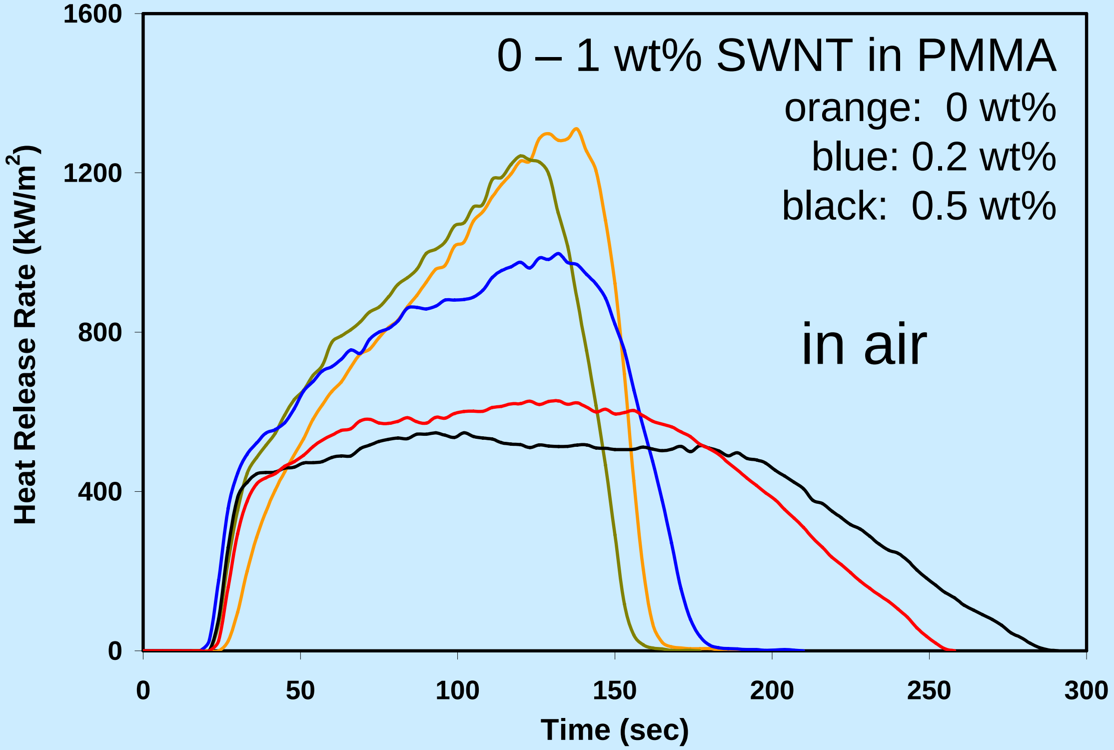
SWNT/PMMA Composites
Shear Storage Modulus

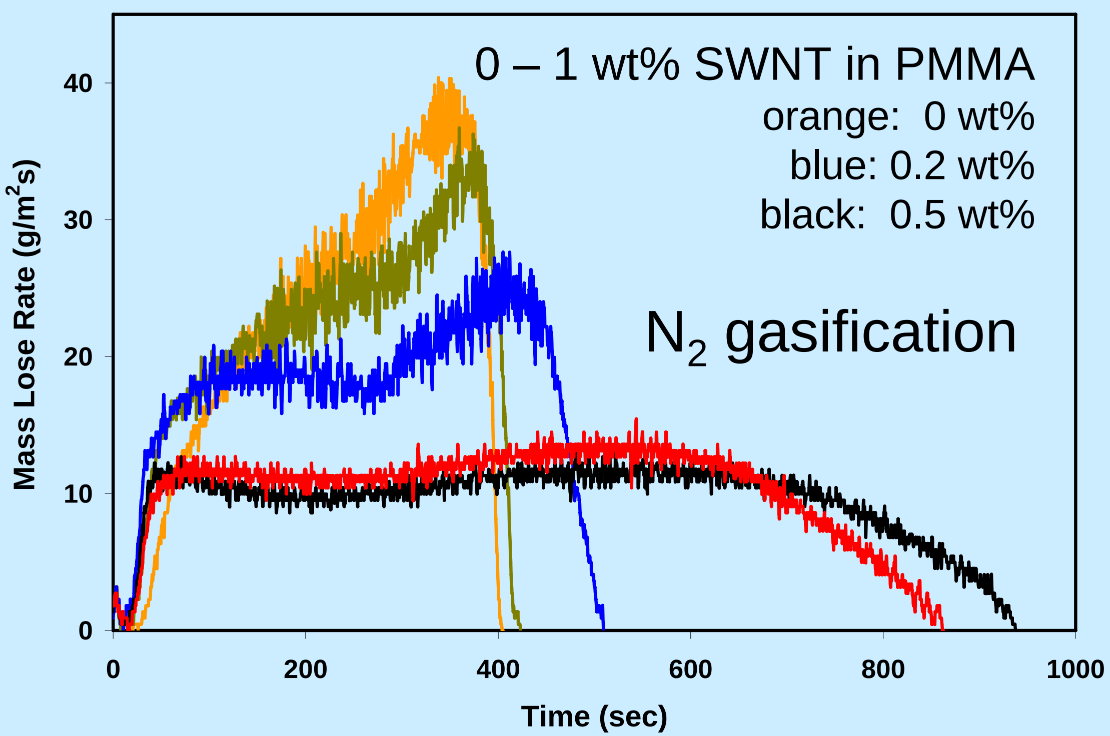


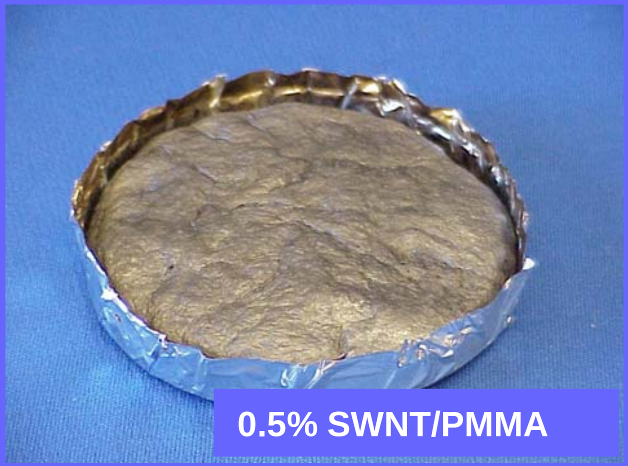
RSAII; 200C, 0.5% strain

Du, et al. *Macromolecules*, 2004.

Effect of nanotube concentration







Residues after nitrogen gasification experiment.

Kashiwagi, et al. *Polymer*, 2005.

Electrical Conductivity: Aspect Ratio

Carbon Nanofibers, Pyrograf® III

After sonication & suspension in DMF

<D> ~77 nm; <L> ~1500 nm

L/D ~ 20

SWNT, Rice University

After sonication & suspension in DMF

<D> ~ 6.9 nm; <L> ~ 310 nm

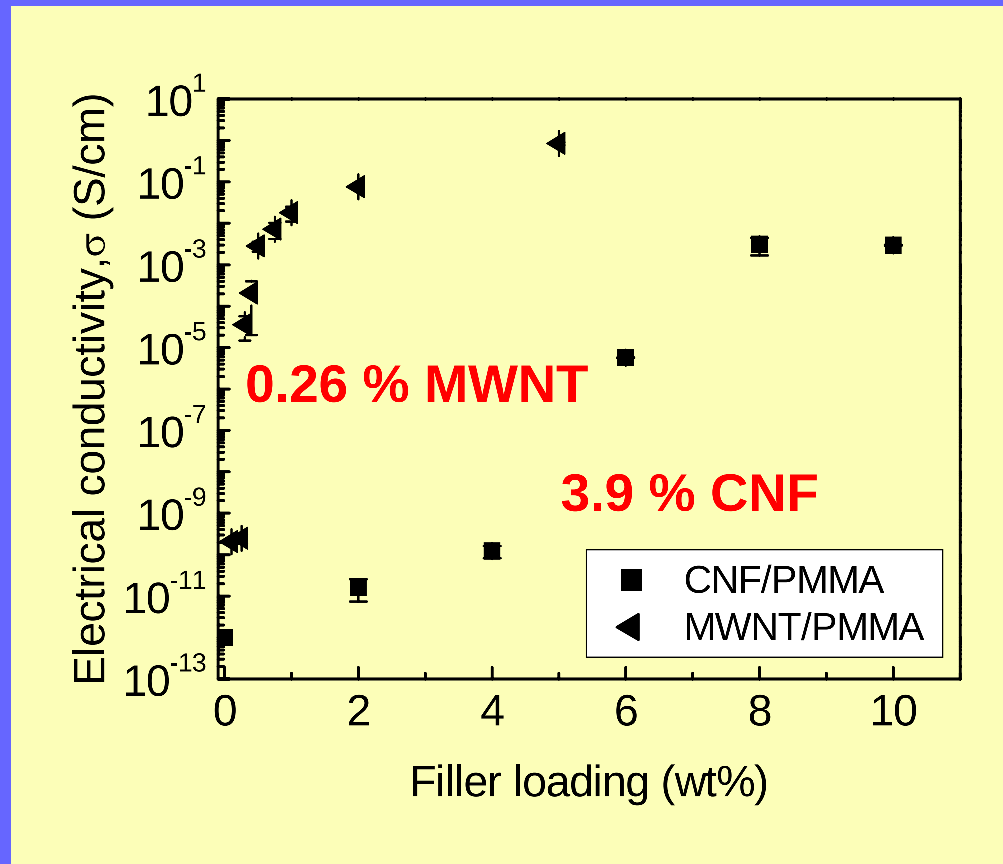
L/D ~ 45

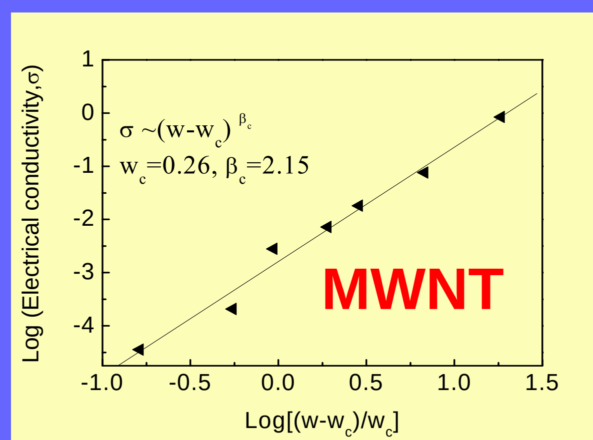
MWNT, Nanocyl S.A.

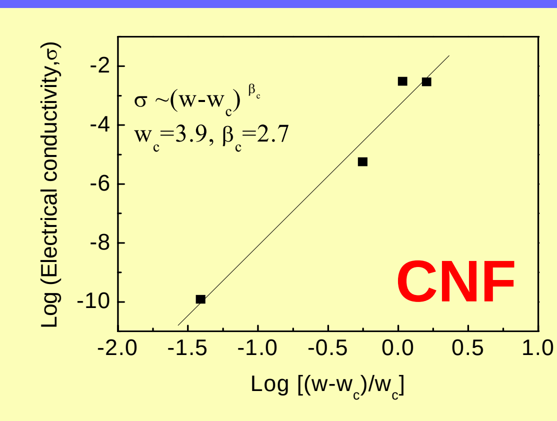
After sonication & suspension in DMF

<D> ~ 6.9 nm; <L> ~ 1338 nm

L/D ~ 190

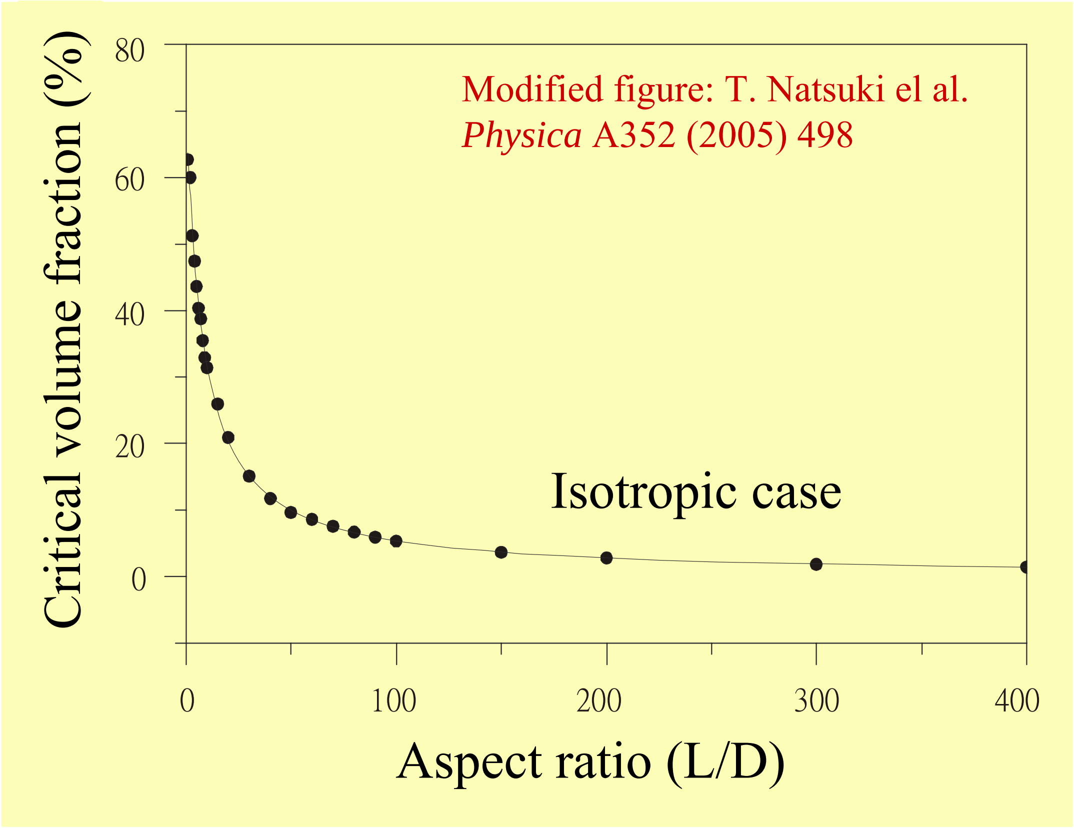


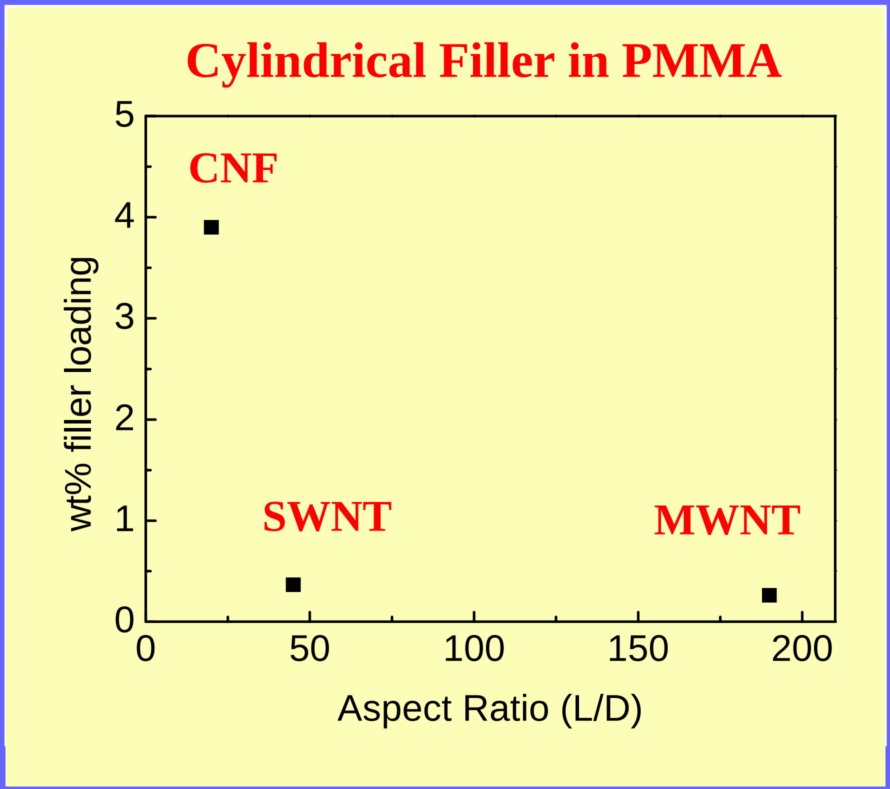




L.-C. Chou, unpublished results

Electrical Conductivity: Aspect Ratio



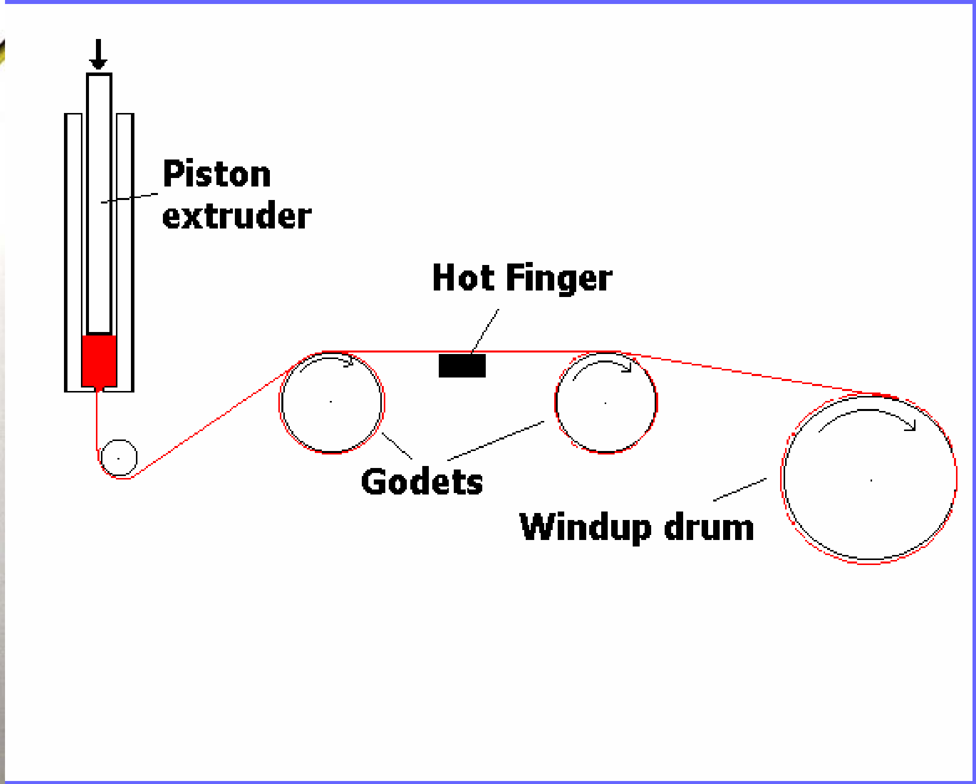


$\sigma \sim (w-w_c)^{\beta c}$

Aspect ratio (L/D) ↑ ; w_c ↓

Less effect at L/D > 40

Melt Fiber Spinning
Extensional Flow to Align SWNT



Control SWNT alignment in composite with…

1. hole diameter of spinneret
2. piston velocity
3. rotating speed of windup drum

Haggenmueller, et al.,
Chem. Phys. Lett. 330 (2000)

X-Ray Analysis of Nanotube Orientation

Scattering:

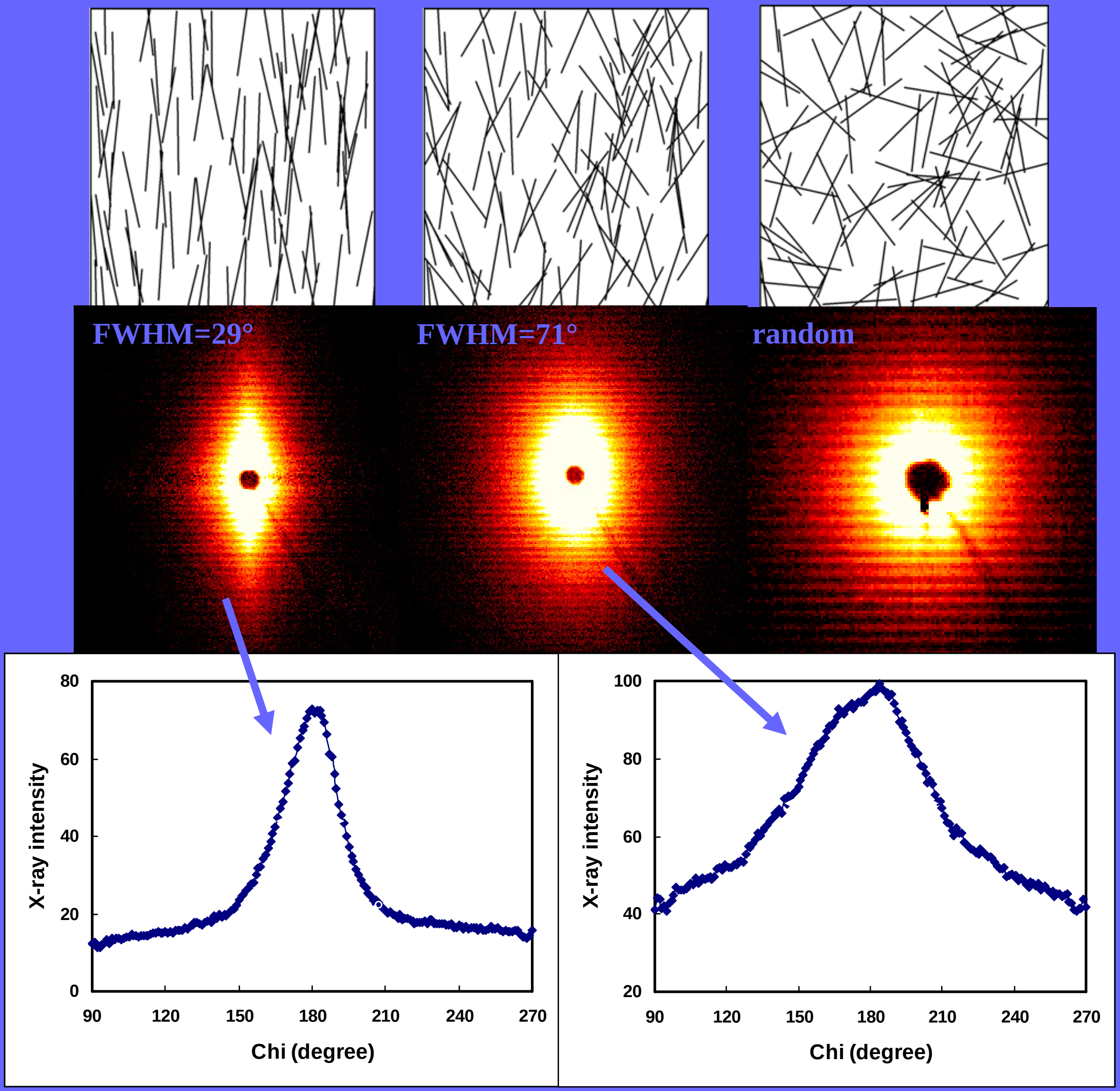
• Form factor scattering due to inherit shape of SWNT. ***Strong.***

• Bragg diffraction due to hexagonal packing in SWNT bundles. ***Weak.***

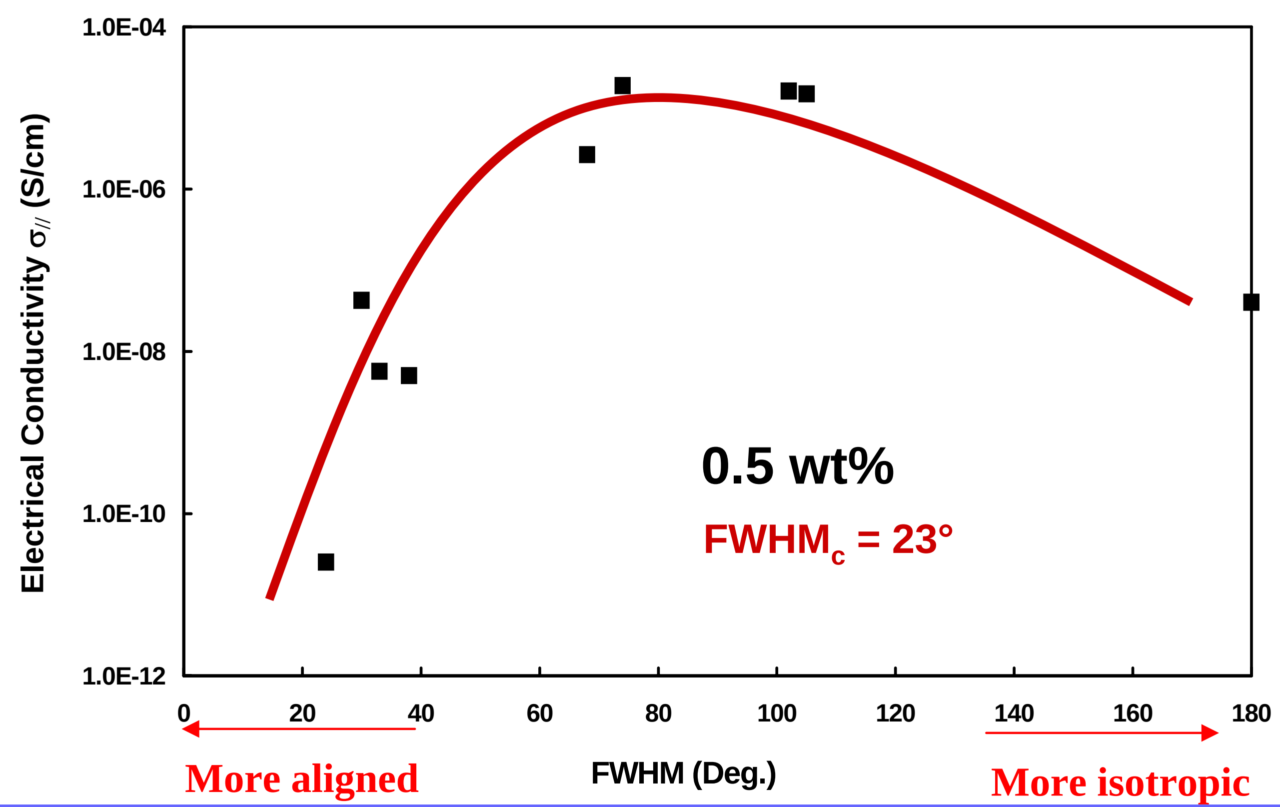
Azimuthal Distribution:

• Anisotropic dependence of scattering indicates SWNT orientation.

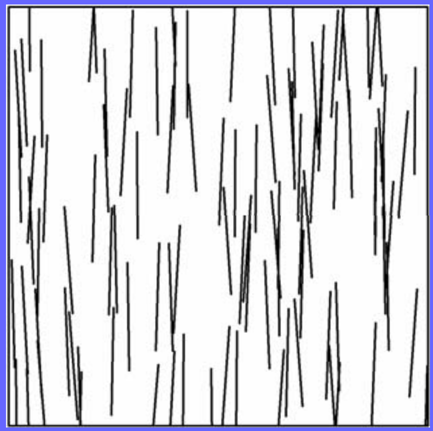
• Quantify distribution by fitting Lorenzian to azimuthal distribution and reporting the FWHM.



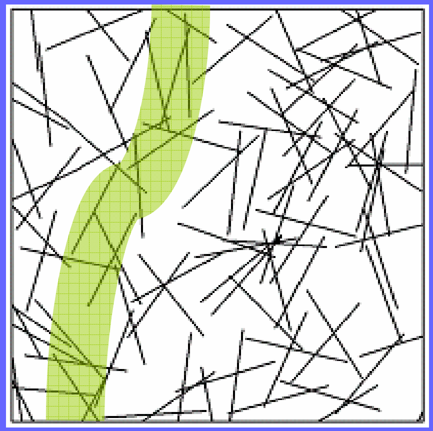
Electrical Conductivity: SWNT Orientation



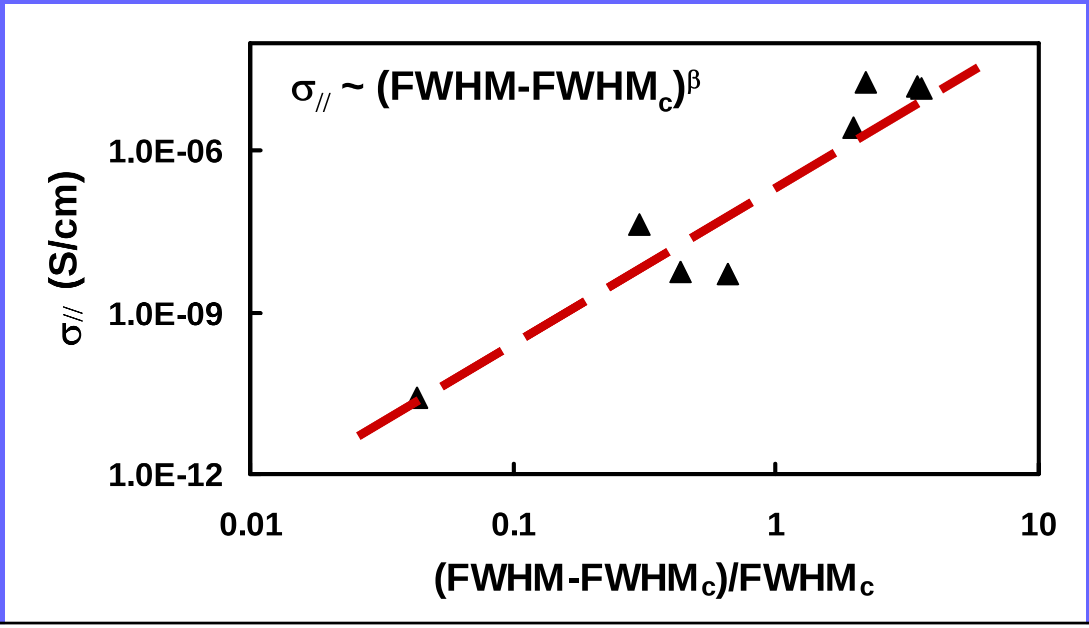
100 sticks, aligned (θ=5°), insulting



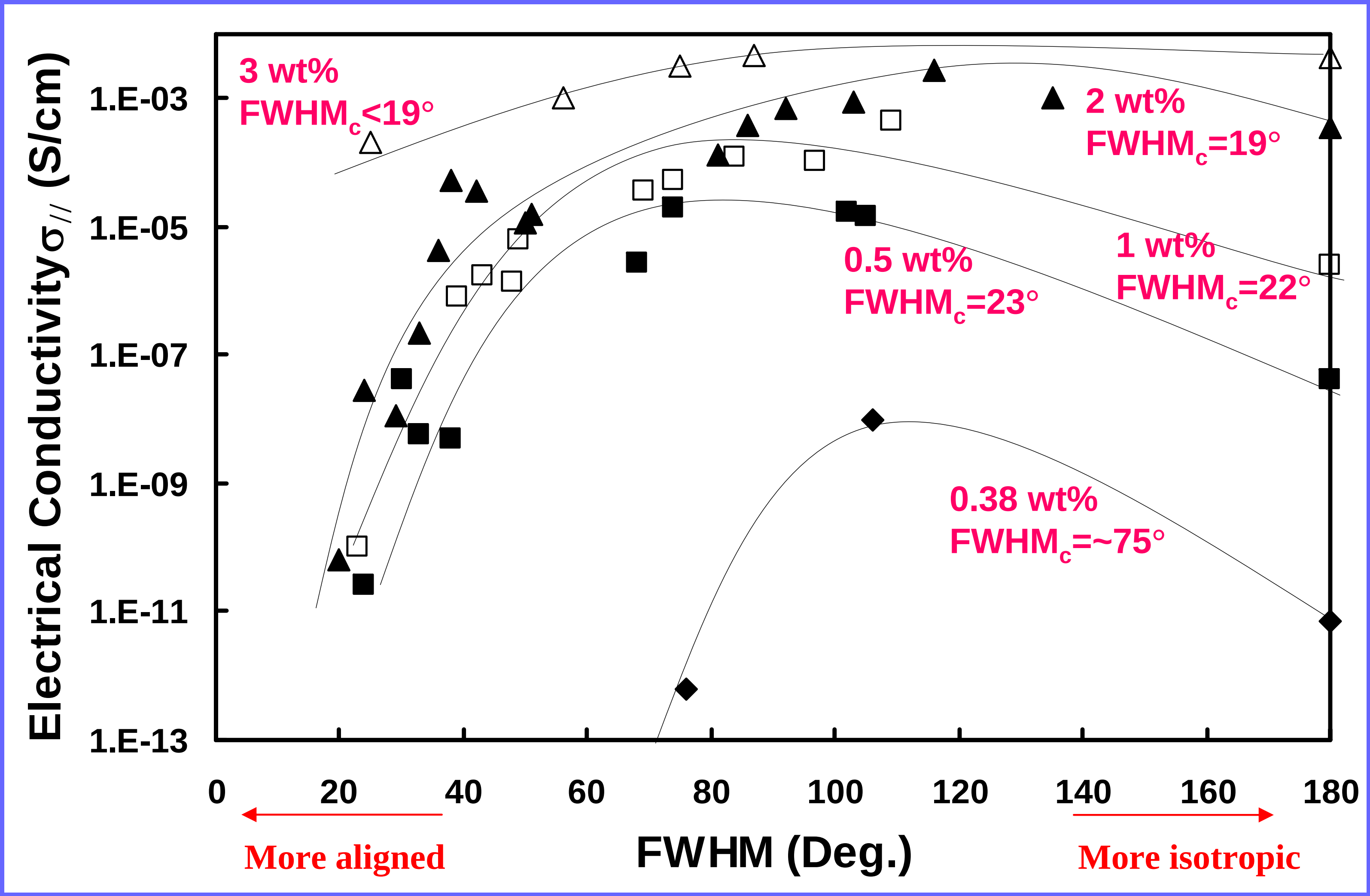
Filler orientation



100 sticks, isotropic, conducting

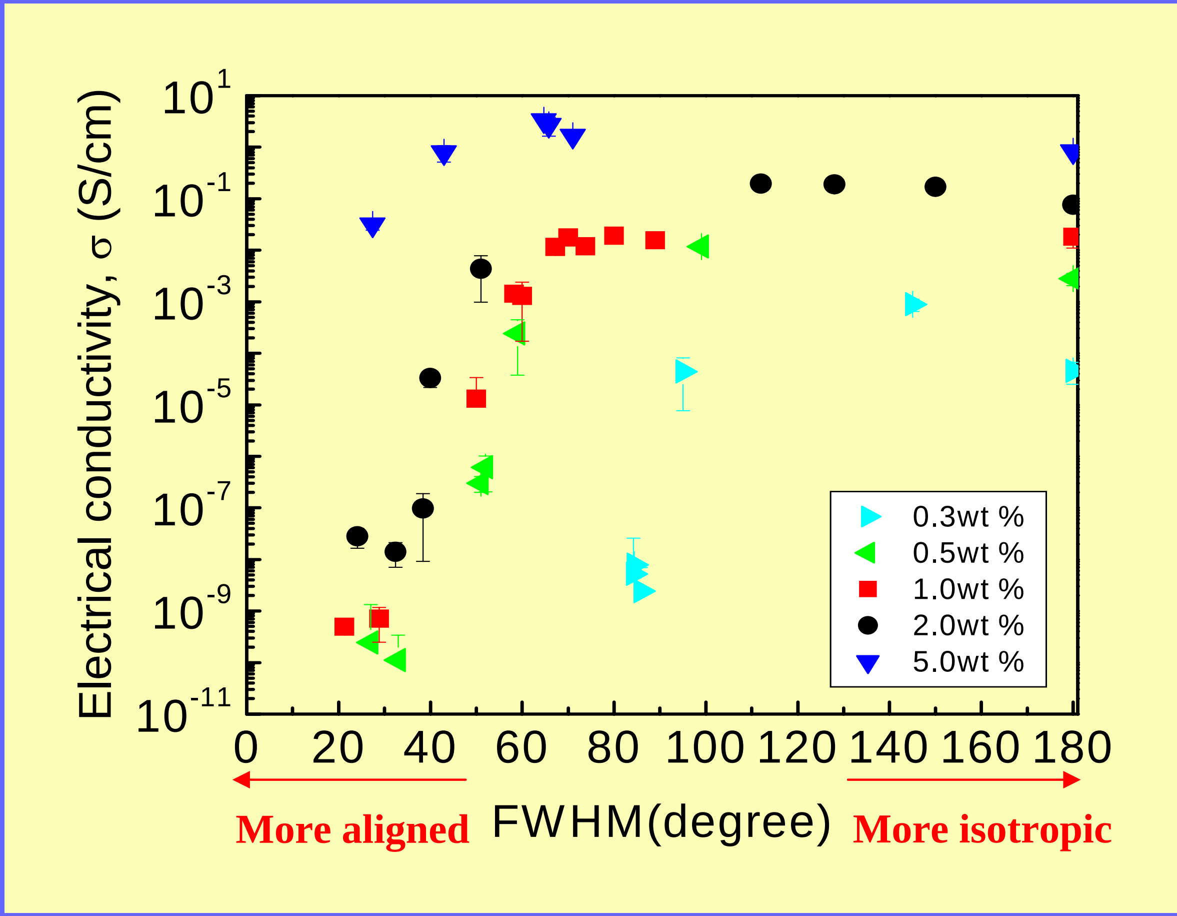


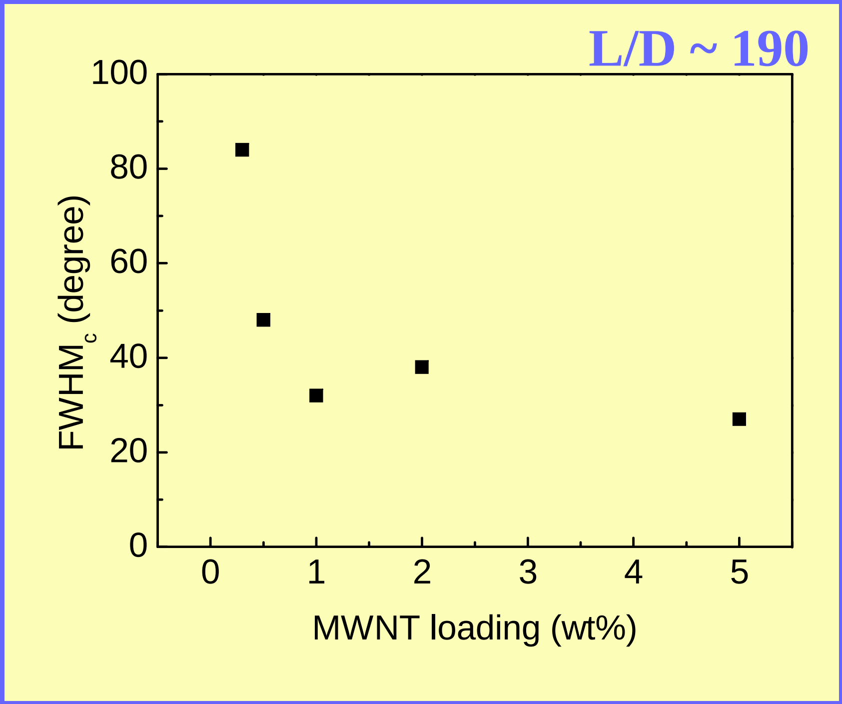
SWNT Loading Effects on Orientation Percolation



1. FWHM$_c$ ↓, as SWNT% ↑
2. Existence of σ_{max}
3. Difference = σ_{max} - σ_{iso} ↓, as SWNT% ↑

MWNT/PMMA Composites: Orientation





- $\sigma \sim (\mathrm{FWHM} - \mathrm{FWHM}_c)^{\beta c}$
- FWHM_c ↓ , as MWNT% ↑
- The isotropic sample is not the maximum σ for 0.3, 0.5, 5.0wt%

#1

Electrical conductivity as a function of filler orientation and filler aspect ratio.

- Electrical conductivity in nanocomposites exhibits a percolation threshold with respect to loading and orientation, where the transition from aligned to isotropic produces a dramatic increase in conductivity.
- The effect of aspect ratio on electrical conductivity is greatest below L/D ~ 50.

F. Du, J. E. Fischer, K. I. Winey*, *J. Polym. Sci.: Polym. Phys.*, **41**, 3333-3338, 2003.

F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, K. I. Winey*, *Macromolecules*, **37**, 9048-9055, 2004.

F. Du, J. E. Fischer, K. I. Winey*, *Rapid Communication in Physical Review B*, **72**, 121404(R)-4, 2005.

Funded by DURIP w/ Rice, NSF-MRSEC

#2

Polyethylene morphology in the presence of SWNT.

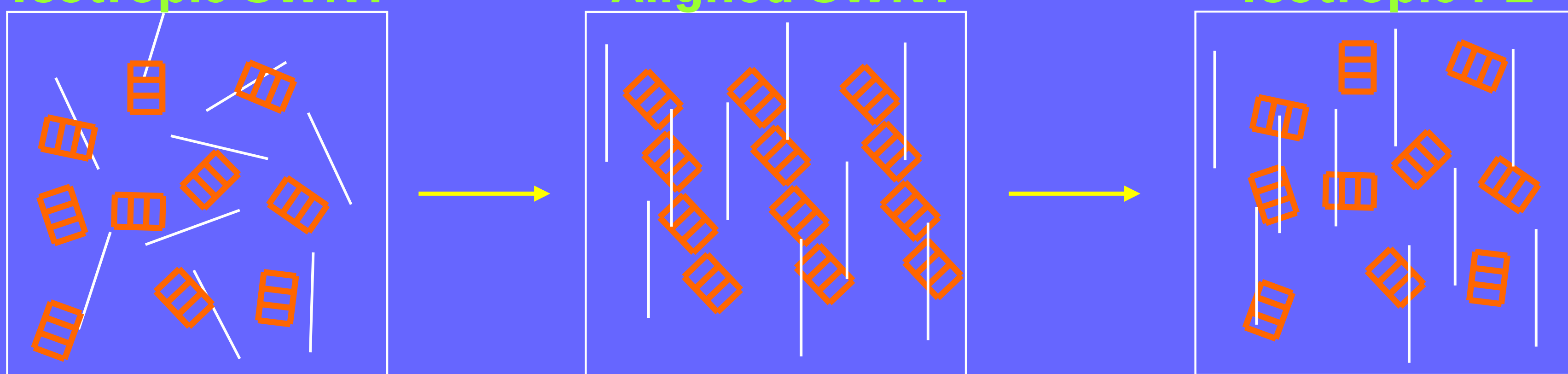
Reto Haggenmueller (UPenn PhD 2005, MEI Charlton, Inc.)
Csaba Guthy (UPenn PhD 2007)
Jack Fischer (UPenn)
Leonard Yowell (NASA JSC)

SWNT and PE Alignment

Type I
Isotropic PE
Isotropic SWNT

Type II
Aligned PE
Aligned SWNT

Type III
Aligned SWNT
Isotropic PE



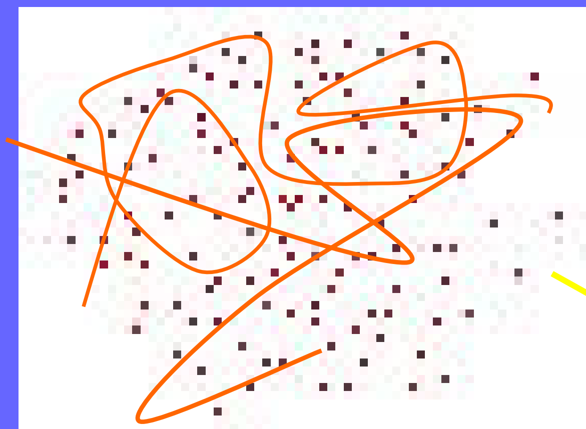
Hot press above T_m (131°C) of PE

Fiber spinning and hot drawing

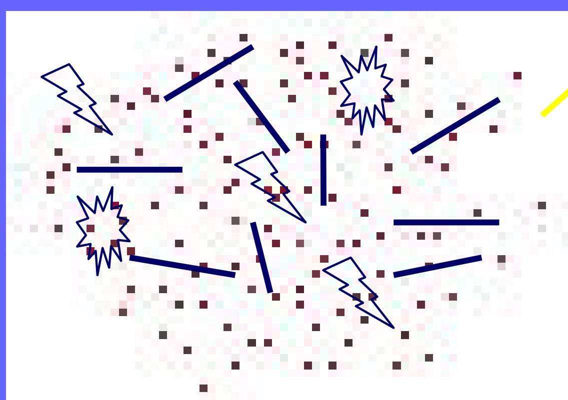
Melting and recrystallizing

Hot Coagulation of PE-SWNT Composites

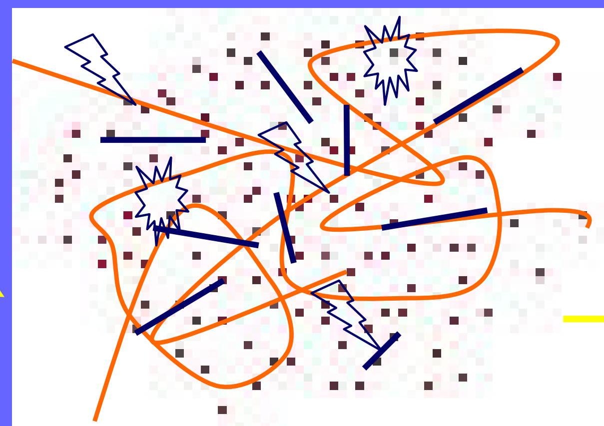
Dissolve PE (20 mg/ml) in 1,2,4-Trichlorobenzene at **115°C**



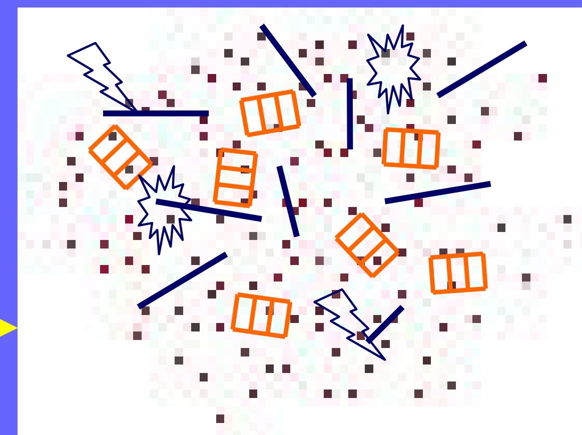
1 – 30 wt% SWNT



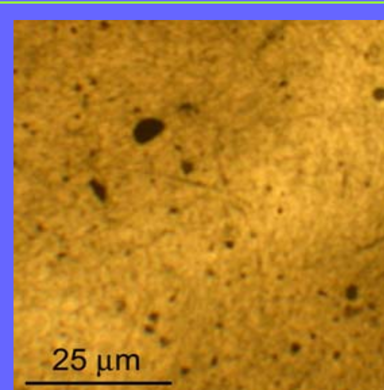
Sonicate HiPco at **RT** in Trichlorobenzene to disperse SWNT, 0.2-0.3 mg/ml



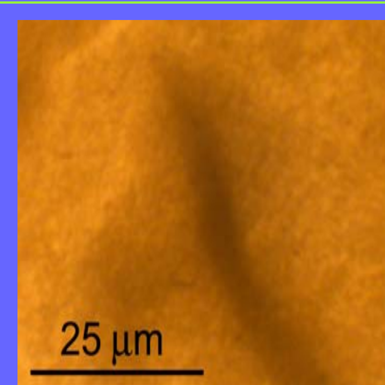
Sonicate 20 min, **95 ° C**



Lower T to coagulate PE

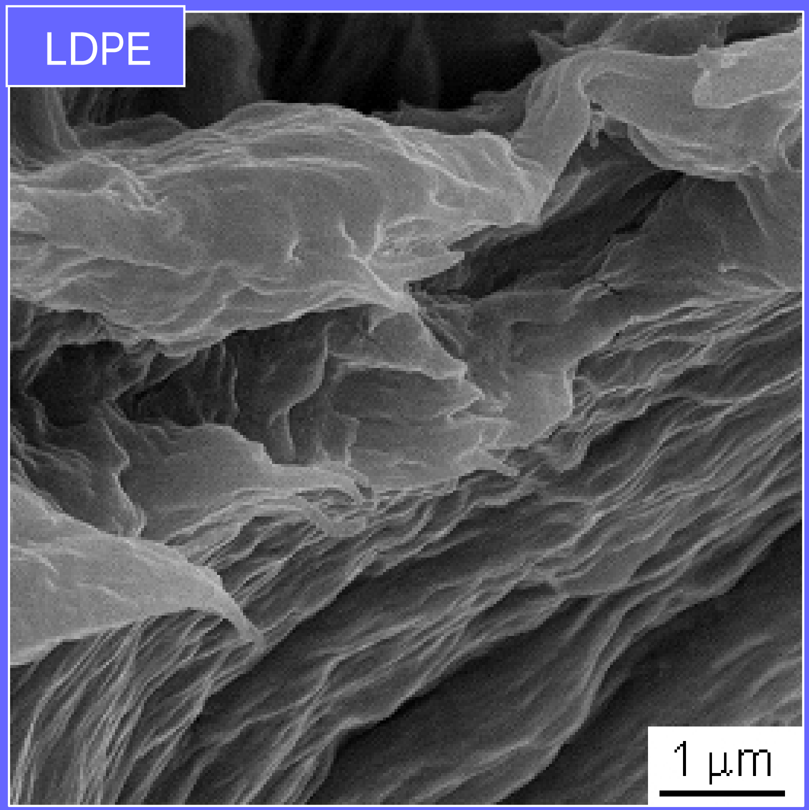


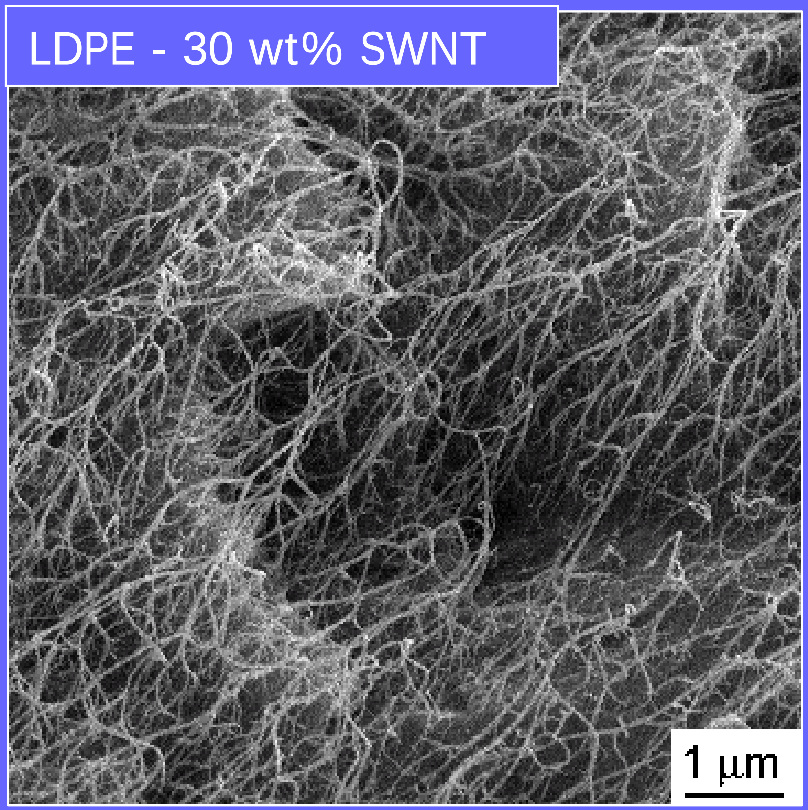
Melt-mixing
10 wt% tubes@rice



Hot-coagulation
20 wt% HiPCO

NASA SWNT Dispersion in PE





SEM of Fracture Surface

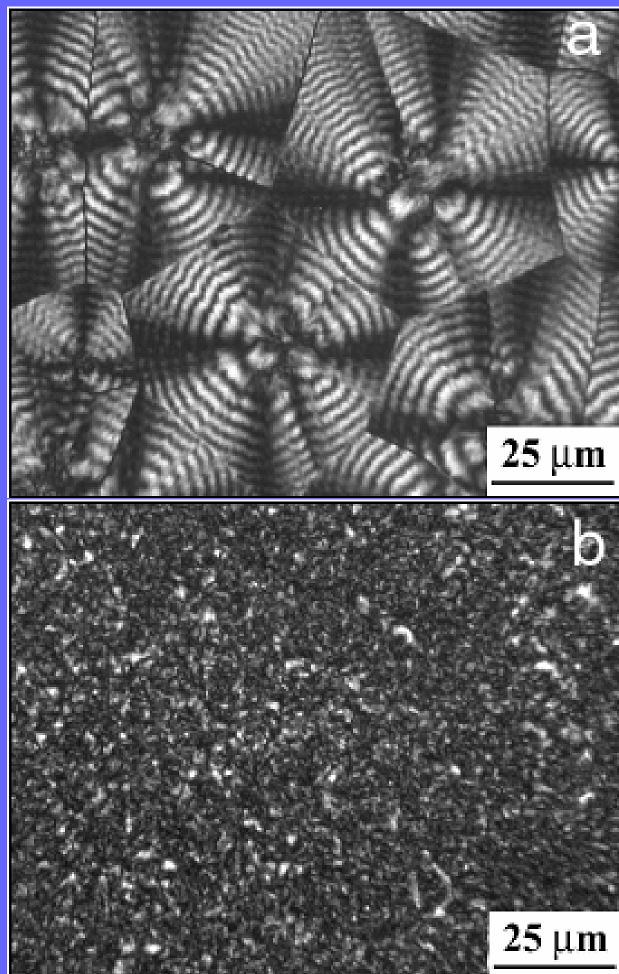
Isothermal Crystallization

TYPE I
Isotropic HDPE
Isotropic SWNT

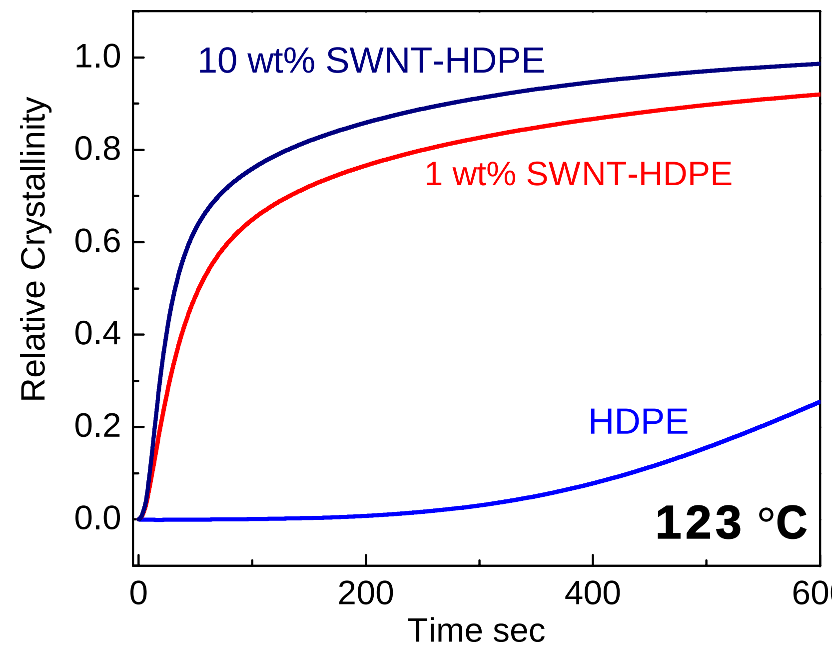
Hot Coagulation
Compression molding

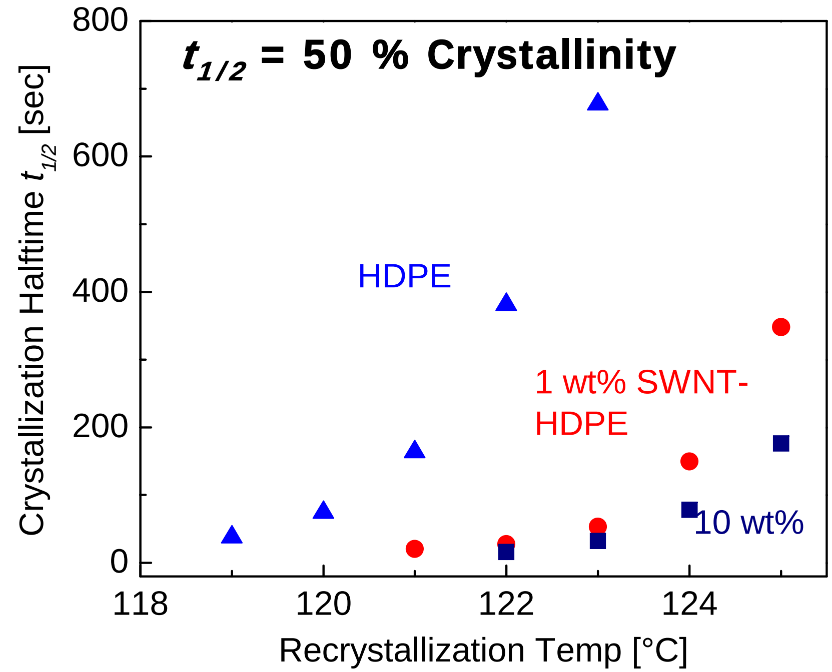
HDPE

0.25 wt% SWNT in HDPE



Transmission optical microscopy with crossed polarizers.

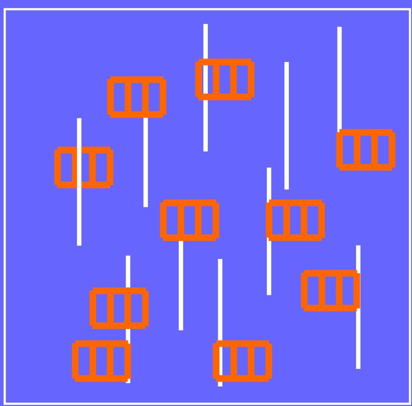




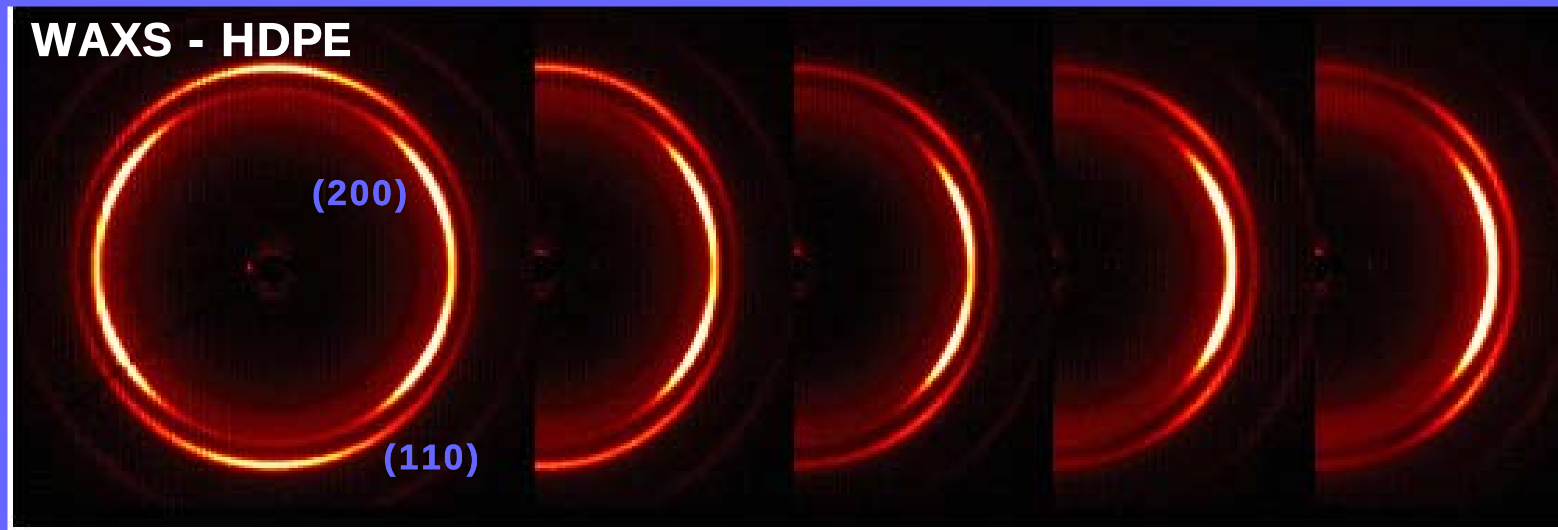
Haggenmueller, et. al., *Macromolecules*, 2006.

Melt Fiber Spinning

TYPE II
Aligned HDPE
Aligned SWNT



Hot Coagulation
Melt fiber spinning
(Extrude 2 mm/min)

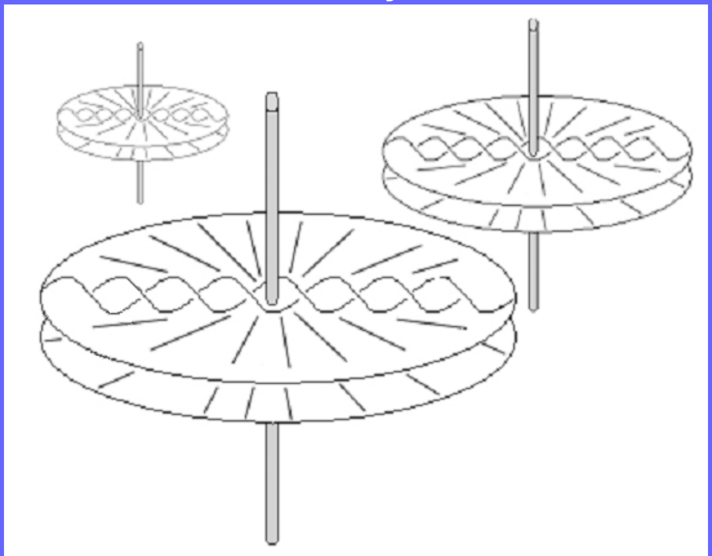


20 m/min 40 60 80 100
Wind-up Speed

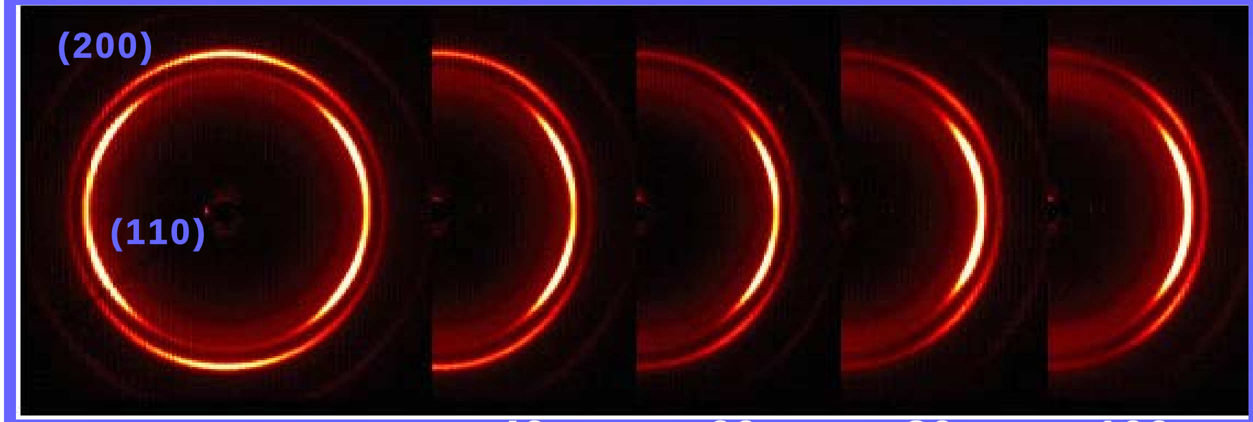
Haggenmueller, et. al., *Macromolecules*, 2006.

Melt Fiber Spinning

Low shish density: kebabs twist

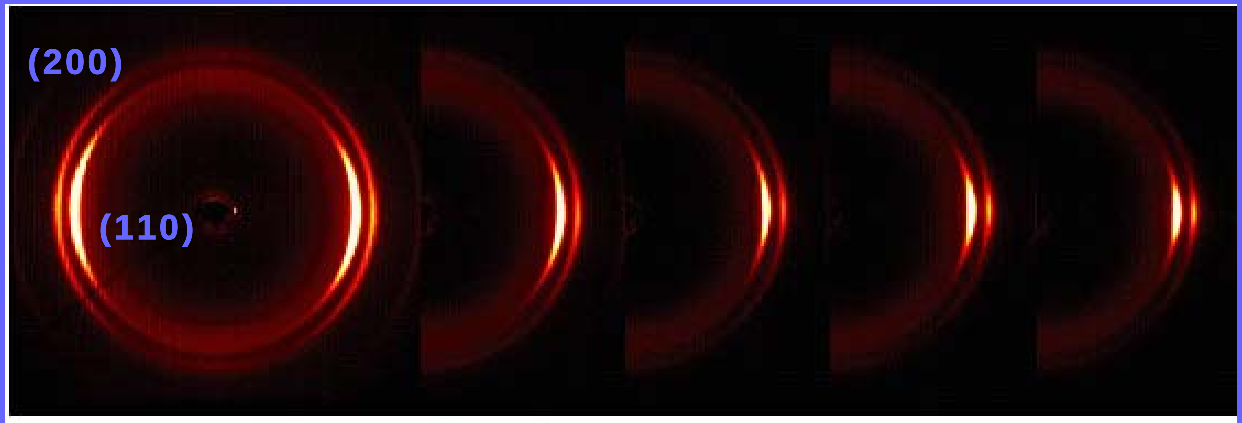


WAXS - HDPE

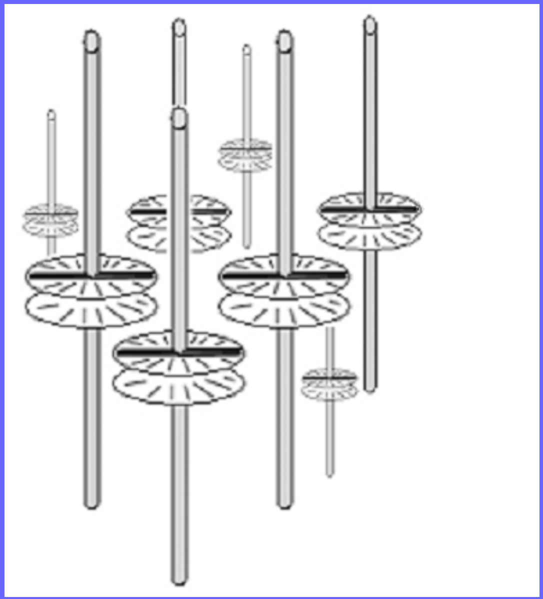


20 m/min **40** **60** **80** **100**
Wind-up Speed

WAXS – 1 wt% SWNT - HDPE

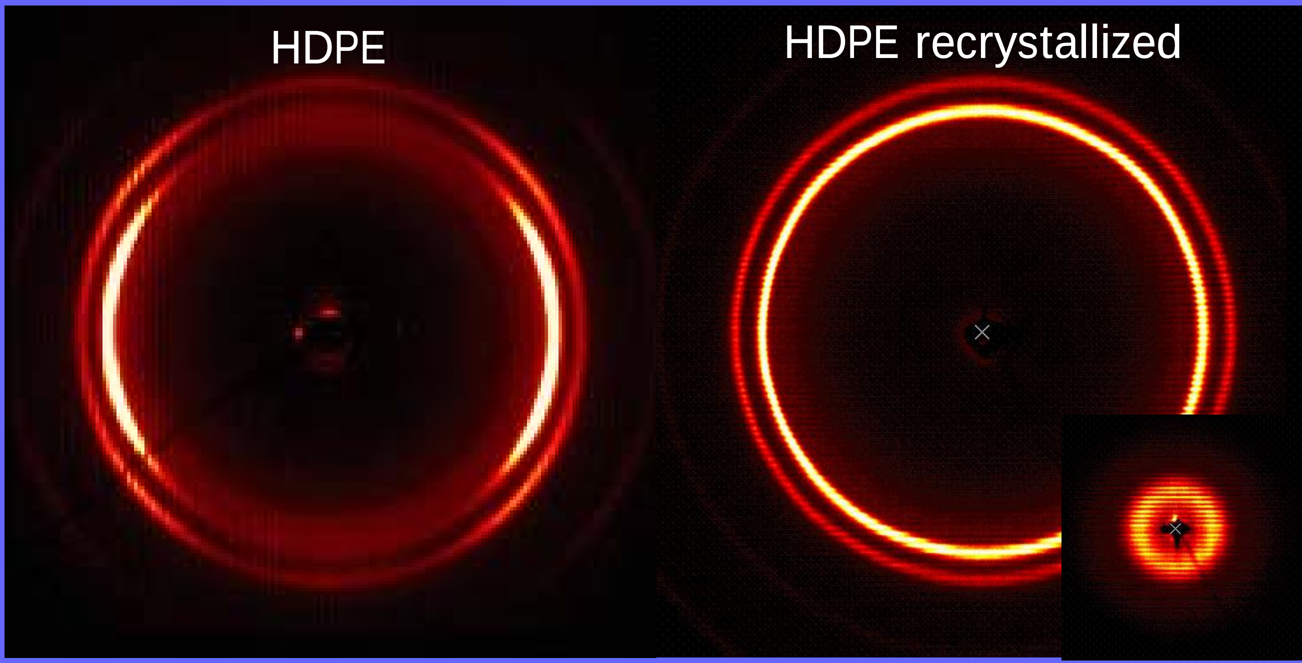


20 m/min **40** **60** **80** **100**
Wind-up Speed



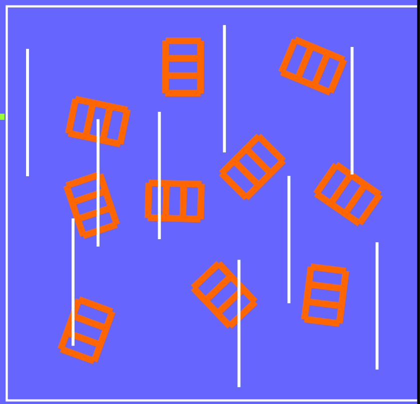
High shish density: kebabs grow straight

Recrystallize Fibers

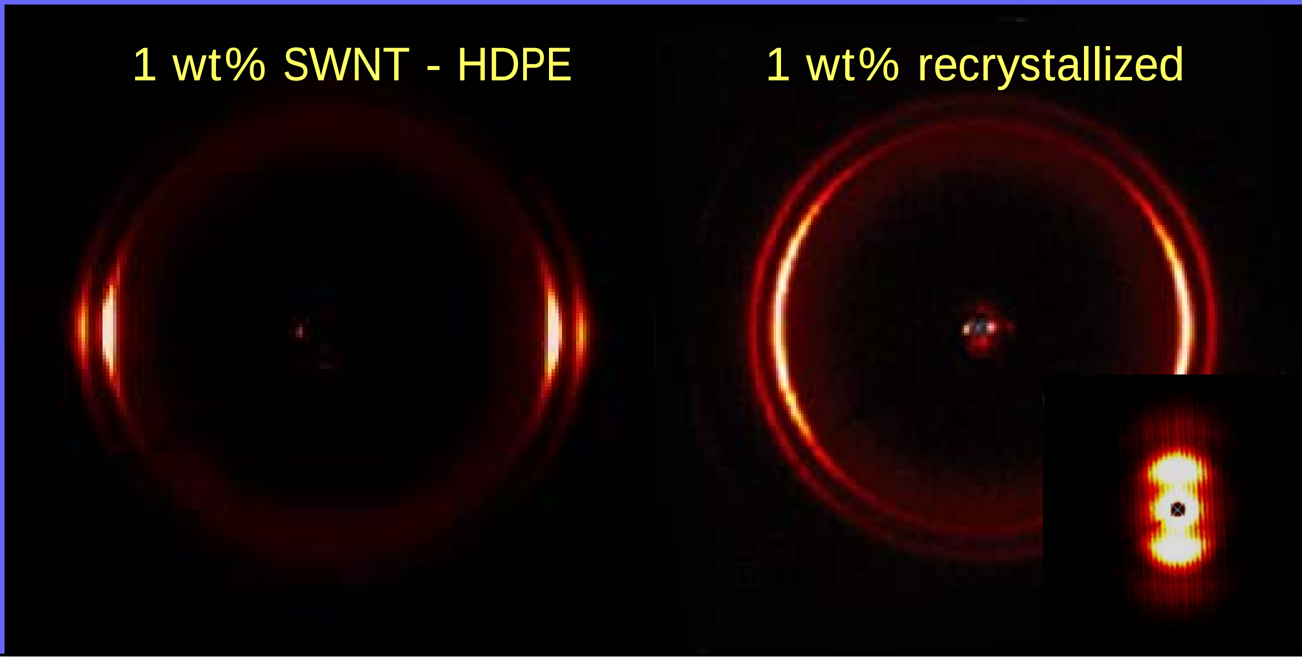


Type III
Aligned SWNT
Isotropic PE

Melting and recrystallizing



PE orientation:
Before: FWHM 45°
fc = 0.388
After: Isotropic

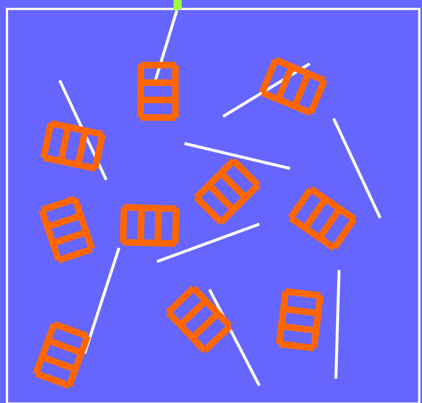


PE orientation:
Before: FWHM 12°
fc = 0.715
After: FWHM 35°
fc = 0.36

SWNT orientation:
Before: FWHM 4.5°
After: FWHM 44°

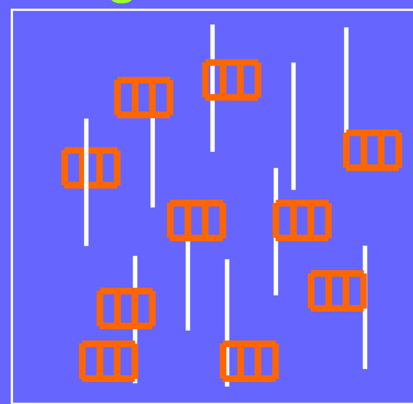
Differentiate SWNT and PE Alignment

Type I
Isotropic PE
Isotropic SWNT



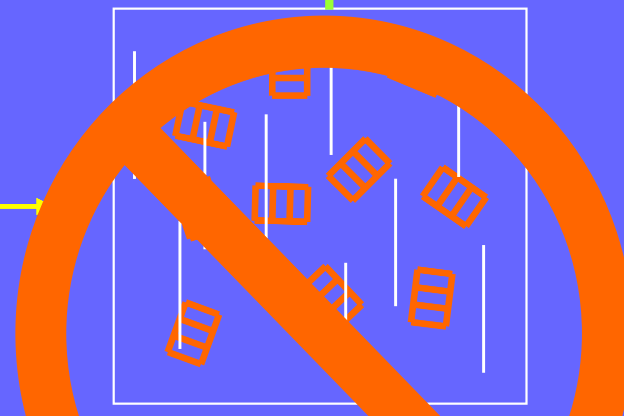
Hot press above T_m (131°C) of PE

Type II
Aligned PE
Aligned SWNT

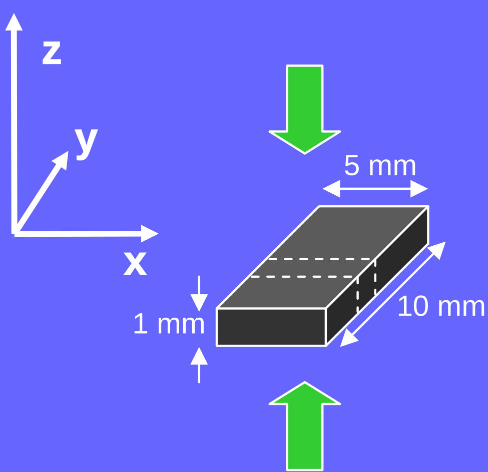


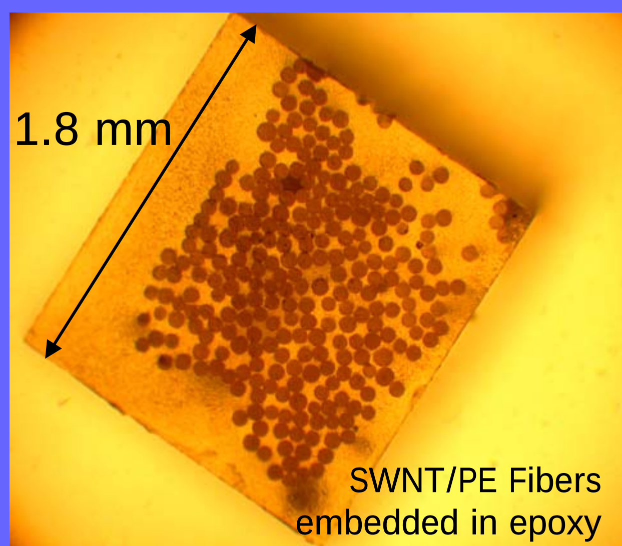
Fiber spinning and hot drawing

Type III
Aligned SWNT
Isotropic PE



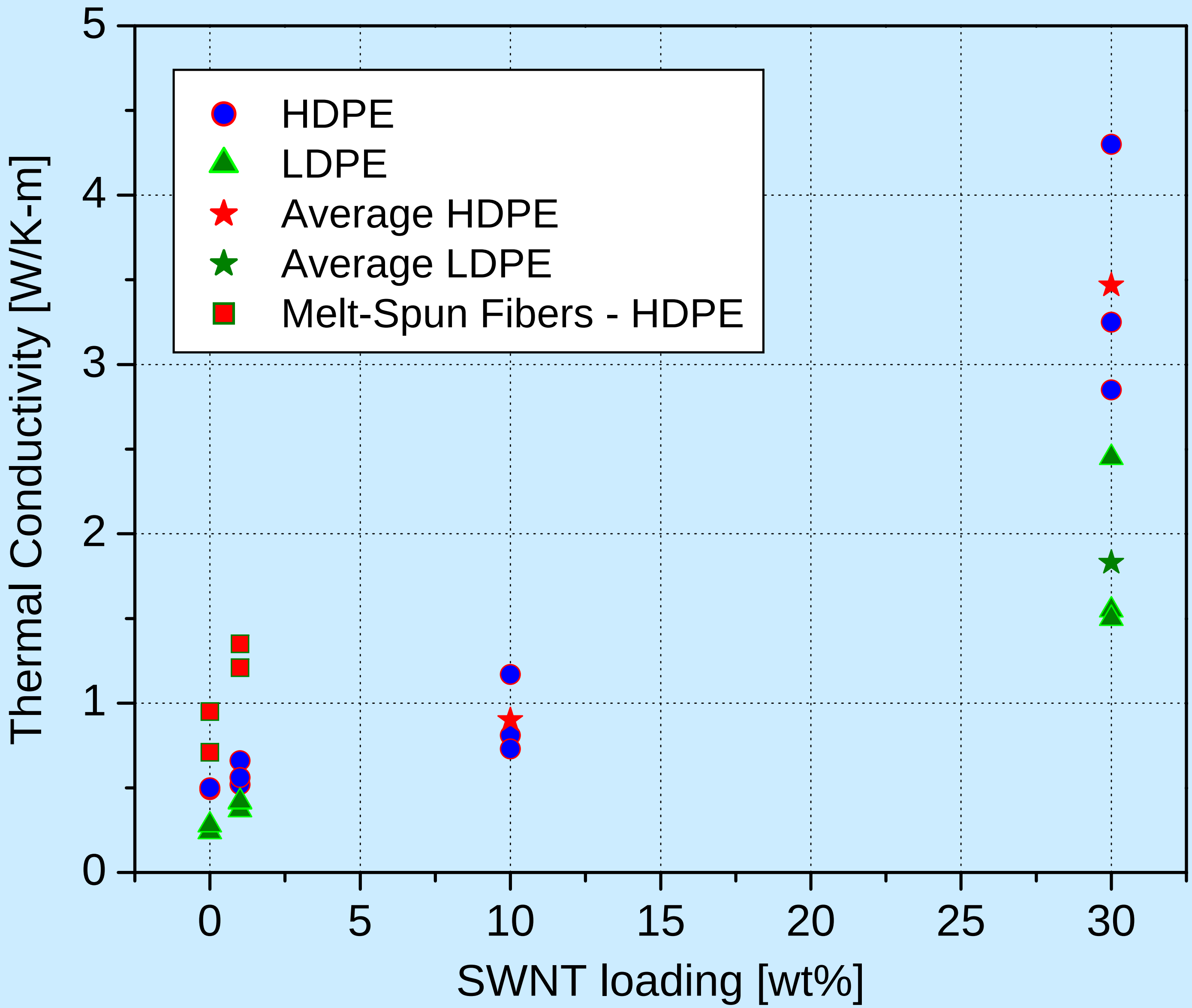
Melting a
recrystallizing

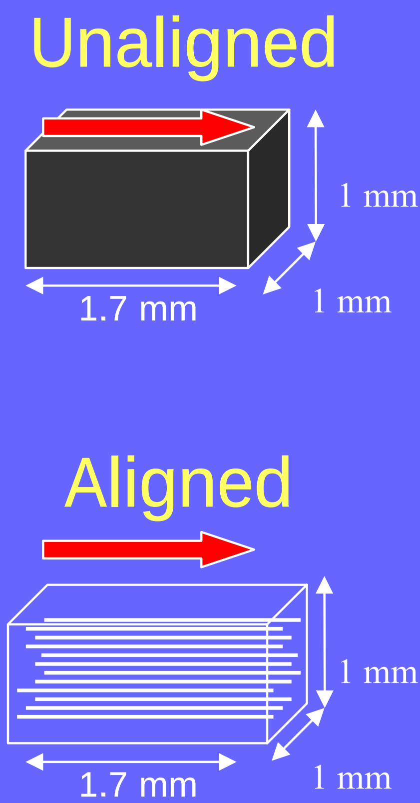




Measure Thermal Conductivity

Thermal Conductivity SWNT - PE





Measured thermal conductivity by the comparative method.

#2

Polyethylene morphology in the presence of SWNT.

- Single walled carbon nanotubes nucleate the crystallization of PE and template the growth of PE lamellae perpendicular to the SWNTs.

- Thermal conductivity of PE increaeses with the addition of SWNT, particularly when the SWNT and PE are aligned.

R. Haggenmueller, J. E. Fischer, K. I. Winey*, *Macromolecules*, **39**, 2964-2971, 2006.

R. Haggenmueller, C. Guthy, J. R. Lukes, J. E. Fischer, K. I. Winey*, *Macromolecules*, **40**, 2417-2421, 2007.

Funded by ONR

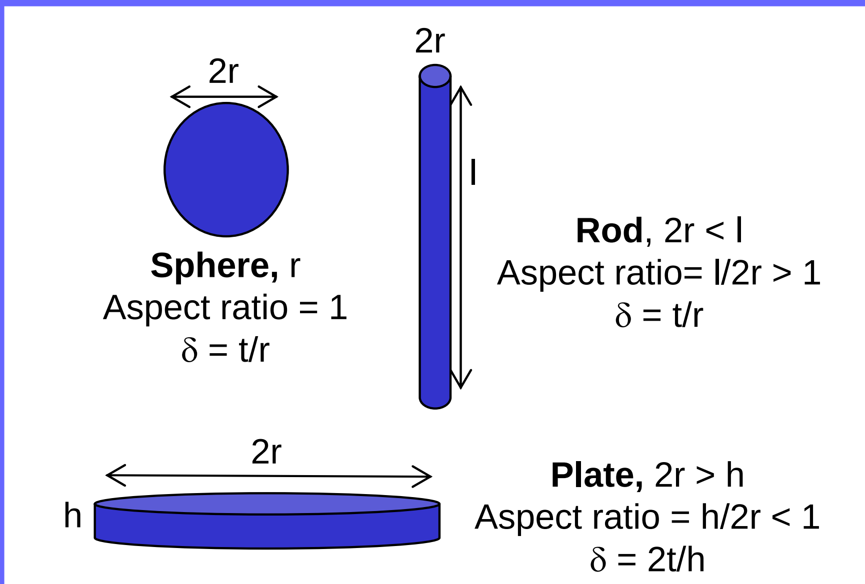
#3

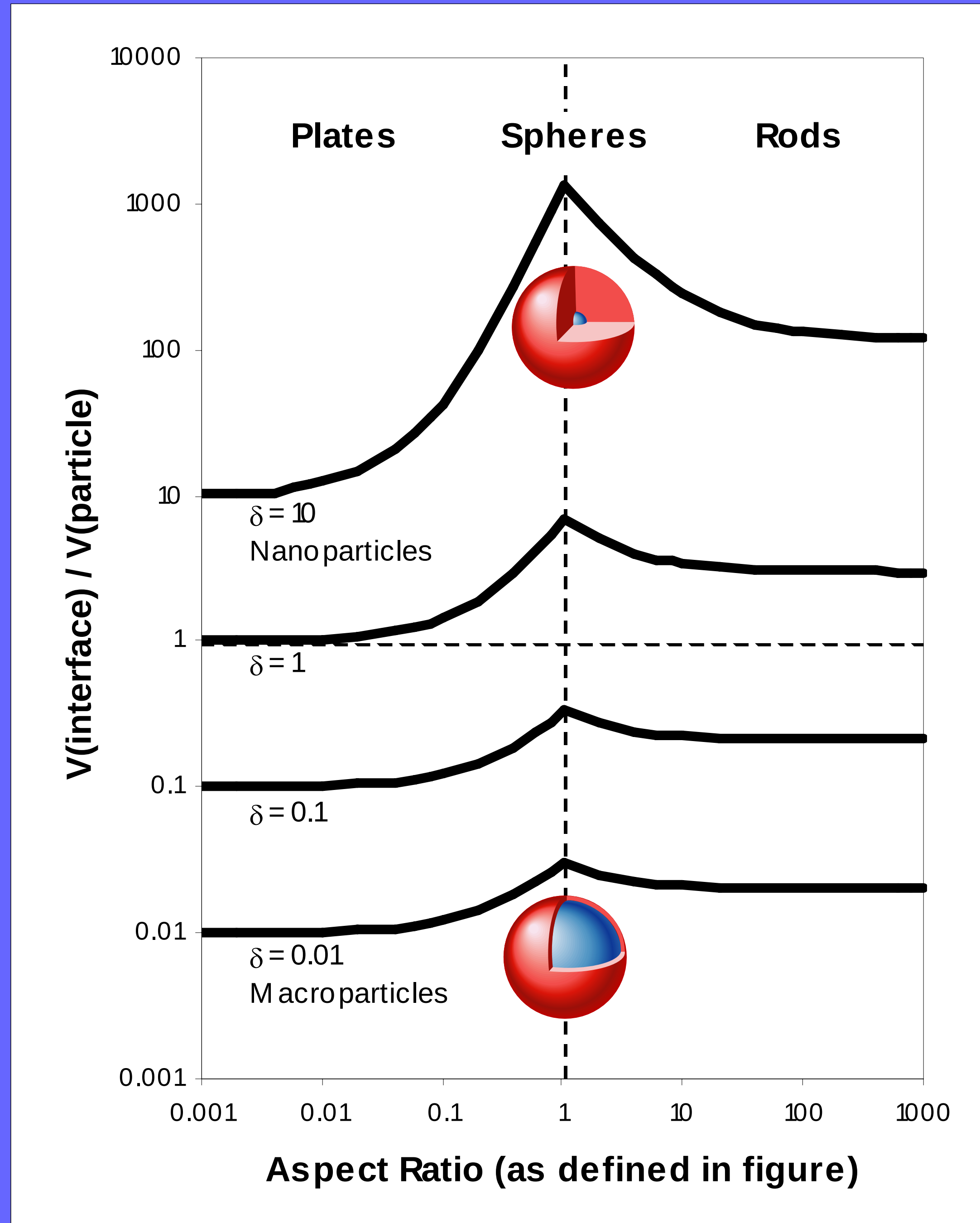
Controlling mechanical properties by tuning the polymer / filler interface.

Minfang Mu (UPenn)
M. Moniruzzaman (UPenn, postdoc)
Ed Billips (Rice University)

What's different about nanocomposites?

"Polymer Nanocomposites." Winey and Vaia, *MRS Bulletin*, to appear in **April 2007**.



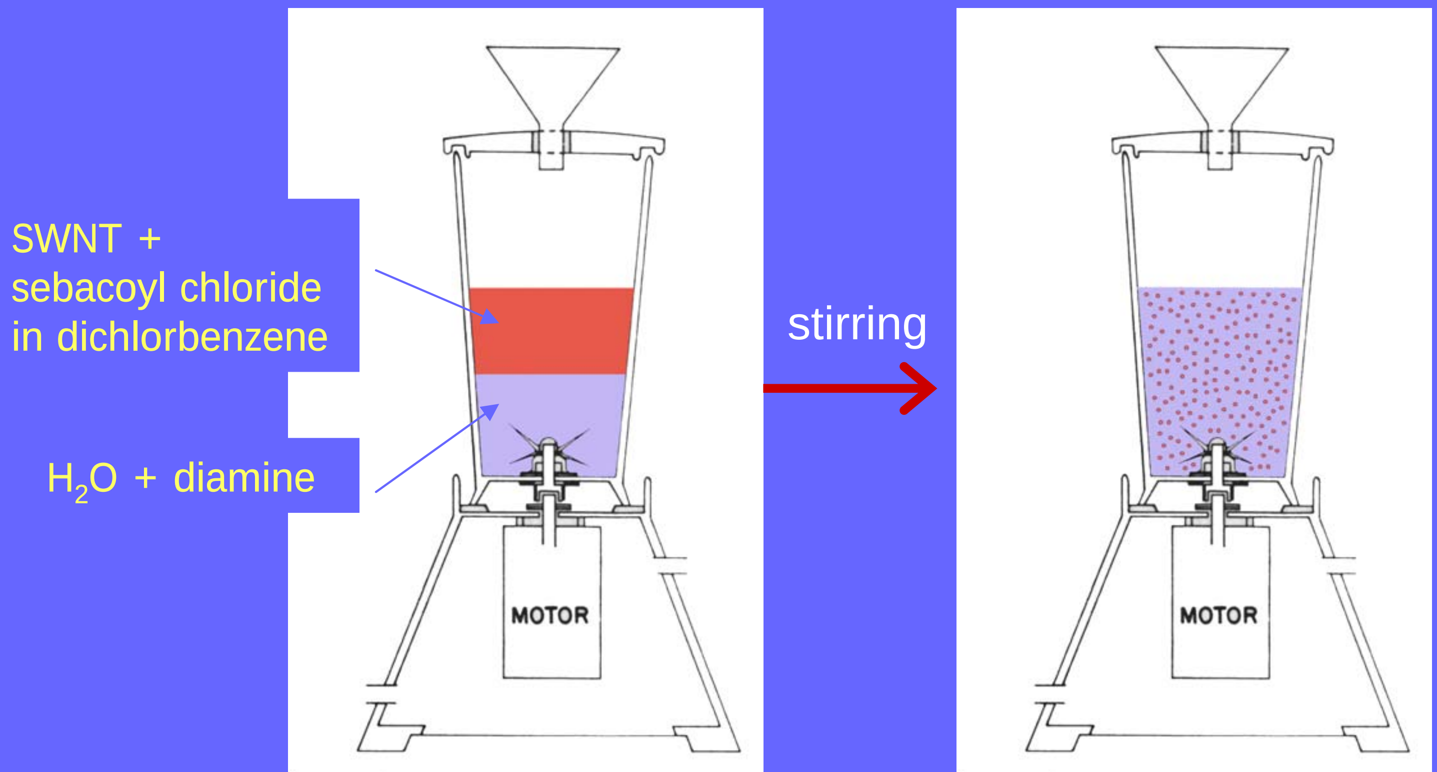


t - thickness of the interfacial volume, that is the thickness of the polymer matrix perturbed by the filler particle, ~ 1 - 10nm.

δ - size of particle relative to **t** and as δ increases the filler particle decreases in size.

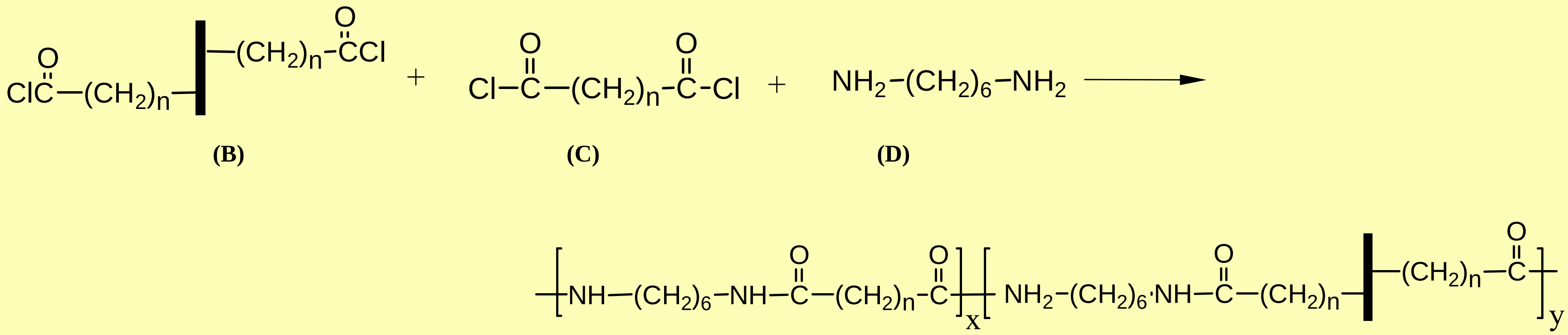
➢ The volume of the interfacial region *exceeds* that of the particle volume as the filler become nanoscale.

Interfacial In Situ Polycondensation of SWNT/nylon



Haggenmueller et al. *Polymer* **2006**, *47*, 2381-2388.
Winey et al U.S. Patent 2006, US 7,148,269.

Functionalized SWNT and Nylon 6, 10 Interfacial In Situ Polycondensation



N = 4, 9

~ 1 acid chloride per 32-35 carbon atoms

Two phases: water, dichlorobenzene

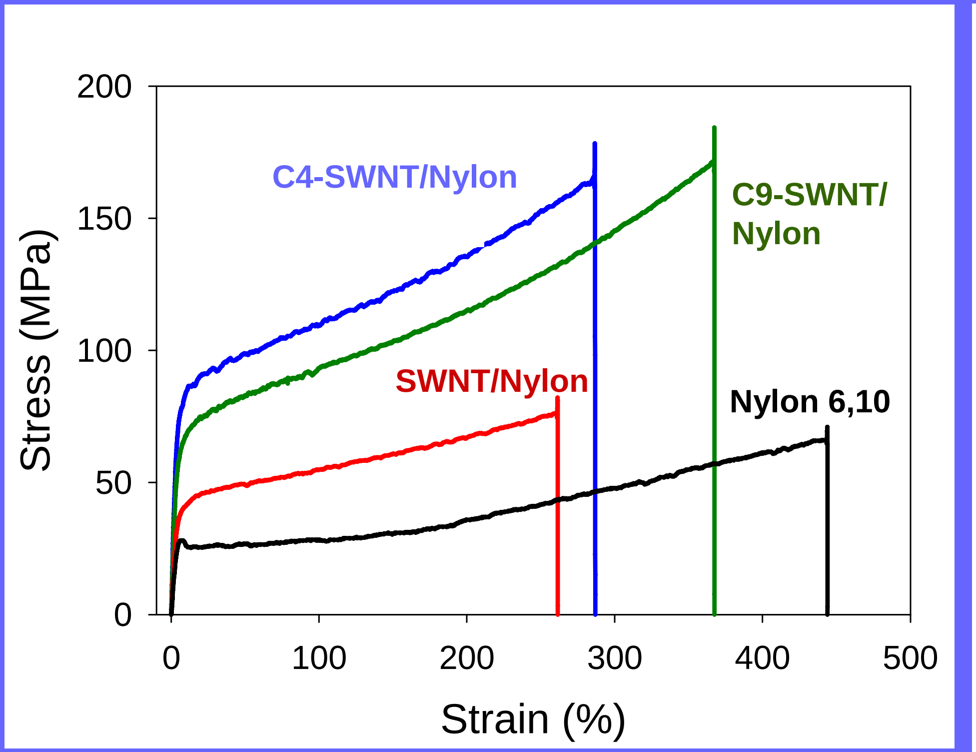
Raman Spectroscopy – covalent bond with SWNT

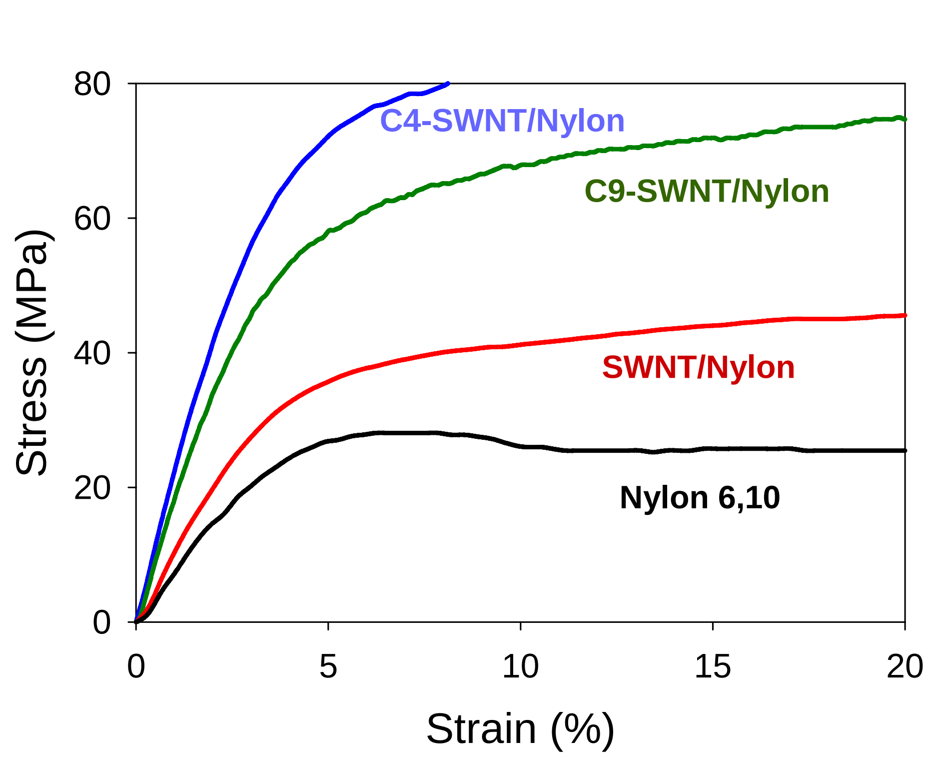
FTIR Spectroscopy – acid chloride combines with diamine

Ed Billups, Rice University

Moniruzzaman, et. al., *Nano Letters* 2007.

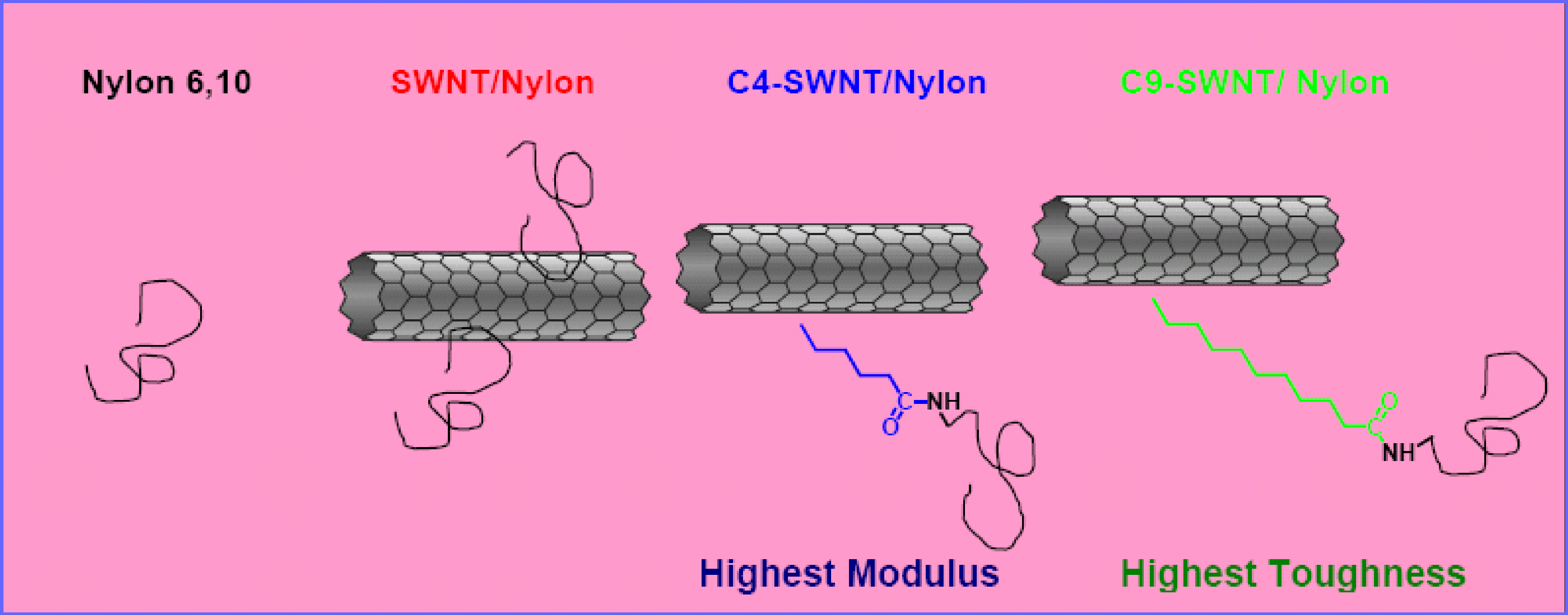
Mechanical Properties of the Composite Fibers (1 wt% filler)





- Composite fibers have higher Young's modulus and strength than nylon 6,10.
- C4-SWNT and C9-SWNT composite fibers have significantly improved strain at break compared to SWNT composite fibers.

Moniruzzaman, et. al., *Nano Letters* 2007.

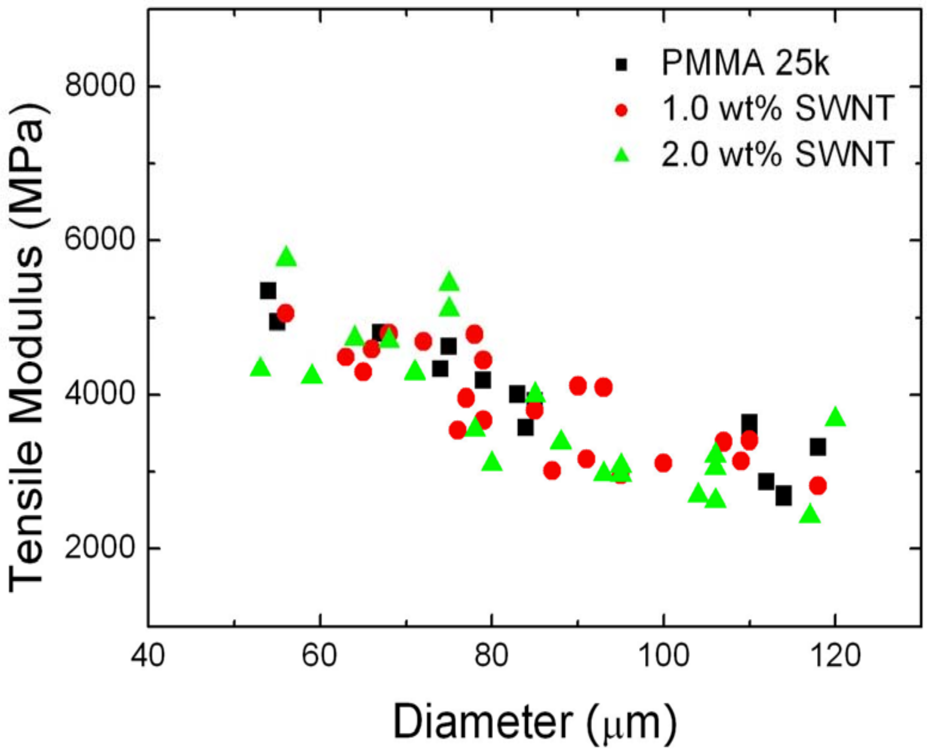


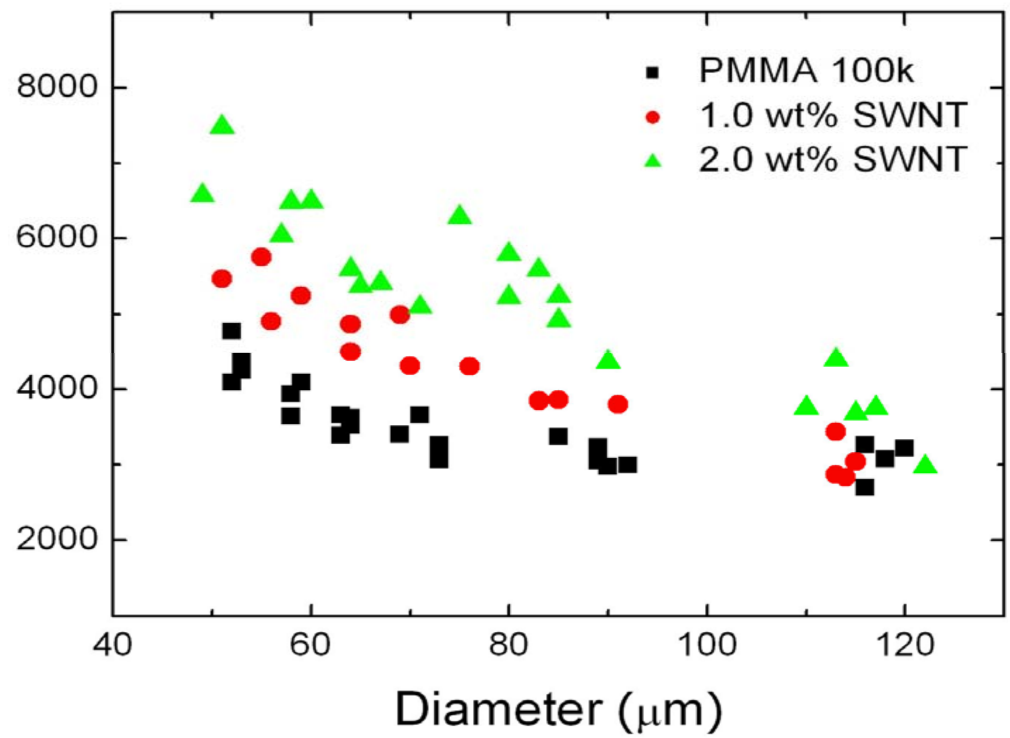
1 wt% filler	Nylon 6,10	SWNT	C4-SWNT	C9-SWNT
Young's modulus (MPa)	879 ± 65	1217 ± 86	2309 ± 78	1955 ± 73
% change		38%	**162%**	**132%**
Tensile strength (MPa)	67.4 ± 6	79 ± 7	168 ± 7	177 ± 6
% change		17%	**149%**	**163%**
Toughness (MPa)	177 ± 18	152 ± 21	365 ± 21	417 ± 24
% change		-14%	**106%**	**136%**
Strain at break (%)	440 ± 7	262 ± 5	290 ± 6	368 ± 7

Moniruzzaman, et. al., *Nano Letters* 2007.

Molecular Weight Effect

Coagulation method
Melt fiber spinning



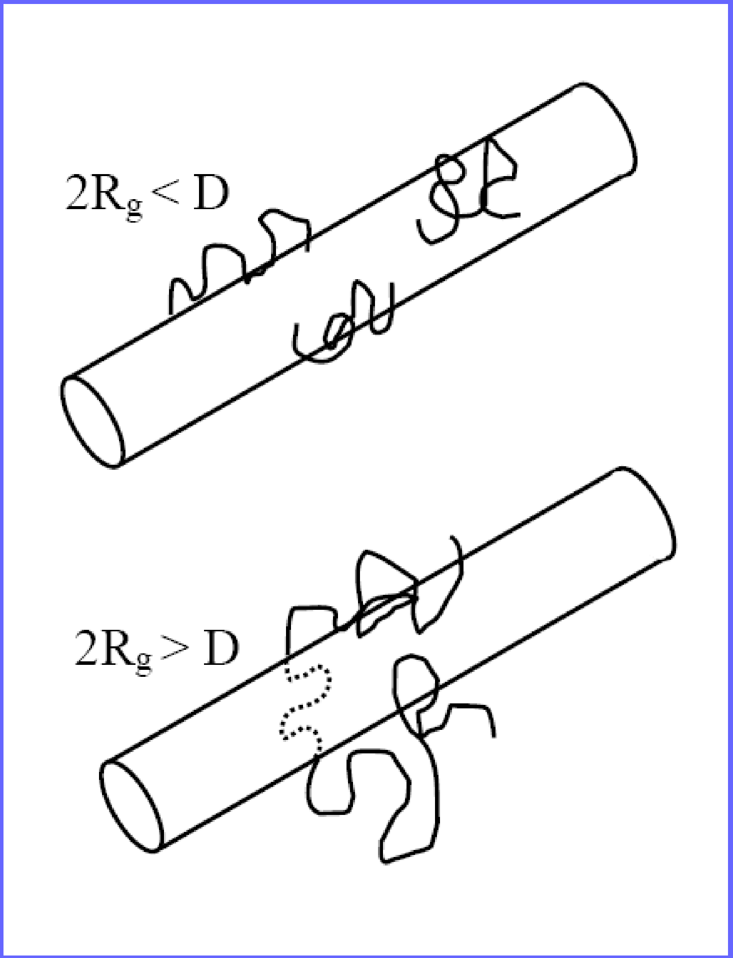


Both sets of composites exhibit comparable SWNT distribution (Raman mapping) and SWNT orientation (x-ray scattering).

Mu, et. al., *J Phys. Chem B*, in press.

Molecular Weight Effect

composite	$2R_g/D$	α (μm^{-1})	[a-D] (nm)
1.0 wt% SWNT in 100k PMMA	1.79	3.33	85.5
2.0 wt% SWNT in 100k PMMA	1.79	6.66	57.7
1.0 wt% SWNT in 25k PMMA	0.90	3.33	85.5
2.0 wt% SWNT in 25k PMMA	0.90	6.66	57.8
6.4 wt% CNF in 100k PMMA	0.22	3.33	192.7
17.7 wt% CNF in 100k PMMA	0.22	9.19	85.5



2Rg/D: relative filler size

α: specific interfacial area

(a-D): filler-filler separation

Mu, et. al., *J Phys. Chem B*, in press.

#3

Controlling mechanical properties by tuning the polymer / filler interface.

- In nylon 6,10, an alkane spacer of 4 or 9 carbons significantly improves modulus, strength and toughness relative to unfunctionalized SWNT.

- In amorphous polymers, a relative size (2Rg/D) greater than one improves modulus.

M. Moniruzzaman, J. Chattopadhyay, W. E. Billups, K. I. Winey*, *NanoLetters*, **7**, 1178, 2007.

M. Mu, K. I. Winey*, *J. Phys. Chem. B*, in press.

Funded by NSF MRSEC, NASA, Nanotechnology Institute (PA)