Challenges of High Performance Polymer Nanocomposites

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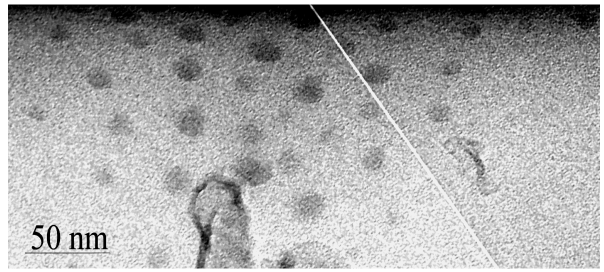
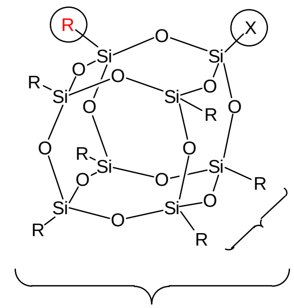
Polymer Nanocomposites

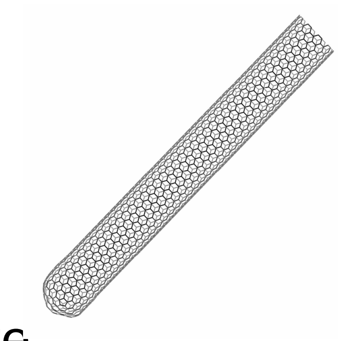
- Introduce small amounts of Nanoparticles to achieve dramatic changes in
  - Mechanical, Thermal, Physical, Electrical and / or Chemical Properties
  - Minimal change in density of the polymer
  - Possibly Inexpensive
- Challenges:
  - Dispersion (Equilibrium; Kinetics; Processing)
  - Interface Control
  - Optimization & Pricing

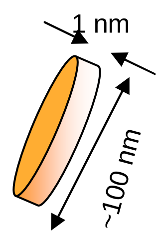
Nanoparticles

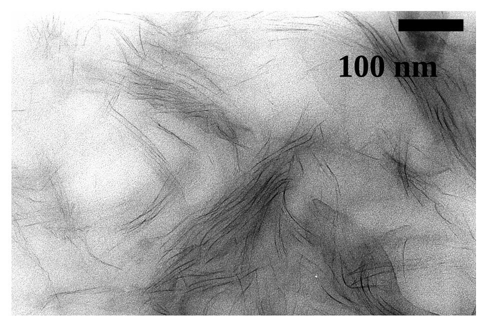
- ► Nanoparticles
  - ► Silica Nanoparticles
  - ► Silsequioxanes
  - ► Carbon nanotubes
  - ► Layered silicates
- ► Isotropic or Anisotropic
  - ► Usually possess Hierarchy of Structure
- ► Functionalized or Pristine
  - ► Controls Thermodynamics
  - ► Might Compromise Properties











A New Paradigm or A Re-invention of Filled Polymers?

- Hierarchical morphology – property correlations?
- Confined polymer behavior - Different from thin film and coating technology?

New Issues:

Preponderance of interface

Diminishing volume fraction of ‘bulk’

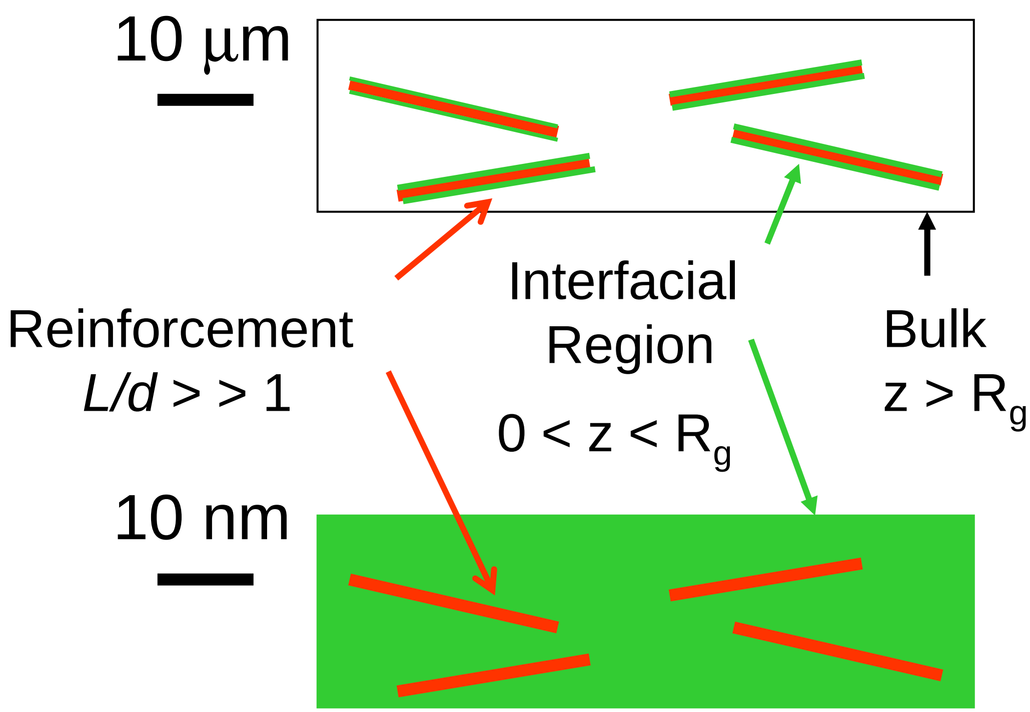
Aspect ratio of constituents

Dissimilar mechanical properties of matrix and filler

Hierarchical morphology with more than one length scale

Morphological Scale

<u>"Macro"-composite</u> *d = 1 µm*



1 x 25 µm fibers

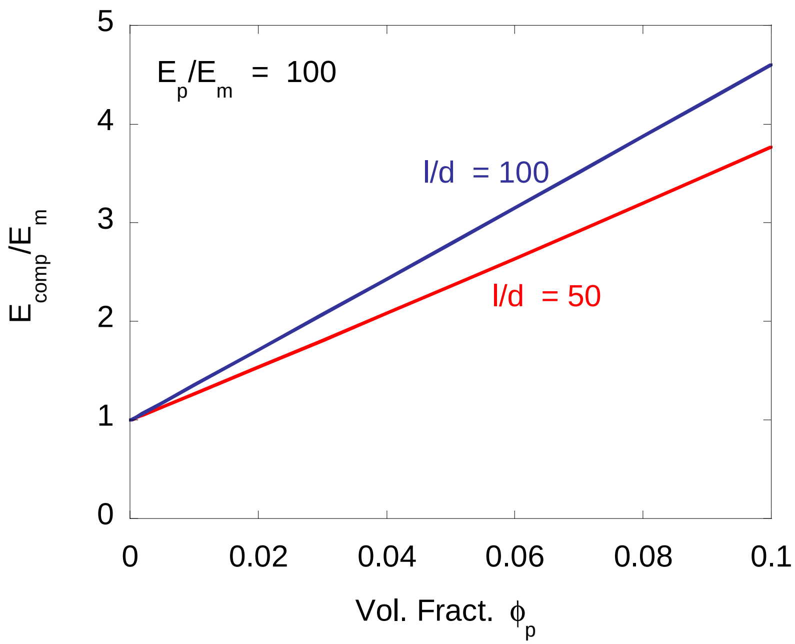
1 x 25 nm fibers

<u>"Nano"-composite</u> *d = 1 nm*

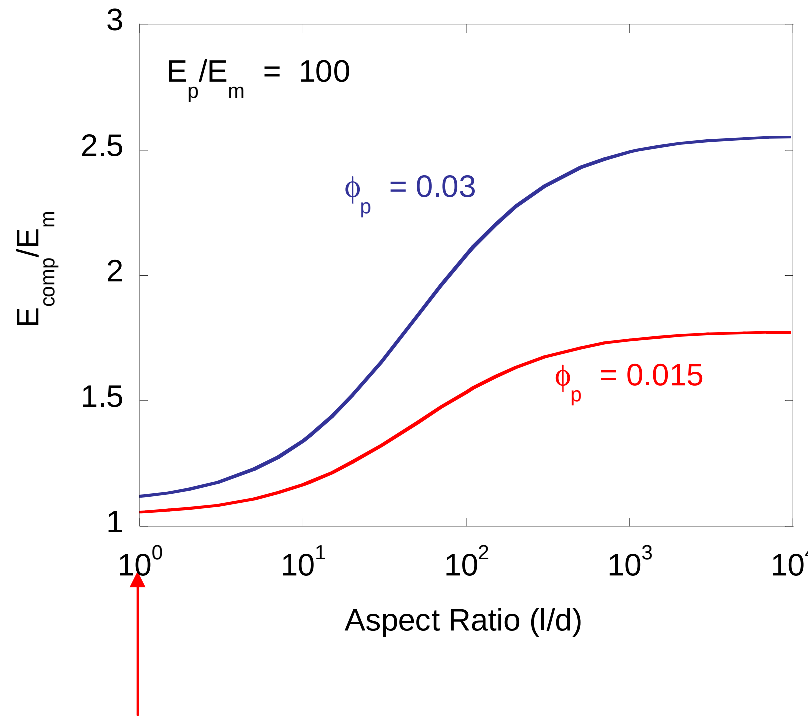
Vaia, R. A.; Wagner, H. D.

Modulus Enhancement

Continuum Halpin – Tsai Model



Influence of Aspect Ratio on Modulus

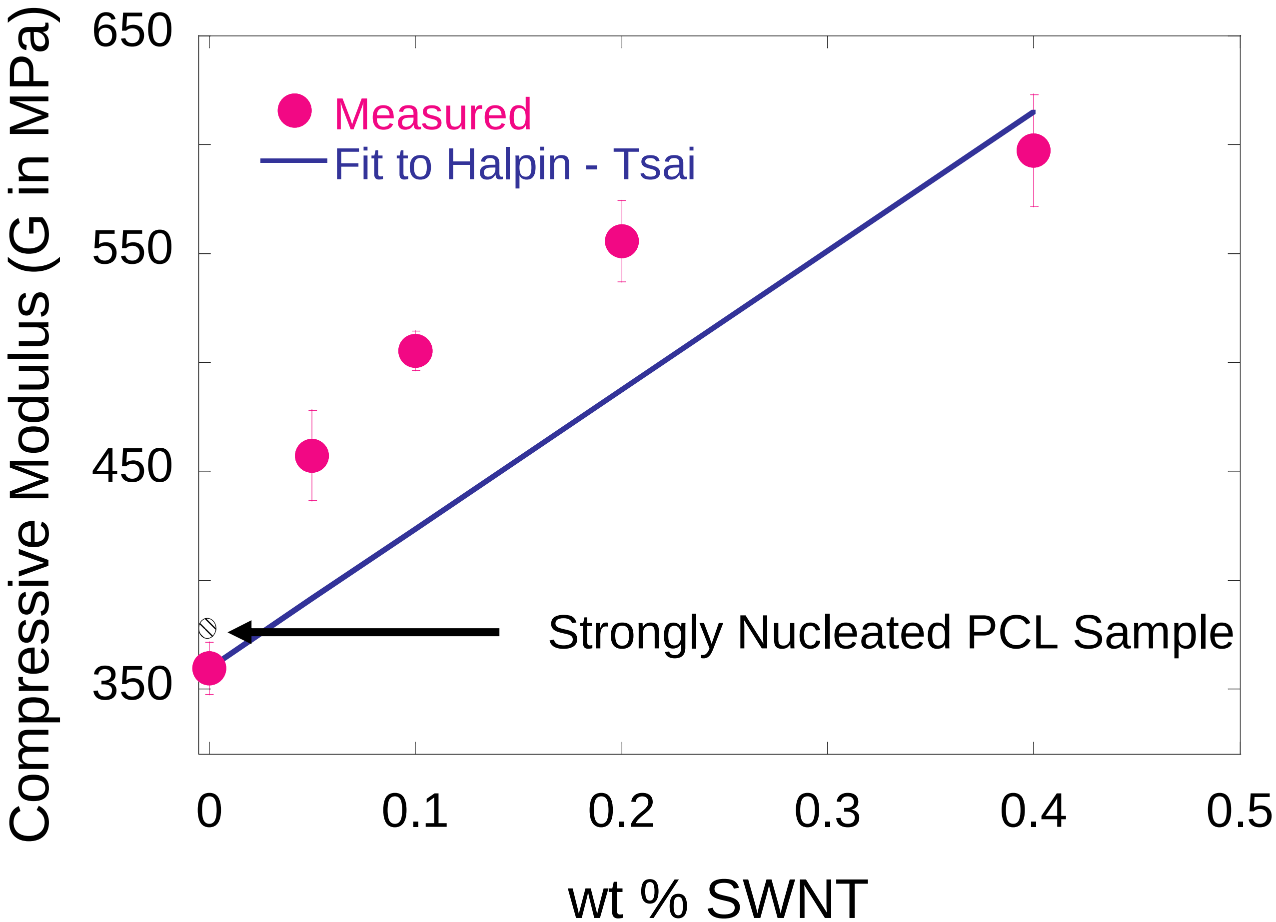


Einstein: $1 + 2.5\ \phi_p$

Montmorillonite:: Aspect ratio: 100 – 400; E_p : 170 GPa

SWNT:: Aspect Ratio: 500 – 10000; E_p: 640 GPa

Reinforcement by SWNTs of PCL



Randomly oriented SWNTs

Geometrical and Electrical Percolation @ ~ 0.08 wt % SWNT

Strong Nucleators of PCL Crystals

G_{SWNT} = 640 GPa

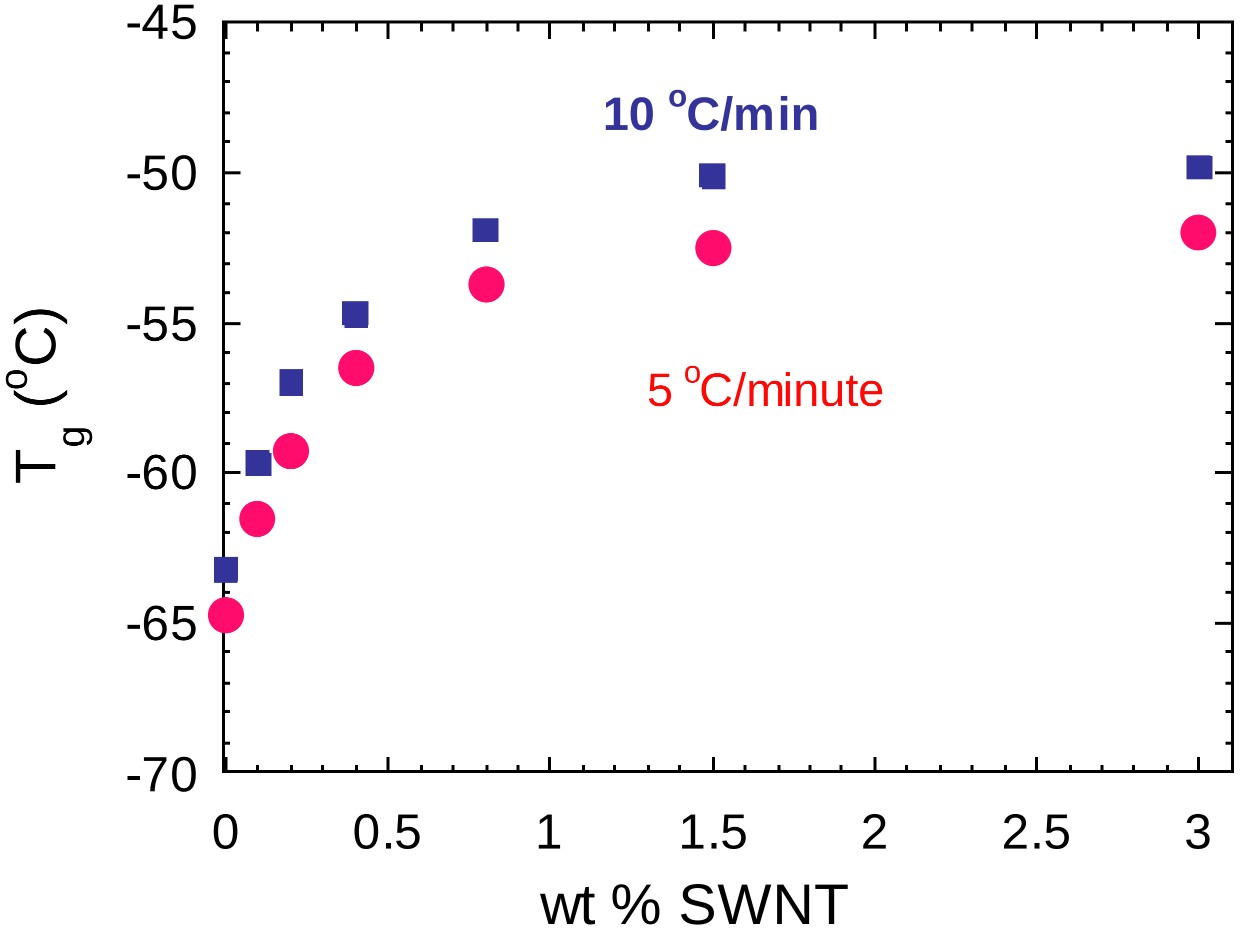
ρ_{SWNT} = 1.0 g/cm^3

l_{SWNT}/d_{SWNT} = 1000

► Reinforcement at low concentration

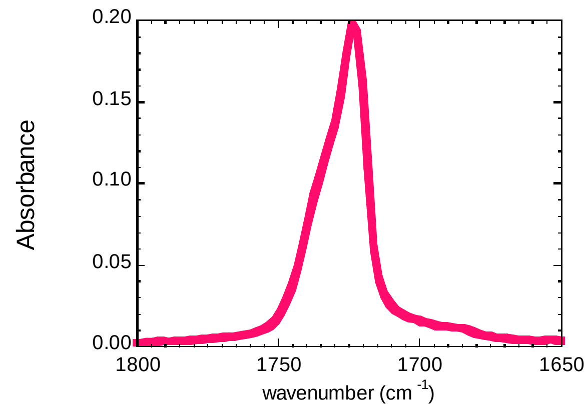
→ *better than Halpin - Tsai*

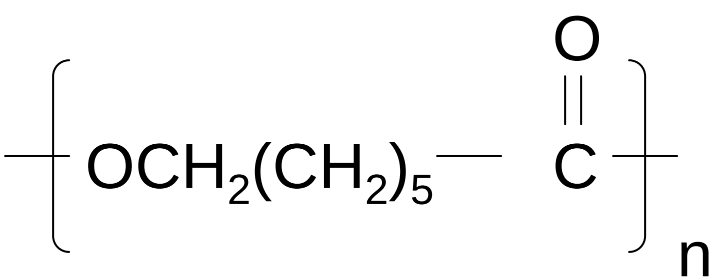
Glass Transition Temperature



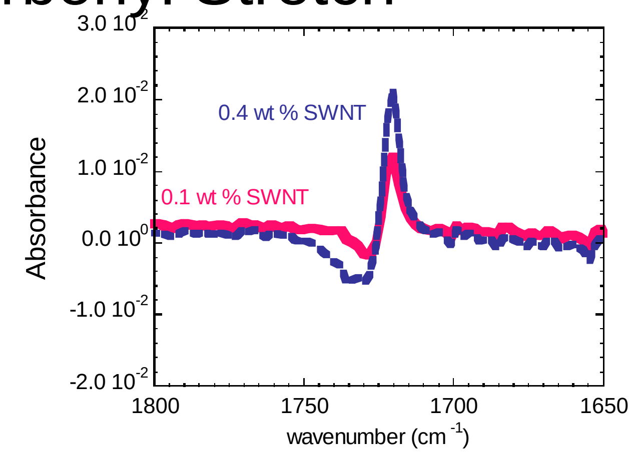
Mechanism of Dispersion

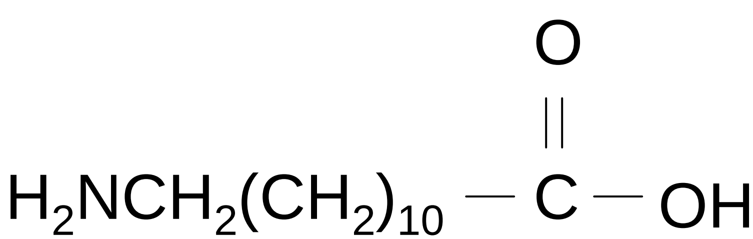
- Hydrogen bonding between surfactant and polymer and attractive interactions between surfactant and SWNT.





Difference FTIR Spectroscopy Carbonyl Stretch



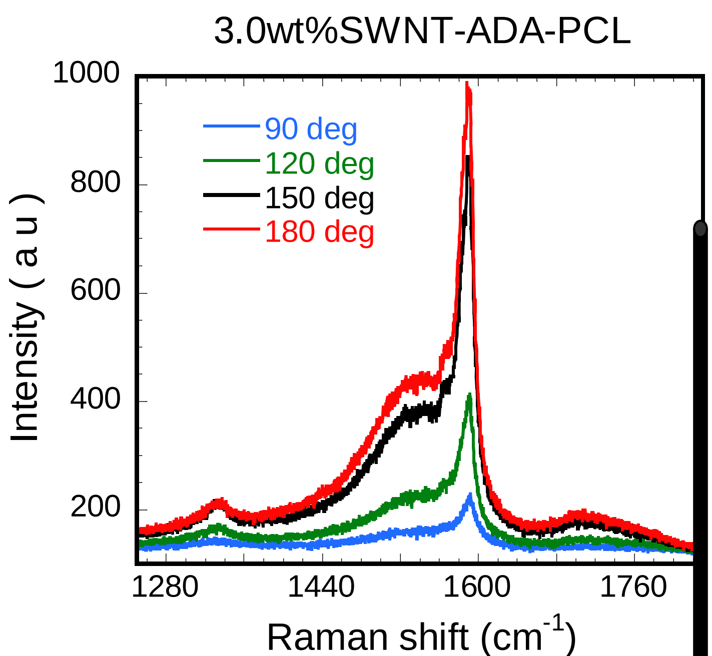


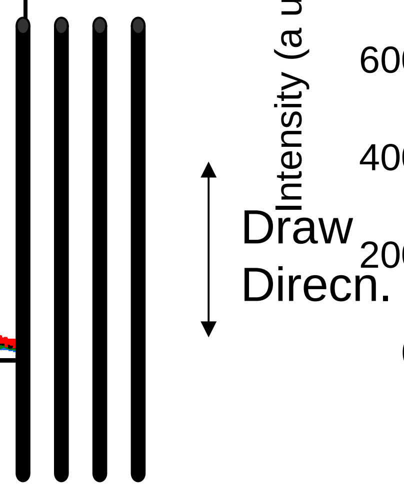
Establishment of Favorable H-bonding

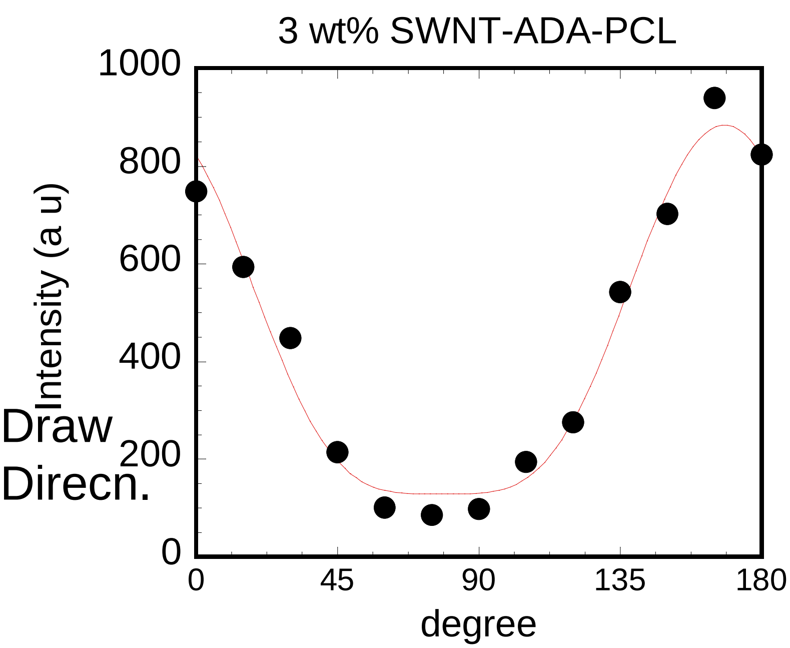
Crystallization in Oriented Nanocomposites

w/Hadjiev

Uniaxial Orientation





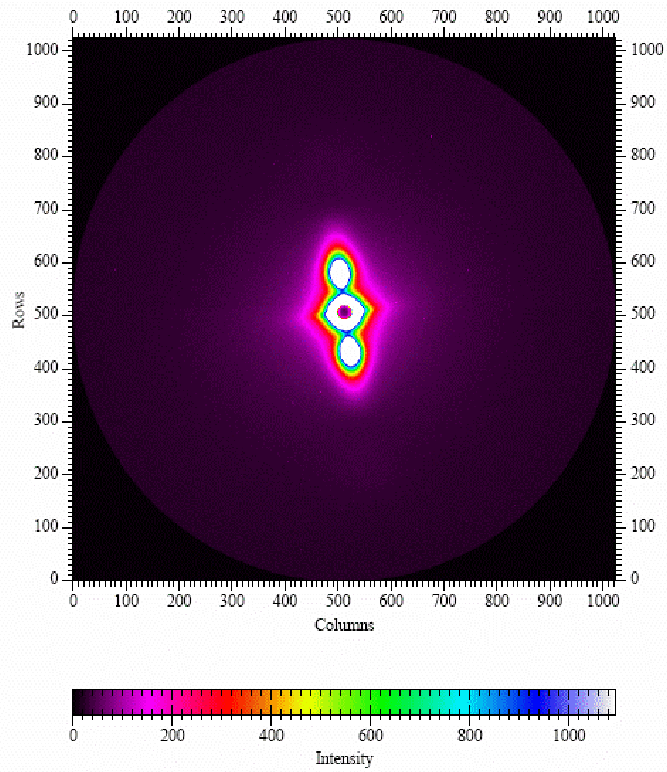


Crystallization in Oriented Nanocomposites

Uniaxial Orientation – Preservation of Orientation with repeated thermal cycling

Draw in Melt; Crystallize and Heat to Melt; Isothermal at 43 °C;

Melt; Isothermal at 50 °C

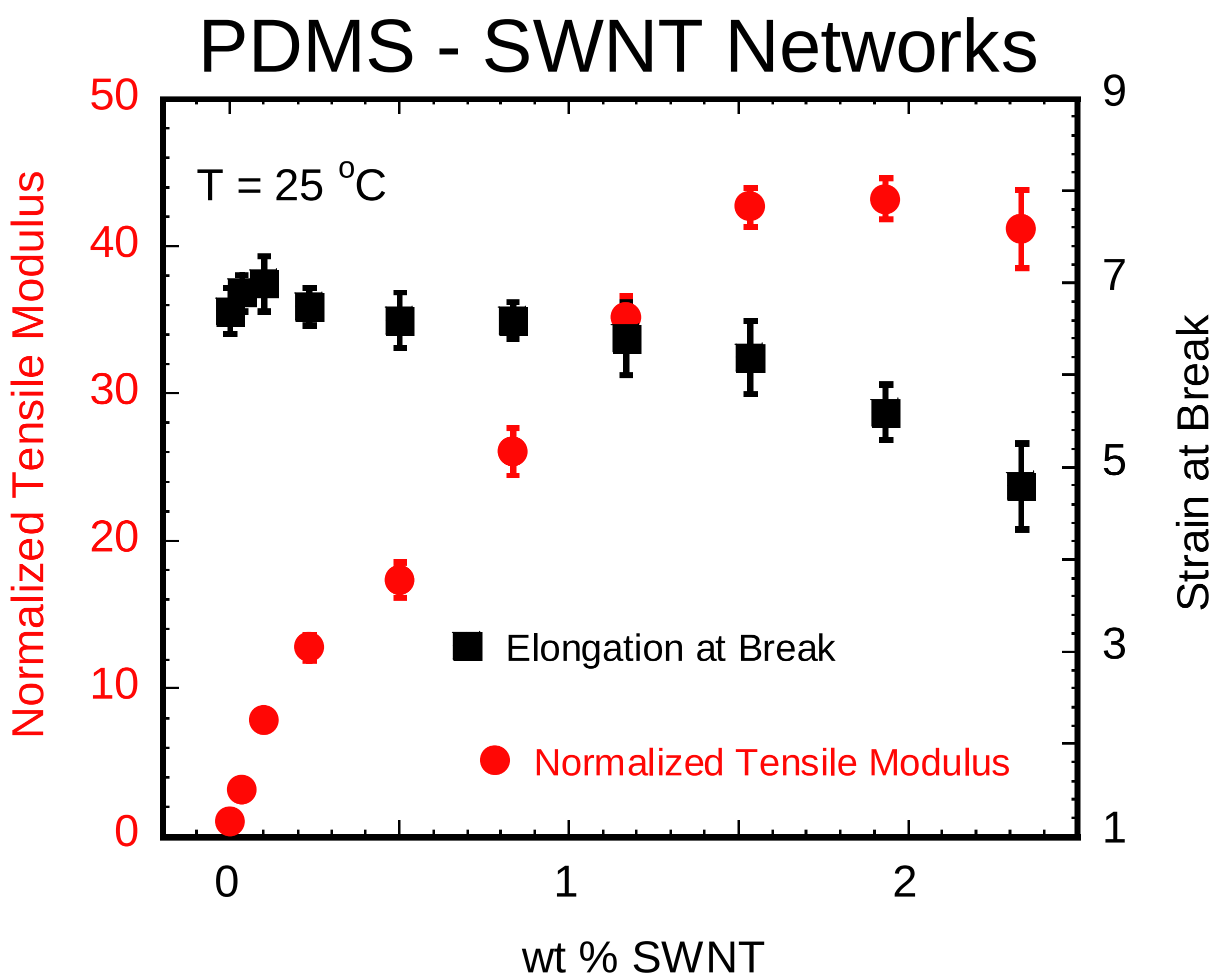


Draw direction

T=55^0 C

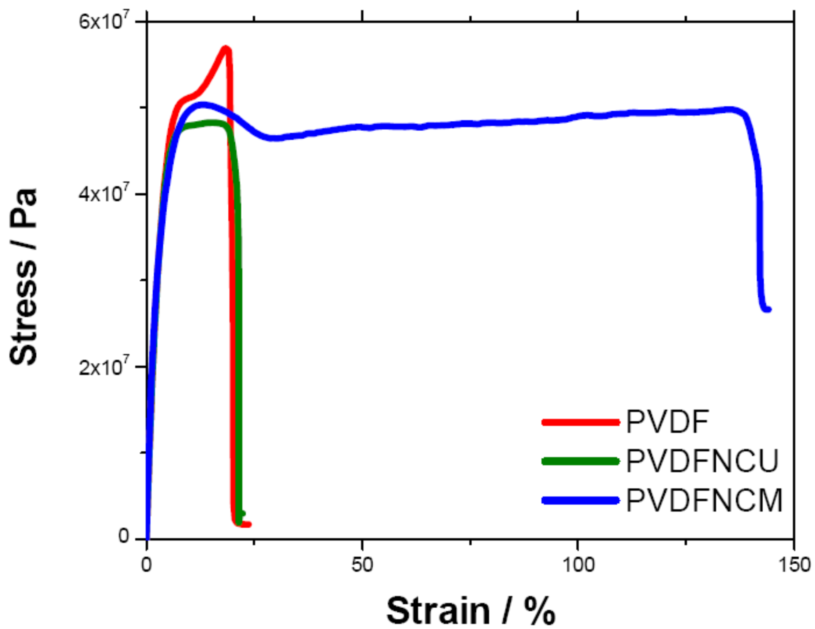
Elastomer Nanocomposites

w/Tour



Trade-offs Can Be Avoided

Giannelis et al



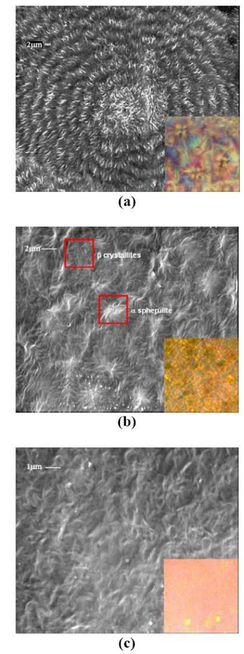
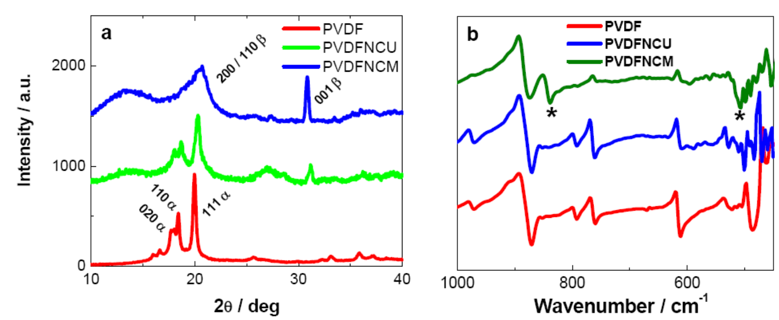


Fig. 3 SEM images with POM insets showing crystal morphology of (a) PVDF, (b) PVDFNCU, (c) PVDFNCM.

	Y (GPa)	Strain
PVDF	1.30	0.2
PVDF + O-MMT	1.80	1.4

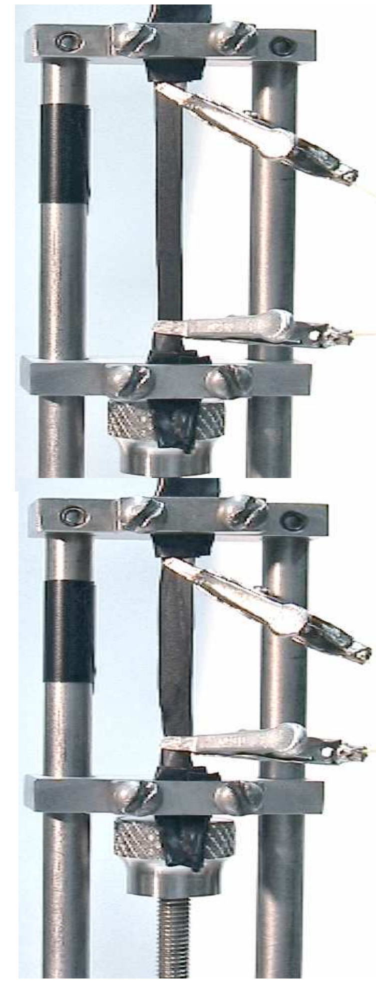


Shape-Recovery

Vaia et al

IR Light

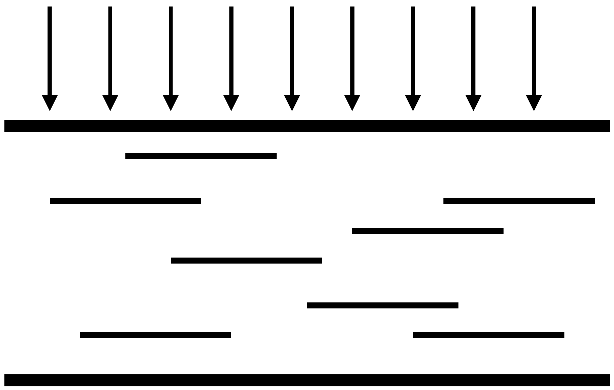
Current



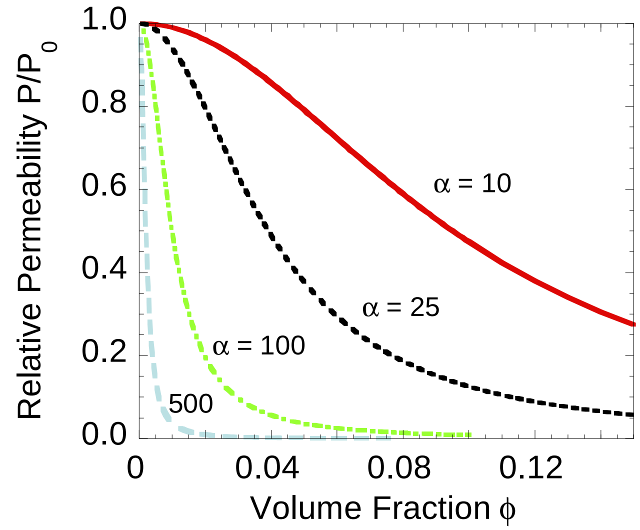
0.3% CNT/elastomer composite

Nanocomposites for Enhanced Impermeability

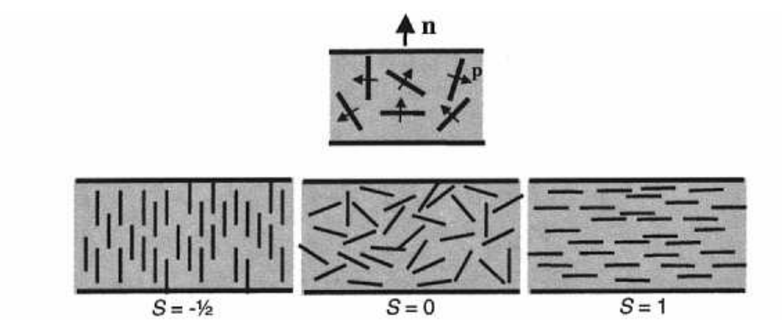
Influence of Layered Silicate on Permeability



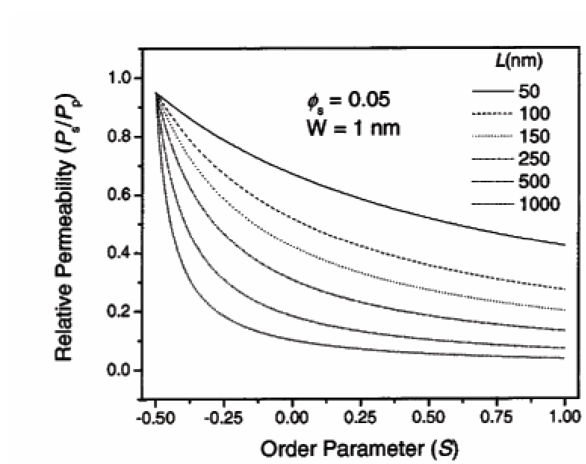
Layered Impermeable aspect ratio α



Cussler et al. J. Memb Sci., 1998

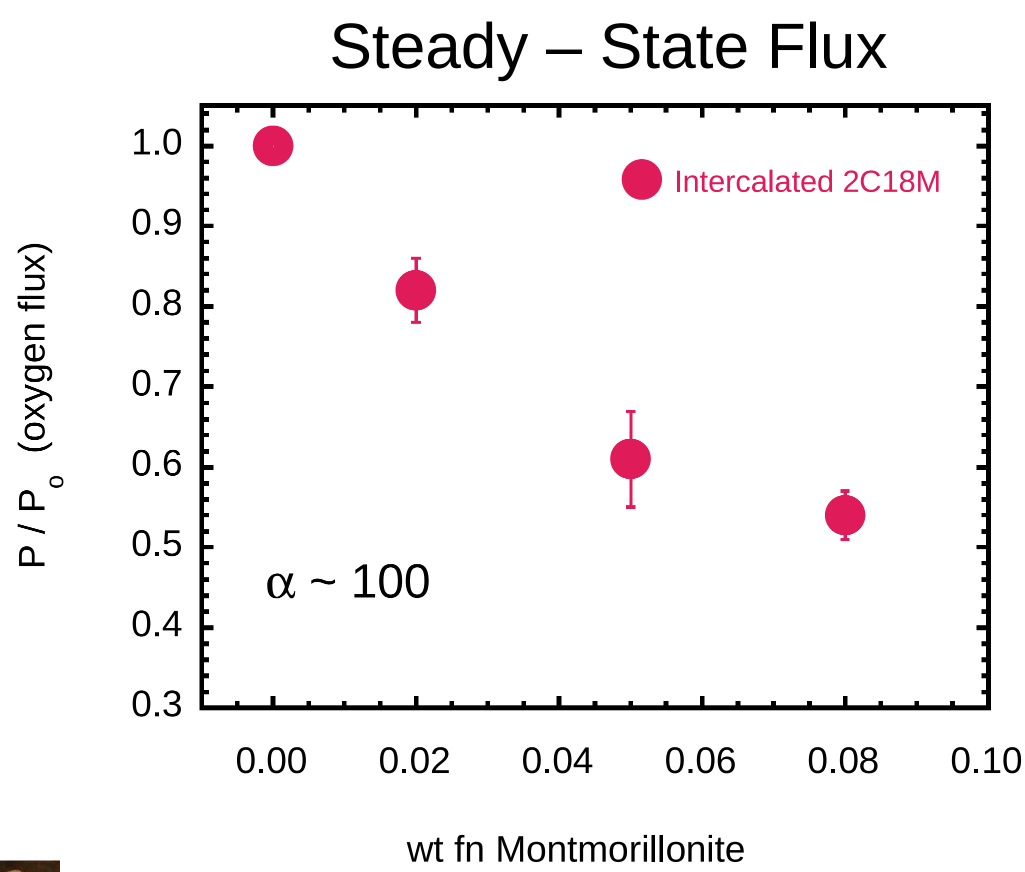


$$S = \frac{1}{2}\left\langle 3\,\mathrm{Cos}^2\theta \ - \ 1\right\rangle$$



Bharadwaj *Macro*. **34**, 9189 (2001).

Role of Layered Silicates on O_2 Permeability



PIB Based Polymer

2C18 Modified Montmorillonite

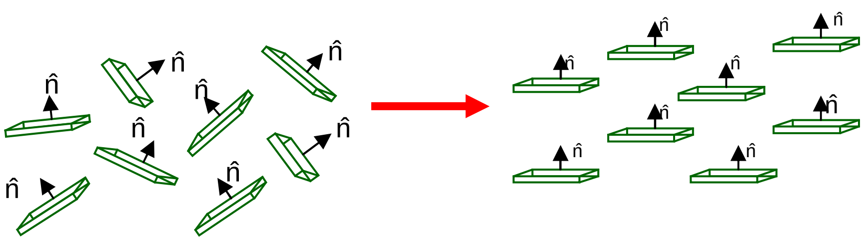
Intercalated Nanocomposite

Randomly Oriented

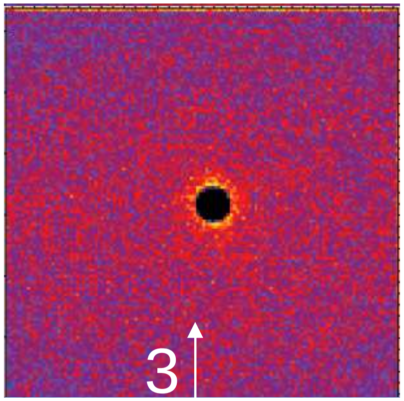
Oxygen Permeability at 25 ^oC

Alignment of Nanoparticles

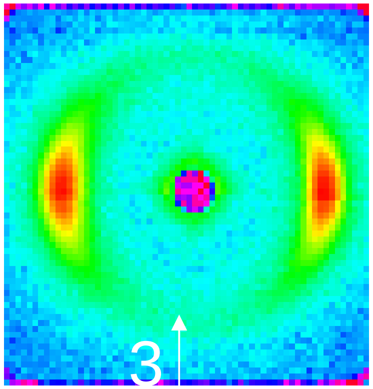
Aligned Sample Prepared by large amplitude oscillatory shear.



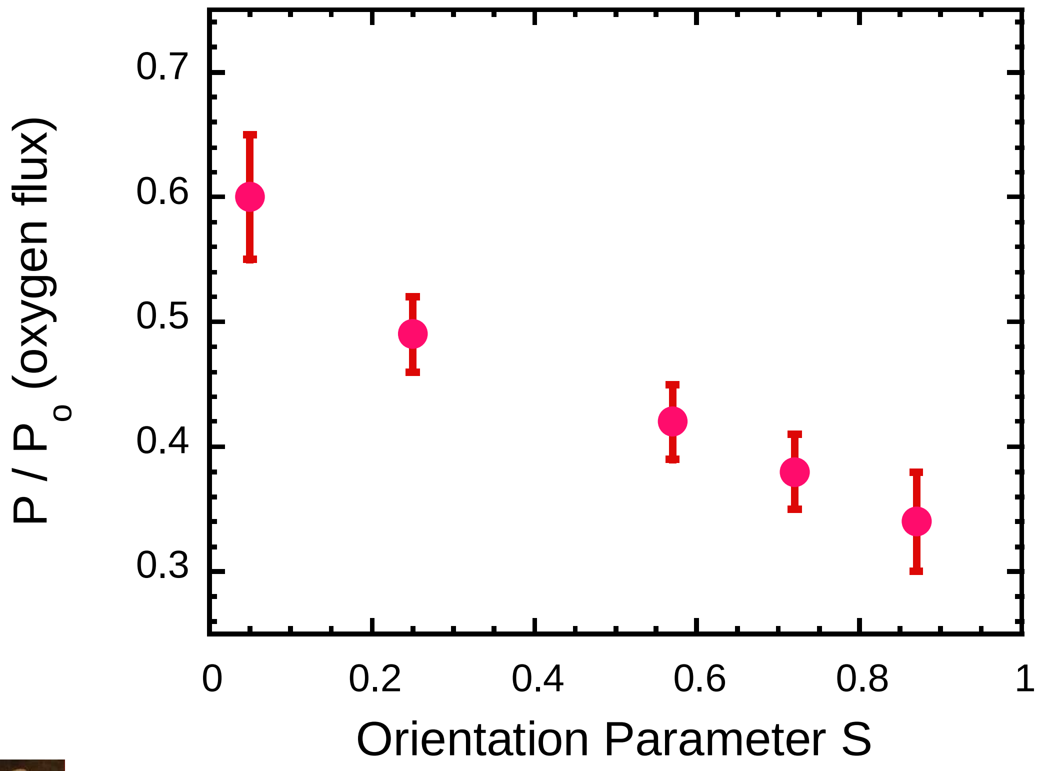
Radial



Tangential



Effect of Orientation on Permeability



PIB Based Polymer

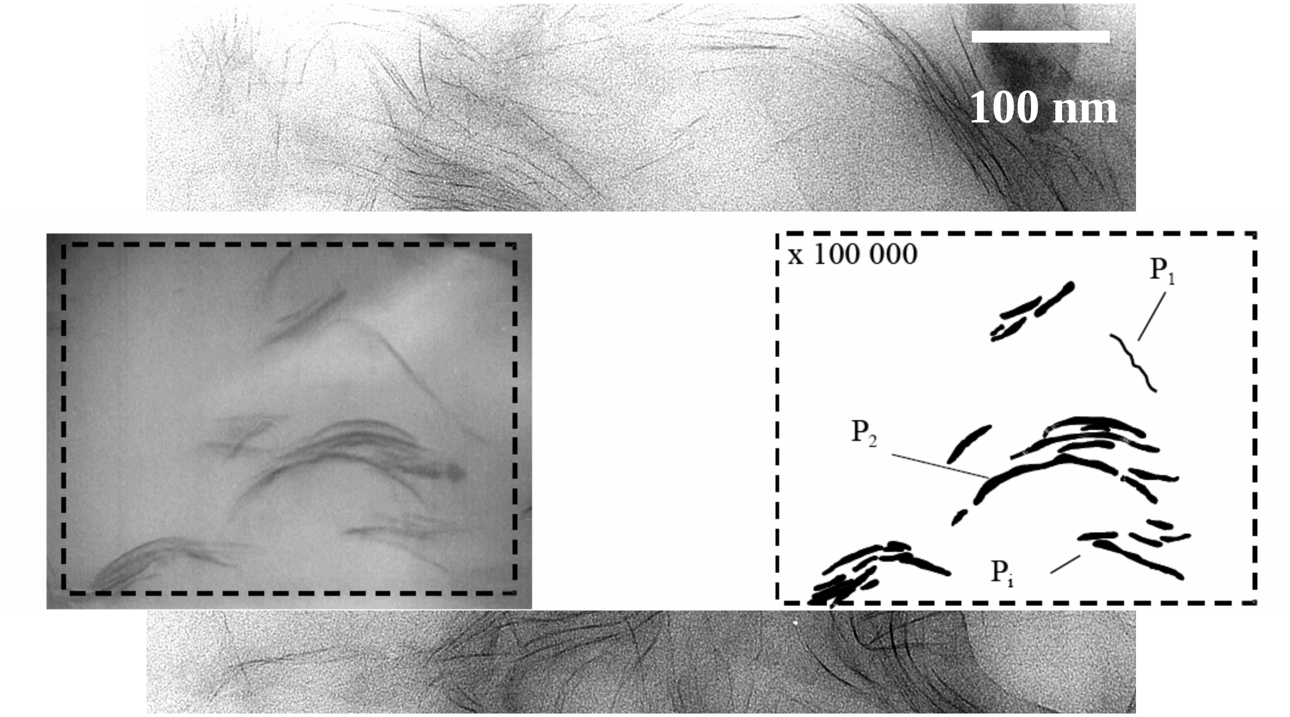
2C18 Modified Montmorillonite

Intercalated

Oriented by Oscillatory Shear

5 wt. % Montmorillonite

Intrinsic flexibility of Clay Layers



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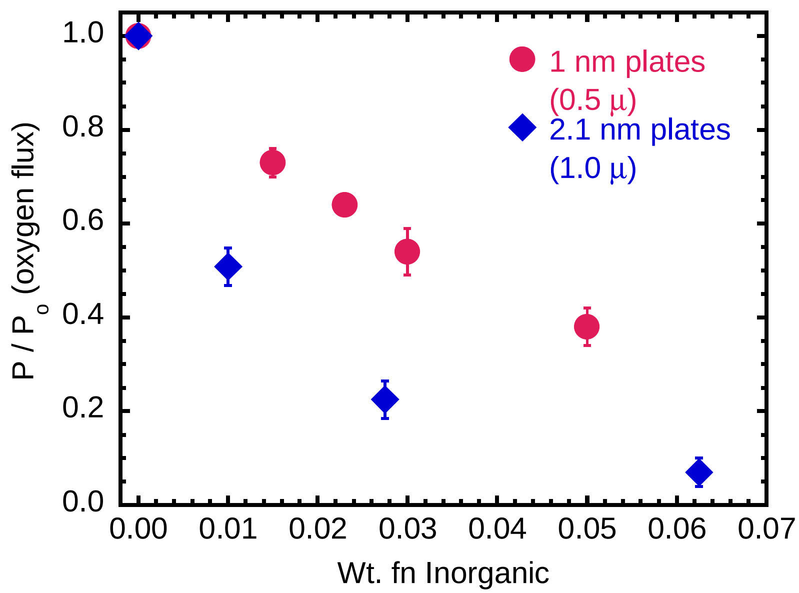
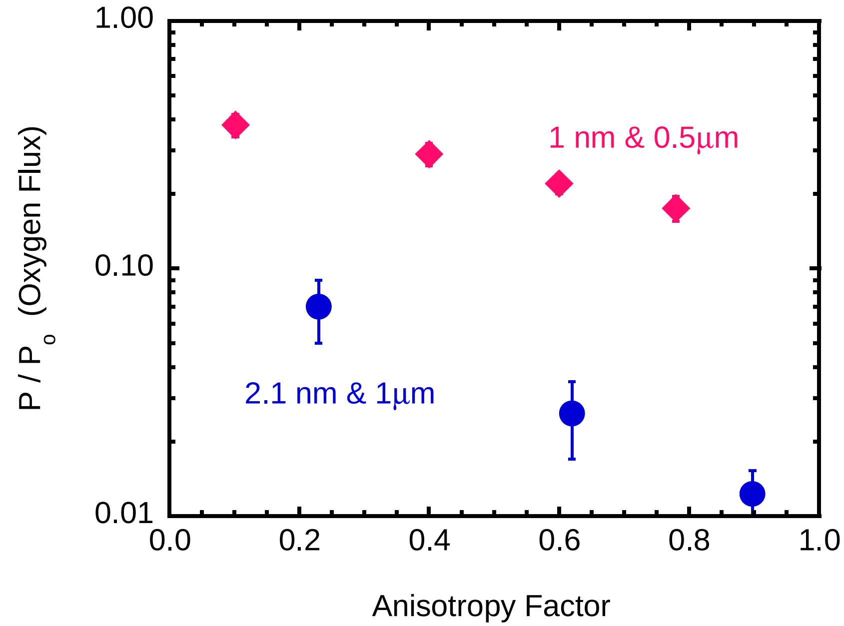
Role of Anisotropy and Orientation on Permeability

Elastomer – Layered Nanoparticle Composites

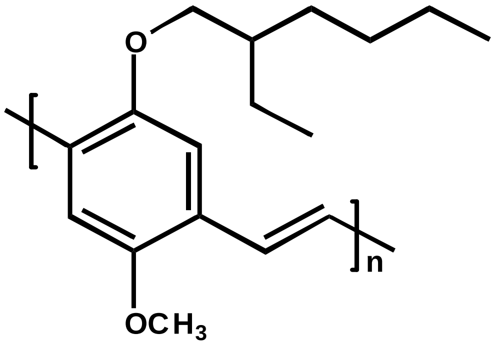


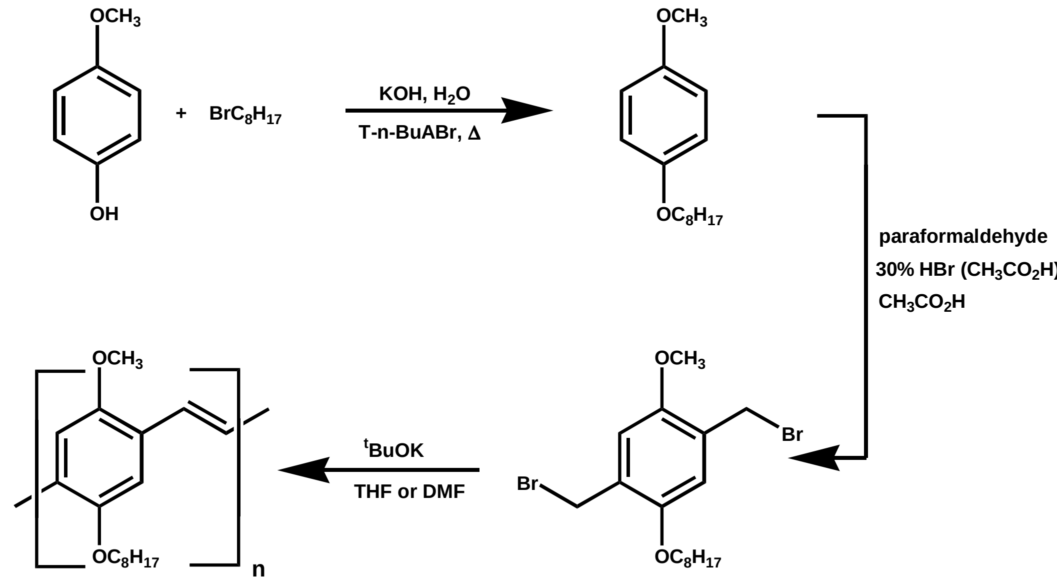


Magadiite indicates an aspect ratio of > 500!

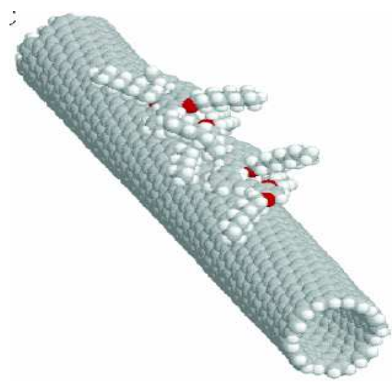
Dispersed Nanotubes in OLEDs (MEH-PPV)

In Collaboration with Randy Lee and Gobet Advincula at UH.



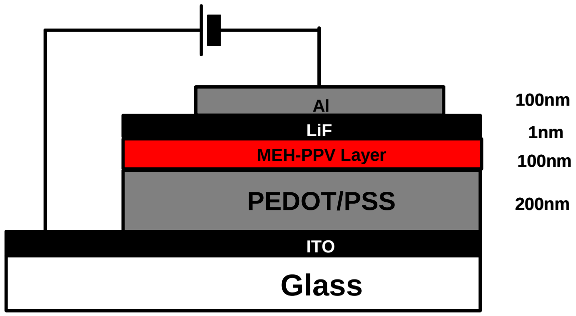


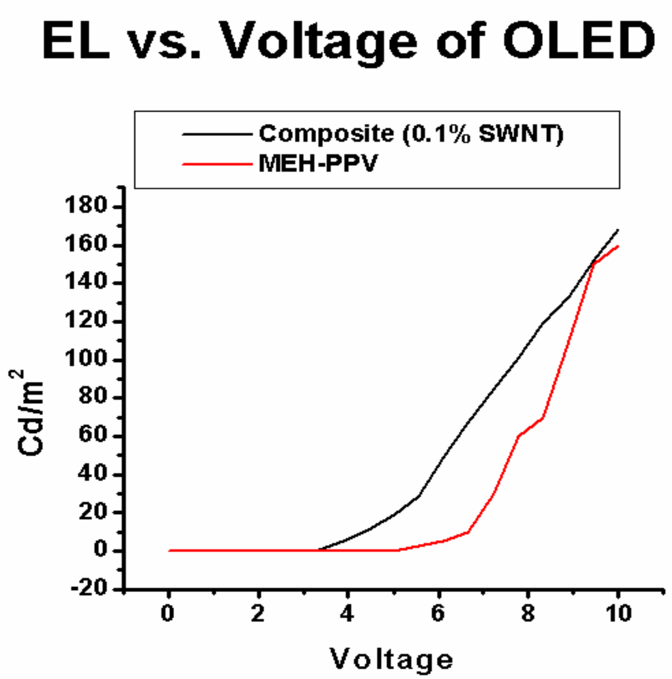
In – situ polymerization of MEH – PPV in DMF (using a modified Gilch Method)

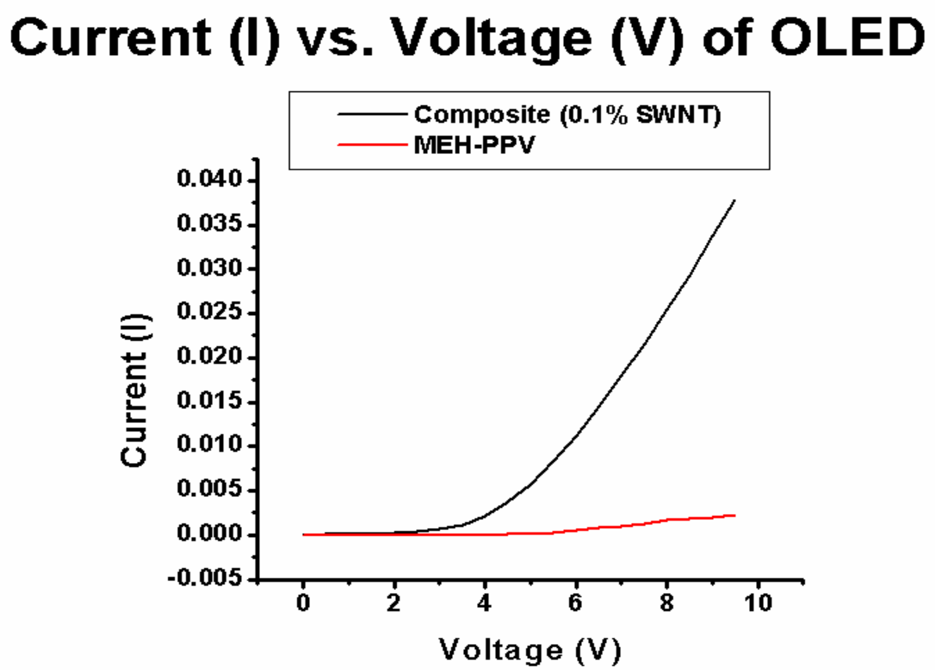


Parekh B. P., Newaz S. S., Sanduja S. K., Ashraf A. Q., Krishnamoorti R., Lee T. R., "*The Use of DMF as Solvent Allows for the Facile Synthesis of Soluble Highly Cis MEH – PPV*." Macromolecules, 37, 8883 – 8887 (2004)

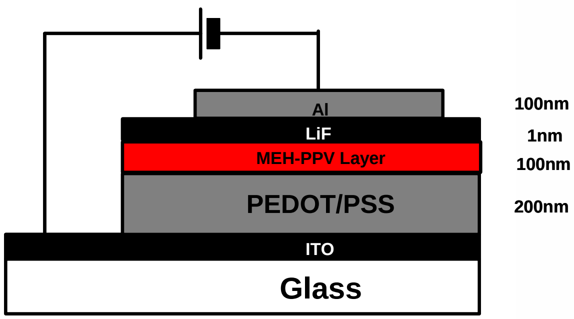
OLED Characterization

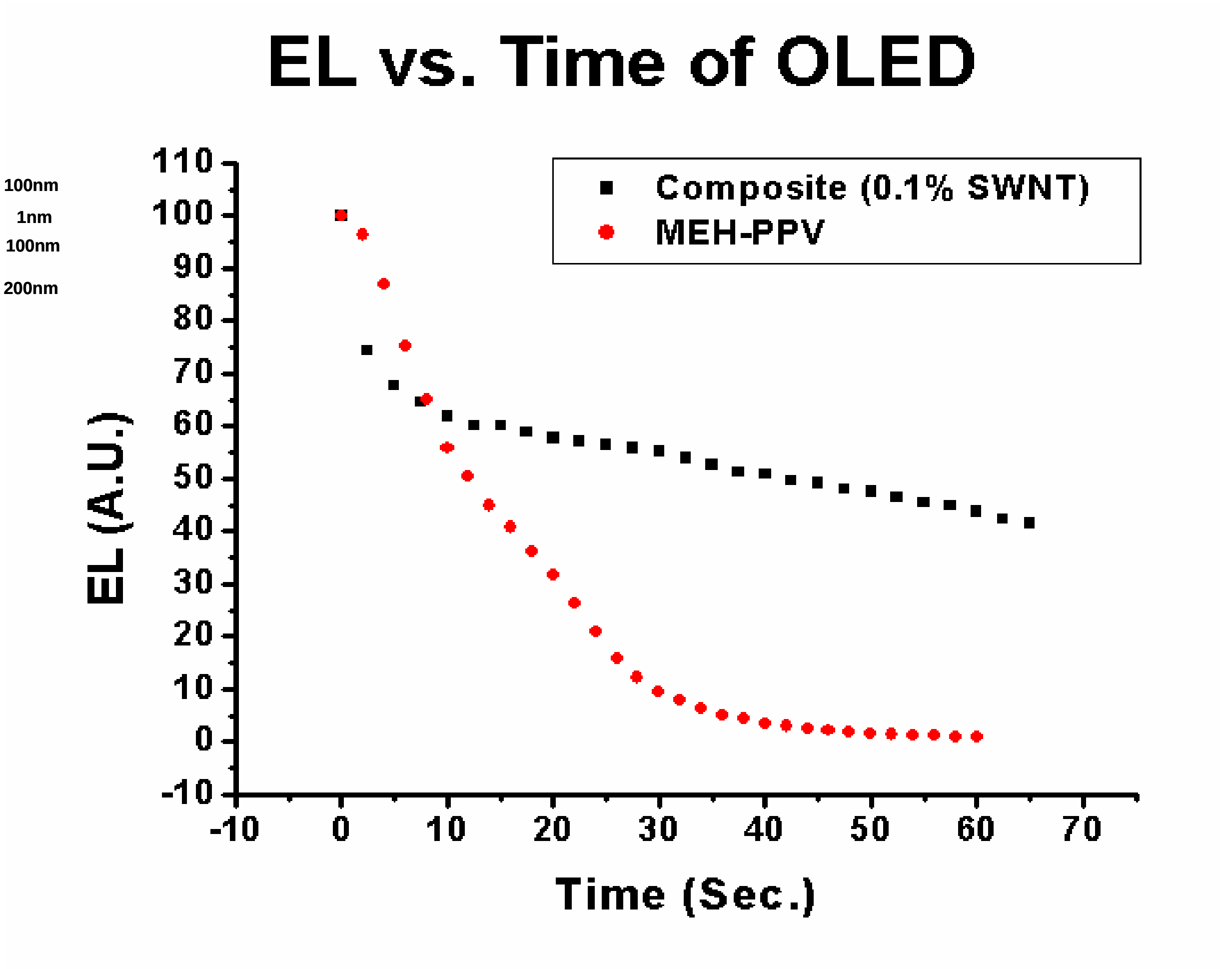




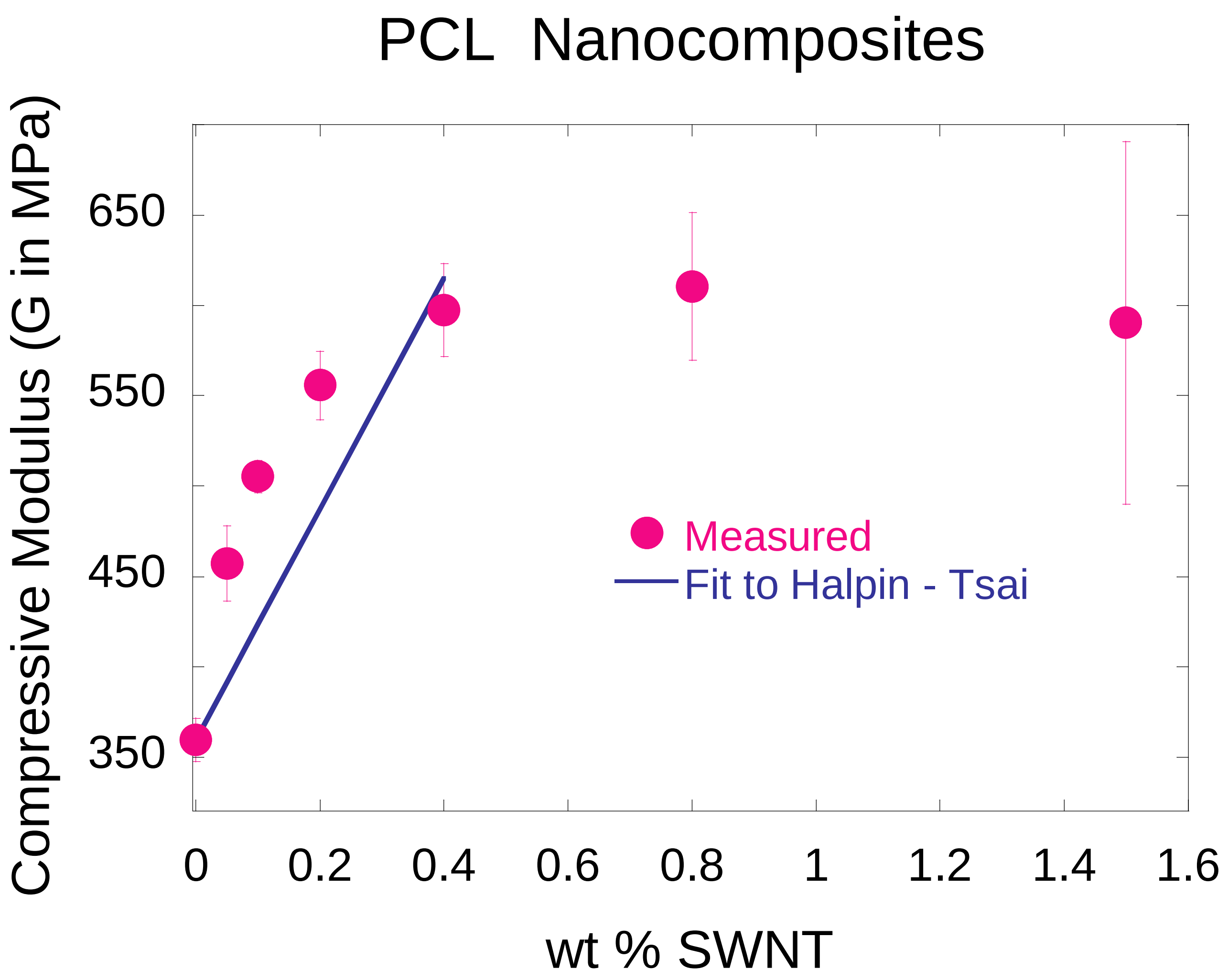


OLED Characterization





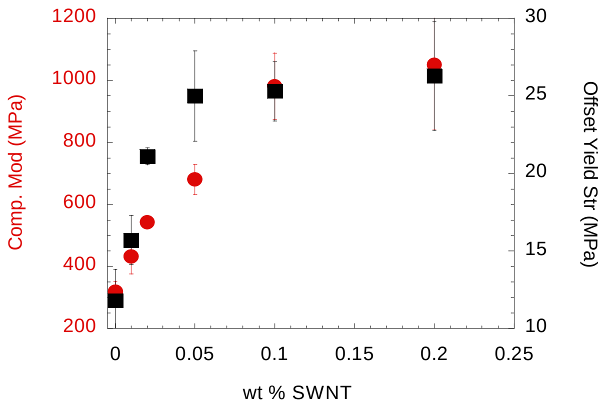
The Challenges

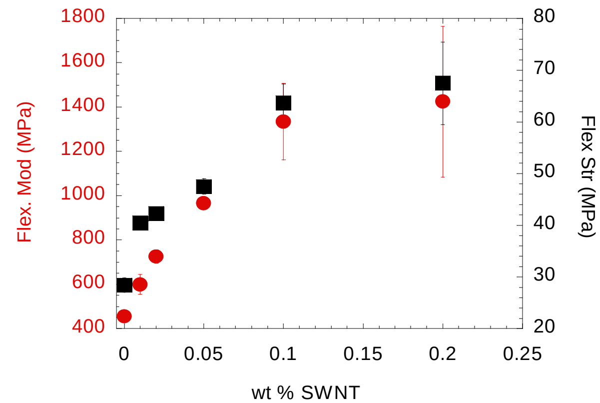


Challenge of Mechanical Reinforcement

This failure to enhance mechanical properties beyond the low concentration cases is generic to all nanocomposites prepared with SWNTs:
(PCL, PPF, PS, & Epoxy)

Poly(propylene fumarate) – functionalized SWNT





These SWNTs perhaps
Form domains at higher concentrations
& the reinforcement mechanism is changed
from individual tube to rope reinforcement

$$\phi_{r,c} \approx \frac{8}{x_r}\left(1 - \frac{2}{x_r}\right)$$

Conclusions

- There are a few examples where nanoparticles at low concentrations can in fact exceed the expected “rule – of – mixtures” based properties.
  - However, for instance, thermal conductivity remains elusive.
- Can the limitation of concentration over which property enhancement can be achieved be overcome in a cost effective manner?

Thanks: Dr. Cynthia Mitchell, Dr. Jiaxiang Ren, Dr. Adriana Silva, Barbara Casanueva and Tirtha Chatterjee; Charlie Shi
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