Sustainable Flame retardant Polymer Nanocomposites

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NIST

National Institute of Standards and Technology

NIST

...working with industry to foster innovation, trade, security and jobs

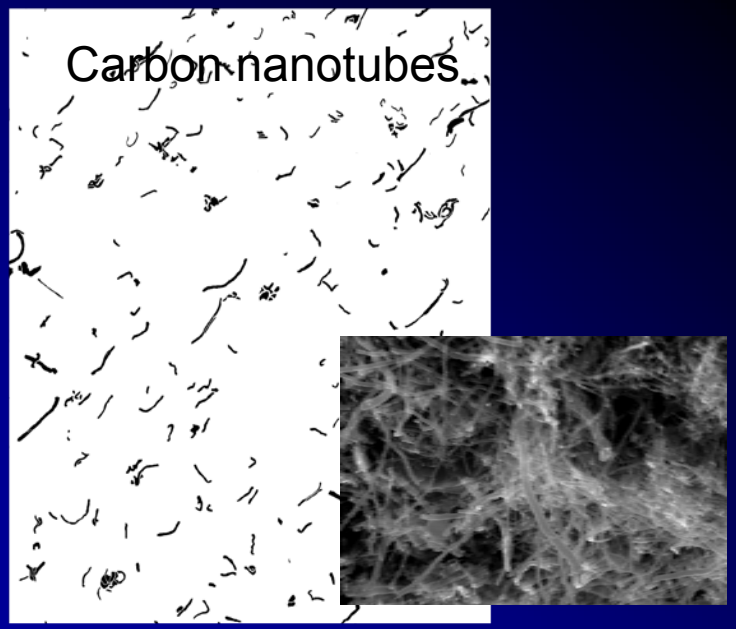
Nanocomposites

Materials:
Nano-particle, organic modifier, polymer matrix

Processing Techniques:
- Solution mixing and film casting
- Melt mixing (extrusion)
- In situ polymerization

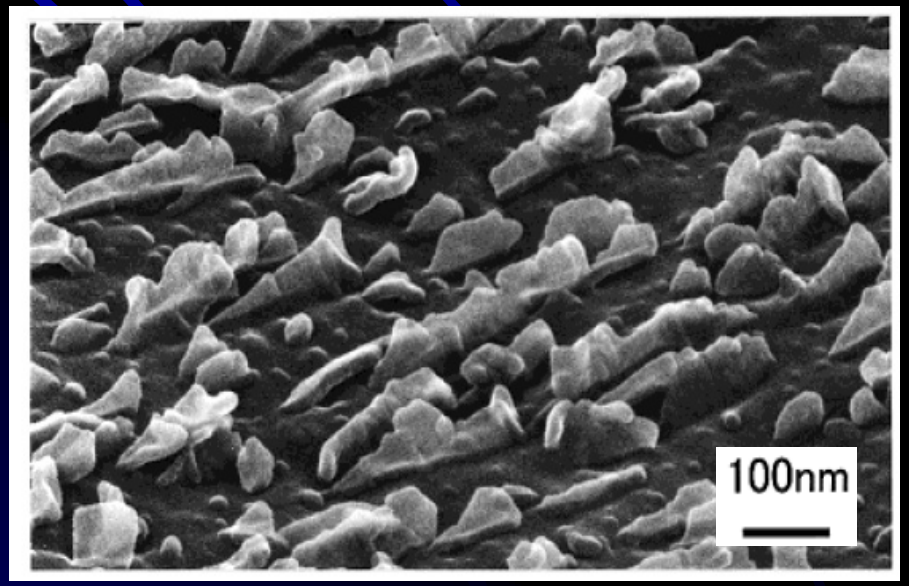
Properties:
- Flame resistance
- Improved gas permeability
- Higher stiffness
- Scratch resistance
- Higher glass transition
- Improved thermo-mechanical response

Carbon nanotubes



Zammarano et al Polym Adv Tech, 2008

Clays



Usuki et al. 2001, Nano Letters

Barriers to Success

- Lack of tools for characterization of dispersion of clay in polymer
- Limited processing window due to low thermal stability of organo-clays
- Incomplete mechanistic understanding of property enhancements

J. W. Gilman, T. Kashiwagi, A. B. Morgan, R. Harris, Jr., L. Brassell, M. Vanlandingham, and C. L. Jackson., ”Flammability of Polymer Clay Nanocomposites Consortium: Year One Report,” , July 2000, NISTIR 6531.

Barriers to Success

- Sustainability
  - "To meet the needs of the present without compromising the ability of future generations to meet their own needs."

As nanotechnology slowly matures from lab scale to industry disruptor, large global companies are taking increasingly <u>selective</u> approaches to innovation and R&D*. Corporations Are Adopting a More Discerning Approach to Nanotechnology

* Lux Research Nanomaterials Intelligence 1; **Nanotechnology Corporate Strategies**

Opportunity

Fig. 2: Corporation Have High Awareness of Nanotech, But Don't Make it Priority

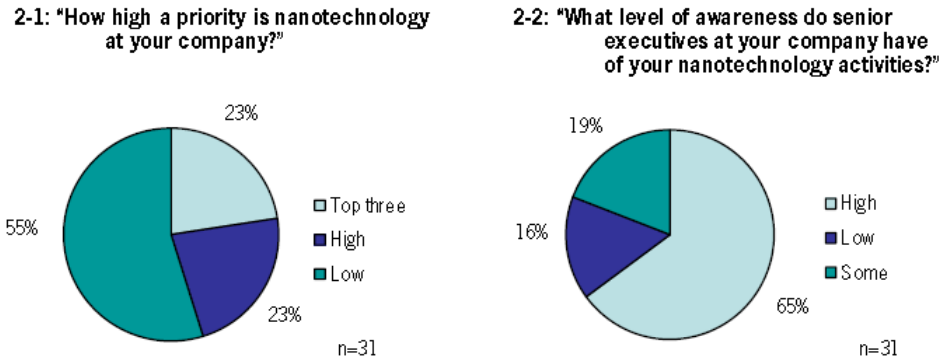
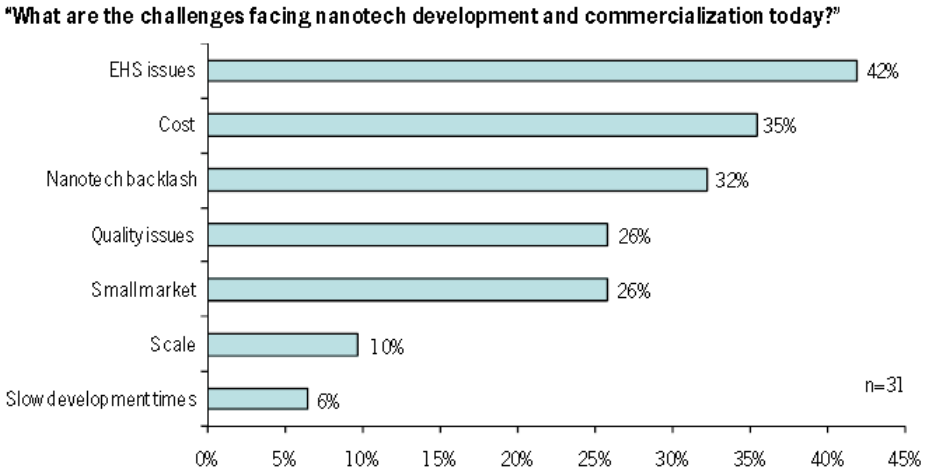
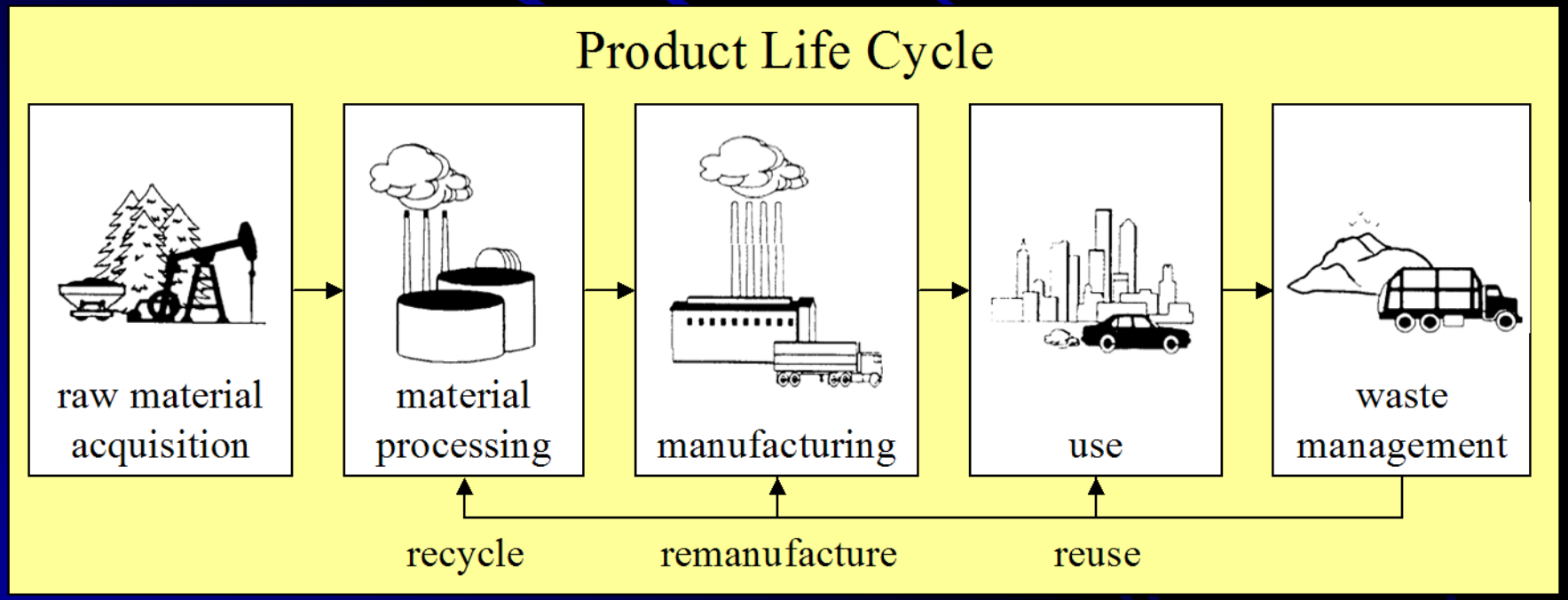


Fig. 3: Corporations Face Diverse Challenges in Exploiting Nanotech



- **Corporations are looking to external innovators to complement internal nanotech efforts.** As large companies shy away from investing large amounts into basic R&D, in nanotech or otherwise, companies see collaborations with universities, government labs, or start-up companies as very attractive alternatives (see Figure 4). Corporations are applying this "open

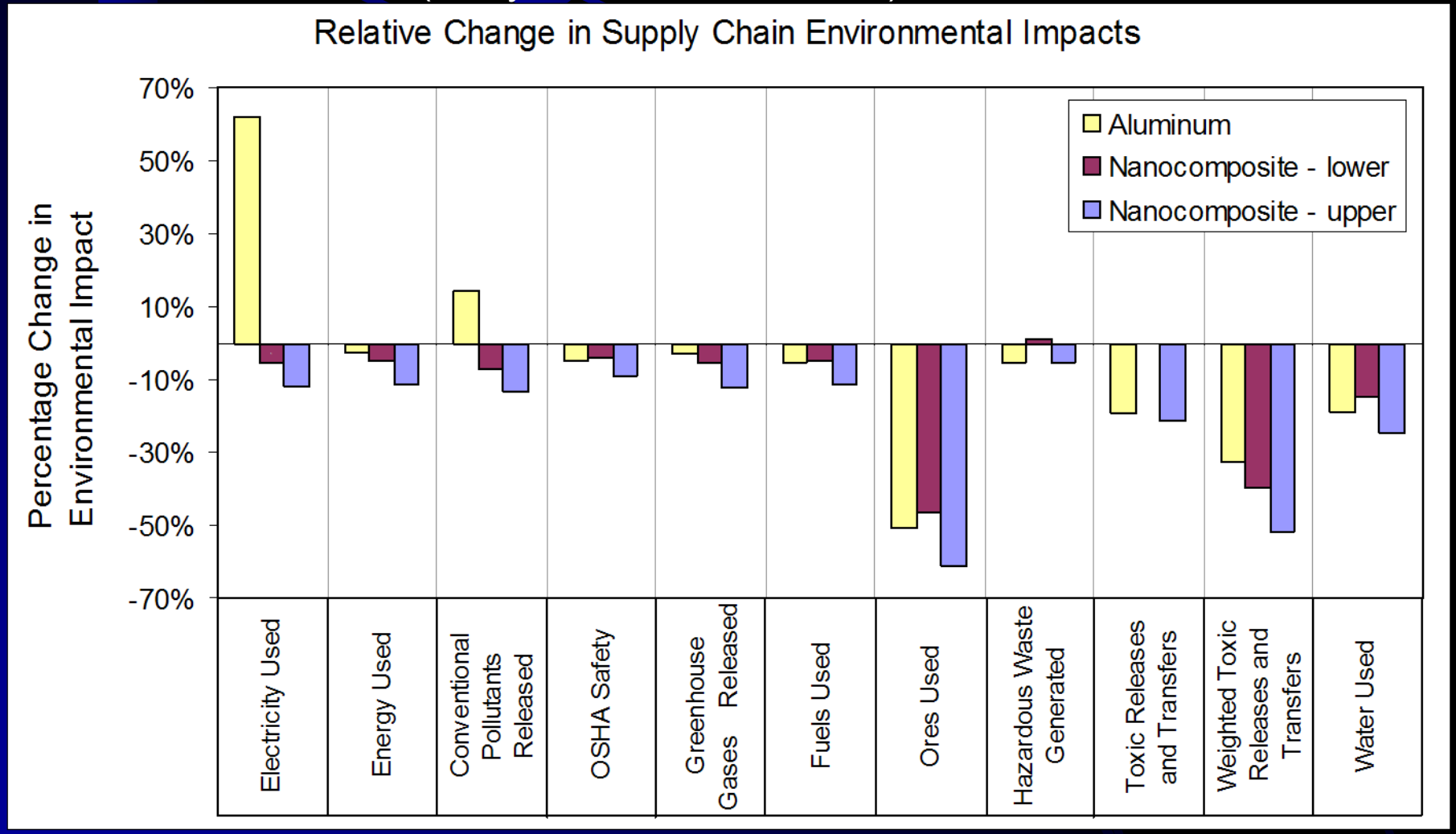
Life Cycle Assessment (LCA) A Technical Decision-making Tool



Source: Lloyd and Lave, ES&T, Vol. 37, No. 15, pp. 3458-3466, 2003

Life Cycle Assessment

(one year's fleet of vehicles)



Source: Lloyd and Lave, ES&T, Vol. 37, No. 15, pp. 3458-3466, 2003

Life Cycle Supply Chain Effects

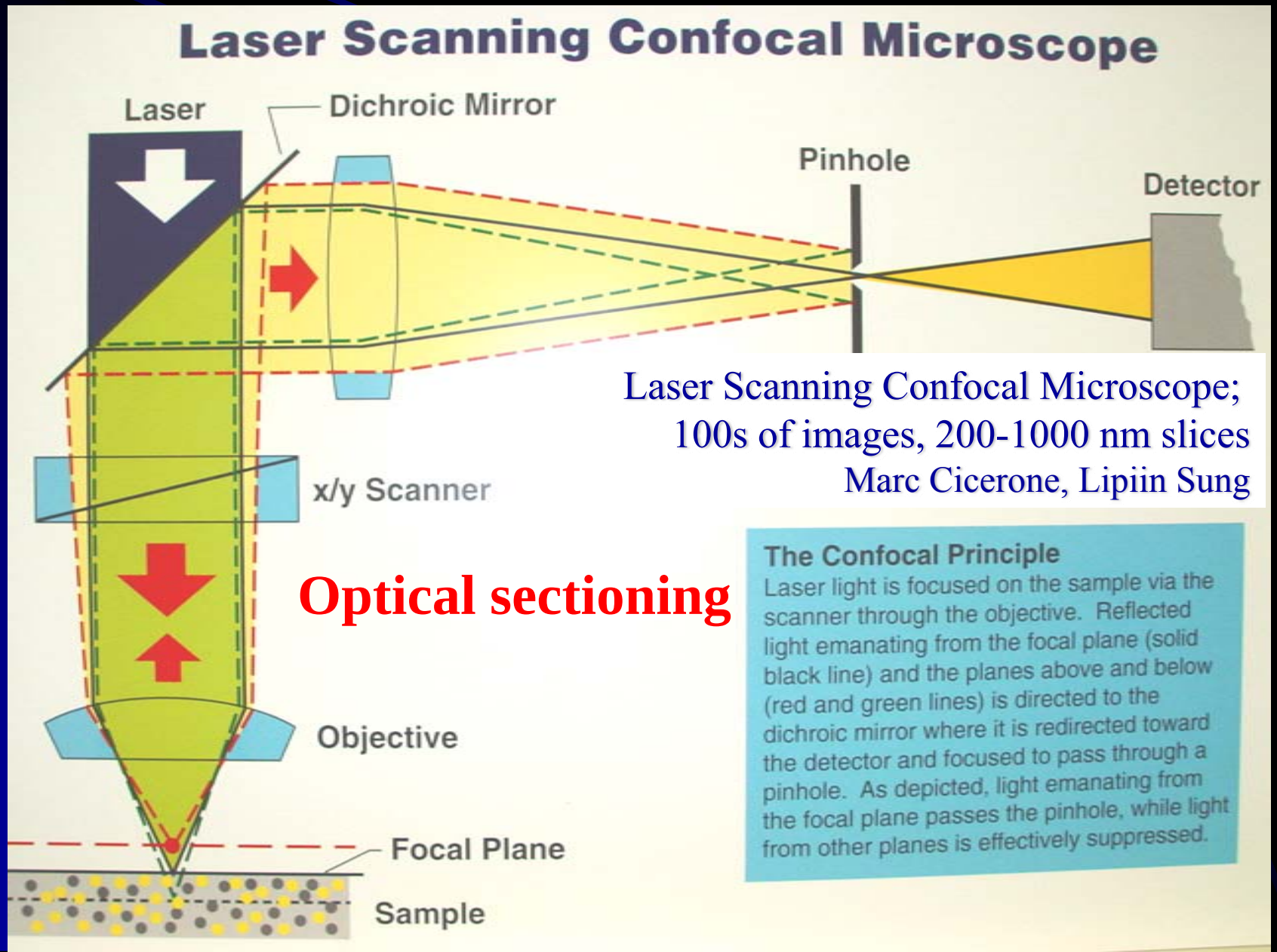
"U.S. consumers have little interest in greater fuel economy, and so this technology is unlikely to be developed and employed in this application without government intervention."

Source: Lloyd and Lave, ES&T, Vol. 37, No. 15, pp. 3458-3466, 2003

Barriers to Success

- Lack of tools for characterization of dispersion of clay in polymer
- Limited processing window due to low thermal stability of organo-clays
- Incomplete mechanistic understanding of property enhancements
- Sustainability

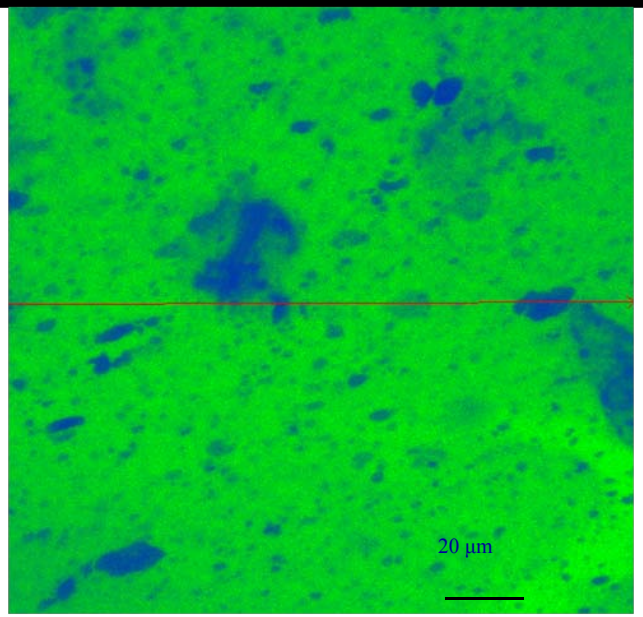
Confocal Characterization of Nanocomposites

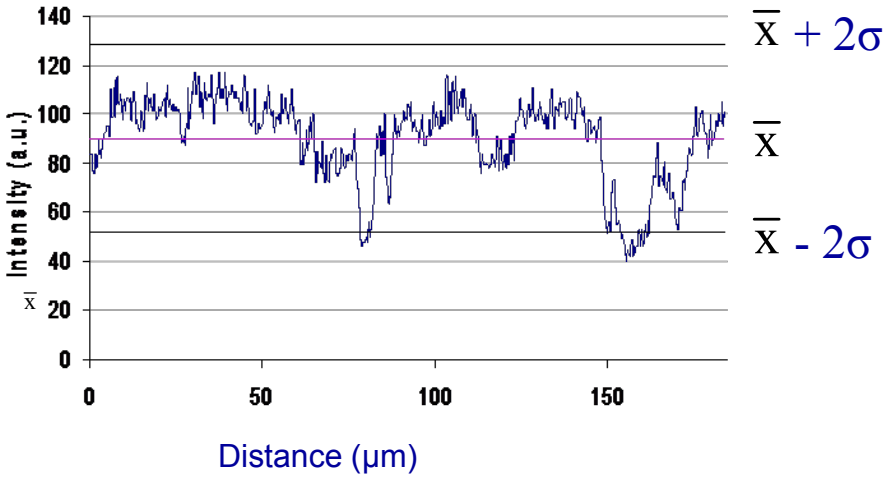


Laser Scanning Confocal Microscope;
100s of images, 200-1000 nm slices
Marc Cicerone, Lipiin Sung

Optical sectioning

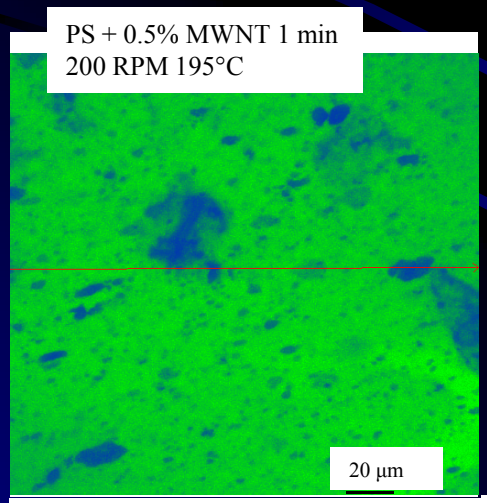
Confocal Characterization of Nanocomposites

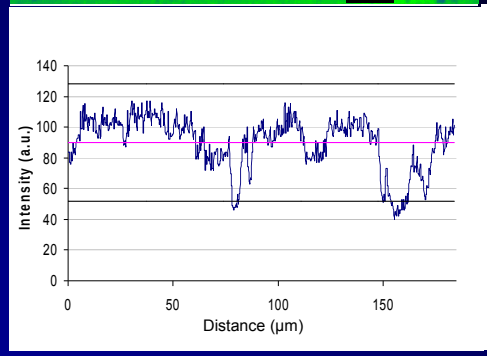


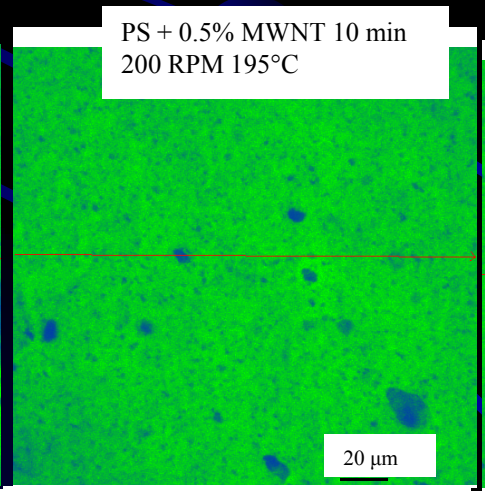


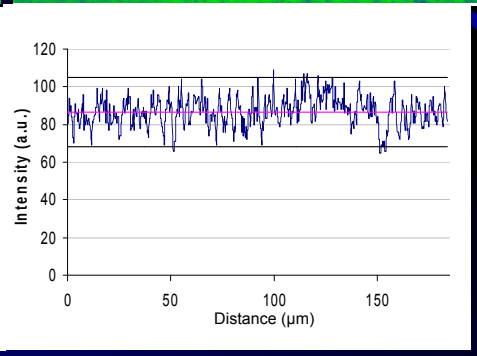
PS + 0.5% MWNT (NB) 1 min

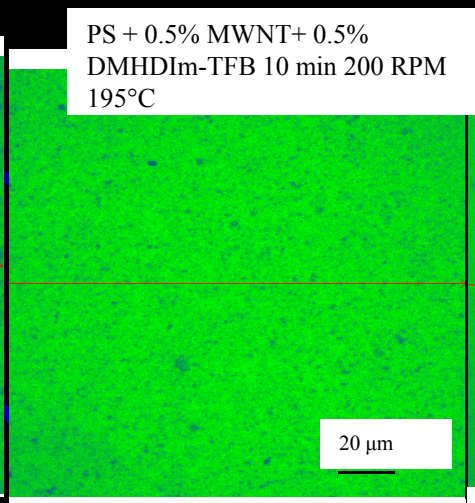
Confocal Microscopy of PS-MWNT

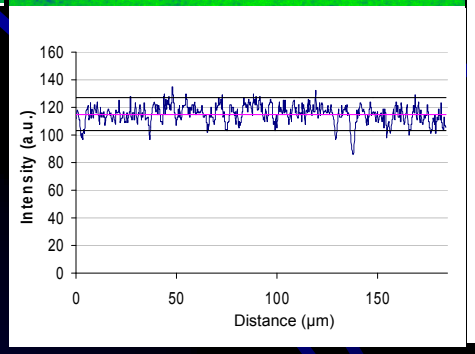


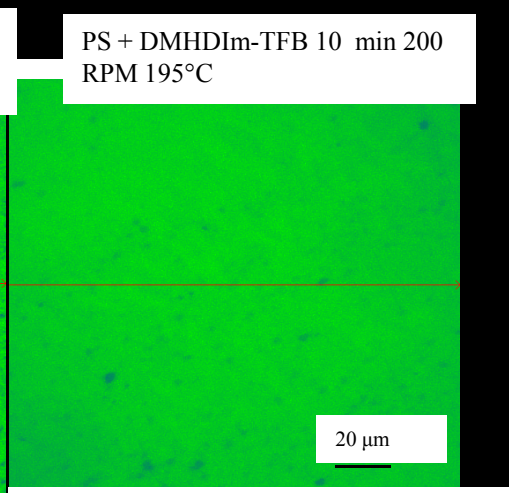


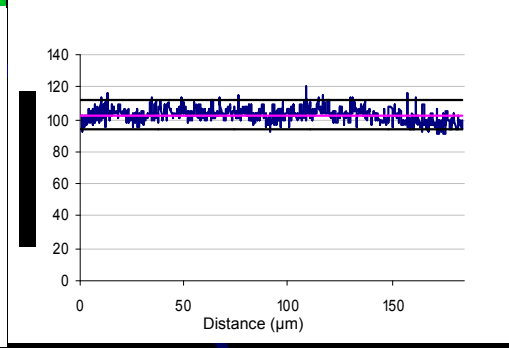


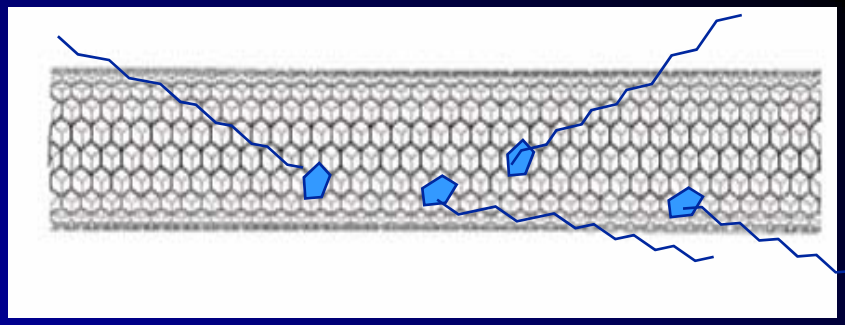










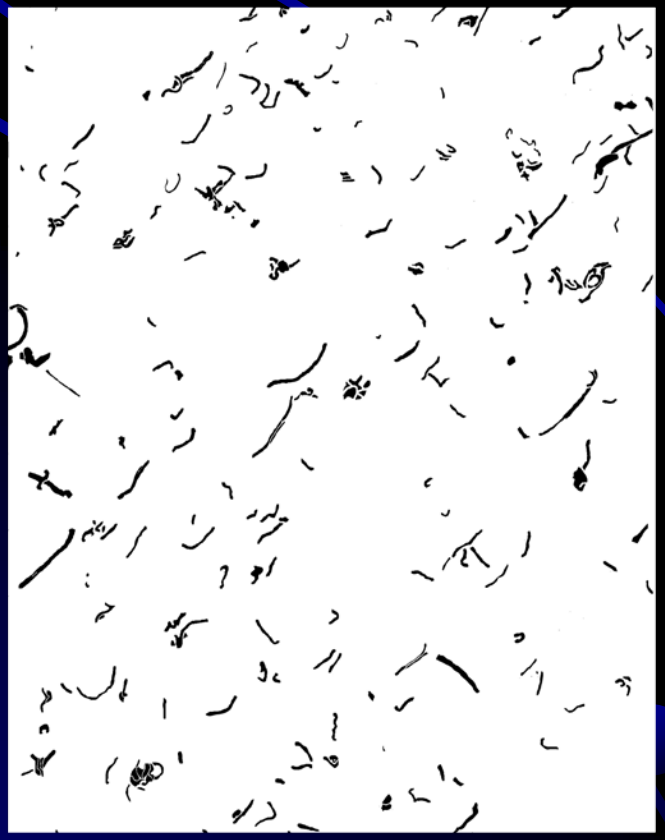


Imidazolium Surfactant and MWNT

Bellayer, S. Gilman, J. et al. *Adv. Funct. Mater.* 2005

Image Analysis of TEM

TEM picture : PS/MWNT binary image

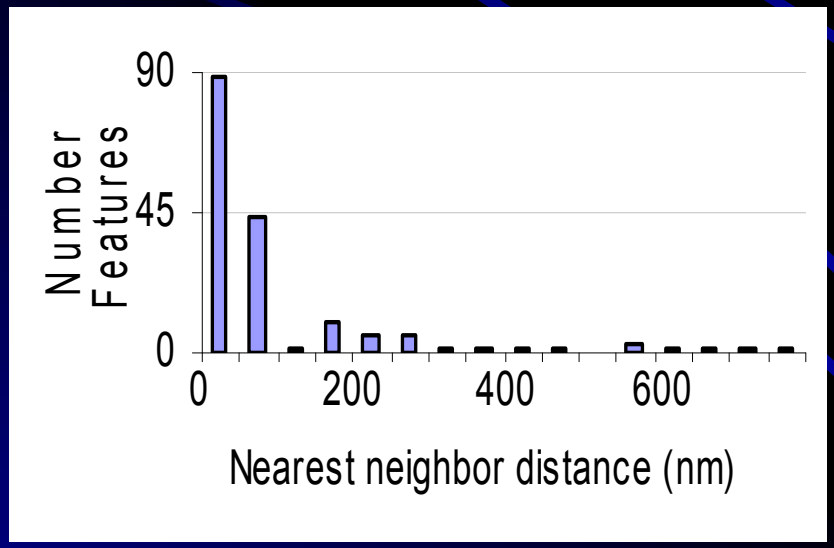


TEM picture : PS/MWNT (1:1) DMHDIm TFB binary image

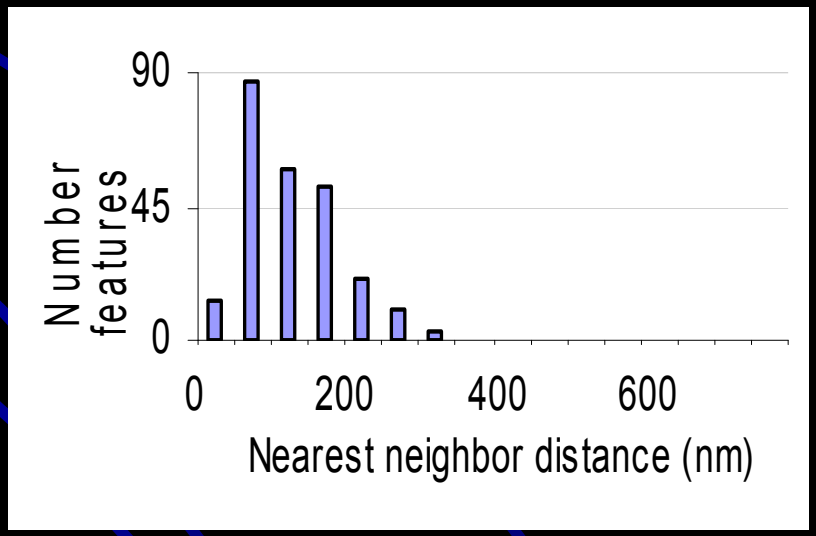
- (Adobe photoshop + Fovea Pro plug-in)
- convert into binary image
- Locate features
- nearest neighbor distance

Quantitative Measurement of Dispersion

PS/MWNT

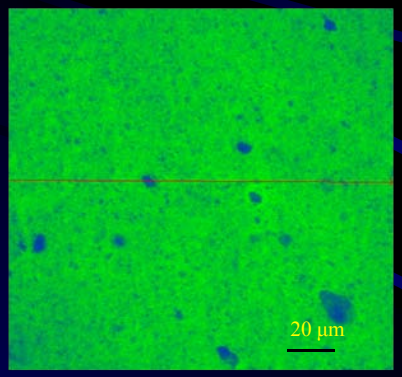


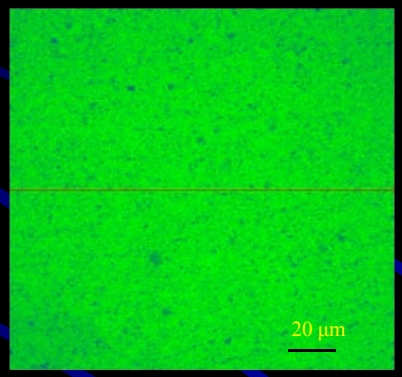
PS/MWNT (1:1) DMHDIm TFB



Nearest MWNT distance
- Median = 38 ± 13 nm
Calculated
- Random = 120 nm ±15 nm

Nearest MWNT distance
-Median= 109 ± 6 nm
Calculated
- Random = 132 nm ± 20 nm,

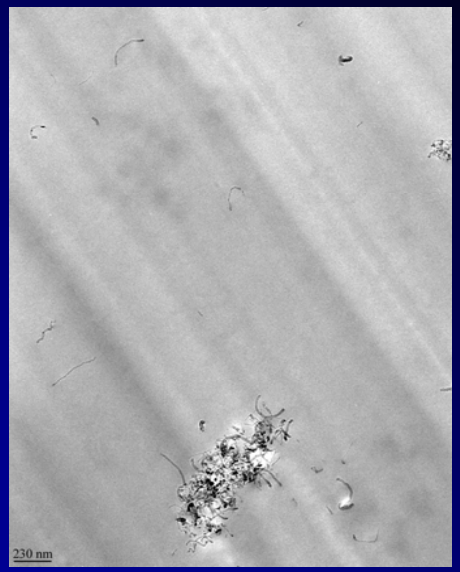




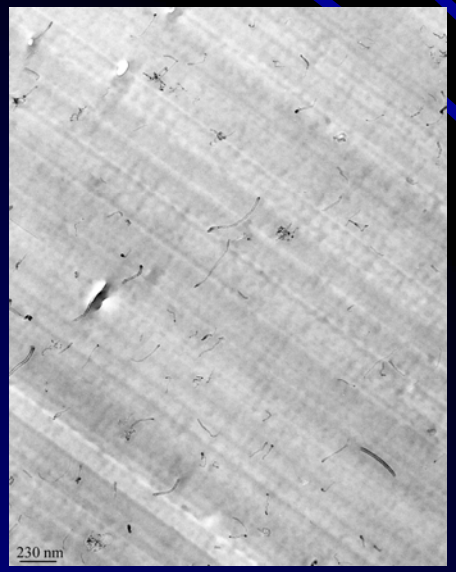
Confocal

Processing samples : 0-1 Hour

Scanning and image analysis : ½ day



PS/MWNT



PS/MWNT (1:1)
DMHDIm TFB

TEM

Processing samples : 1 Hour

Microtoming : ½ day

TEM Analysis : ½ day

Developing and scanning : ½ day

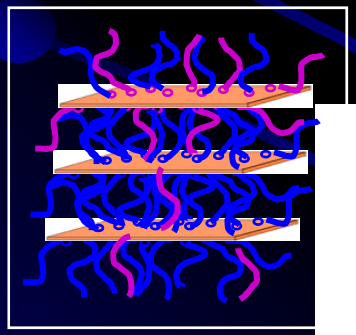
Image analysis : 1 days

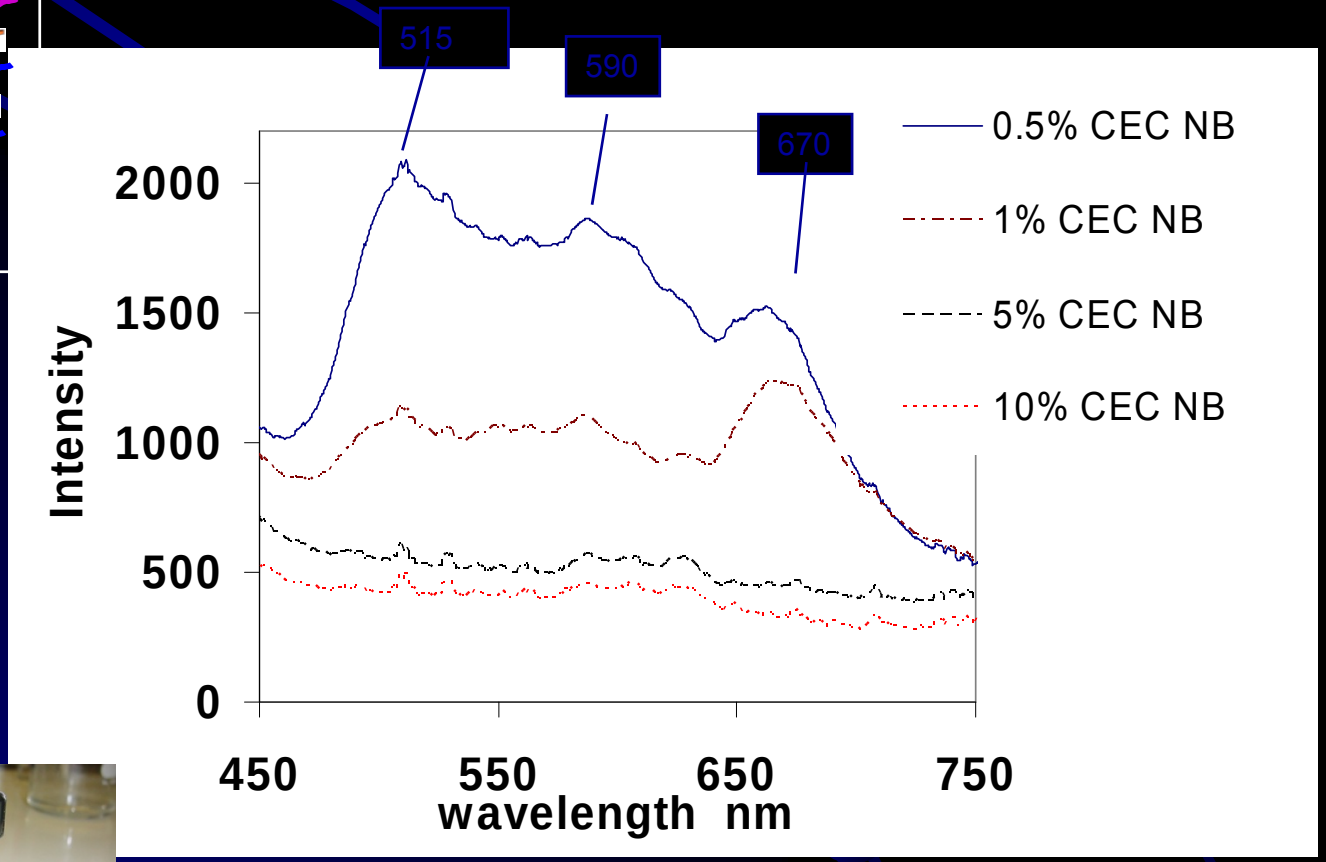
Total = ~3 days

Bellayer, S. Gilman, J. et al. *Adv. Funct. Mater.* 2005

Fluorescence of NB-MMT Clay

Nile-Blue-clay

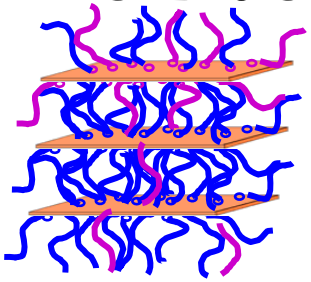


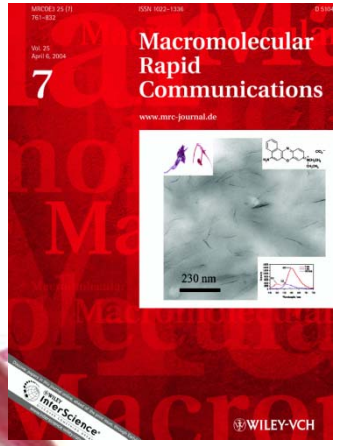


407 nm Laser Induced Fluorescence Spectroscopy
:Tony Bur, Paul Maupin

Optical Monitoring of Exfoliation

Nile-Blue-clay





Micro/intercalated

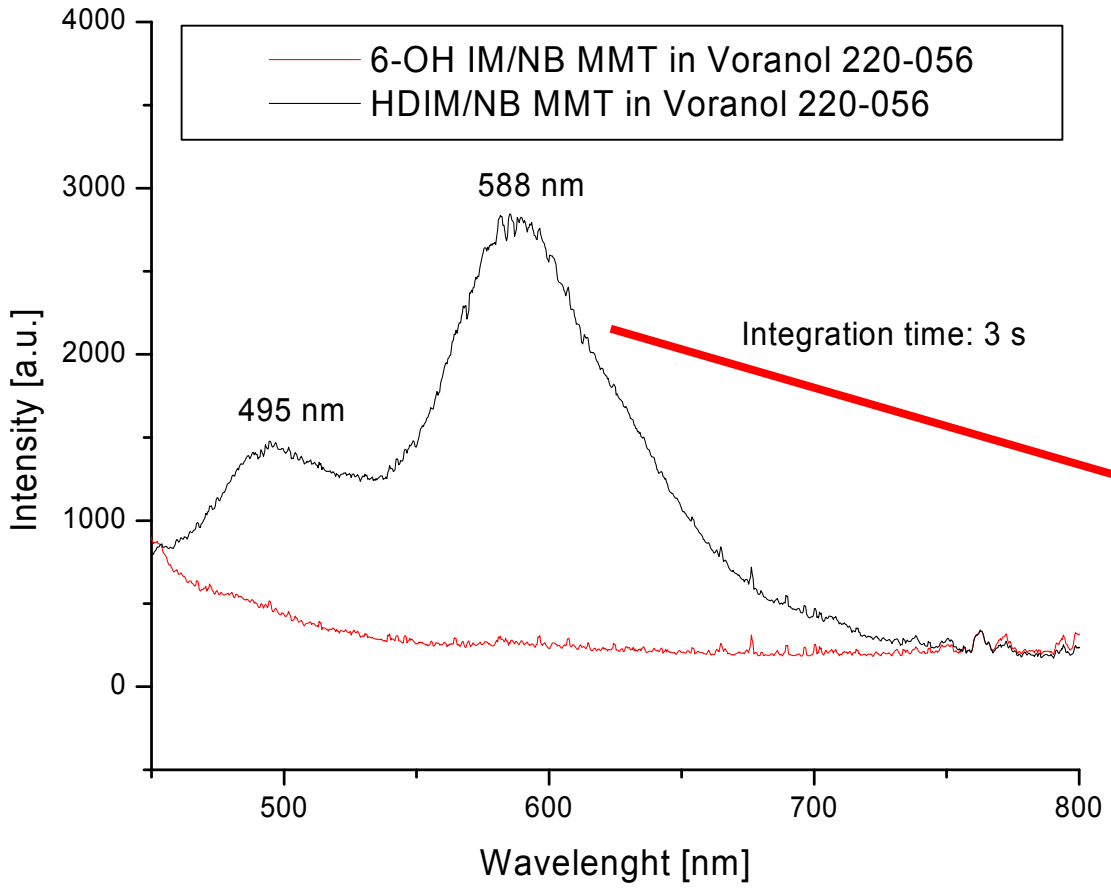
PA-6 2% IM/NB MMT extruded-1 min

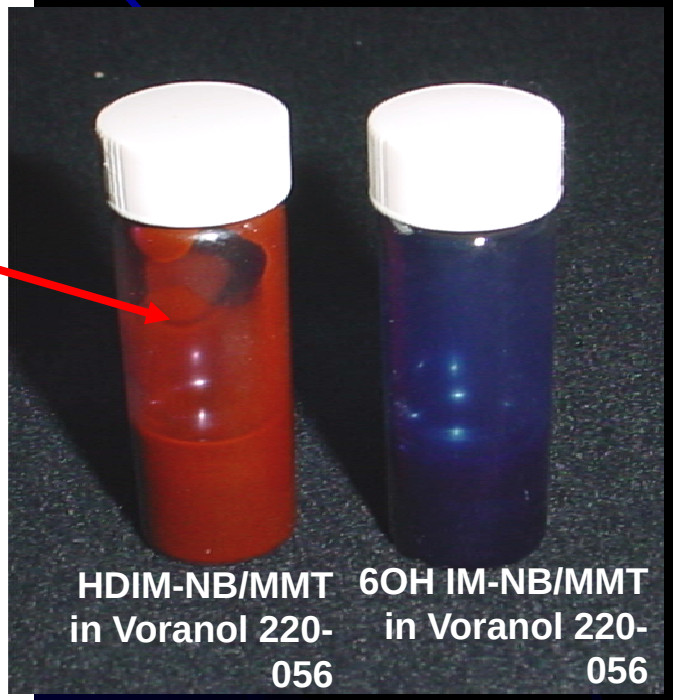
Disordered exfoliated

PA-6 2% IM/NB MMT extruded-7 min

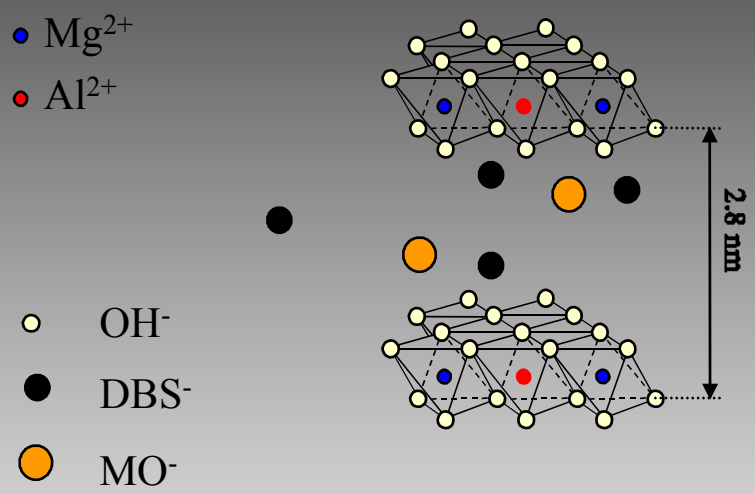
Maupin, et al, Macromol. Rapid Comm. April, 2004
Gilman et al, PMSE, 2004, and 2005

Nano-dispersion Using Fluorescent Dye Labeled Montmorillonite





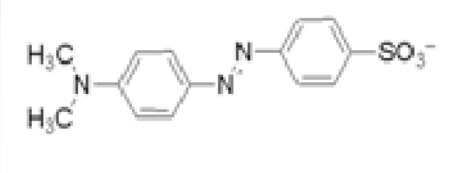
Organo Modified Layered Double Hydroxides



Nominal Formula:
$Mg_4Al(OH)_{10}(DBS)_{0.95}(MO)_{0.05} \cdot nH_2O$

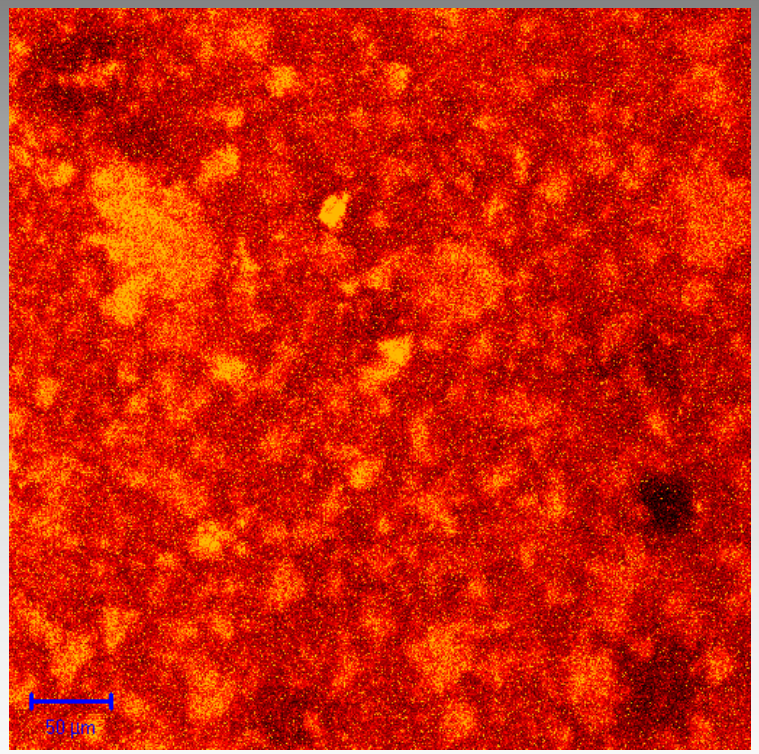
DBS^- =

MO^- =



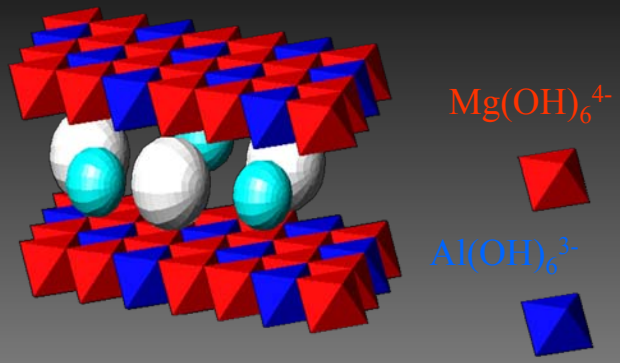
Confocal Microscope

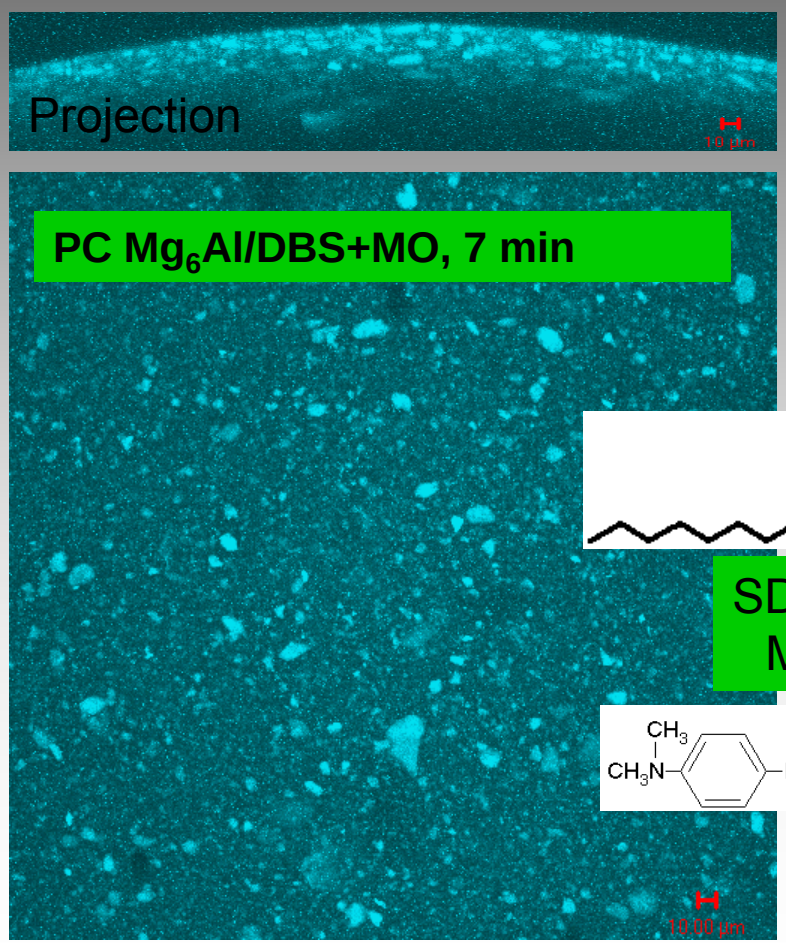
X-Ray Diffraction

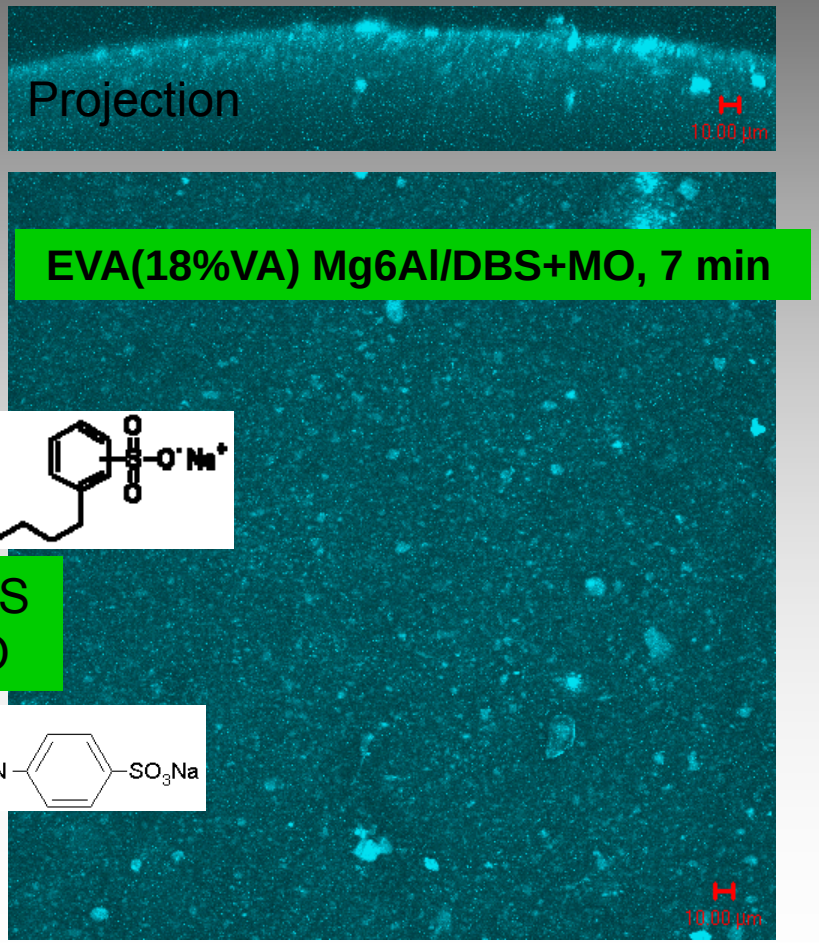


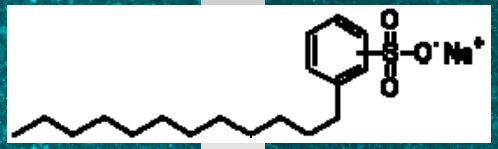
Matrix (polyurea) quenching,
Weak aggregate fluorescence

Confocal Imaging of LDH Nanocomposites



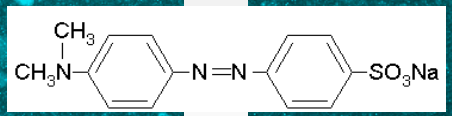






SDBS

MO



Confocal characterization of EVA/OM-LDH

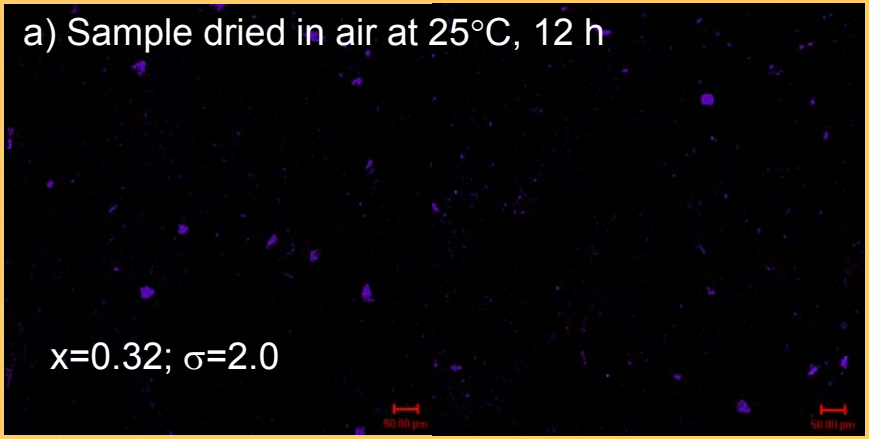
Increased drying conditions

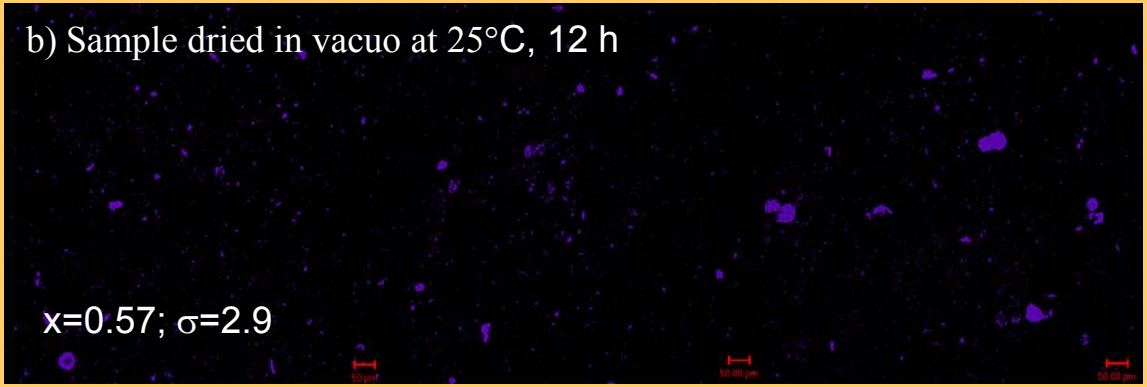
Image Analysis

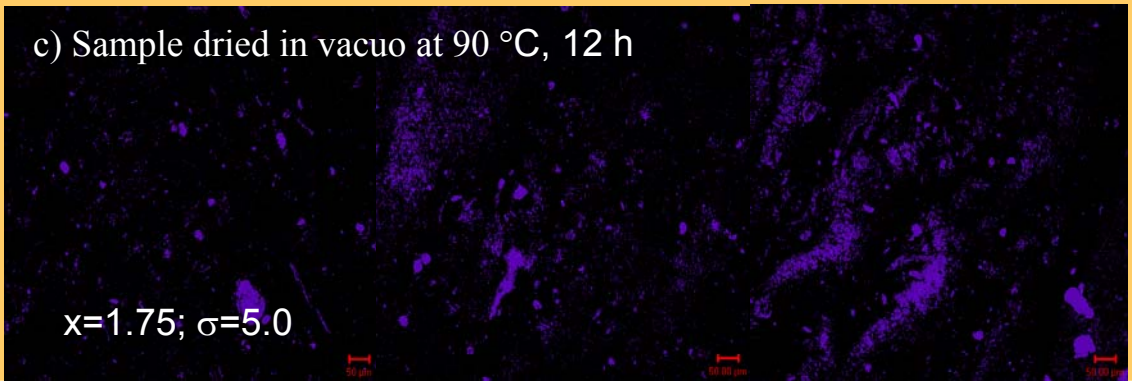
- **DBS-MO-LDH is fluorescent**
- **EVA quenches Methyl Orange fluorescence**

X = mean fluorescence intensity

σ = std. dev. Noise



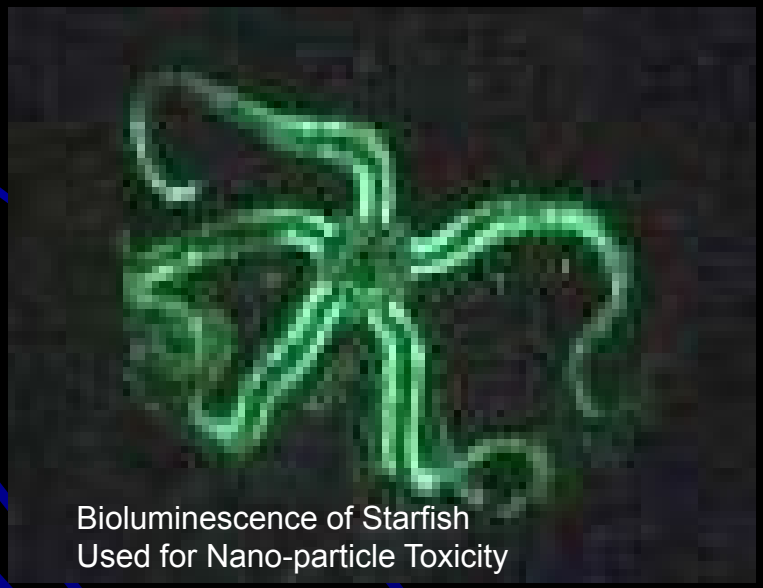




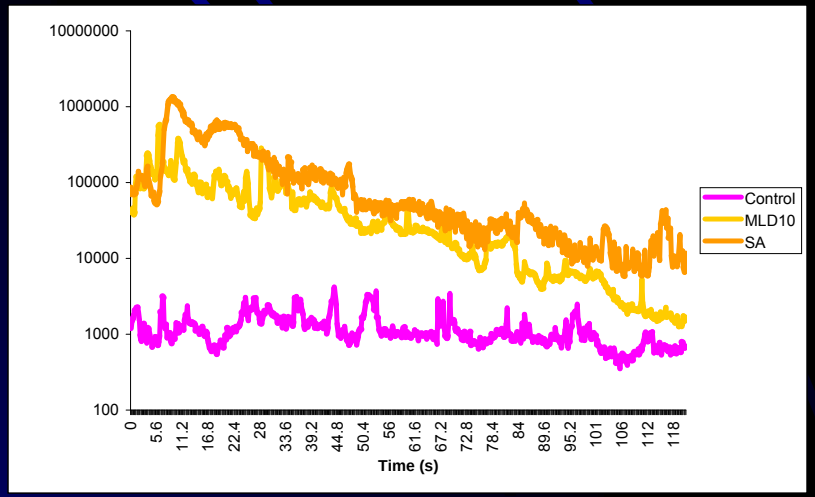
Methodologies to Determine Health and Environmental effects of Nano-particles

- Dimitri D. Deheyn, Ph.D.
  Marine Biology Research Division,
  Scripps Institution of Oceanography,

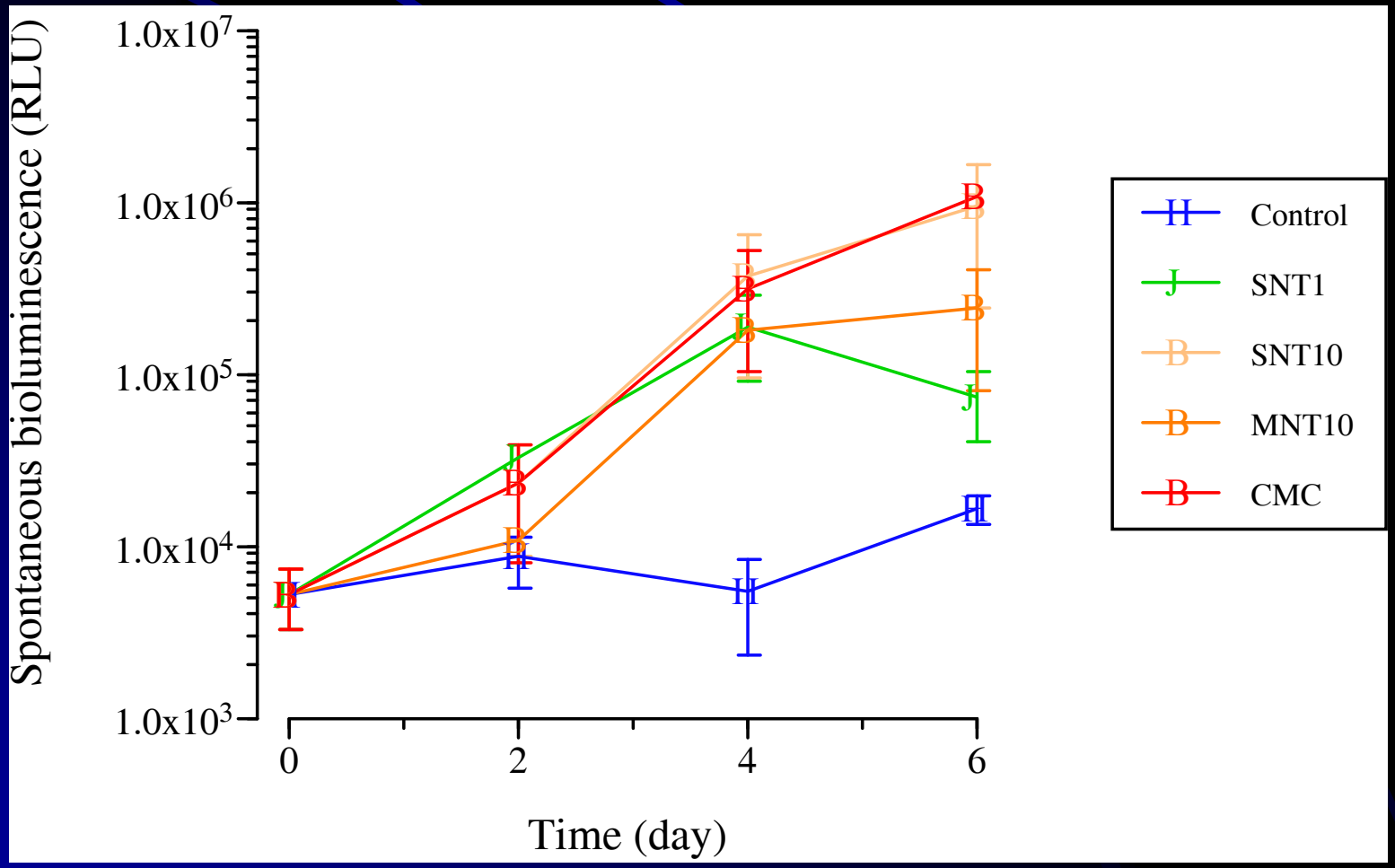
  University of California, San Diego



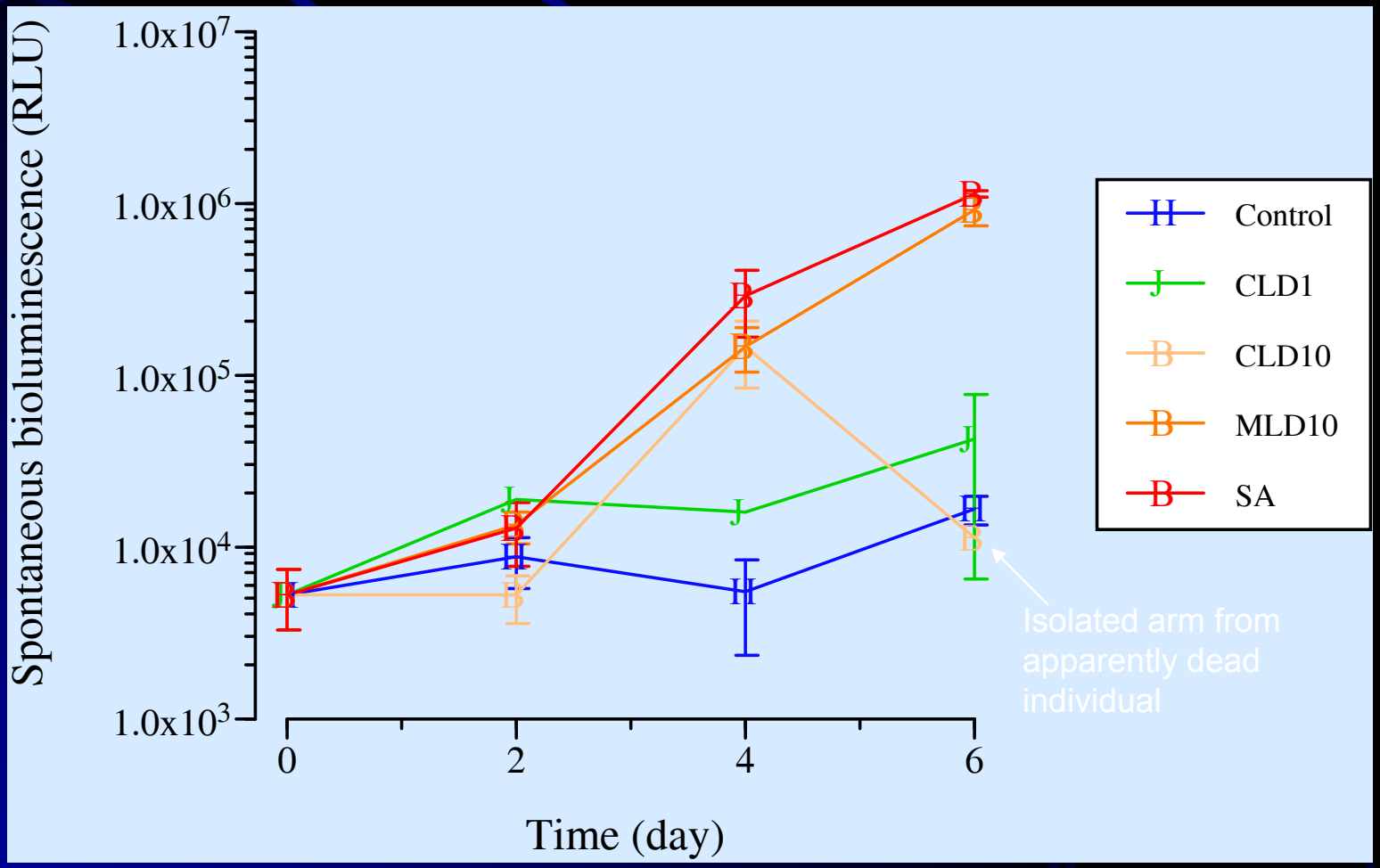
Bioluminescence of Starfish
Used for Nano-particle Toxicity



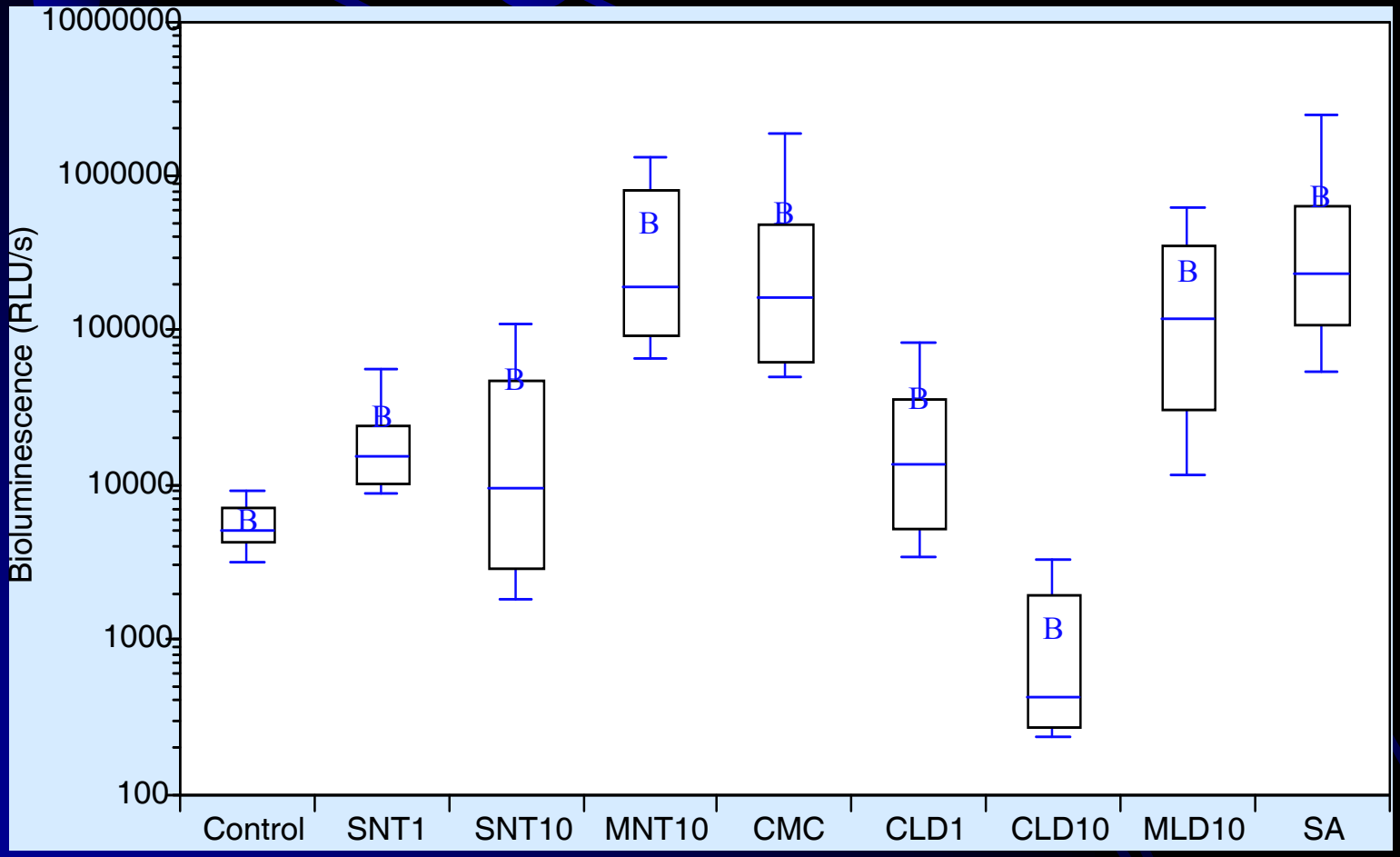
Time variation of the spontaneous light Nanotubes



Time variation of the Brittlestar Bioluminescence from Nanoparticles



Variations of light stimulated by Ach – Day 6



Dimitri D. Deheyn, Ph.D.
Marine Biology Research Division,
Scripps Institution of Oceanography

Barriers to Success

- Lack of tools for characterization of dispersion of clay in polymer
- Limited processing window due to low thermal stability of organo-clays
- Incomplete mechanistic understanding of property enhancements
- Sustainability

Improved Thermal Stability via Extraction

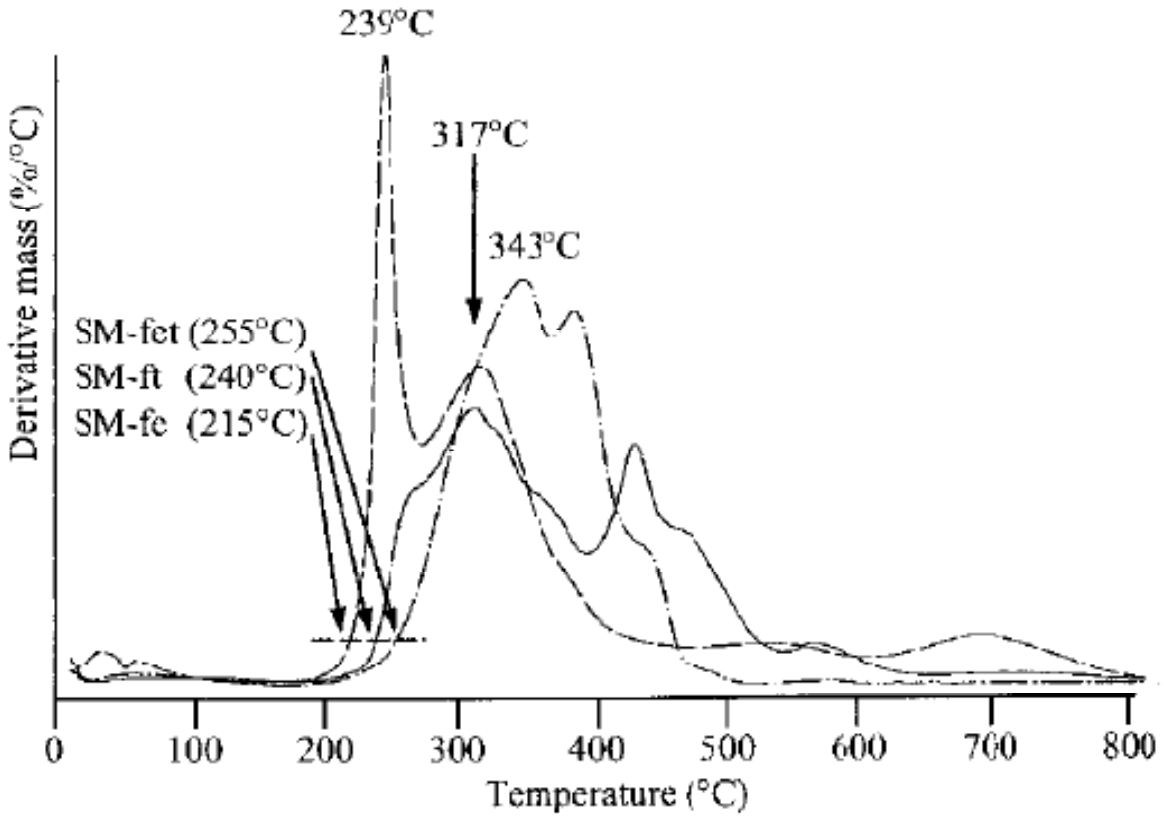
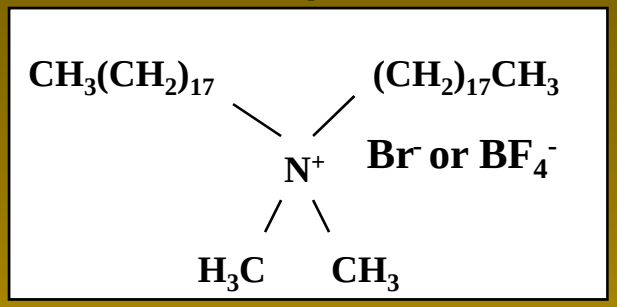


Figure 3. Thermograms of DMDODA-SM samples SM-fe, SM-ft and SM-fet. Exothermic peaks above 500°C represent the decomposition of aromatized pre-char formed from degradation of the DMDODA. Note that the two-solvent-extraction approach increases the thermal stability of the ionically bound organic modifier by ~40°C.

Davis RD, Gilman JW, Sutto TW, et al., Improved thermal stability of organically modified layered silicates, Clays and Clay Minerals, 52 (2): 171-179, 2004.

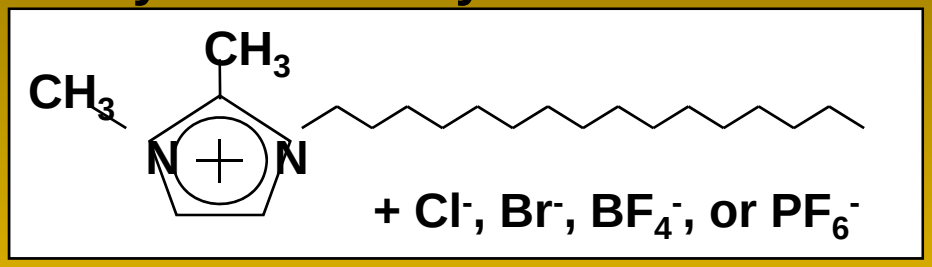
Organic Cations for Clays

- **N,N-Dimethyl-N,N-Dioctadecylammonium salts**



Tdec = 215° C

- **1,2-Dimethyl-3-hexadecylimidazolium salts**



Tdec = 300° C

- **1,2-Dimethyl-3-(benzyl ethyl iso-butyl POSS)imidazolium Chloride**

Tdec = 350° C

Gilman, Awad, Davis, Shields, Harris, Davis, Morgan, Sutto, Calahan, Trulove and De Long, *Chem. Mater*. 2002.

Awad, W.; Gilman, J.; Harris, R.; Sutto, T.; Calahan, J.; Trulove, P.; De Long, H. *Thermocmem. Acta*, 2003

Fox, DM; Gilman, JW; De Long, HC; Trulove, P. C., *Journal of Chemical Thermodynamics*, 2005.

Langat, J., Bellayer , S., Hudrlik, P., Hudrlik , A., Maupin, P.H., Gilman J.W. Sr., Raghavan, D., *Polymer*, 2006.

Barriers to Success

- Lack of tools for characterization of dispersion of clay in polymer
- Limited processing window due to low thermal stability of organo-clays
- Incomplete mechanistic understanding of property enhancements
- Sustainability

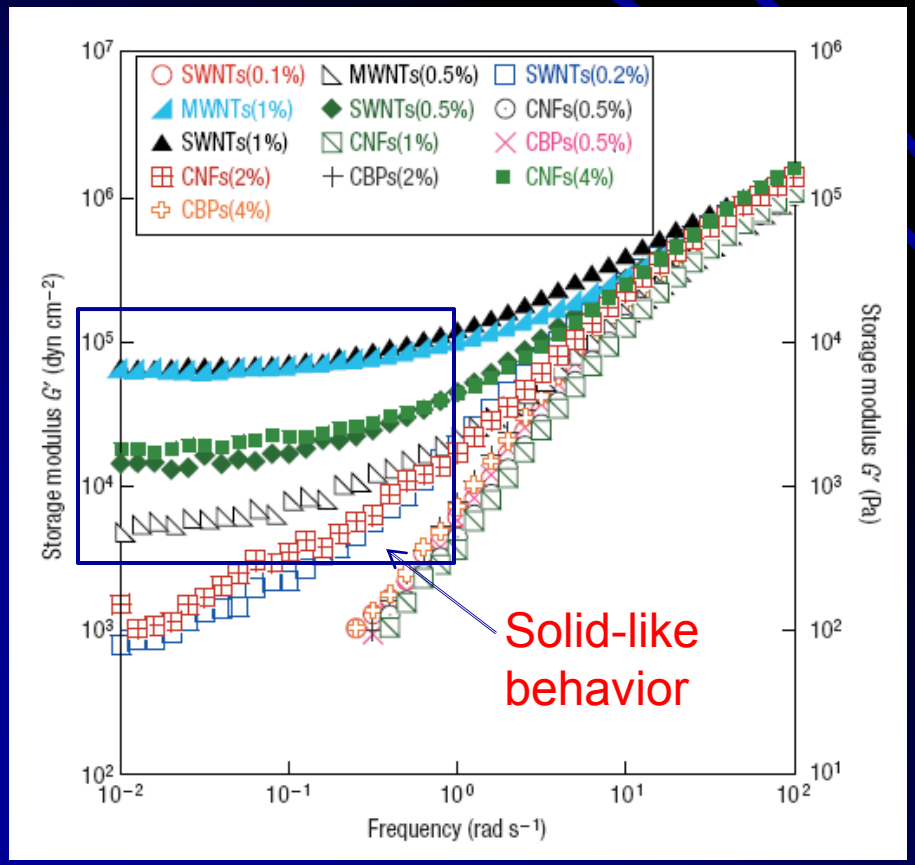
Non-Newtonian Fluids

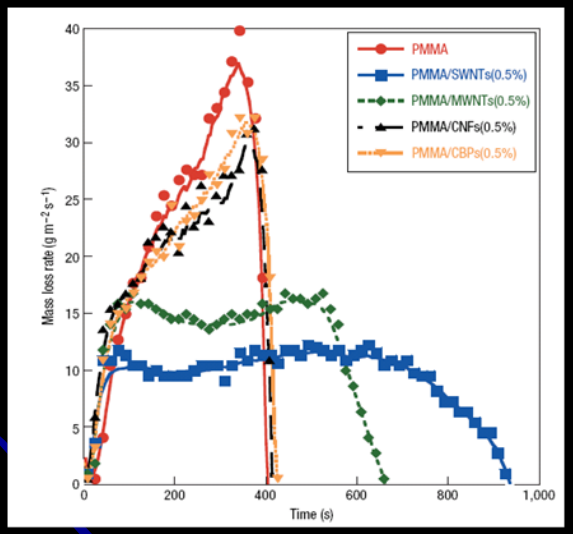
- http://www.youtube.com/watch?v=f2XQ97XHjVw

Effect of Network formation on Polymer nanocomposites Flammability

- Formation of network of nanoparticles significant reduction melt dripping during degradation, heat and mass release rate during burning

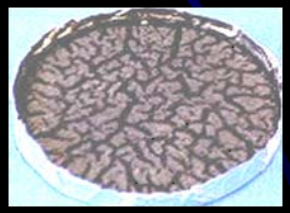
- The critical network formations and hence the flame resistance changes with the type of particles eg. 0.5wt% for SWCNT and 9 wt% for carbon black.





Pure PMMA

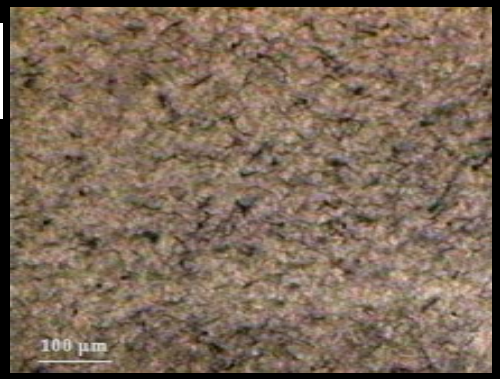
PMMA+0.5wt% SWCNTS

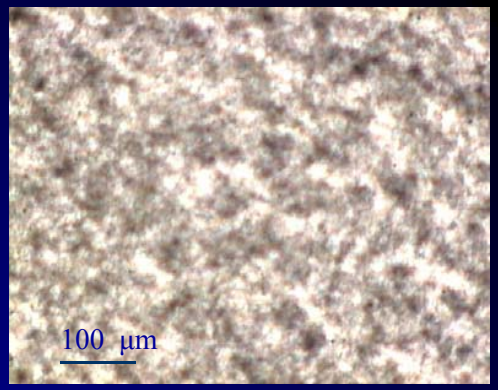


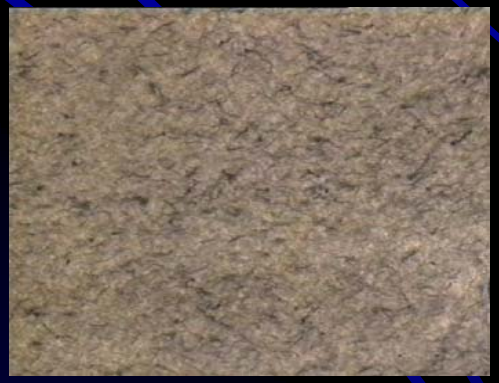
PMMA+ 0.5 wt%MWCNTS

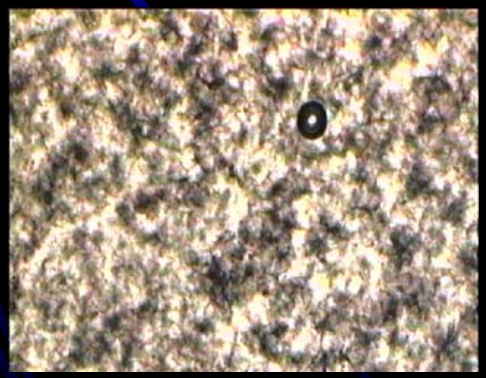
Shear induced flocculation

After waiting for 1hour without applying shear

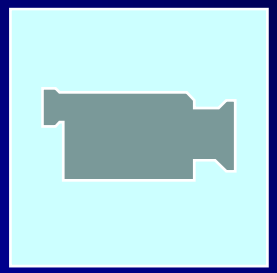








After applying low shear rate



Shear Induced flocculation

Nanocomposite + Conventional Flame Retardant enabled
A lower cost Approach

- Nanocomposites + additional flame retardants have resulted in final materials that pass regulatory tests and have superior balance of properties.
  - Successful commercial approaches* remove some of existing FR package, replace with nanocomposite.
    - ***Kabelwerk Eupen: EVA + Organomontmorillonite + $Al(OH)_3$. – cable insulation, passes UL1666**
    - ***PolyOne: (polyolefin nanocomposite – UL-94 V-0 @ 3.0mm)**
    - ***Albemarle – ATH or MgOH and OMC**
    - ***Nanocor – Phos. Clay - UL94 V0**

Barriers to Success

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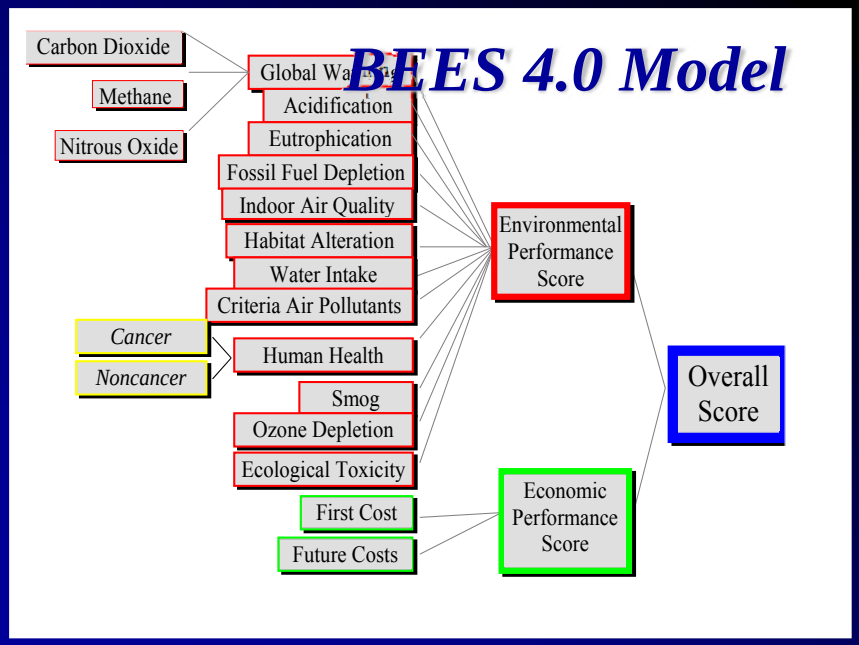
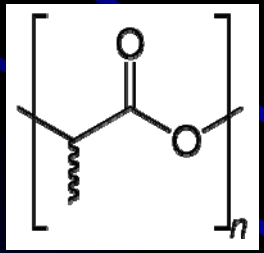
- Limited processing window due to low thermal stability of organo-clays
- Incomplete mechanistic understanding of property enhancements
- Sustainability

Biopolymer Nanocomposites



Challenges for Bio-based Polymers



NatureWorks LLC

- Poly lactide –PLA
  - Narrow processing window
  - Difficult to flame retard
  - Blends cannot be easily recycled

- Innovation Takes Root Conference 2008:
- Dr. Masatoshi Matsuda of the **Toyota Motor Corporation laid out Toyota's ambitious vision of establishing technology for 20 weight % usage of ecoplastics and recycled plastics by 2015**
- **But PLA limitations include:** the low HDT, impact strength, and hydrolytic stability, and in process, the relatively higher molding cycle times

Natural Polymer Nanocomposites

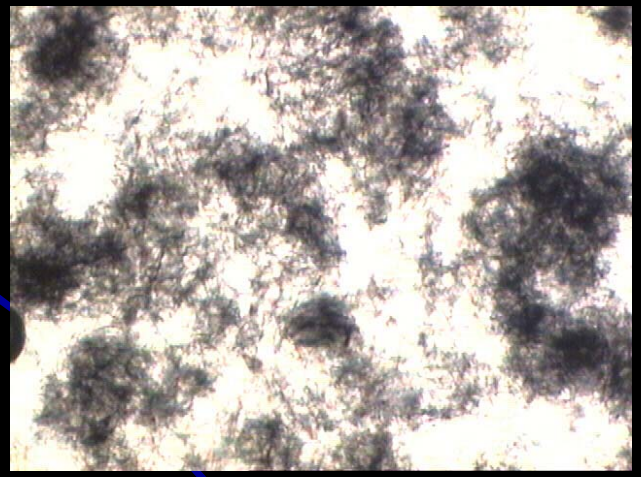
PLA, Cellulose, NOP…

- Goals

1) Characterize effects of aspect ratio, surface chemistry and processing on nanoparticle network formation in natural polymer nanocomposites.

2) Use ionic liquids, natural surfactants, to prepare and process sustainable nanoparticles.

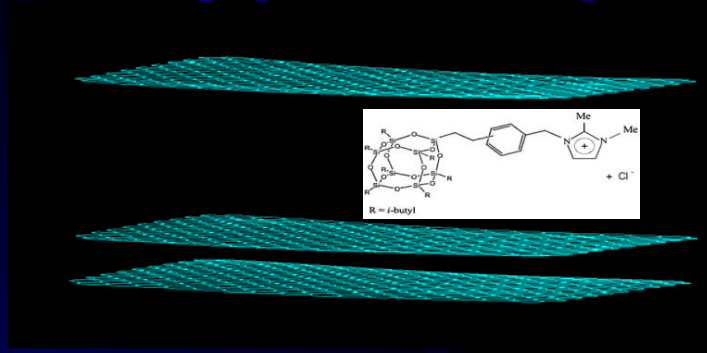
3) Develop high throughput methods for preparation and characterization of natural polymer nanocomposites

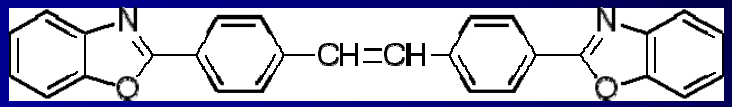


nanoparticle networks

Rahatekar et al. Adv. Mat. 2008

POSS-IM functionalized graphene





2-(benzoxazolyl)-stilbene

Schmidt. al., J Sol-Gel Sci Techn 2006

Natural Polymer Nanocomposites

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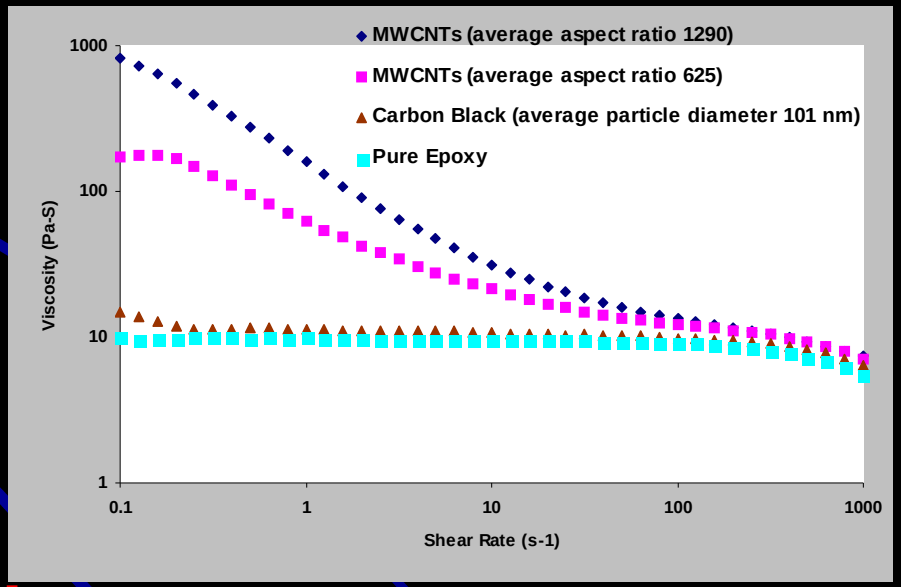

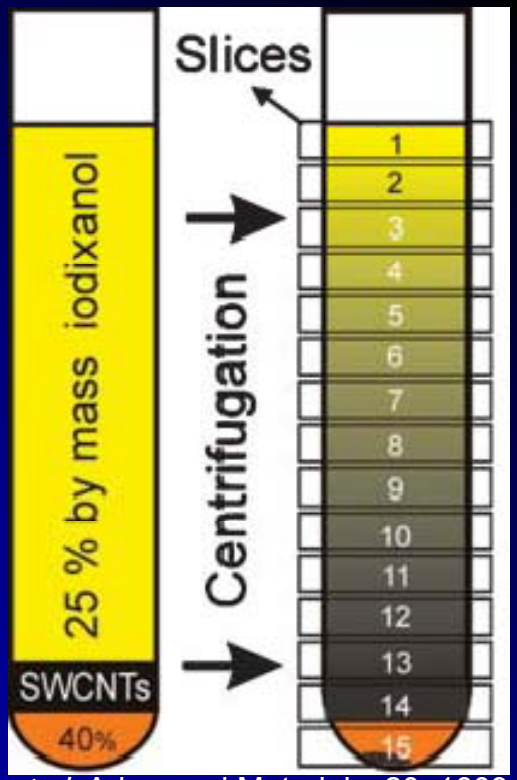

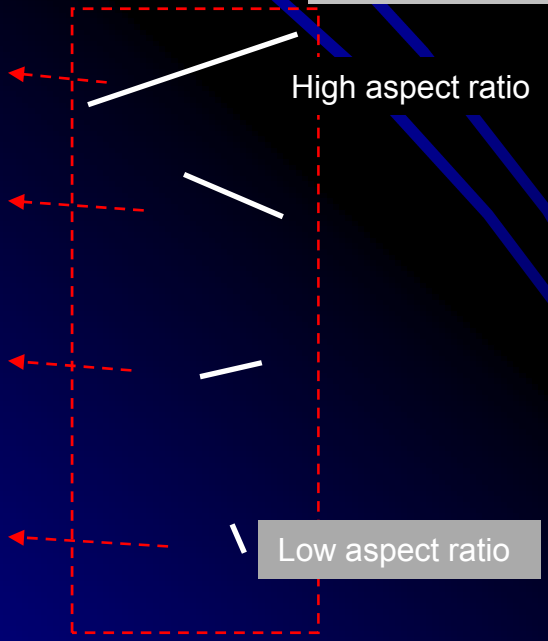

Graphene

Cellulose NF/whiskers

LDH

In PLA, Cellulose, …

Fagan *et al.* Advanced Materials, 20, 1609, 2008

Natural Polymer Nanocomposites

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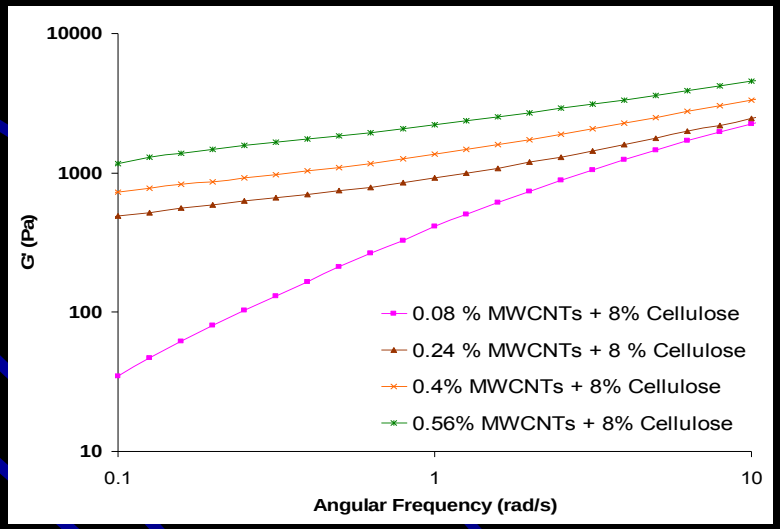
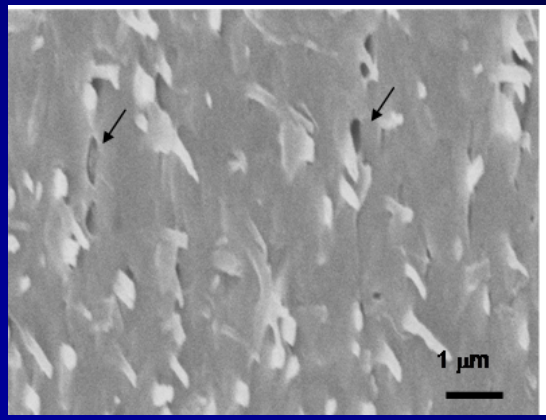
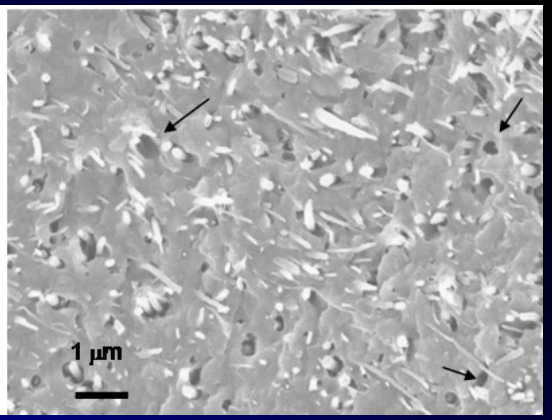


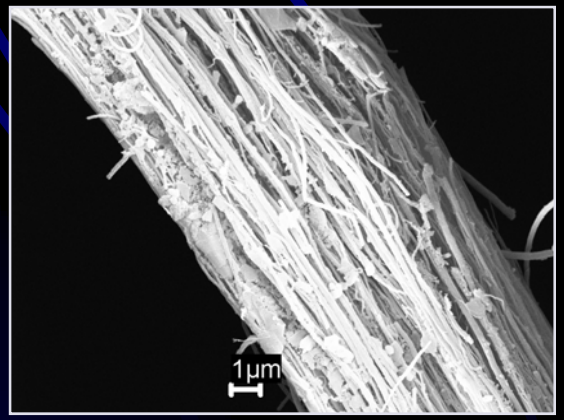
A

3-D Confocal image MWCNT in epoxy in shear cell

Jeffrey Urbach, Dan Blair -Georgetown University







Cellulose MWCNT composite fibers wet spun from ionic liquid solution, S. Kumar Ga Tech

Natural Polymer Nanocomposites: Plans

- Goals

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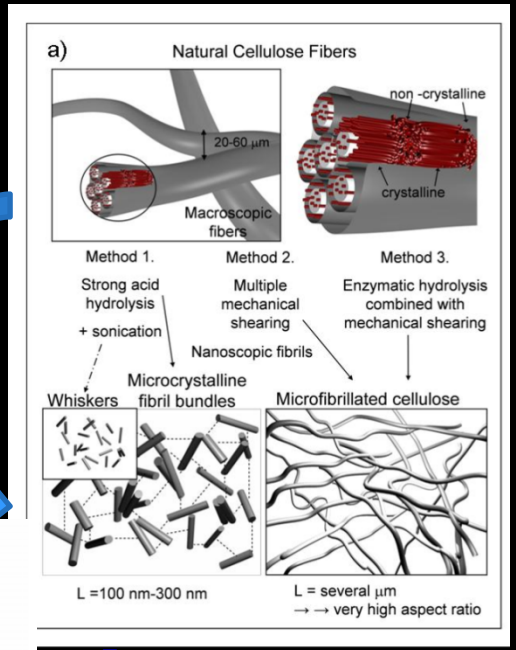
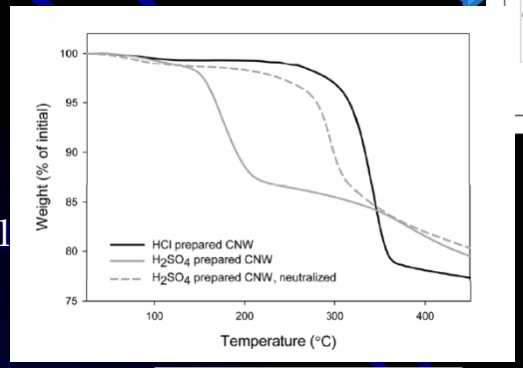
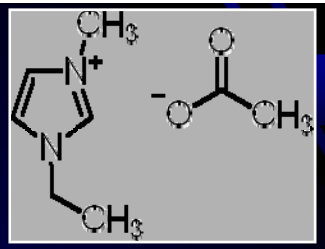
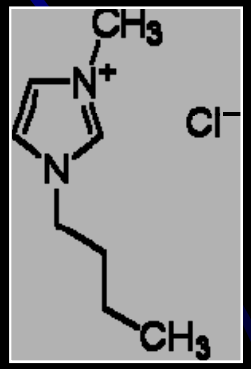
3) Develop high throughput methods for preparation and characterization of natural polymer nanocomposites

ionic liquids









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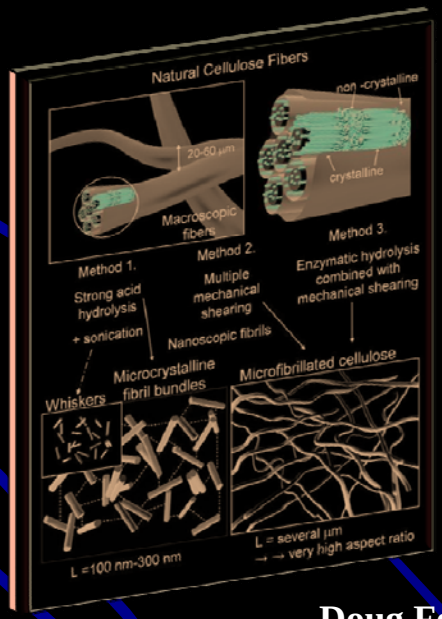
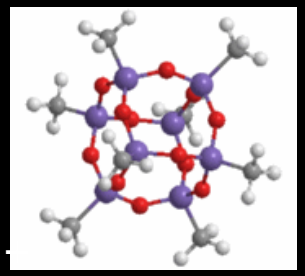
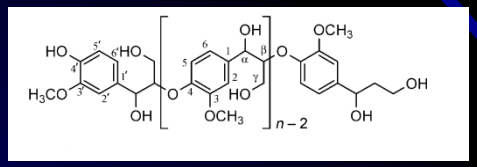




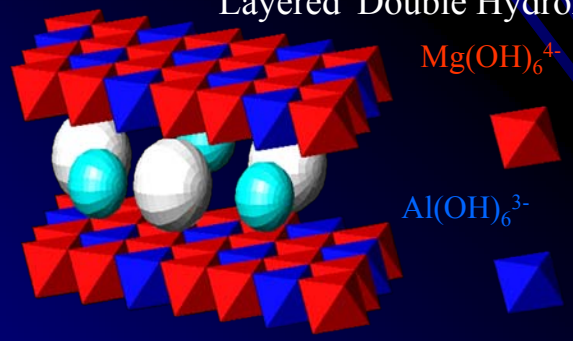
POSS functionalized cell-NF

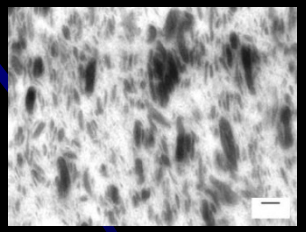
Doug Fox – American University



Lignin

Layered Double Hydroxide





P. Mather; U. Conn

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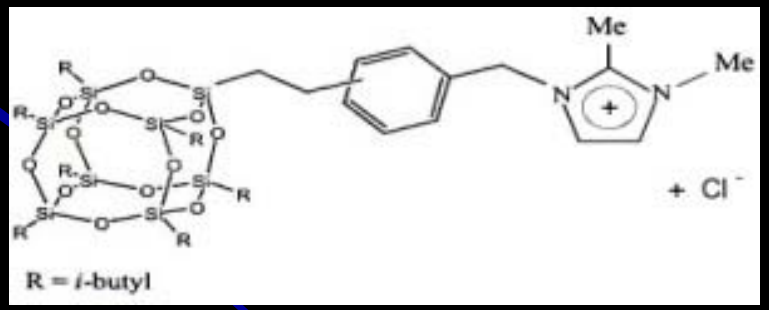
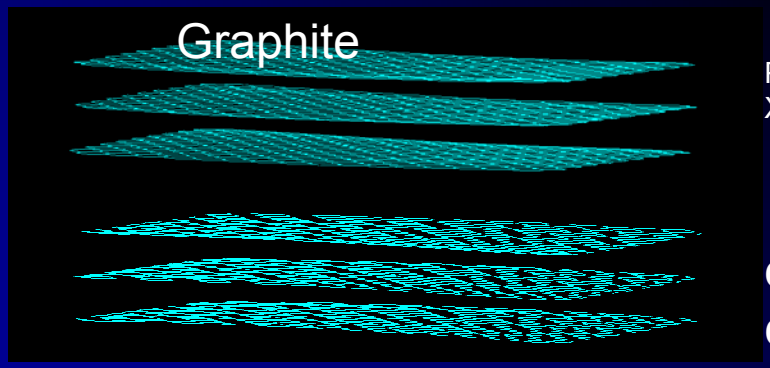


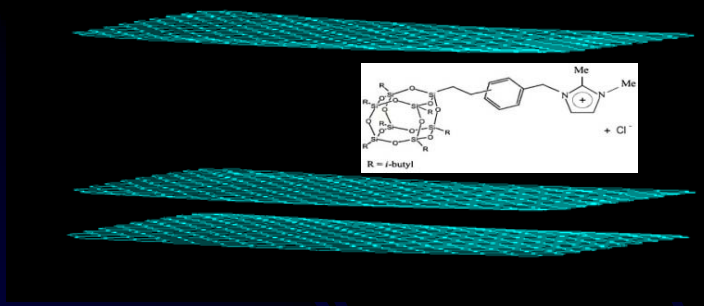
POSS-IM functionalized graphene

Paul Trulove- US Naval Academy



POSS-IM+
X-

electro chem



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T. E. Sutto, P. C. Trulove and H. C. DeLong, Electrochem. Solid-State Lett., (2003) 6, A50-A52.
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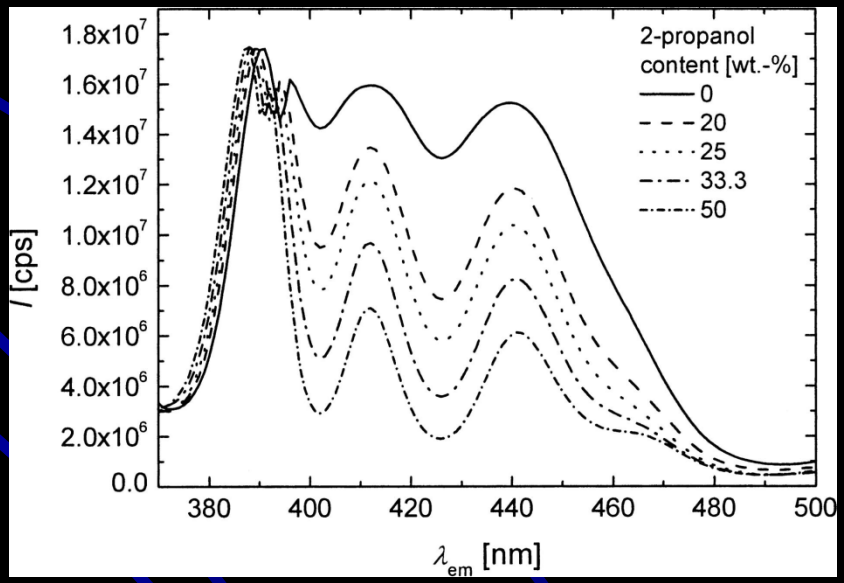
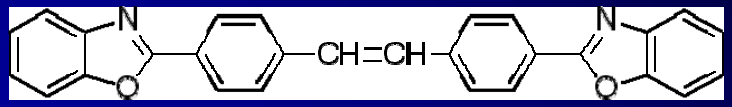


Maupin et al., Macro. Rapid Comm.



2-(benzoxazolyl)-stilbene

Schmidt. al., J Sol-Gel Sci Tech. 2006

Progress

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Funding ($): Air Force Office of Scientific Research, Department of State –US Egypt Program, Navy, FAA, Ashland, Dupont, NIST Consortia: (**Foam**: Air Products, Foamex, So. Clay, Multina, Boeing, Dow, Bayer MS), (**High Throughput**: Dow, So. Clay, Rhodia, Air Force Research Lab), (**Nanocomposites**: Dow, So. Clay, Nanocor, Raychem, 3M, Nyacol Nanotech.)

We thank: Kalman Migler, Steve Hudson and Jeff Fagan for use of the Polymer Division Lincam shear cell, LIF spectrometer, and Lipiin Sung and Marc Cicerone for use of the LSCM

WORKSHOP AGENDA