A DuPont perspective on Nano Environmental, Health, and Safety

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June 10, 2008

The miracles of science™

Outline

Characterization Challenges in Nanomanufacturing

- Characterization of dispersion and/ or particle size distribution in dilute suspension, through processing and into final part
- Nano or suface coatings on nanoparticles
- Nanoparticle/ polymer interphase
  - How does the presence of the nanoparticle influence or affect nearby polymer molecules

Outline

Characterization Challenges in Nano

- Characterization of dispersion and/ or particle size distribution in

- Nano or suface coatings on nanoparticles
- Nanoparticle/
  - How does the presence of the nanoparticle influence or affect nearby

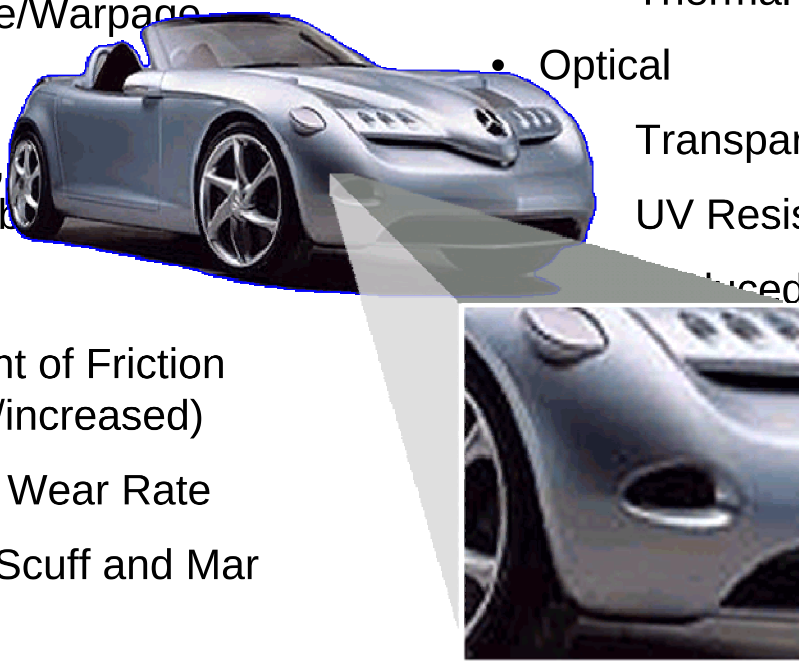
Outline

Characterization Challenges in NanoEHS

- Characterization of dispersion and/ or particle size distribution in water, air, in complex mixtures, cells, tissues, and selected organisms
- Nano or surface coatings on nanoparticles
- Nanoparticle interactions
  - How does the presence of the nanoparticle influence or affect nearby tissue
- Sampling issues (water, air)
- Safe practices in the work place
- Collection and sharing of basic physical data
- Particle size, surface chemistry, etc. in ground water, soil, cells, tissues…

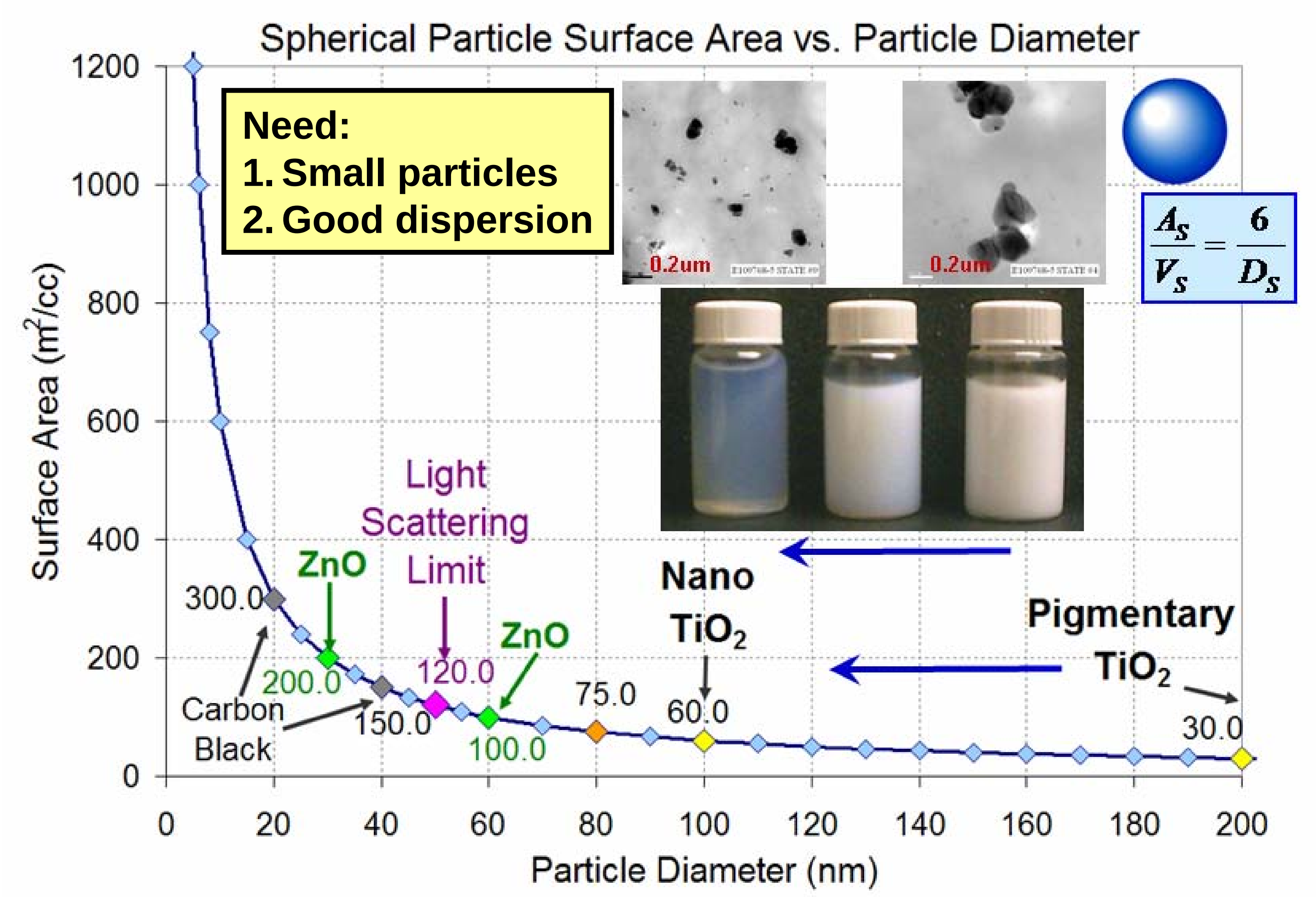
Polymer Nanocomposites - Property Enhan

- Mechanical
  - Modulus
  - Tensile Strength
  - Toughness
  - Shrinkage/Warpage
- Barrier
  - O2, H2O, Hydrocarb
- Tribology
  - Coefficient of Friction reduced/increased)
  - Reduced Wear Rate
  - cratch, Scuff and Mar
- cal
  - onductivity
  - orona Discharge Resistance
  - ielectric and Magnetic



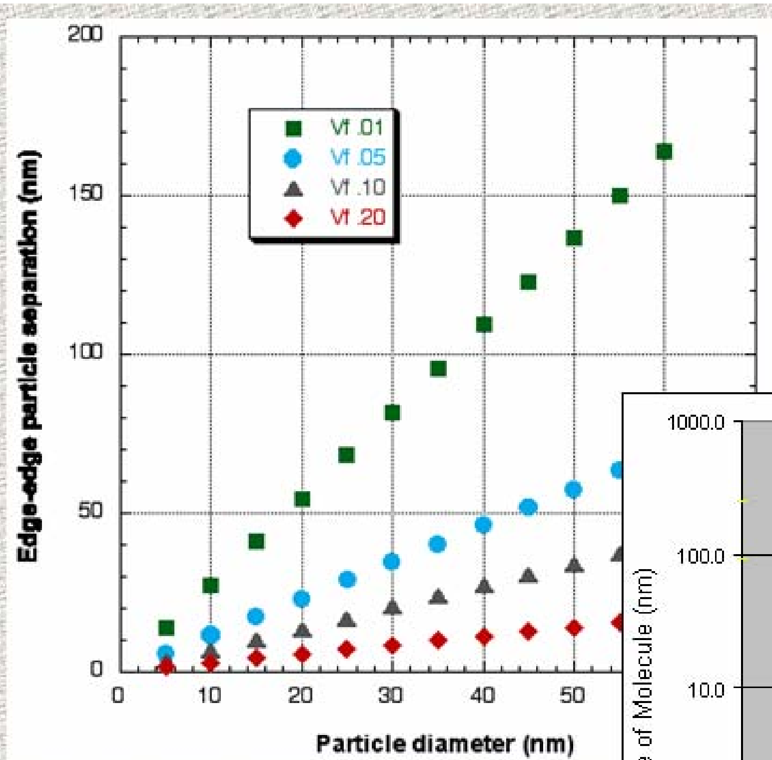
- Thermal
  - Heat Distortion Te
  - Coefficient of Line Expansion
  - Thermal Conducti
- Optical
  - Transparency/ Re
  - UV Resistance
  - ced IR Transmission
  - e Resistance
  - mation
  - jation
  - lification
  - cosity at low shear rates (low creep)
  - Small filler effect on viscosity at high shear rates

TiO_2 for UV Durability: Importance of Particle Surface Area and Dispersion



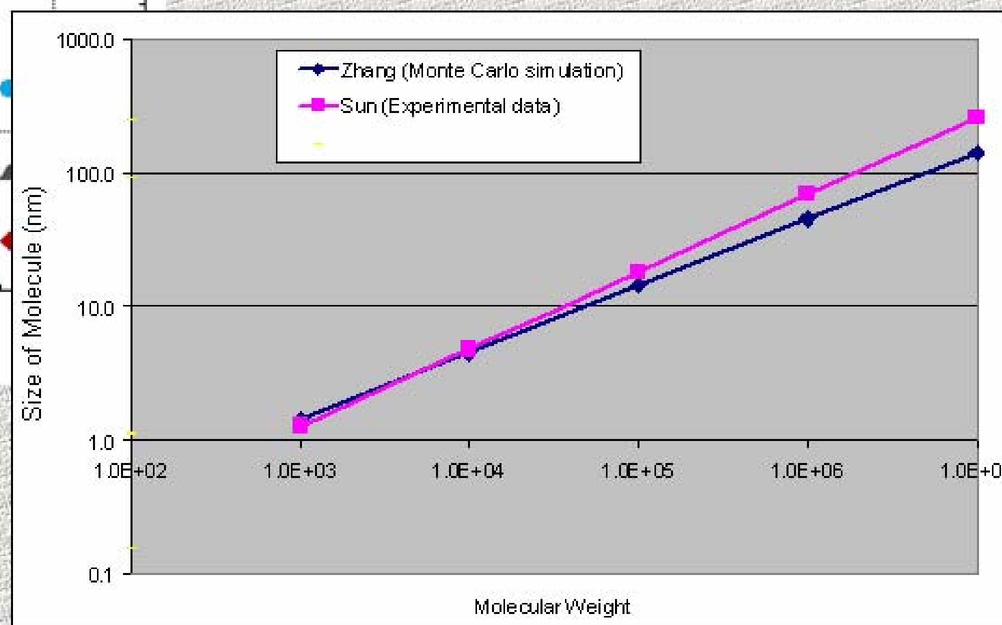
Wetzel

Polymer Interphase



When the distance between particles is less than or equal to the size of the polymer molecules themselves unusual things can happen!

Constrained Polymers



Does This Nano TiO_2 Pose an EH&S Risk?

- TiO_2 photo and surface chemistries are well known
  - Effects of surface modification/passivation?
- With increased surface area, are TiO_2 nanoparticles hazardous to human health and the environment?
  - Different than micron-scale cousins?
    - **Harmful, benign or beneficial?**
    - Can they pass through tissue (lung, skin, eye, etc.)?
  - Form in the product/process/use chain?
    - **Free primary particles or agglomerates?**
- Specific EH&S issues for polymer processing?
  - Extrusion and compounding
  - Molding, shaping and forming
  - Machining, sanding, grinding, cutting, etc.
  - Recycling, landfill, incineration, etc.

Nanocomposites Product Stewardship

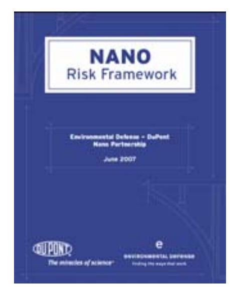
Research → Manufacturing → Post process → End-use → End of Life

- EH&S culture and practices
- DuPont/Environmental Defense "Nano Risk Framework"
  - **DuPont standard for nanotechnology**
  - **Rigorous, data-driven process**
    - Supplier & Customer relationships
    - **Research and development phase ✓**
    - **Pilot-scale processes ✓**
    - Manufacturing
    - Technical Service, …
    - Toxicology and Environmental Fate

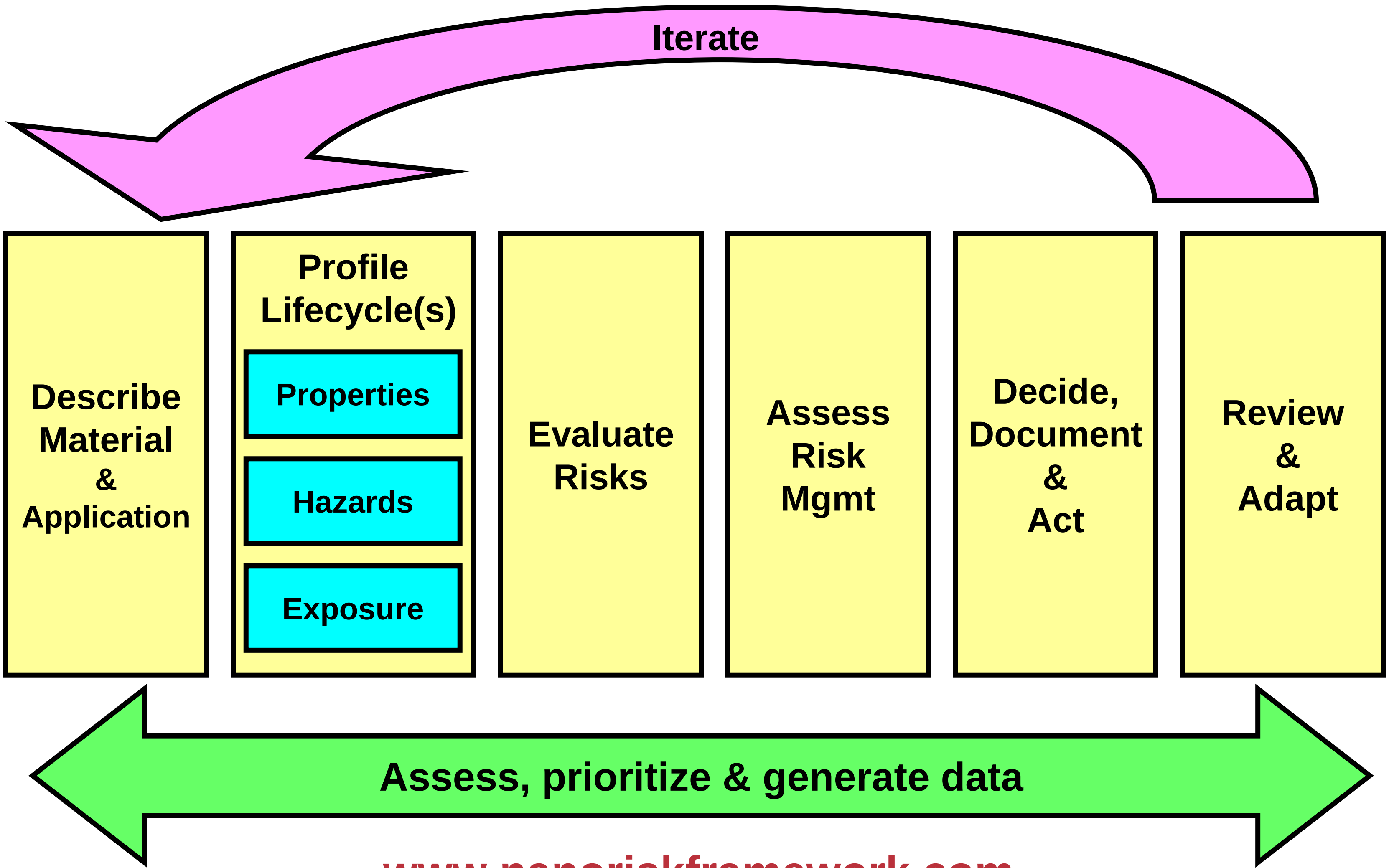
DuPont – Environmental Defense Nano Risk Framework

"A framework to facilitate the responsible development, production, use and disposal of nano-scale materials"

- Collaboration begun in October 2005
- Objectives: A systematic and disciplined process, developed with broad collaboration to
  1. **identify, manage and reduce potential health, safety and environmental risks throughout the lifecycle of such nanomaterials**
  2. **provide a model and tool for industry, public interest groups, academia and government**
  3. **make available information, tools and methods developed**
- Framework published on June 21, 2007



The Nano Risk Framework Process



www.nanoriskframework.com

Nano Risk Framework & Case Studies

NANO
Risk Framework

http://www.nanoriskframework.com

A Partnership of Environmental Defense Fund and DuPont

- Home
- Download Framework
- Case Studies
- Frequently Asked Questions
- About this Partnership
- For the Media
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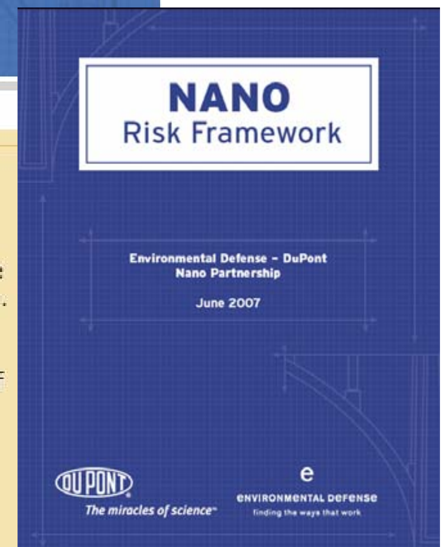
ENVIRONMENTAL DEFENSE FUND
Finding the ways that work



Case Studies

DuPont conducted three demonstration projects in order to evaluate the comprehensiveness, practicality, and flexibility of the Framework. The three nanomaterials under consideration differed in terms of composition, structure, intended application, stage of development, and DuPont's role in the development, evaluation, or potential use of the material.

DuPont™ Light Stabilizer 210

The first material, DuPont™ Light Stabilizer 210, is a surface-treated high-rutile phase titanium dioxide. DuPont generated a complete Output Worksheet for this product, addressed all of the base sets, completed a risk evaluation, and selected risk management measures.

- DuPont™ Light Stabilizer 210 Summary [PDF]
  A four-page overview of the case study
- DuPont™ Light Stabilizer 210 Output Worksheet [PDF]
  The full Output Worksheet for the case study

Carbon Nanotubes

The second material, carbon nanotubes (CNTs), consists of cylindrical carbon molecules whose novel properties make them potentially useful in a wide variety of applications (e.g., electronics optics, and materials). Both single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) are being tested.

Product Stewardship (TiO_2 commercial offering)

Product R&D (CNTs)

Approach: Apply and Adapt Existing EH&S Principles and Practices to Nanocomposites

- Apply the Nano Risk Framework
- Develop rational approaches to mitigate risks
  - **Nanomaterials are treated as potentially hazardous**
    - until EH&S data prove otherwise
  - **Engineering controls designed for the application**
  - **Standard Operating Procedures (SOPs)**
  - **Personal Protective Equipment (PPE)**
    - **PPE as last line of defense**
- Consultation with experts and nano-advisory groups
- Hazards review and change management processes
- Operations occupational health monitoring
- Line management responsibility

Nano Risk Framework CNT Case Study:

Step 1) Describe Material & Application, stage of development, past experience, benefits & risks

CNT supplier data

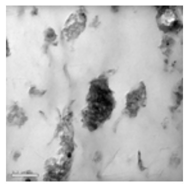
Material	CAS Number	Composition
MWCNT	7782-42-5 (Graphite)	Carbon (> 95%)

Issue: nano-filler material supplier data may be insufficient

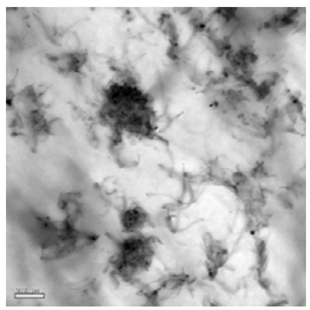
Application:

CNT nanocomposite

1) **Batch mixer melt blending**
2) **injection molding**

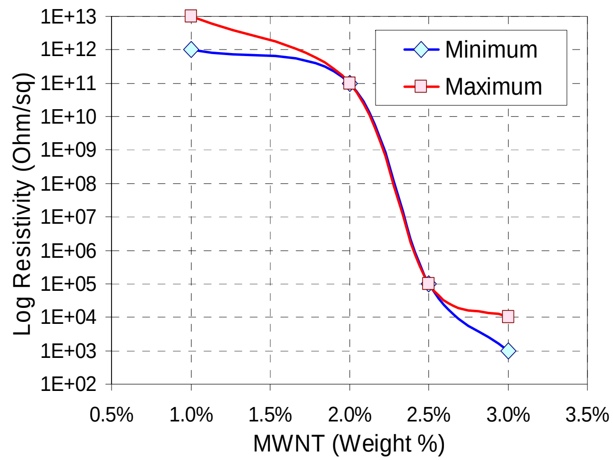


Poor dispersion, no conductivity



2.5% MWNT

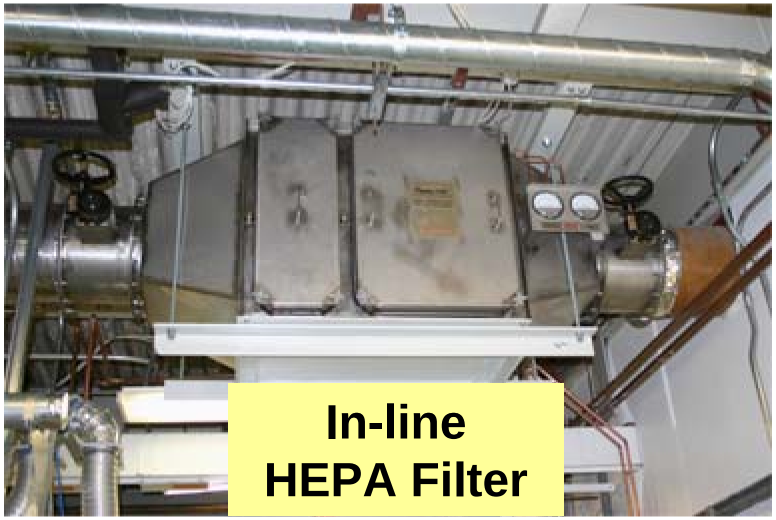
2-pt. Surface Resistivity



Injection molded bars

Properties: mechanical, electrical, etc.

Laboratory R&D Prototyping:
Nanocomposites Synthesis and Evaluation



Laboratory designed for Nanocomposites Processing

- **Sample preparation and handling**
- **Small-scale melt processing technologies:**
  - Micro-compounding and batch mixers
  - Laboratory compounding extruders
  - Lab-scale shaping and forming
- **HEPA* filtration to isolate ventilation system**

***HEPA: High Efficiency Particle Air filtration**

Sample Preparation & Identifying Risks and Mitigating Hazards during Handling

- **Enclosure designed for localized containment**
- **Specific SOP for nano-filler handling, cleanup and spill response**
- **PPE for handling nano-fillers**

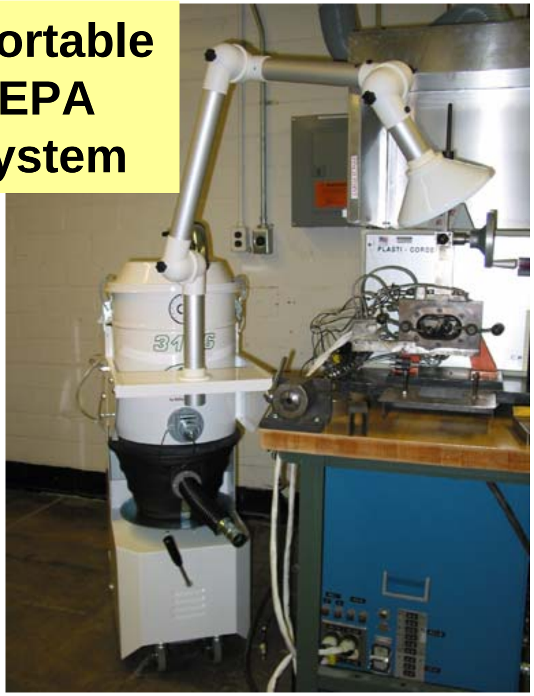
Double-bagged plastic packaging may be insufficient

Electrostatic potential (CNT, plastic, metal, RH, etc.)

Incidents or events are analyzed and documented to improve engineering controls, SOPs or PPE

Filler Handling during Batch Melt Processing

Portable HEPA system



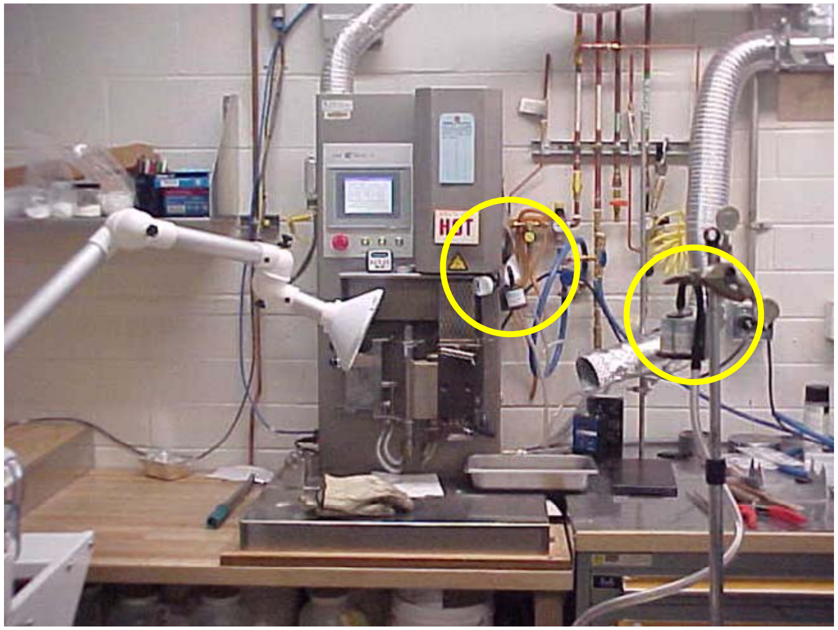
Localized Engineering Control

Melt Blending

Injection Molding

- **Specific SOPs for nano-filler handling, cleanup and spill response**
- **Portable HEPA system during nano-filler addition and cleanup**
- **PPE for hot melt processing *and* handling nano-fillers**
  - PPE for nano-fillers used until monitoring establishes low exposure potential and toxicology data determine that the material has low hazard

Step 3) Evaluate Risks: Air monitoring of Carbon Nanotube Compounding



Air Monitoring

Sample #	*Type / Name or Location*	Time (min)	Vol (liters)	Analyzed for	Results (mg/m^3)
NANO-051219-01	Personal / Technician (BZ)	130	351	**Total Dust**	ND < 0.28
NANO-051219-05	Area / right side of DSM	134	331	**Total Dust**	ND < 0.30
NANO-051219-07	Area / top of hood enclosure	132	317	**Total Dust**	ND < 0.32
NANO-051219-08	Area / base of the enclosure	135	320	**Total Dust**	ND < 0.30
NANO-051219-10	Blank	N/A	N/A	**Total Dust**	--

- For non-detects (ND) the results indicated with a '<' value represents the reporting limit for that analysis
- Breathing Zone (BZ): Limit of Quantification (LOQ) = 0.1 mg / sample

Using conventional air monitoring (NIOSH method 0500 for total dust)
- **CNT's did not produce measurable nanoparticles in the air**
- **Engineering controls effective**

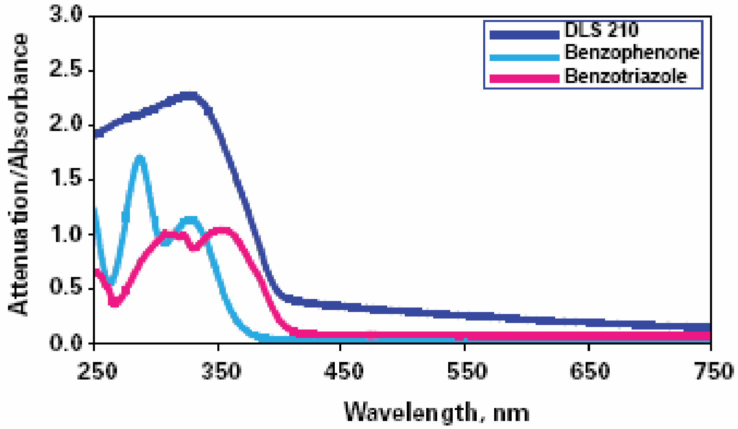
Sub-micron particles detected near powder samples
- **TSI P-Trak Model 8525P instrument (new technology - NOSH consortia)**

Step 4) Assess Risk Management - Summary

- CNTs are handled as if they are potentially hazardous materials
  - Environmental and Health data inconclusive
- A PEL (Permissible Exposure Limit) to be established as more monitoring data are collected in laboratories using CNTs for different applications
  - Example: development of a CNT nanocomposite product requiring a continuous compounding process
    - New or modified engineering controls
    - Air monitoring evaluations

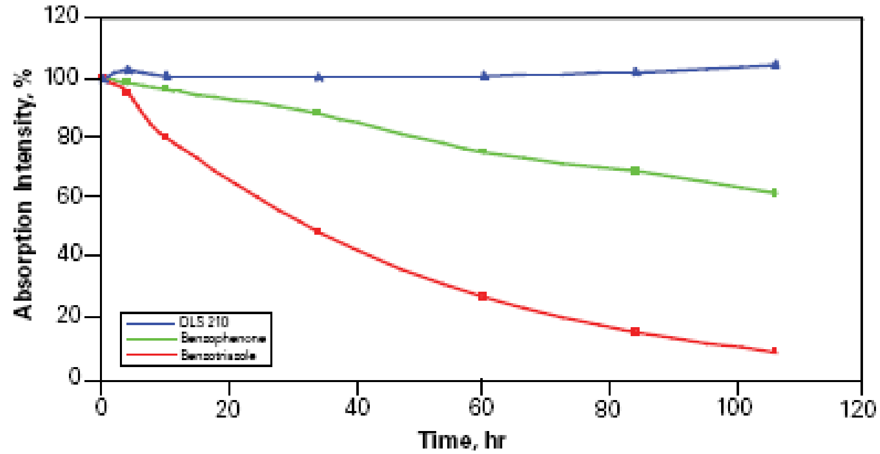
DuPont™ Light Stabilizer 210

Figure 1. UV Visible Attenuation/Absorbance of DuPont™ Light Stabilizer 210 and Organic UV Absorbers



1.0 wt.% loading in 2 mil LDPE films

Figure 3. Accelerated Migration Study at 70°C Exposure



Presence of each component followed by attenuation/absorbance at optimum wavelength.

http://www2.dupont.com/Titanium_Technologies/en_US/sales_support/about_us/product_stewardship/index.html

The next stage of development:
Lab-scale extrusion compounding of nano TiO_2

Lab extruder with Cutter

Feed System Powder Handling

Engineering controls for TiO_2 powder handling & containment

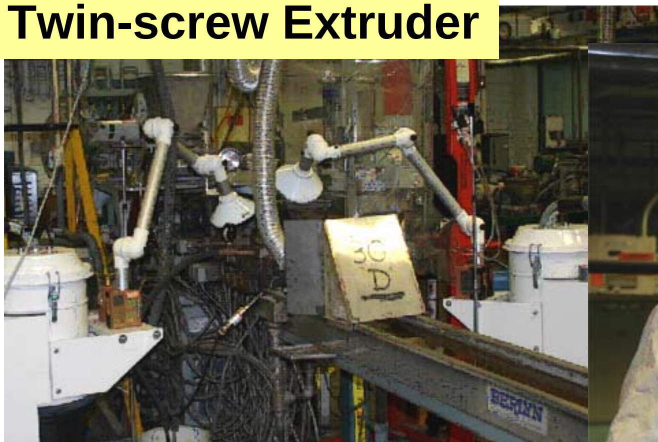
- **Increased nano-filler volumes**
- **Exposure sources**
  - ***Are nano-particles generated (feeder, die, quench, cutter)?***
  - ***Opening and cleaning the extruder & feeder***

Air Monitoring

Sample #	*Type / Name or Location*	Time (min)	Analyzed for	Results (mg/m^3)
BC010405-01	Operator	364	TiO_2	0.012
BC010405-02	Desk near door	381	TiO_2	<0.006
BC010405-03	Control panel	384	TiO_2	<0.006
BC010405-04	Operator	387	Total Particulate	0.112
BC010405-05	oven on top	382	Total Particulate	<0.065
BC010405-06	Control panel	384	Total Particulate	<0.065
BC010405-07	Blank	--	TiO_2	--
BC010405-08	Blank	--	Total Particulate	--

Nano TiO_2 Nanocomposite Compounding Process Scale-Up

Twin-screw Extruder



Feeder Loading

Powder Containment

Semi-works compounding:

- **Large volumes at high rates**
- **Continuous process**
  - **repetitive loading of feeders**
  - **dust generation (feeds, vents)**
- **Engineering controls & SOPs**
  - **tailored to the operation**
  - **PEL can be established**

Air Monitoring

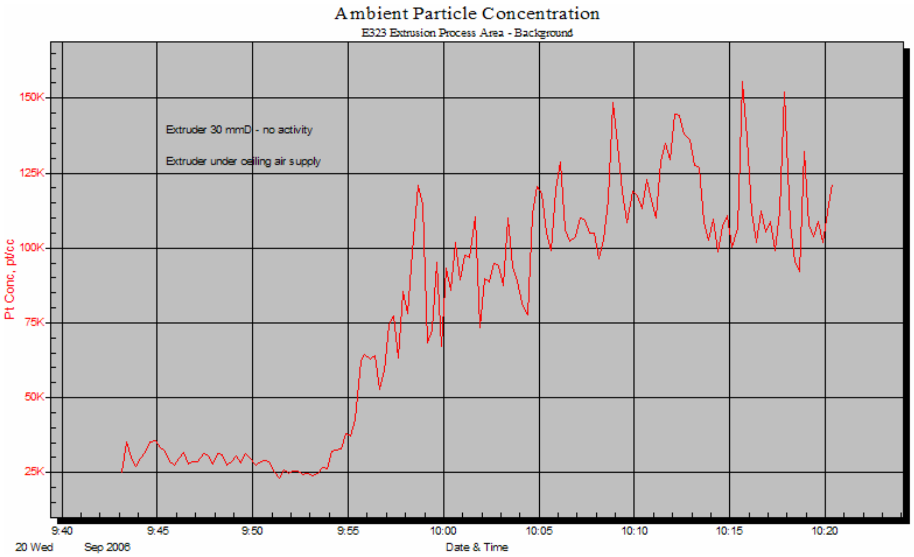
Description	Sample Duration	Resp Dust (mg/m^3)	Resp. TiO_2 (mg/m^3)
Personal: Operator handling TiO2 at feeder, transfers to bag, cleaning of enclosure	125 min	<0.16	<0.01
Area: Chamber, adjacent plastic sheet/access	34 min	<0.58	<0.04
Area: Extruder side	147 min	<0.14	<0.01
Area: Pellitizer	103 min	<0.19	<0.01

Wetzel

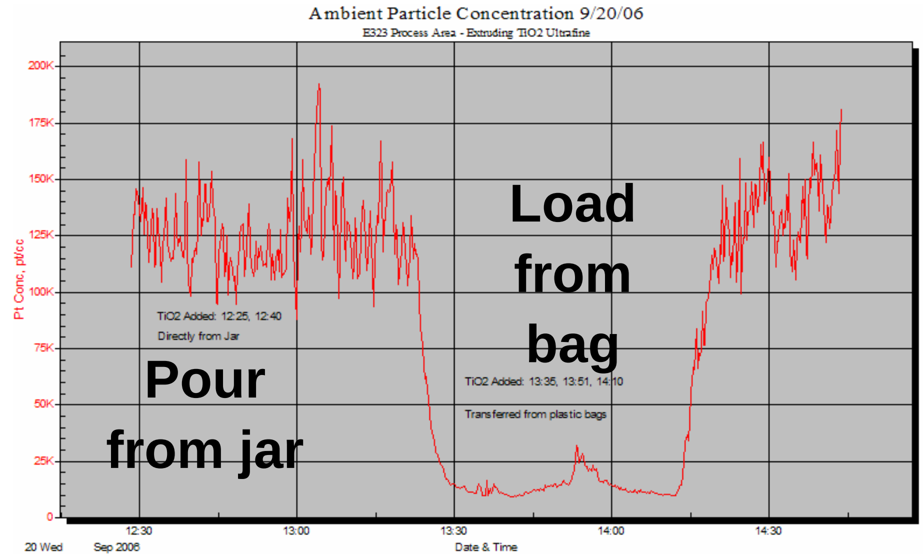
DUPONT

P-Trak model 8525P portable sub-micron particle detection: DLS 210 TiO_2 Compounding

Extrusion Area Ambient Conditions (no TiO_2)



30mm Extrusion: Methods to Load Feeders



P-Trak as a qualitative tool:

- **Counts particles < 1μm**
- **Sensitive to ambient state**
- **Sensitive to H_2O vapor**

Characterization challenges, more questions than answers!

Grand Challenges still…

- Nanocoatings on nanoparticles
- Dispersion of nanomaterials in host matrices and characterization from synthesis through processing to final article.
- Measurement of chemistry and properties on nano-length scales.
- Structure and Chemistry of Buried Interfaces.
- Predict macro or end use properties from nano measurements

- Particle size distribution!!

Particle size distribution measured by multiple techniques

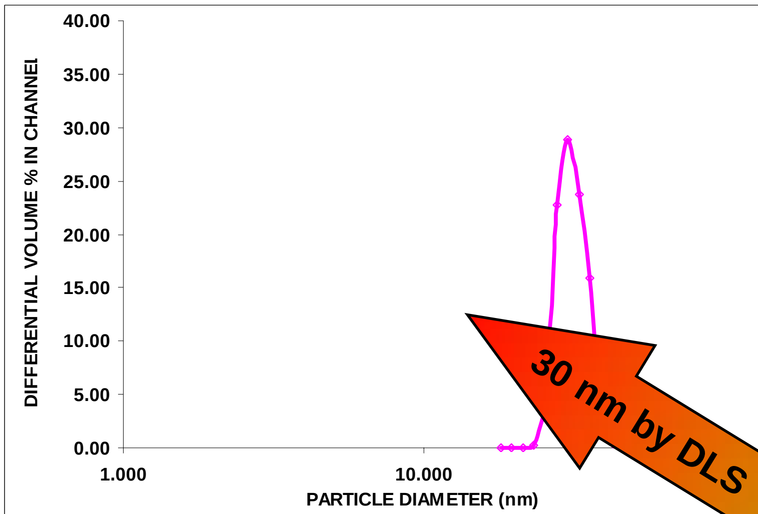
- NIST reference standard:

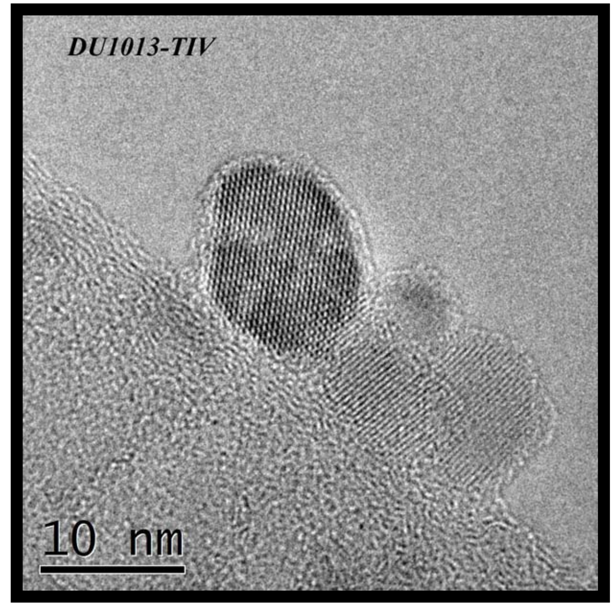
Table 1. Reference Value Mean Size and Expanded Uncertainty [a]
Average Particle Size (Diameter), in nm

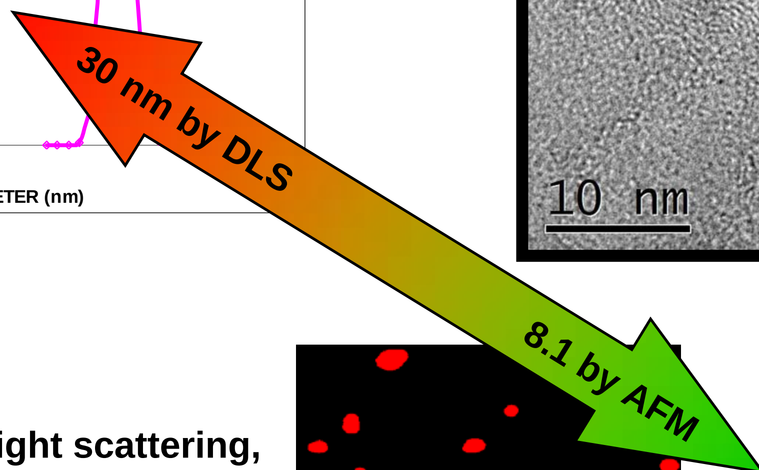
Technique	Analyte Form	Particle Size (nm)
Atomic Force Microscopy	dry, deposited on substrate	8.5 ± 0.3
Scanning Electron Microscopy	dry, deposited on substrate	9.9 ± 0.1
Transmission Electron Microscopy	dry, deposited on substrate	8.9 ± 0.1
Differential Mobility Analysis	dry, aerosol	11.3 ± 0.1
Dynamic Light Scattering	liquid suspension	13.5 ± 0.1
Small-Angle X-ray Scattering	liquid suspension	9.1 ± 1.8

Very nice start, but… We need more standards with different sizes, chemistry, surface coatings. And does anyone wonder why these techniques do not agree with one another??

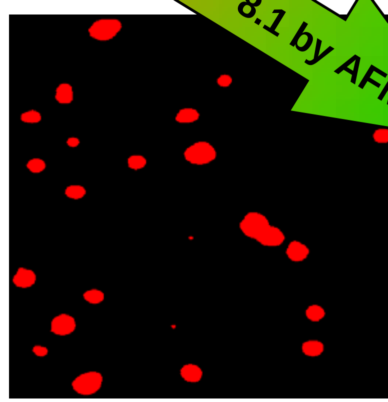
Dynamic Light Scattering

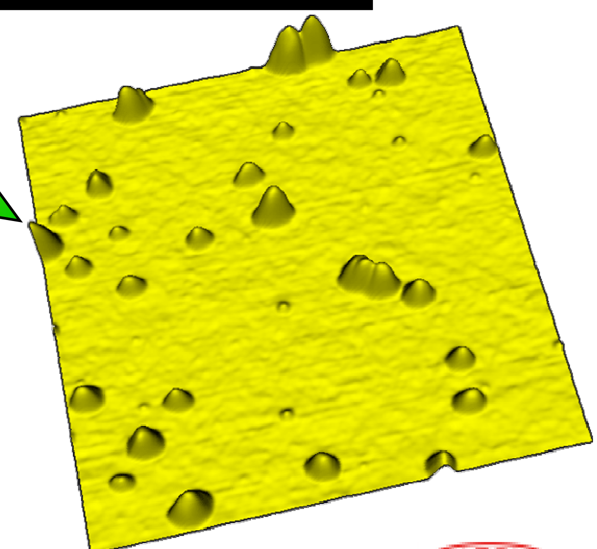






Everyone does Dynamic Light scattering, but… the PSD often depends on concentration, is model dependent, varies considerably depending on sample prep, and often does not agree with other techniques!

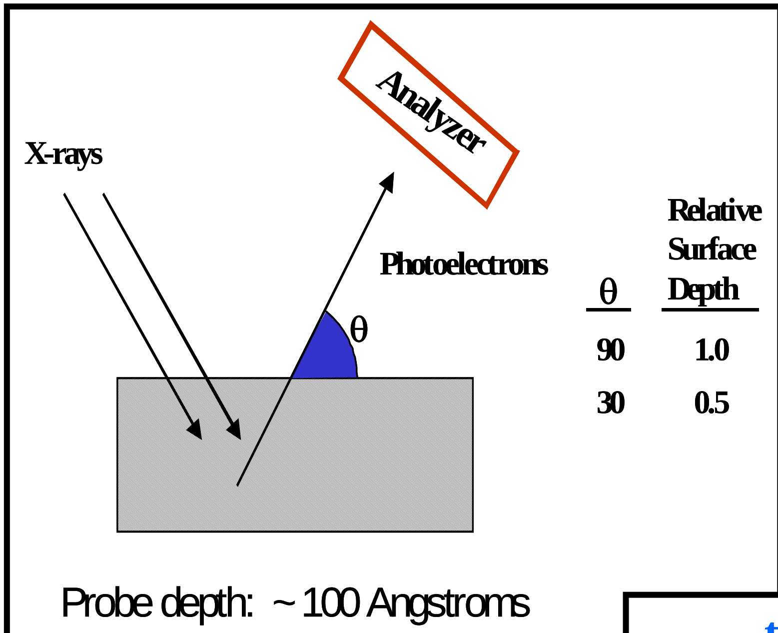




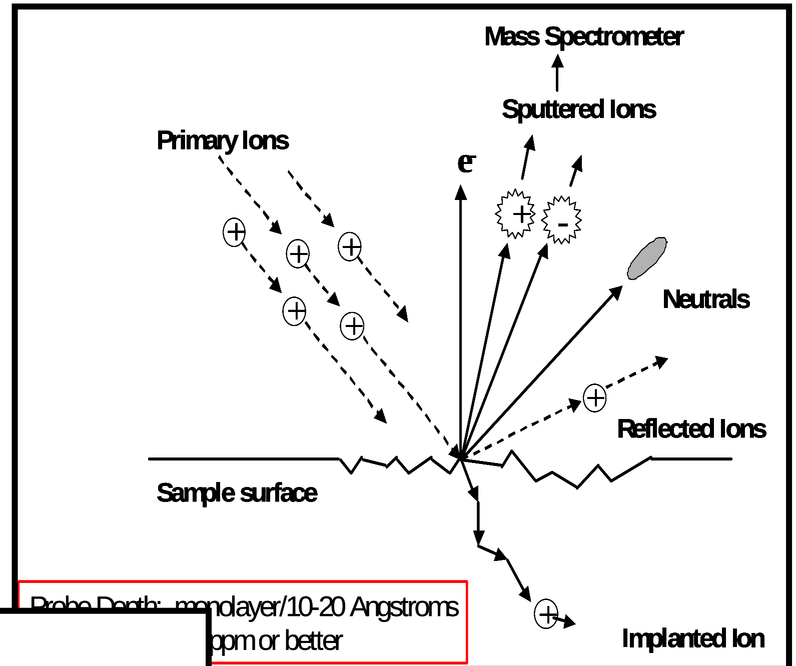
Kourtakis, Khalili, Subramoney, Blackman

Statistical particle size by AFM

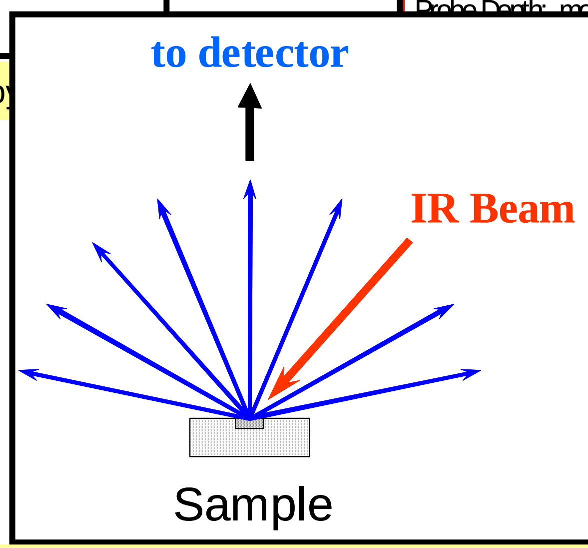
State of the art Surface Analysis tools



X-ray Photoelectron Spectroscopy

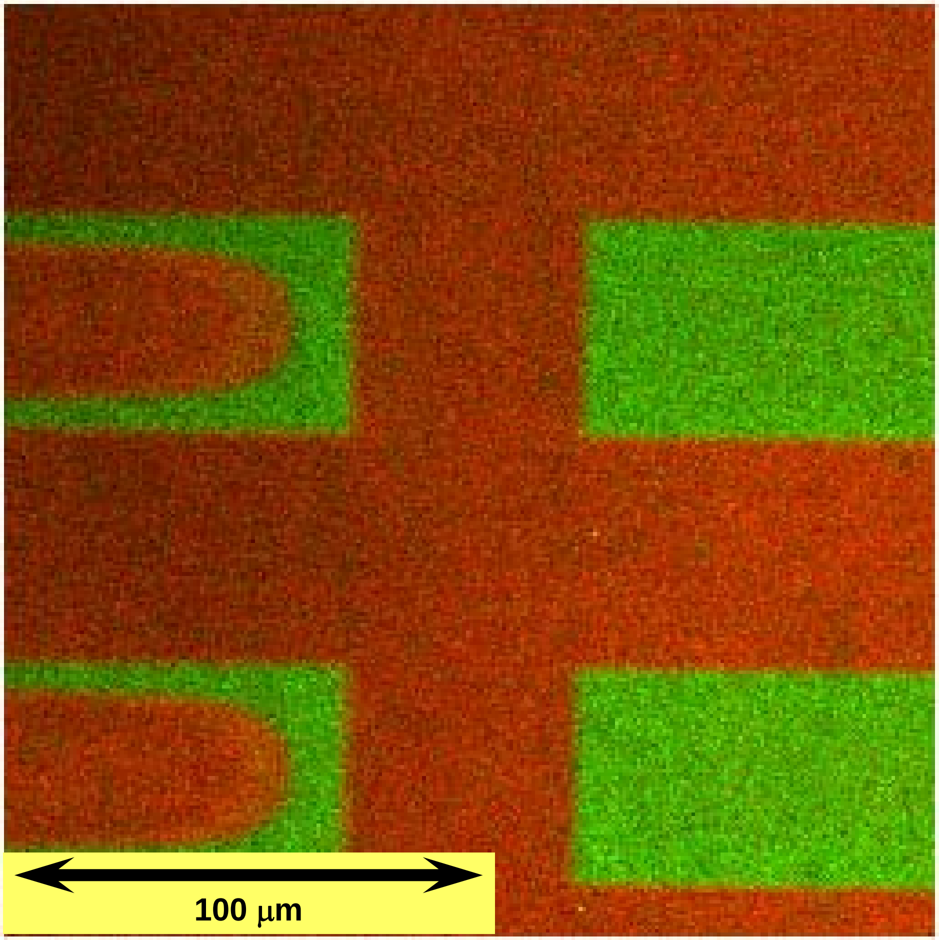


ght Secondary Ion Mass Spectrometry



Diffuse Reflectance Infrared Spectroscopy

Surface chemistry using ToF-SIMS



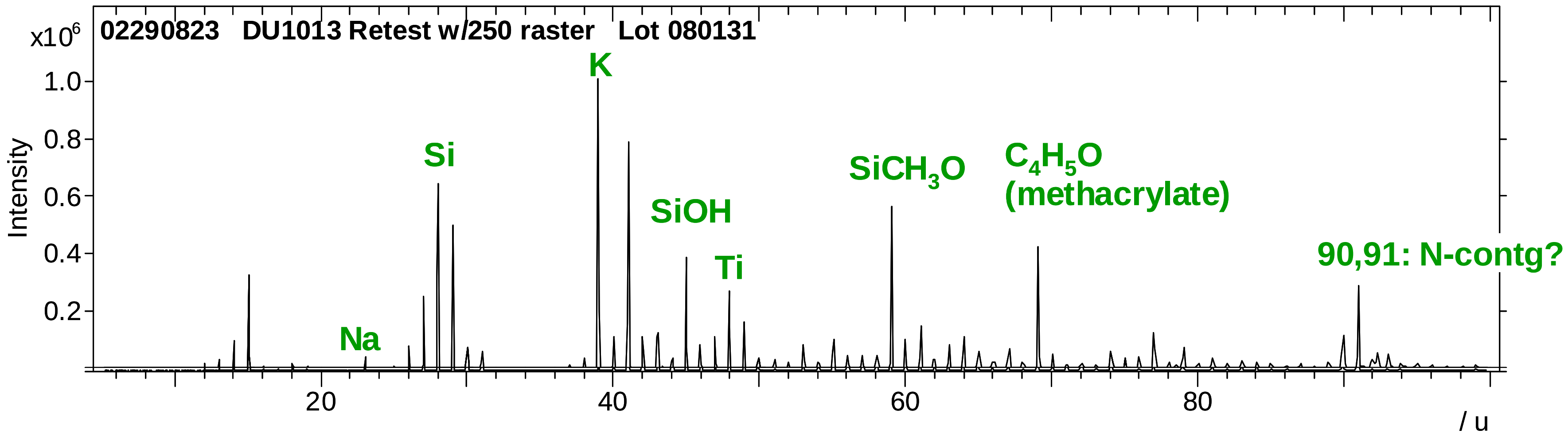
Hexadecane Thiol

Gold

- Superb surface sensitivity
- Direct chemical information
- But only ~1 micron spatial resolution

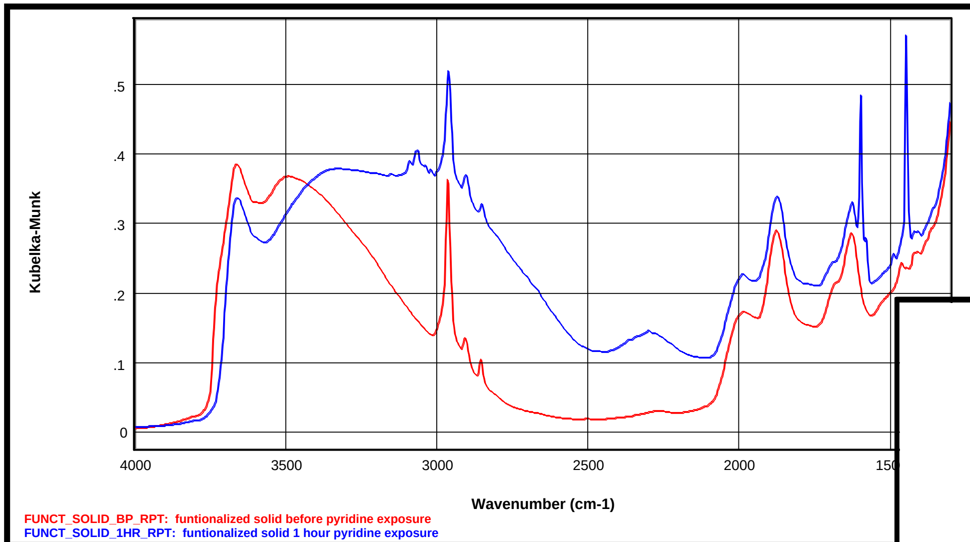
Lloyd, Sharp, Jagota, Blackman

ToF-SIMS Spectra from surface functionalized Nanoparticles



Thin coatings on large ensembles of nanoparticles. If the coating is > 1 nm thick, no substrate peaks will be detected!

High surface area enable other techniques to probe the surface chemistry of nanoparticles



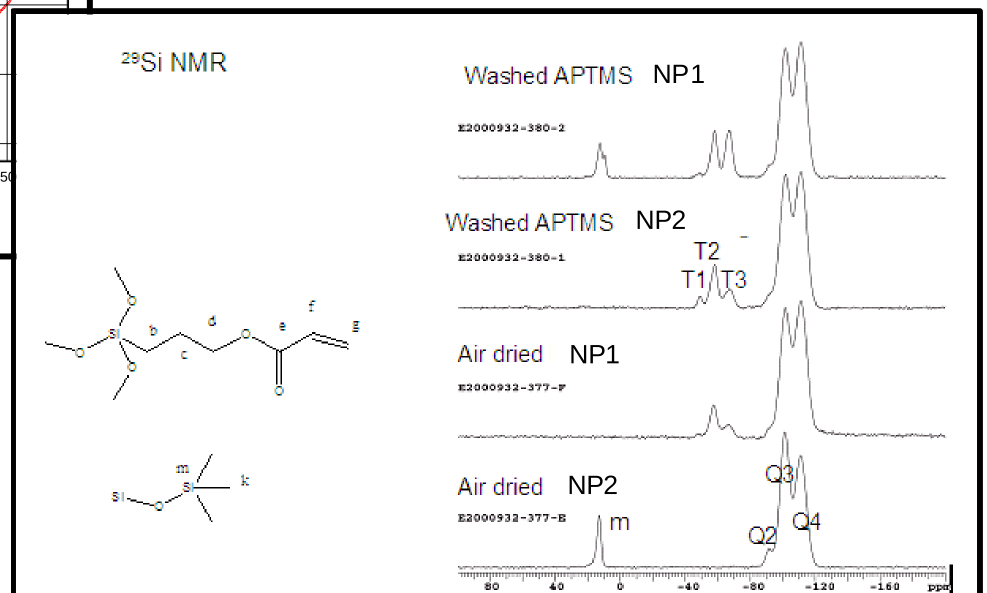


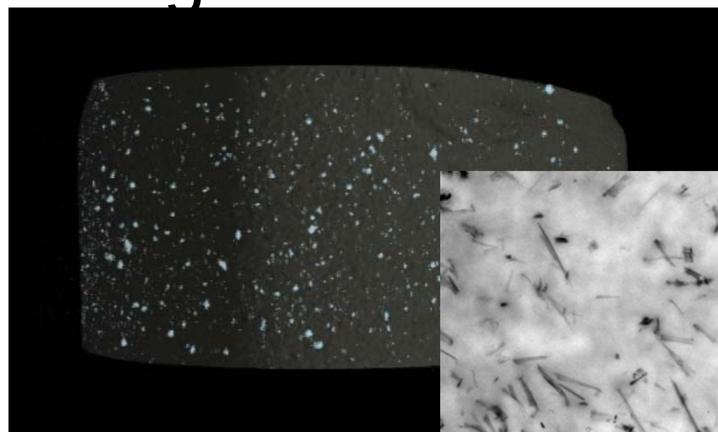
Figure 3. [29]Si solid state CPMAS NMR spectra.

DRIFTS and ^{29}Si NMR can detect chemical reactions at the surface of nano-silica particles

Walls, Mccord, Kourtakis

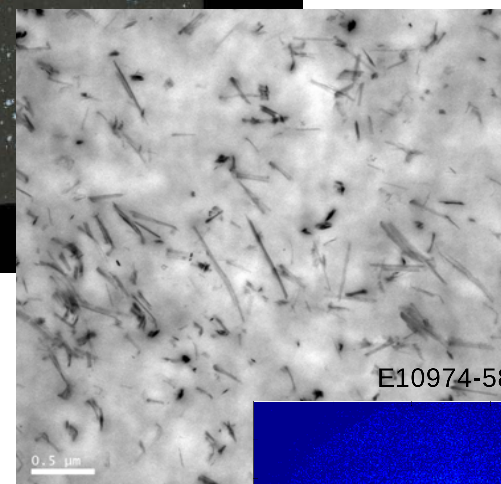
Integrated Approach to Understanding Nanocomposite Morphologies

- X-ray Tomography
  - **Size µm-mm**
  - 3-D



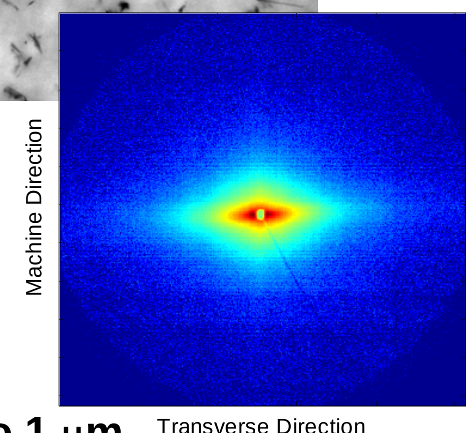
TEM –

- **Size 1 nm to 10 µm**
- High resolution



- **Complete characterization requires multiple analytical methods**
- **Length scale spans 6 orders of magnitude**

SAXS



- **Size 1 nm to 1 µm**
- Statistical distribution

Rosenfeld, Wood, Londono

Critical Enabling technology: stable aerosol generation

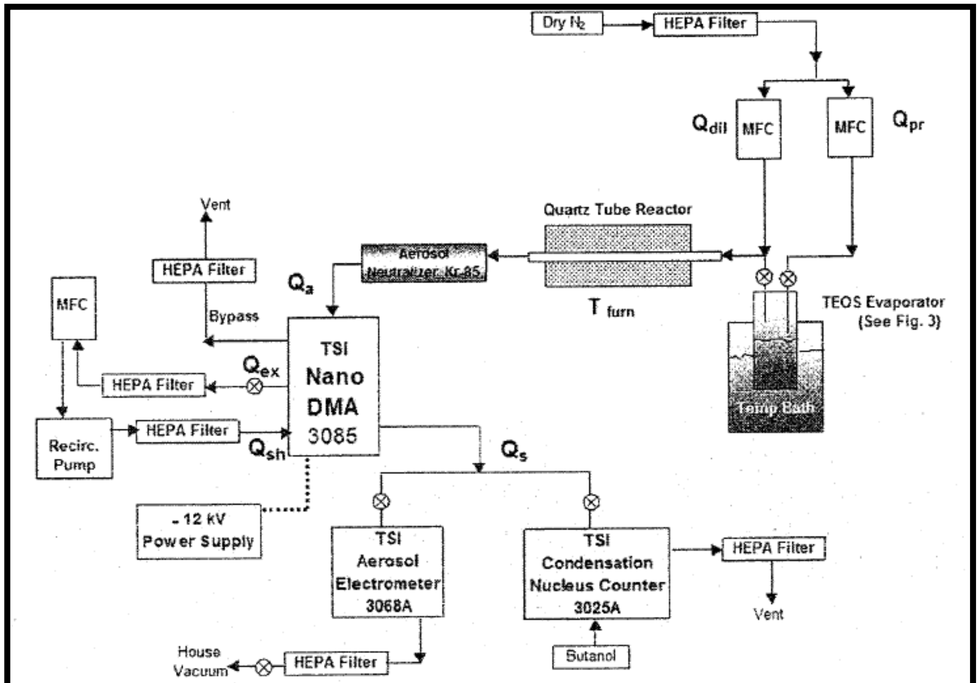


FIGURE 1. Schematic of an SiO_2 aerosol nanoparticle reactor with a classification and detection system to produce SiO_2 aerosol nanoparticles with controlled d_{50} and number concentration

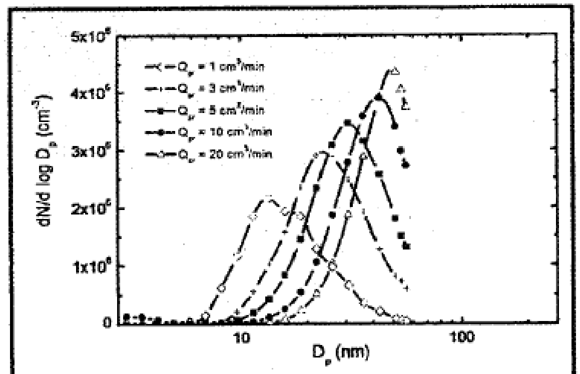


FIGURE 5. Particle size distributions corresponding to the schematic in Figure 1 as measured by a nano-DMA as a function of Q_{pr} and constant T_{furn} = 950°C. The d_{50} and σ_g of these particle size distributions are tabulated in Table I.

Reliable, controllable size and surface chemistry

- Controlled exposure studies
- PPE testing
- Controlled E-fate studies

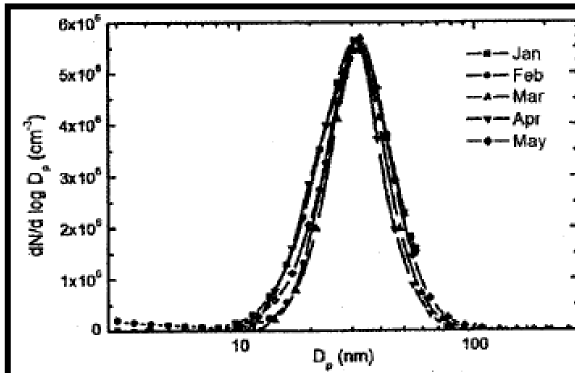


FIGURE 10. Particle size distributions at Q_{pr} = 10 cm^3/min and T_{furn} = 850°C are recorded on a daily basis to monitor daily reproducibility of the aerosol particle synthesis. Randomly selected data collected during each of 5 successive months illustrate the long-term stability of the reactor scheme.

Ostraat, J Occupational and Environmental Hygiene, 5, 390 (2008)

Conclusions

- The Nano Risk Framework provides a rigorous method for identifying potential hazards and reducing risks
  - Developed protocols for safe handling of nanopowders and processing of polymer nanocomposites based
- Still many questions about nanocharacterization
  - Particle size distribution still not as easy as it sounds
  - It is possible to monitor dispersion of particles when they are incorporated into a polymer
  - We can probably measure surface chemistry of nanoparticles
  - **but what happens to particle size, state of agglomeration, and surface chemistry of nanoparticles when exposed to the environment, biological fluids, cells, tissues, organisms???**

The miracles of science™

Thank You