# Engineered Nanoparticles: Safer Substitutes for Toxic Materials, or a New Hazard?


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Toxics Use Reduction Act 20th Anniversary Symposium and Conference
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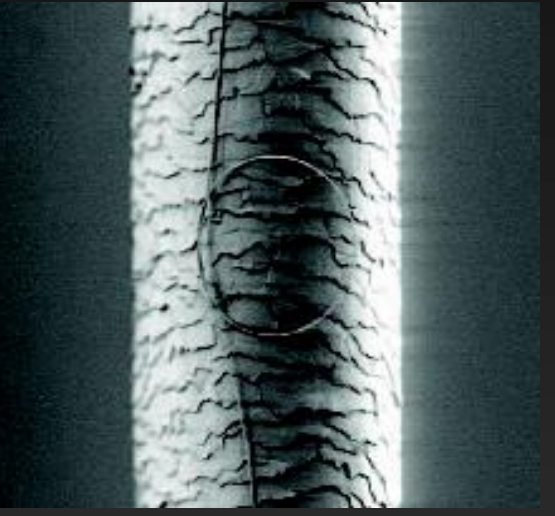
# Outline

- Definitions
- Current products available using engineered nanoparticles
- Current knowledge concerning nanoparticle toxicity
- Exposure assessment work at CHN
- Use of nanomaterials as substitutes for toxic materials
- Conclusions and recommendations

# What is Nanotechnology?

- “Nano-” = $10^{-9}$ unit
- Refers to particles or structures with at least 1 diameter in 1-100 nm Size range
- Compare to:
  - Human Hair = 60 – 120 micrometers
  - DNA = 2 – 12 micrometers
  - Red Blood Cell = 7,000 nm
  - Water molecule = 0.3 nm

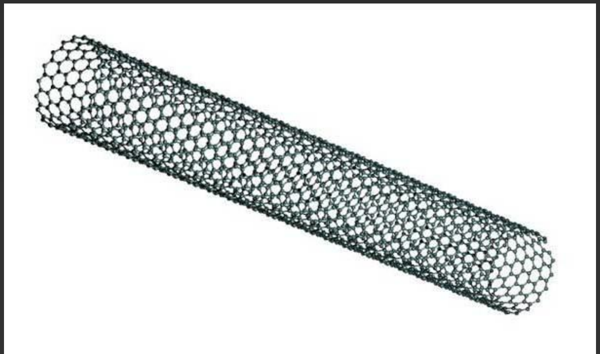


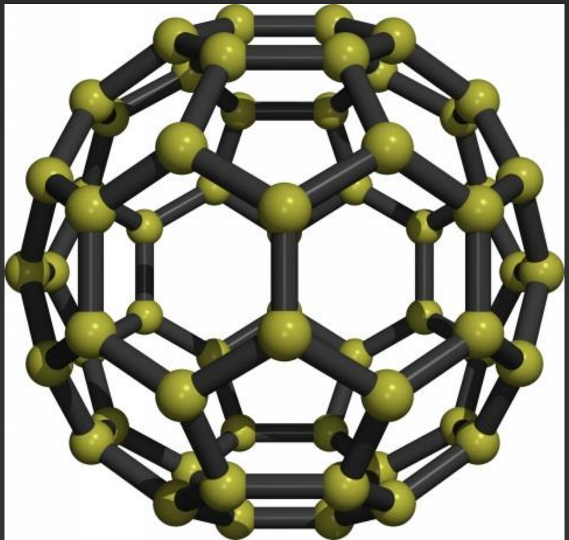
# What is a Nanoparticle?

- US Federal Office of Science and Technology Policy: nanotechnology is "R&D…in the length scale of approximately 1 – 100 nanometer range…"
- Some consensus that a nanoparticle is any particle with at least one dimension less than 100 nm

# Categories of Nanoparticles

- Naturally-occurring
  (*e.g.*, forest fires, volcanoes)
- Industrial
  (*e.g.*, welding fume, diesel exhaust)
- Engineered
  (*e.g.*, carbon nanotubes, fullerenes)





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# Woodrow Wilson Institute

- Project on Emerging Nanotechnologies
- Nanotechnology Consumer Products Inventory
- Currently lists 807 products, from
  - AccuFlex Evolution golf shaft, to
  - Zelens C-60 Fullerene Night Cream

http://www.nanotechproject.org/inventories/consumer/

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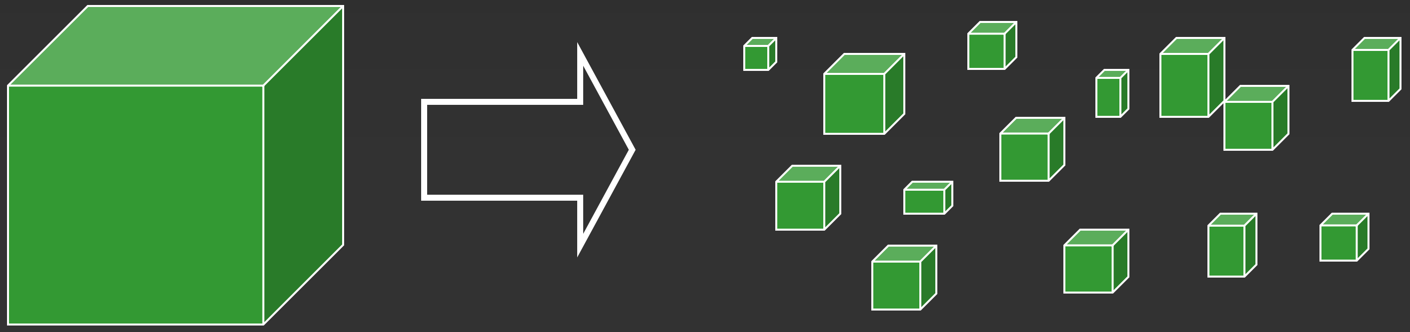
# Crucial Factor in Nanoparticle Toxicity

**Question**:

What makes nanoparticles different from larger particles of the same composition?

**Answer**:

Particle surface-to-volume ratio increases as the particle diameter decreases



# The Message

- Surface area and particle number become much more important as the particles become smaller, compared to mass

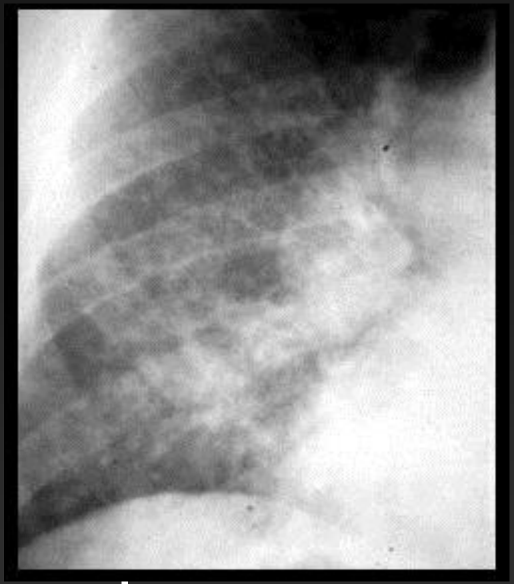
- Toxicological end points that depend on mass may be less important than end points that depend on surface area or number

# Particle Mobility

- As particles reach the nanometer size range, they may become more biologically mobile
  - Cross cellular boundaries from the alveolar region into the circulatory system
  - Pass through the skin
  - Travel through the olfactory nerve to the brain

# Emphasis on CNT Toxicity

- Many studies published in the last 2-3 years
- End point studied:
  - Fibrosis
  - Inflammation
    - Lung tissue
    - Cardiac tissue
- Mesothelioma



Donaldson: "…there is no experience of a workforce being potentially exposed to a biopersistent fibre of this degree of thinness."

Donaldson, et al., Carbon nanotubes: a review of their properties in relation to pulmonary toxicology and workplace safety Toxicol Sci 92: 5-22, 2006

# NIOSH Inhalation Studies

- Purified SWCNT’s
- Mice
- Aspiration – 0,10,20,40 µg/mouse
- Ultrafine carbon black and $SiO_2$ used as control
- Dose equivalent to a worker exposed to the graphite Permissible Exposure Limit (5 $mg/m^3$) for 20 work days

# Effects on Lung

- Both *inflammation* (acute response) and *fibrosis* (chronic response) were found
- Effects were dose-dependent
- No fibrosis and greatly reduced inflammation found with the reference materials

# Is This of Concern?

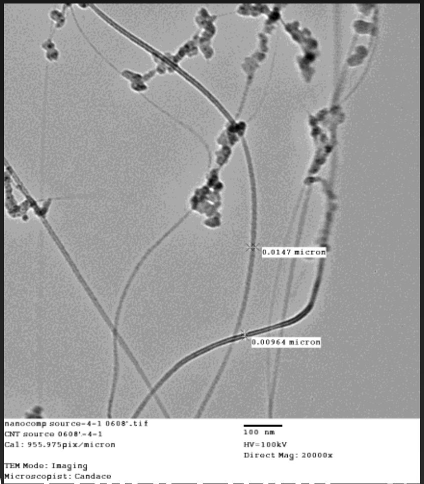
- Mouse dose equivalent to airborne concentration of 5 $mg/m^3$ for 8 h/day for 20 days
- 5 $mg/m^3$ CNT → $10^{17}$ $CNT/m^3$

  = $10^{11}$ $CNT/cm^3$!!

  - Highest concentrations we have measured anywhere in any lab :

    < $10^6$ $particles/cm^3$

# CNTs cause Mesothelioma?




- Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in 2 pilot studies.
- Poland, et al., Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. Nature Nano. 3:423-8, 2008.
- Induction of mesothelioma in p53+/- mouse by intraperitoneal application of multi-wall carbon nanotube.
  Takagi, et al., Induction of mesothelioma in p53+/- mouse by intraperitoneal application of multi-wall carbon nanotube J. Toxicol. Sci 33:105-15, 2008.

# Mesothelioma, Cont.

- Those studies used intraperitoneal injection
- Just published – an inhalation study
- “Inhaled carbon nanotubes reach the subpleural tissue in mice”
  - “multiwalled carbon nanotubes reach the subpleura in mice after a single inhalation exposure of 30 mg/m$^3$ for 6 h.”

- Ryman-Rasmussen, et al.,

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Published by Tsai et al.

- NANO 3(4):301-309, 2008.
- Journal of Aerosol and Air Quality Research, 8(2):160-177, 2008.

Published by Tsai et al.

- Journal of Nanoparticle Research, 11(1): 147-161, 2009.
- Annals of Occupational Hygiene, 2009.

# Many Processes Studied

Published by Tsai et al.

- Environmental Science and Technology, 43 (15): 6017–6023, 2009.

# Conclusions from Exposure Evaluations

- Significant exposures were measured in some laboratories.
- Engineering and administrative controls are effective to reduce exposure.
- Fume hoods may not offer adequate protection for handling nanoparticles.
- Proper design and operation of ventilation are required for effective control.

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# Potential Advantages of Nanomaterials

- The unique properties of nanomaterials, *e.g.*, high surface-to-volume ratio, may provide advantages when used as substitutes for toxic chemicals
- The same properties, however, may contribute to *their* toxicity
- On balance, is their an advantage to using them?

# Potential Advantages of Nanomaterials, Cont.

- This question must be answered on a case-by-case basis
- Alternatives assessment tools must be used in making the judgement
- Incomplete information, especially concerning toxicity, may be available when making the decision

# Substitutes for VOCs?

- Solvents cannot be directly substituted with NPs
- However, NPs may be a **component** of a water-based substitute
- There are very few examples in the literature that this is actually done

# Substitutes for VOCs?

One example – solvent-based paints

- Manufacturers of water-based paints **claim** they contain NPs
- ZnO or $TiO_2$ NPs may make the paint surface more **durable**, leading to thinner paint layers & a reduction in chemical use
- Nanometer-sized powder coatings may be an effective substitute

# Substitutes for VOCs?

- Another example – nanoemulsions of chemicals in water
  - Used in some alternative dry cleaning formulations
  - What is the toxicity of the chemical in the emulsion?

# Example – Nanoclays and Wire & Cable Insulation

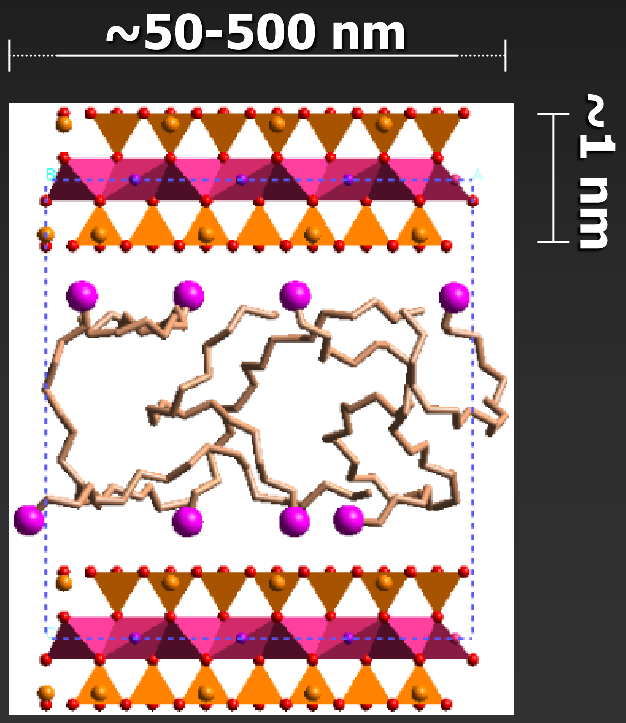
- One of the most promising areas of current research into NP substitution
- Research performed by Prof. Dan Schmidt, with TURI funding
- Focus on replacing lead and phthalate plasticizers in PVC insulation
- Responds to EU requirement to eliminate Pb in consumer electronics, starting in 2008

# Polymer Nanocomposites

- Nanoparticulate fillers have been shown to improve a wide range of properties
  - Mechanical: Stiffness without embrittlement
  - Barrier: Reduced permeability
  - Thermal: Higher degradation temperatures
  - Fire: Char formation and reduced heat release
- Nanofillers have also shown synergy with other additives
- Nanoparticles can also present new hazards!

# Why "Nanoclays"?

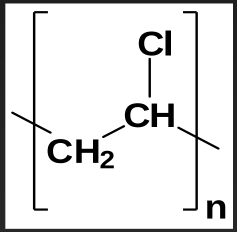
- Nanoclay = Montmorillonite (MMT)
  - Produced via weathering:
    Mica → Vermiculite → MMT
  - Found in dirt, rivers worldwide
  - "Nano" when dispersed in a medium; otherwise primarily <u>micron</u>-sized
- Readily modified by quaternary ammonium salts
  - Bio-derived & biodegradable
  - Long safety record in detergents, fabric softeners, etc.
- Inexpensive (as low as ~$3/lb) compared to other nanofillers
- Low toxicity, good sustainability → relatively "green" as well?




(image courtesy of D. Shah, Cornell University)

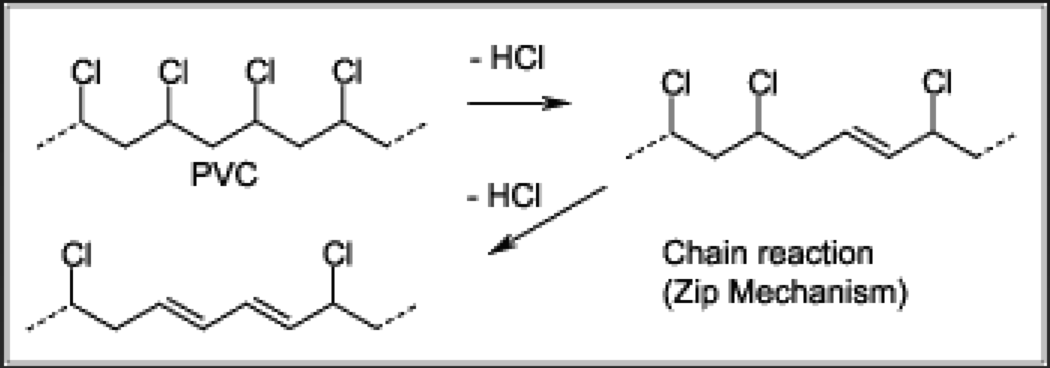
# System of Interest: Flexible PVC

- Advantages
  - Versatile, inexpensive, widely utilized
  - Polar, rubbery
    → Good for nanocomposite formation!



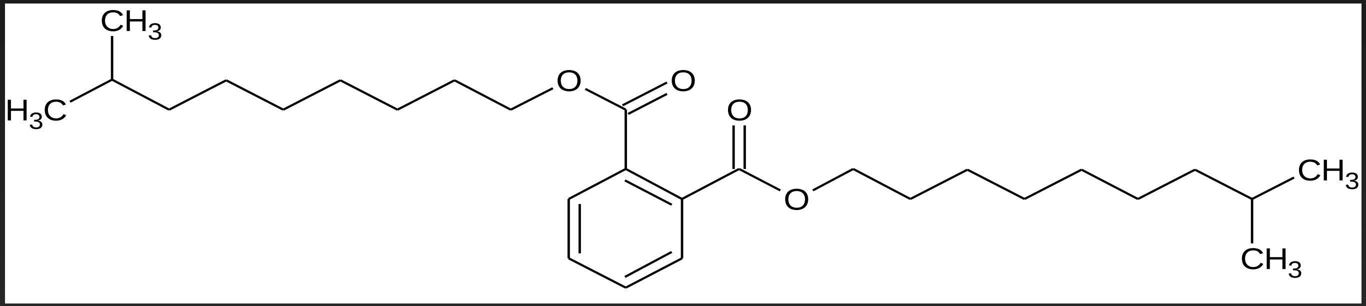

- Challenges
  - Difficult to process (degrades before melting)
  - Formulation space is huge because PVC contains so many additives
  - PVC formulations can raise health concerns
- Few PVC nanocomposite studies, fewer with realistic formulations / processing

# Problem I: Toxic Thermal Stabilizers




- Thermal stabilization of PVC is required to prevent zip dechlorohydration (above)
- Most effective and inexpensive heat stabilizers are also lead-based and toxic
- 3.5 million pounds of lead compounds used in MA alone in flexible PVC for wire & cable
- Studies show lead can be leached out

# Problem II: Concerns over Plasticizers




***Diisodecyl phthalate (DIDP)***

***(a typical plasticizer for wire & cable applications)***

- Plasticization of PVC is required for flexibility appropriate for wire and cable
- Most effective and inexpensive plasticizers are phthalates, suspected endocrine disruptors
- A typical wire and cable formulation can easily be ~30 wt% plasticizer
- Phthalates can also leach out over time

# Motivation for Study: In Summary

- Flexible PVC is cheap and versatile, will not go away
  - Problematic additives are cheap and effective
  - Alternatives cost more and / or perform less
- A high-performance alternative
  - Nanoclay – provides properties enhancements at low levels
  - Ca/(Mg)/Zn stabilizers – provide stability without lead
  - ELO plasticizer – improves clay dispersion and stability
- Practical?
  - Nanoclays: ~2 wt% → ~$0.06/lb more?
  - Stabilizers: Pb-free in use, a matter of time before Pb ban
  - ELO: Expensive at $0.90/lb, but from plants, <u>not petroleum</u>

*Time will tell…*

# Nanocor is Producing Nanoclay-containing Insulation

**Coaxial cable (1/2") with an LSO0H-nanocomposite based jacket**

# Question: Nanoclay toxicity?

- Nothing specific in the literature
- Nanoclays are “thought” to be nontoxic or of very low toxicity
- TOXNET: 0 results
- ICON: 0 results
- Can we assume that nanoclay is less toxic than lead and phthalate plasticizers?

# Question: Nanoclay toxicity?

"NIST has begun to work with the CPSC and Scripps Institution of Oceanography to evaluate whether any of these nanomaterial-based fire retardants are toxic…testing…conducted to date suggests the surfactants used to ensure the nanomaterials disperse throughout the materials to which they are added may be more toxic than the nanomaterials themselves."

Betts, K, New thinking on flame retardants, *Environ Health Perspect.* 2008 May; 116(5): A210–A213.

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# Conclusions

- Engineered nanoparticles have the **potential** to substitute for toxic materials
- Few examples are available today
- Wire & cable insulation may be the best current example
- Must always compare the toxicity of the NP to the current process
- The toxicity of most engineered NPs is not well-understood at this time

# Q & A

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