Update on Carbon Nanotubes and Related Nanofibers

To: Science Advisory Board
Date: 18 Nov 2020
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What is Nanotechnology

- The study of the controlling of matter on an atomic and molecular scale
- Engineered nano objects: at least one dimension between 1 to 100 nanometers (nm)
  - roughly 100,000 times smaller than the diameter of a human hair
R&D and Use – Spanning multiple technology sectors

Nanotechnology

- Aerospace
- Food and agriculture
- Medicine
- Bio-technology
- Advanced materials/textiles
- National security
- Transportation
- Energy/Env
- Cosmetics
- Agriculture
MA is among the top 5 in the country for commercial and R&D activity on nanomaterials/nanotechnology

According to Nanowerk, currently there are 68 companies in MA “with a nanotechnology focus”

https://www.nanowerk.com/nanotechnology/Nanotechnology_Companies_Research_and_Degree_Programs_in_Massachusetts.php
Types of Engineered Nanomaterials

Broad Categories: Engineered Nanomaterials

- Carbon-based
  - fullerenes, carbon nanotubes

- Metal
  - Silver, gold, copper

- Metal Oxides
  - Titanium dioxide, zinc oxide, iron oxide

- Dendrimers
  - Hyperbranched polymers, dendrigrift polymers, dendrons

- Composites
  - Nano clays, polymer beads
Engineered nanomaterials in consumer products (Source: Project on Emerging Technologies, Consumer Products Inventory, 2013)
http://www.nanotechproject.org/cpi
Engineered nanomaterials: enhanced performance compared to their bulk counterparts

- At nano-scale:
  - material properties change - melting point, fluorescence, electrical conductivity, and chemical reactivity
  - Surface size is larger - more material comes into contact with surrounding materials and increases reactivity
Physical-chemical properties: key to performance AND inherent hazard

Can we tune these properties to enhance their technological benefit AND reduce their potential hazard to ensure the safe development and use of engineered nanomaterials?
Overview: Carbon Nanotube Environmental and Occupational Health and Safety
Engineered Carbon Nanotubes – What are They?

• Divided into 2 broad categories:
  – Single-walled CNTs (SWCNTs)
  – Multi-walled CNTs (MWCNTs)
• Carbon nanofibers (CNFs) – similar but cylinders are not perfectly formed
• Important: CNTs/CNFs are not a single material. ~50,000 SWCNTs and likely even more potential combinations of MWCNTs
  – Vary based on size, shape, chemical composition, reactivity, etc.
“IBM Scientists Find New Way to Shrink Transistors”

- CNT field effect transistors
- Increase speed and/or reduce power use by a factor of 7
Emerging as substitutes for toxic chemicals

Anti-fouling marine paints [substitutes for tributyltin, copper boat paints, etc]

Flame retardants for electronics, wire/cable, textiles, foams [substitutes for halogenated flame retardants]
Journal of Cleaner Production, 2017: Carbon nanomaterials as potential substitutes for scarce metals. Rickard Arvidsson, A. Bjorn


Introducing Sugar-Coated Carbon Nanotubes – A Nontoxic Alternative Source of Power
CNT Toxicity

• Many studies published in the last 20 years
• Primary end points of concern:
  – Pulmonary fibrosis – SWCNT, MWCNT, CNF
  – Inflammation
    • Lung tissue - SWCNT, MWCNT, CNF
    • Cardiac tissue - SWCNT, MWCNT
• Cancer - MWCNT
  – Lung tumor promoter
  – Mesothelioma

Cancer & MWCNTs

- **Tumor promotion** [high aspect ratio MWCNTs]:
  - mouse inhalation study, first exposed to methylcholanthrene (MCA) via intraperitoneal injection.
  - Strong promotion of lung tumors [pulmonary adenomas and adenocarcinomas]
  - Strong promotion of malignant serosal tumors consistent with sarcomatous mesothelioma

Asbestos

CNTs
CNTs cause Mesothelioma?


CNTs cause Mesothelioma?, Cont.

Poland: “Here we show that exposing the mesothelial lining of the body cavity of mice, as a surrogate for the mesothelial lining of the chest cavity, to long multiwalled carbon nanotubes results in asbestos-like, length-dependent, pathogenic behaviour… Our results suggest the need for further research and great caution before introducing such products into the market if long-term harm is to be avoided.”

Dec 2014 – IARC designates “certain MWCNTs” as 2B, Possible Human Carcinogen

Fiber Morphology Important

- In animal studies thus far:
  - SWCNTs do not cause mesothelioma
  - Thin (d < 15 nm) MWCNTs – ditto
  - Thick (d > 150 nm) MWCNTs – ditto

- But – all commercially available MWCNTs:
  - 15 nm < d < 150 nm

- Short (L < 1-5 µm) MWCNTs – ditto

Can we make them all short?
Functionalization can affect Length

Human Studies

• Few human studies to date
  – Case reports of CNTs found in the lungs of 911 first responders
  – Recent case-control study revealed MWCNT manufacturing workers (levels 3x above the NIOSH REL) found biomarkers of effect similar to conclusions from tox studies
    • increase in serum & sputum inflammatory & fibrotic biomarkers[ IL-1β, IL6, TNF-α, inflammatory cytokines, KL-6, TGF-β1]


– We evaluated carbon nanotube/nanofiber (CNT/F) exposure in relation to biomarkers.
– We assessed CNT/F exposure via personal breathing zone, filter-based air sampling.
– We measured fibrosis, inflammation, oxidative stress, cardiovascular biomarkers.
– Inhalable rather than respirable CNT/F was more often associated with biomarkers.
– Sixteen biomarkers were associated with at least three CNT/F exposure metrics.
Emerging Ecotoxicity Concerns

• Daphnids (*Daphnia magna*)
  – Interferes with food uptake & movement at low concentrations [MWCNTs & SWCNTs]; More toxic with longer exposures; Impaired growth and reproduction at very low levels

• Juvenile rainbow trout (*Oncorhynchus mykiss*)
  – Systemic toxicity at very low levels (consistent with GHS classification of “extremely toxic to aquatic life”)

• Powerful anti-microbial agent
  – Implications for sewage treatment plants

*variation in findings given differing physicochemical characteristics

Setting Occupational Exposure Limits

• No consensus between different groups
• Basic difference: mass concentration vs. number concentration
• Mass concentration – easier, cheaper to measure
• Number concentration – more relevant biologically (e.g., asbestos), lower LOD
NIOSH REL for CNT/CNF

• NIOSH CIB 65
• REL = 1 µg/m³ of respirable elemental carbon as an 8-h TWA
• Elemental carbon is readily measured using NIOSH Method 5040
• 1 µg/m³ is the limit of quantification for Method 5040
NIOSH REL for CNT/CNF, Cont.

• “Recent observations indicate that exposure to CNF can cause respiratory effects similar to those observed in animals exposed to CNT”

• Because of residual risk at the REL, “NIOSH recommends that exposures to CNT and CNF be kept below the recommended exposure limit”
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<tr>
<th>Agency or Company</th>
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<tr>
<td></td>
<td>Mass Concentration (µg/m³)</td>
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<td>Bayer Schering Pharmaceuticals</td>
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<td>Japanese National Institute of Advanced Industrial Science and Technology</td>
<td>30 (SWCNT)*</td>
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<td>National Institute for Occupational Safety and Health U.S.</td>
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BUT……

• Depending on CNT fiber dimensions, 1 µg/m³ can correspond to number concentrations ranging from 0.01 f/cm³ (extremely large CNF) to 300,000 f/cm³ (typical CNT)

• BSI – 0.01 f/cm³
TURA Program Resources

• Nanomaterials Fact Sheet

• Nanomaterials EH&S Library Guide

• TURI Webpage on Nanomaterials

• TURI Library
  – Books
  – Reports
  – Databases
Precarious Promise: A Case Study of Engineered Carbon Nanotubes

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