Dermal and Respiratory Protection in Handling Nanomaterials at the Center for High-Rate Nanomanufacturing (CHN)

Kwangseog Ahn and Michael J. Ellenbecker
Toxics Use Reduction Institute
Department of Work Environment
The University of Massachusetts Lowell
Contributors

This presentation includes works of the following people:

- Candace Tsai
  Department of Work Environment
  The University of Massachusetts Lowell

- Jun Lee
  Department of Plastics Engineering
  The University of Massachusetts Lowell

- Marilyn Hallock
  Environment, Health and Safety Office
  Massachusetts Institute of Technology
Center for High Rate Nanomanufacturing (CHN)

- An NSF Nanoscale Science and Engineering Center (NSEC)
  - The University of Massachusetts Lowell
  - Northeastern University
  - The University of New Hampshire

- The primary mission of the CHN is to develop manufacturing processes that move nanomaterials and devices from the laboratory to the production phase
Center for High Rate Nanomanufacturing (CHN) (Cont’d)

- Approximately ten laboratories are working on various aspects of new nanomanufacturing processes
- Since the Center was started in 2004, most of the laboratories are relatively early in the manufacturing development cycle
Environment, Health and Safety

- CHN is committed to developing nanomanufacturing methods that are protective of the environment and of workers
- Offers a unique and challenging opportunity to ensure that proper precautions are followed from early, exploratory research right through to nanomanufacturing processes
Is There a Risk in the Workplace?

- Nanomaterials present new challenges to understanding, predicting and managing potential health risks
- Risk - function of exposure and toxicity
- Exposure to nanomaterials & other toxic chemicals
  - What is the potential for exposure?
  - How often, how long, and how?
  - Repetitive or isolated exposure?
  - Concerns about respiratory and dermal exposure to nanomaterials
- Toxicity of nanomaterials
  - What are the target organ(s)?
  - What is the toxicity of the substance?
- Many knowledge gaps to be filled before we fully understand how to work safely with these materials
Determining Risk & Exposure

- **Survey - questionnaire, interview, walk-through**
  - Process
  - Materials and products
  - Protective measures

- **Monitoring**
  - Airborne number concentration and size distribution
Sample Questions of Questionnaire

- Are researchers wearing any following Personal Protective Equipment (PPE) while working with nanomaterials? (please choose all applied)
  (a) Safety glasses
  (b) Lab coats: cotton, other fabric:
  Other clothing: apron ( ), sleeve ( ), chemical-resistant suit ( ), other:
  (c) Gloves, please indicate the material from the following examples:
  natural rubber, polyvinyl chloride, butyl rubber, nitrile, neoprene, or other:
  (d) Respirators, please indicate the brand and model.
  brand: model:
  (e) Others and comments

- How long do researchers work while handling nanomaterials?
  (a) 15mins or less (b) 15-30mins (c) about 1hr (d) about 2hrs (e) about 4hrs
  (f) 8hrs or more

- How long are gloves being worn before they are replaced with new ones?
  (a) 15mins or less (b) 15-30mins (c) about 1hr (d) about 2hrs (e) about 4hrs
  (f) 8hrs or more
Process and Nanomaterials in the CHN Laboratories

- **Processes**
  - Chemistry - organic synthesis
  - Plastics engineering - nanocomposites, rubber compounding
  - Physics and materials science - thin film deposition
  - Electrical & computer engineering, Mechanical engineering - template fabrication

- **Nanomaterials**
  - Carbon nanotubes, fullerenes
  - Carbon black
  - Nanoclays, Nanoalumina
Process and Nanomaterials in MIT Laboratories

- **Processes**
  - Mechanical Engineering - carbon nanotube furnace
  - Electromagnetic and Electronic Systems - carbon nanotube furnace
  - Department of Materials Science and Engineering - amorphous silica powder transfer
  - Electrospinning

- **Nanomaterials**
  - Carbon nanotubes, fullerenes
  - Amorphous Silica
Process and Nanomaterials in the CHN & MIT Laboratories

- Nanomaterials and nanoprocesses can be either in solution or solid phase
- Nanomaterials are not the only materials subject to health and safety concerns
  - Other toxic chemicals, particularly solvents, are also present
  - High temperature processes
  - High voltage processes
Exposure to Nanomaterials

- Most processes require dermal contact
- Some researchers are exposed to nanomaterials through inhalation
Use of Personal Protective Equipment

- **Respirators**
  - Respirators are not used in most labs
  - Disposable N95 respirators and surgical masks are used in some labs

- **Protective Gloves**
  - Latex and nitrile are the most common protective gloves
  - Neoprene and cotton gloves are used in some labs
  - Gloves wearing time ranges from 15 min or less to about 1 h before they are disposed
  - It appears that presence of the nanomaterials does not affect researchers in choosing glove types and in using disposable gloves
Use of Engineering Controls
Use of Engineering Controls (Cont’d)
Fast Mobility Particle Sizer Spectrometer

- Real-time measurements of size distributions with one-second resolution
- Measure submicrometer aerosols between 5.6 to 560 nanometers
- Reporting a total of 32 channels
FMPS

FMPS, MODEL 3091 CONCENTRATION RANGE
Min values are typical RMS noise with filtered inlet air

Concentration [particles/cm³]

Particle Diameter [nm]
Monitoring Result - Amorphous Silica Powder Transfer

Silica 300 Aerosol Monitoring 011006'-
Source Conc. vs. Breathing Zone Conc.

Source Conc. Stirring Silica - Close Sash
Breathing Zone Conc. Stirring Silica - Close Sash
Ambient Background Conc.
Monitoring Result - Nanocomposite

Avg. Total Conc. = $1.6 \times 10^6$

Avg. Total Conc. = $2.1 \times 10^5$
Nonocomposite
Reducing Risk

- **Inhalation protection**
  - Enclosure hoods or fume hoods are preferred
  - Adequacy of respirators needs to be evaluated

- **Dermal protection**
  - Universal precaution - chemical protective gloves should be worn when handling nanomaterials
  - Gloves should be used to prevent contact with both nanomaterials and other accompanying chemicals
  - Efficacy of protective gloves needs to be evaluated
Adequacy of Metrics

Assuming nanoparticles with a diameter of 100 nm and a density of 1 g/cm³

- 200,000 particles/cc = 0.1 mg/m³
- Carbon nanotube 2 mg/m³ = 3.8 x 10⁶ particles
- Can we use mass concentration as an adequate metric?
Adequacy of Respirators

If breathing zone conc. is 200,000 particles/cc,

- N95 respirator (95% efficiency) - 10,000 particles/cc pass through
- N99 respirator (99% efficiency) - 2,000 particles/cc pass through
- N100 respirator (99.97% efficiency) - 60 particles/cc pass through

- Are these enough?
- Asbestos TLV – 0.1 f/cc TWA
Knowledge Gaps on Efficacy of Protective Gloves

- Guides to chemical resistance, permeation, degradation and breakthrough time available
  - Mostly against liquid and gaseous chemicals
  - ASTM Method F739-96
- Permeation/penetration by solid particles? In nanoscale?
- Lack of any standard test method to test efficacy of protective gloves against nanomaterials
Simple Tests for Determining the Efficacy of Protective Gloves Against Nanomaterials

- **Static test**
  - Small glove pieces were exposed to bulk nanoalumina and nanoclay for one hour

- **Rigorous test**
  - Glove pieces were shaken in the presence of nanoparticles for one hour

- **Scanning electron microscopy (SEM)**
  - Afterward, the surface of the glove pieces was examined using scanning electron microscopy, to see if any of the nanoparticles had penetrated them
Tested Gloves and Nanomaterials

- Three types of gloves
  - Powder-free latex examination gloves
  - Powder-free nitrile medical examination gloves
  - Cotton gloves
- Two types of nanomaterials
  - Nanoalumina
  - Nanoclays
SEM Images of the Surface of the Protective Gloves - Latex
Surface Porosity of Latex Glove by Non-Contact AFM
SEM Images of the Surface of the Protective Gloves - Nitrile
Glove Surface Comparison

Source: Wilshire Technologies, Glove Surface Comparison
SEM Images of the Surface of the Protective Gloves - Cotton
Surface Pores/Intrinsic Voids of Protective Gloves

- Latex and nitrile gloves have intrinsic voids in the micrometer size range
  - The voids do not appear to be going through the glove creating holes and causing the gloves to leak
  - These voids, however, might be vulnerable to the penetration of nanoparticles if the gloves are used under unfavorable conditions, such as in an elongated state or under a severe wear and tear situation
  - In addition, nanoparticles may be treated with special coatings to enhance their dispersion characteristics
  - When those coating materials and glove material are in close contact, the chance of particle penetration could potentially be increased
- There are wider gaps in between the cotton fibers in the cotton glove
Nanoclay - Static Test

Latex  Nitrile  Cotton
Nanoclay - Rigorous Test

Latex  Nitrile  Cotton
Nanoalumina - Static Test

Latex

Nitrile

Cotton
Nanoalumina - Rigorous Test

Latex  Nitrile  Cotton
Test Results

- Latex and nitrile gloves have intrinsic voids (thinner areas) in the micrometer size range.
- Nanoparticles tend to accumulate in the intrinsic voids.
- The degree of the accumulation is different for different gloves, nanoparticles, and contact between gloves and nanoparticles.
- These voids might be vulnerable to the penetration of nanoparticles if the gloves are used under unfavorable conditions, such as in an elongated state, in contact with the coating materials of nanoparticles, or under a severe wear and tear situation.
Future Research

- Realistic use conditions
  - Friction test
  - Pressure test
  - Stretching
- True penetration through the glove
Summary

- Possibility of dermal contact with and/or inhalation of nanomaterials is present in a nano research environment.
- There are other materials/conditions subject to health and safety concerns in the environment.
- Presence of nanomaterials does not appear to change the pattern in selecting and using personal protective equipment.
Summary (Cont’d)

- There are still a lot of unknowns as to whether or not traditional protective measures work against nanoparticles
  - Adequacy of respirators and respiratory exposure metric needs to be evaluated
  - Efficacy of protective gloves in handling nanomaterials needs to be evaluated
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