Characterization of Mechanical and UV-Induced Nanoparticle Release from Commercial Products

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Nano Release at NIST

• NIST-CPSC Projects
  • MWCNT, metal oxide & inorganic nanoparticle release from commercial products
  • Nanomaterial release from fire retardant products

• NIST Projects
  • MWCNT release from composite materials
  • MWCNT release visualization
  • Impact of weathering on nanoparticle release from composite materials
Mechanically induced MWCNT release from nanocomposites

• Characterization of intact nanocomposite materials
  • Raman, SEM & TEM
  • Commercial materials often have carbon fibers as well as MWCNTs - additional analytical challenges

• Mechanical release - cutting, sawing, abrasion

• Released particle collection and analysis
  • Passive collection, MOUDI, electrostatic precipitator, filtering
  • Real-time particle analysis - CPC, SMPS
  • Release particle analysis - Raman, SEM/STEM, LM
Passive sample collection from sawing and cutting

- Mostly μm- to mm-sized particles consisting of fiber bundles, resin pieces, paint chips, etc.
- Might contain bare or small clusters of nanoparticles.

Loss of resolution due to defocus & possibly no detection

Electron beam focused on top of a large particle

Some loss of resolution due to defocus

Low resolution mode

NP

High resolution mode

Electron beam focused on top of a small particle

Severe loss of resolution due to defocus

Some loss of resolution due to defocus
Aerosol sampling challenges

Loss during aerosol collection
- Flow rate
- Collection substrate efficiency
- Total collection efficiency

Loss during transport
- Tube type, length, size
- Flow geometry
- Mismatched flow velocity

Loss or contamination from sampling chamber
- Contaminants from abrading tip, sample holder, etc.
- Position of intake port
- Speed of inlet air/chamber air flow
- Net positive or negative flow

Loss during realtime analysis
- Flow rate
- Charge neutralization
- Analytical speed

Loss during aerosol collection
- Flow rate
- Collection substrate efficiency
- Total collection efficiency
Nanoparticles from cutting debris

- **What do we mean by released MWCNT?**
  - Partially embedded
  - Attached
  - Loose

- **Are rod shaped particles MWCNTs?**

- **What about other nano-sized particles?**
STEM in SEM

- STEM in SEM can provide MWCNT distribution and size information.
- Easier, faster and cheaper than dedicated TEM investigation.
- Cannot visualize the wall structure in epoxy matrix (but it can do it with free-standing CNTs).
Size separated sampling helps but ...

- Relatively high resolution (30 nm x 30 nm pixel) imaging is needed to locate individual CNT particles
- Manual survey is not realistic.

2500 images needed to cover the sampling area fully!

35+ GB of images
Automated SEM imaging

25 mm

1” MOUDI substrate

1 mm
Challenges for nanorelease characterization

- Better process control for particle sampling
  - Loss through diffusion?
  - Setup (tube length, inlet location, flow rate, collection substrate, etc.) dependent variations
  - Effective size separated sampling
- Automated and faster imaging and analysis process
  - Very small objects (nano) in a large field of view (statistics)
- Data management must be part of the solution

Quantitative analysis of release may be difficult until experimental processes are fully characterized
Release Pathways of Nanoparticles (NP) During the Life Cycle of Nanocomposites: Mechanical, Matrix Degradation, Chemical Dissolution, Fire/Incineration, etc.

**Mechanical abrasion**

- **Polyurethane (PU) flooring coatings on wood substrates**
  - SiO$_2$
  - Al$_2$O$_3$

- **Latex Coatings on a dry-wall substrate**
  - TiO$_2$
  - ZnO
  - Ag

**Matrix Degradation via UV**

- **Model Epoxy (EP)**
  - MWCNT
  - SiO$_2$

- **Exterior Coatings and Paints**
  - SiO$_2$-PU
  - ZnO -Latex

*Abrasion after UV exposure*

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**Goal:**

- To develop test methods and measurement protocols for determining the quantities and properties of nanoparticles released from polymer nanocomposites.
- To understand the mechanism that causes nanoparticles to leave the polymer matrix during exposures to the environments.

→ Providing data needed for assessing and managing potential EHS risks of NP release during nanocomposites’ life cycles.

# Airborne release particles - working with Indoor Air Quality Group/EL
1. Characterize abraded surfaces (LSCM, SEM, EDX)
2. Remove Particles from Abraded Surface (TEM grid pressed against the surface or using an Adhesive Tape)
3. Collect residues from abrasion wheels

2 & 3 → Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), SEM/EDX
• Commercial rotary abraser can be used for nanoparticle release study, but commercial abrading wheels that are composed of a polymer binder and inorganic abrasives → release their own particles → not suitable

- CS10 wheel
- CS-10 wheel
- CS-17 wheel
- S-35 wheel (Metal)

- Tungsten wheel
- Large grooves
- Fewer particles
- 150 μm x 150 μm

• NIST-made deep cross-patch (MW2) or sandblasted (MW4) noncorrosive stainless steel (e.g., 316 SS) wheels having a root mean square (RMS) surface roughness between 5 μm and 7 μm, are suitable for reproducibly abrading in water and in air for coatings and paints containing nanoparticles.
Laser scanning confocal microscopy (LSCM) in combination with image analysis is a good, relatively fast method for quantifying the number and size distribution of metal-oxide/inorganic particles accumulated on abraded surfaces having particle size greater than 100 nm (detection limit).

To identify the particles on surface ➔ SEM/EDX, ICP-OES
SEM images: particles from Abraded Surfaces (TEM grid pressed against the surface)
Case-Study: SiO$_2$-PU Exterior Coatings

- Neat PU and 5 % (by mass) nanosilica in PU (commercial, containing UV absorbers)
- Nanosilica (surface treated) in suspension
- Exposed on NIST SPHERE at 50 °C and both dry (0%RH) and humid (75% RH) conditions (PU: $T_g = 40.4 \pm 3^\circ C$)

Release Pathways:
Polymer matrix degradation via UV exposure
  → Simulated rain test
  → Abrasion test

Characterization
- Chemical Degradation (rates, mechanism)- FTIR, UV-vis, and XPS
- Surface Morphologies (AFM, SEM, EDXS)
- Release: amount & rate by ICP-OES
Nanoparticle Release Process and Collection

Mechanical abrasion
- Taber rotary abraser (ASTM D 4060-14, organic coatings)

Matrix Degradation via UV
- NIST SPHERE High Throughput, High Intensity UV Chamber

Abrasion parameters:
- MW2 metallic wheels
- Fixed loading
- 100 cycles

To be analyzed by ICP-OES
FTIR – Intensity

(a) CH$_2$ bending at 1468 cm$^{-1}$

(b) N-H bending at 1535 cm$^{-1}$

(c) Acid C=O at 1706 cm$^{-1}$

Mass loss

Rates of chemical degradation and weathering-induced mass loss of commercial PU nanocoating (ENC) were lower than those of the neat PU, indicating that surface-treated silica nanoparticles had photostabilized the PU matrix.

ENC: SiO$_2$-PU
Silica nanoparticles were observed to accumulate and cluster on the nanocoating surface with increasing UV exposure time and eventually release from the nanocoating.
Total Si collected: 16.9 µg ± 0.5 µg

PU: 2.8 mg/m² ± 0.1 mg/m² after 103 days
Model epoxy: 83.1 mg/m² ± 0.2 mg/m² after 72 days
### Surface morphology & mass loss before and after abrasion

#### 50 °C and dry (0%RH)

**Exposure days**: 0, 10, 20, 40, 60

**Surface morphology**

- **Before**
  - 50x magnification
  - 150x magnification

- **After**
  - 50x magnification
  - 150x magnification

<table>
<thead>
<tr>
<th>Exposure days</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>60</th>
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</thead>
<tbody>
<tr>
<td>$M_{\text{before abrasion}} - M_{\text{after abrasion}}$ (mg)/samples</td>
<td>0.15 ± 0.10</td>
<td>0.73 ± 0.39</td>
<td>2.20 ± 0.27</td>
<td>1.82 ± 0.52</td>
<td>1.98 ± 0.17</td>
</tr>
<tr>
<td>Mass of Si (µg) by ICP*</td>
<td>2.2 ± 1.4</td>
<td>2.01 ± 0.51</td>
<td>1.92 ± 0.50</td>
<td></td>
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</tr>
</tbody>
</table>

* Collected from abrasion wheels averaged of 4 samples
Surface morphology after abrasion – at different UV exposure times

0 d

10 d

20 d

40 d

60 d

Total Surface Particle Count (1/mm²)

Particle Size (µm)

Total Surface Particle Count (1/mm²)

Particle Size (µm)

Total Surface Particle Count (1/mm²)

Particle size (µm)

Exposure time (d)

0 20 40 60
Silica nanoparticles were observed to accumulate and cluster on the nanocoating surface with increasing UV exposure time and eventually release from the nanocoating.

The trends (as a function of exposure time) of released Si mass collected from simulated rain process and the mass loss & total surface particle counts from abrasion process are similar.
Concern: Harmful effects of surface-exposure and release of nanomaterials during the life cycle of polymer nanocomposites?

• How to capture released particles?

• Evidence of particle release – detection? Can you detect discrete nanoparticles?
  - High resolution microscopy –SEM/TEM –labor intensive
  - ICP – element analyses
  - Others

• The size and form of released particles?
  - Size: range from “nano” to “micro” depends on release mechanism
  - Form: free nanoparticle? nanoparticles embedded in polymer matrix?
  - Can we distinguish between agglomerates and aggregates of nanoparticles?

• What are the best methods available to answer these questions? Reference?
  - Experimental data are needed for assessing and managing potential EHS risks of nanoparticles release during nanocomposites’ life cycles.
  - Need guidelines and protocols!