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

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QEEN Workshop 2015

July 7th, 2015

Arlington, VA

National Institute of Standards and Technology

U.S. Department of Commerce

Acknowledgements

NIST

MML (Materials)
EL (Engineering)
ITL (Information Science)
CNST (NanoFab)
PML (Physics)

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CONSUMER PRODUCT SAFETY COMMISSION

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Nano Release at NIST

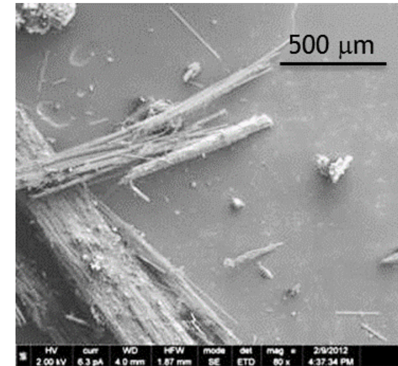
- NIST-CPSC Projects
  - MWCNT, metal oxide & inorganic nanoparticle release from commercial products
  - Nanomaterial release from fire retardant products
- NIST Projects
  - MWCNT release from composite materials
  - MWCNT release visualization
  - Impact of weathering on nanoparticle release from composite materials

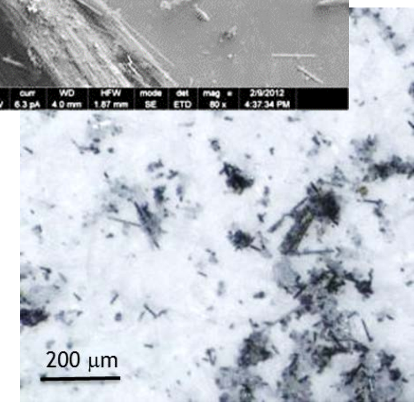
Mechanically induced MWCNT release from nanocomposites

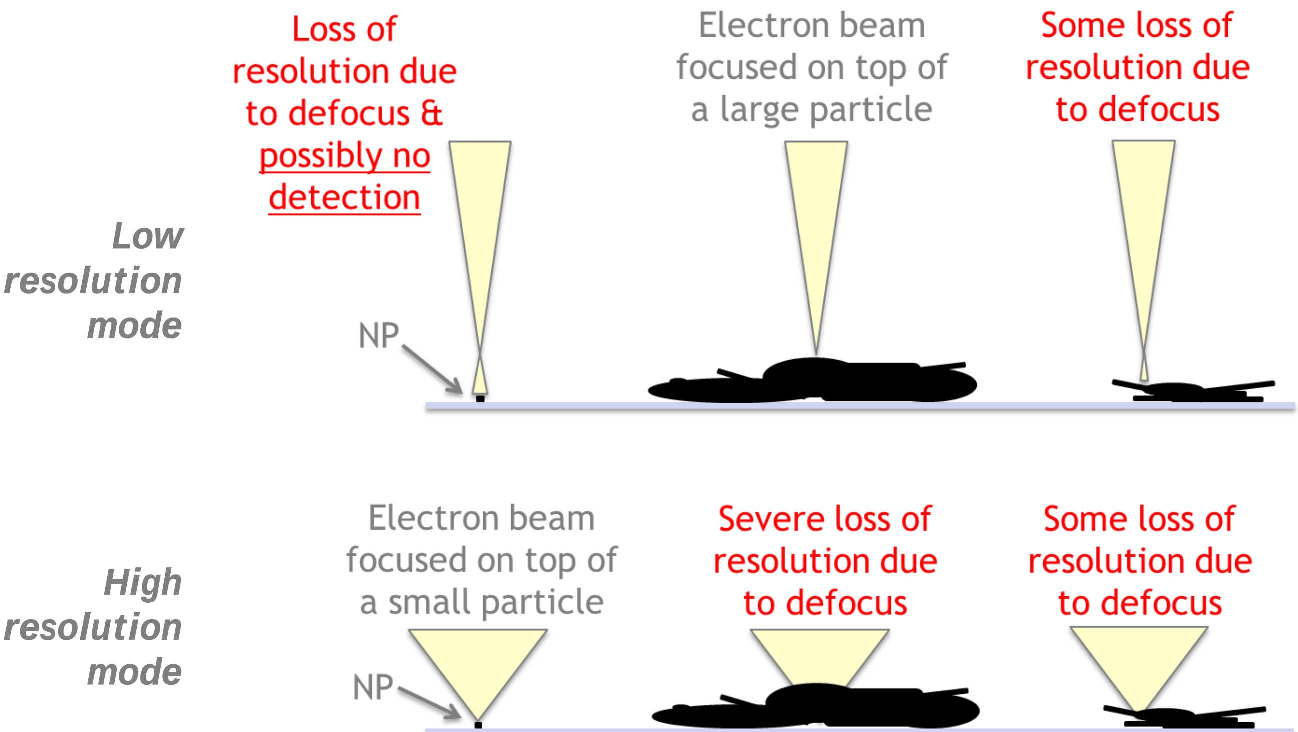
- Characterization of intact nanocomposite materials
  - Raman, SEM & TEM
  - Commercial materials often have carbon fibers as well as MWCNTs – additional analytical challenges
- Mechanical release - cutting, sawing, abrasion
- Released particle collection and analysis
  - Passive collection, MOUDI, 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 fiber bundles, resin pieces, paint chips, etc.
- Might contain bare or small clusters of nanoparticles.



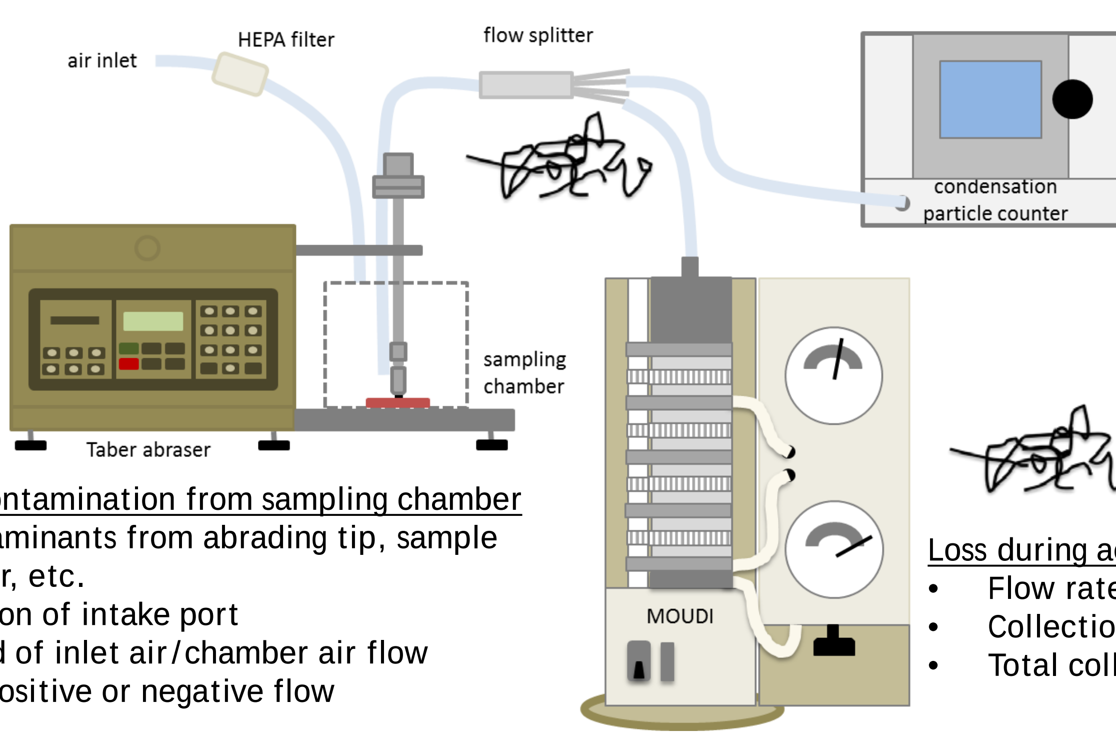




Aerosol sampling challenges

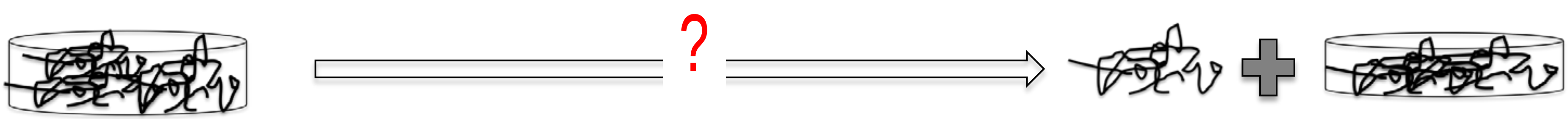
Loss during transport
- Tube type, length, size
- Flow geometry
- Mismatched flow velocity

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



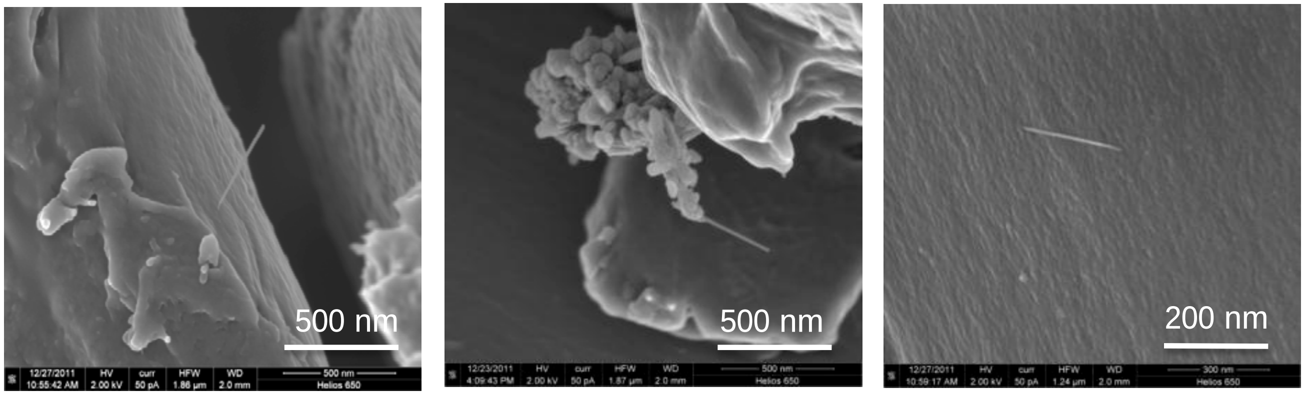
Loss or contamination from sampling chamber
- Contaminants from abrading tip, sample holder, etc.
- Position of intake port
- Speed of inlet air/chamber air flow
- Net positive or negative flow

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

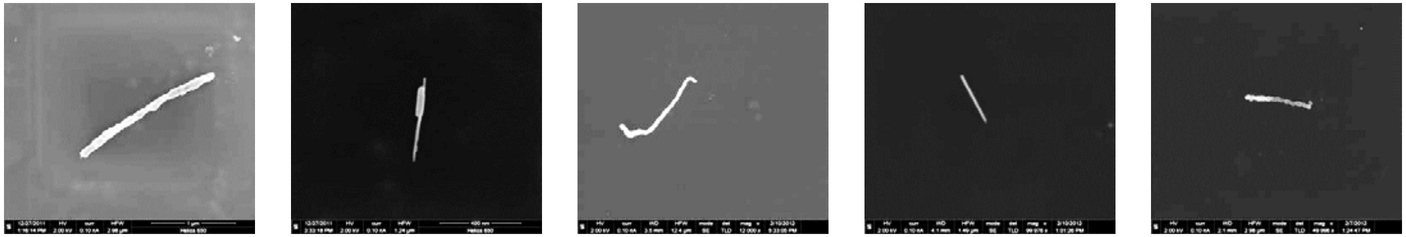


Nanoparticles from cutting debris

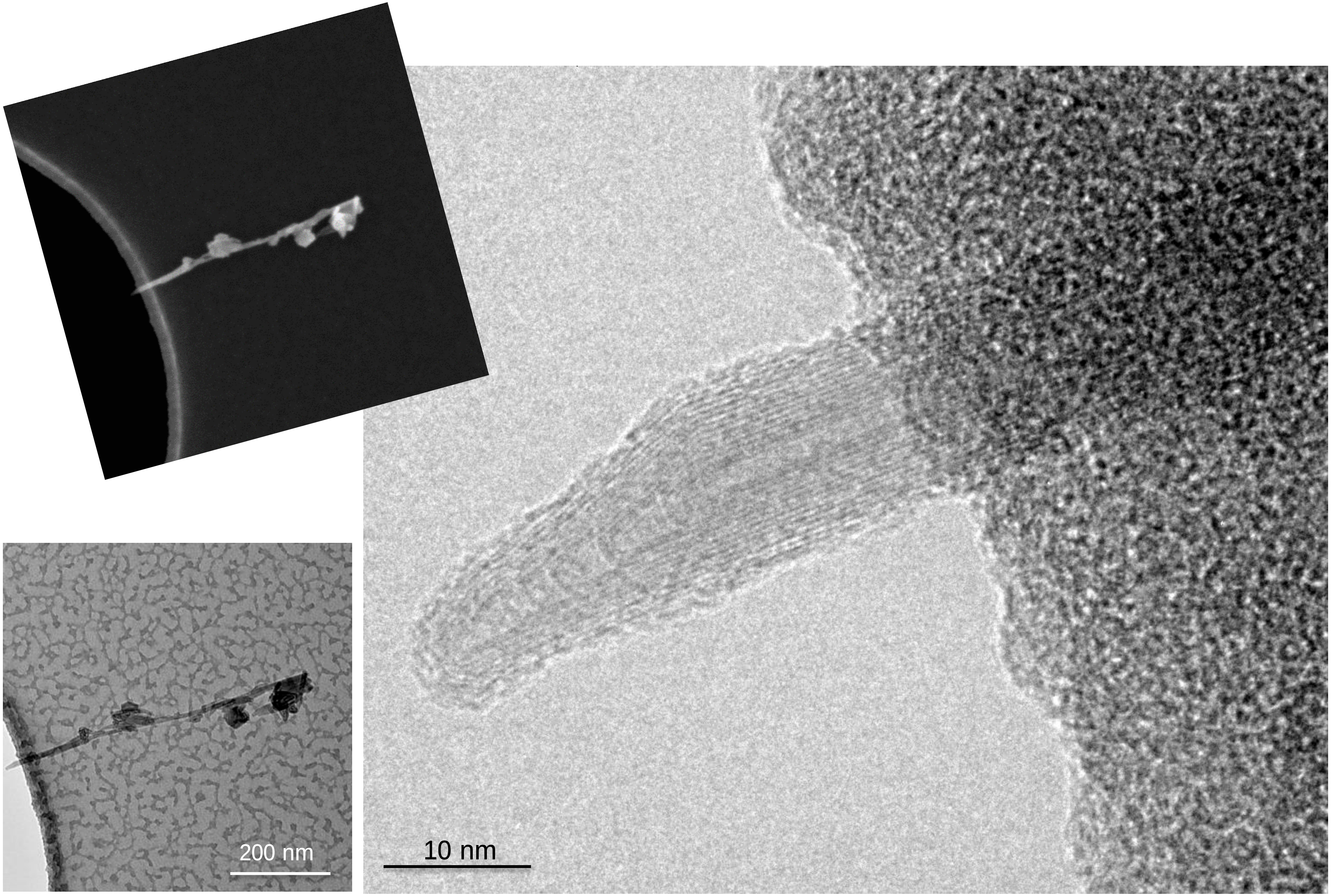
- *What do we mean by released MWCNT?*
  - Partially embedded
  - Attached
  - Loose



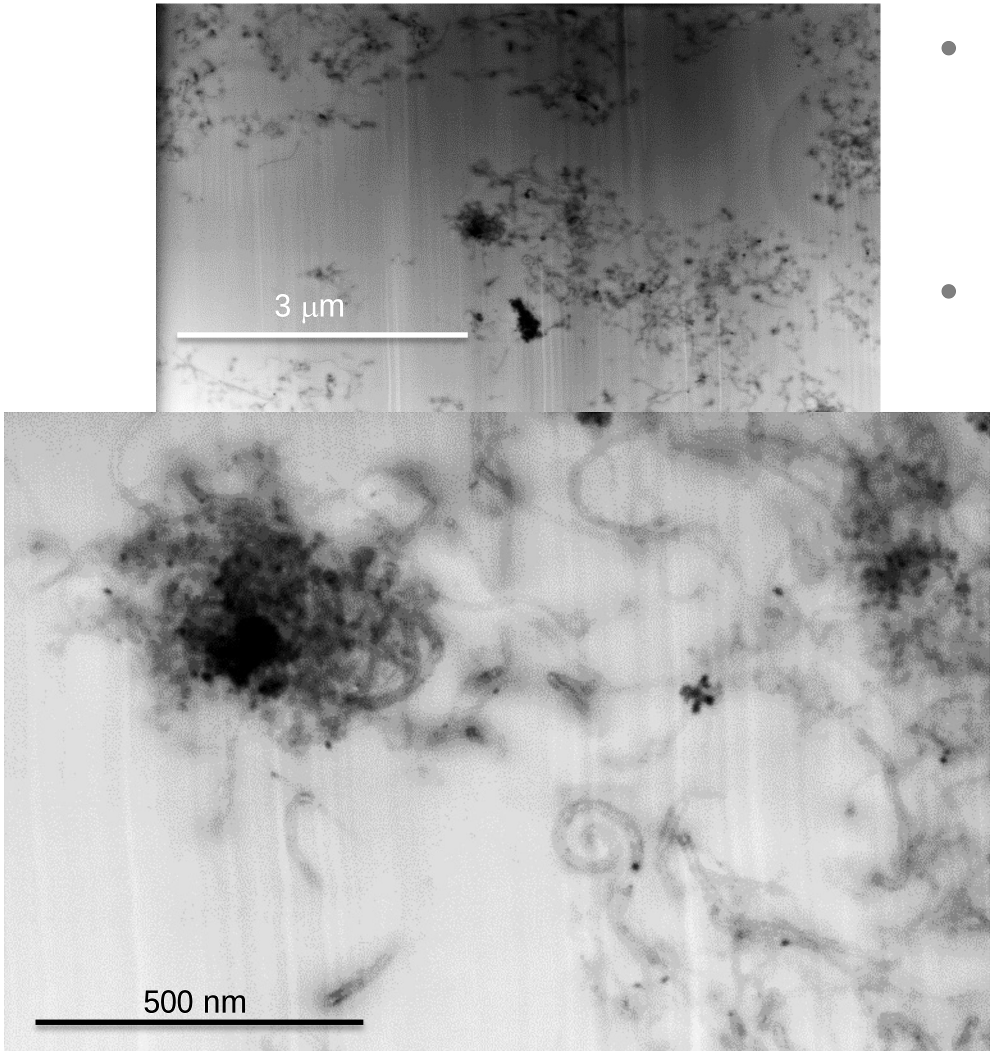
- *Are rod shaped particles MWCNTs?*



- *What about other nano-sized particles?*


200 nm
10 nm

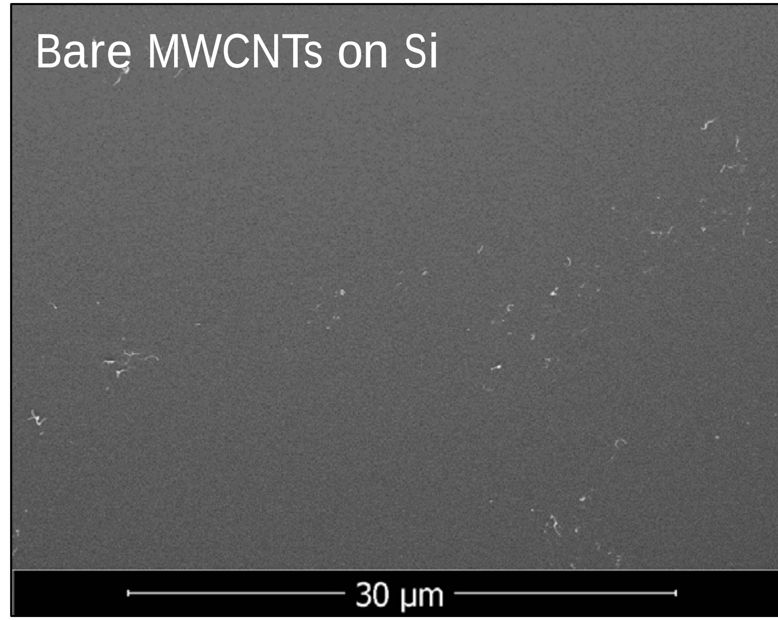
STEM in SEM

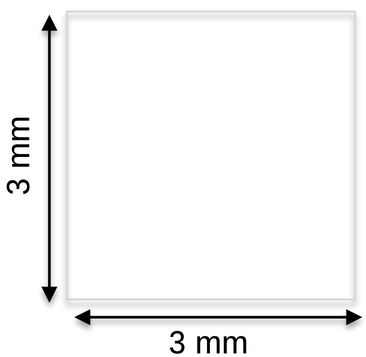


- STEM in SEM can provide MWCNT distribution and size information.
- Easier, faster and cheaper than dedicated TEM investigation.
- Cannot visualize the wall structure in epoxy matrix (but it can do it with free-standing CNTs).

Size separated sampling helps but ...

- Relatively high resolution (30 nm x 30 nm pixel) imaging is needed to located individual CNT particles
- <u>Manual survey is not realistic.</u>

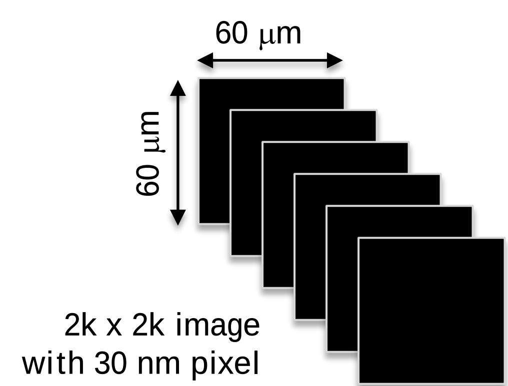




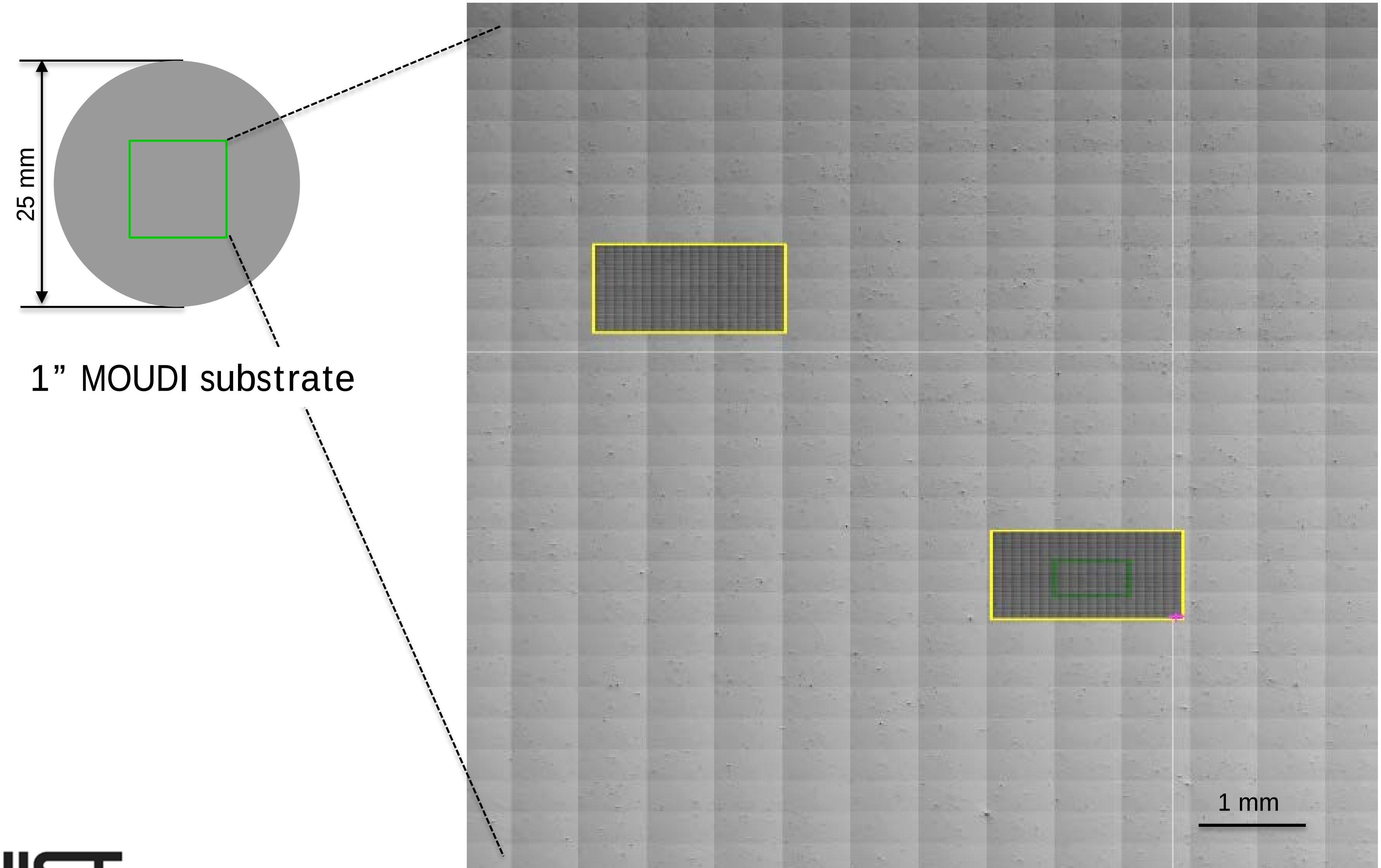
Total sampling area

2500 images needed to cover the sampling area fully!

35+ GB of images



Automated SEM imaging



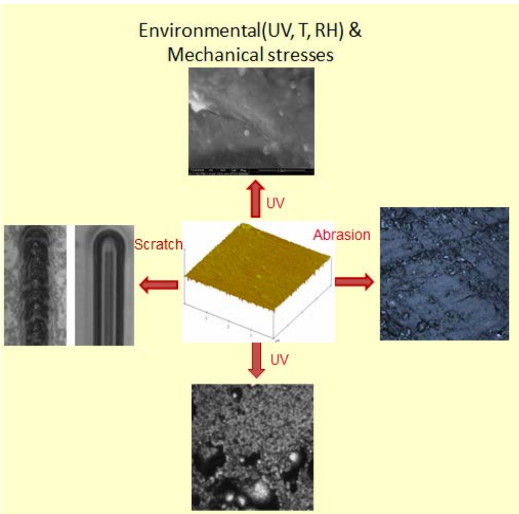
Challenges for nanorelease characterization

- 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)
- <u>Data management must be part of the solution</u>

Quantitative analysis of release may be difficult until experimental processes are fully characterized

NIST/EL – CPSC Nanoparticle Release Research

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_2O_3

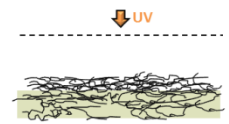
Latex Coatings
on a dry-wall substrate

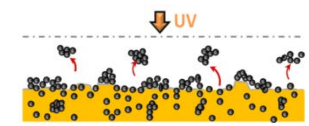
- TiO_2
- ZnO
- Ag

Matrix Degradation via UV

Model Epoxy (EP)

- MWCNT
- SiO_2





Exterior Coatings and Paints

- **SiO_2-PU**
- ZnO -Latex

***Abrasion after UV exposure**

Airborne release particles- *working with Indoor Air Quality Group/EL*

Goal:

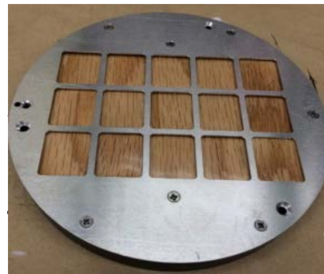
- To develop test methods and measurement protocols for determining the quantities and properties of nanoparticles released from polymer nanocomposites
- To understand the mechanism that causes nanoparticles to leave the polymer matrix during exposures to the environments

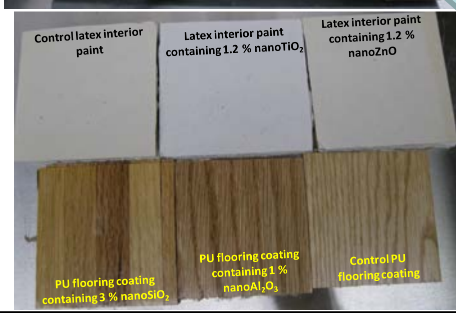
→ Providing data needed for assessing and managing potential EHS risks of NP release during nanocomposites' life cycles.

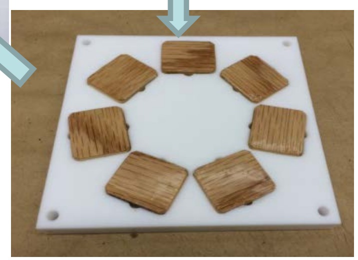
Nanoparticle Release Process and Collection

Mechanical abrasion

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





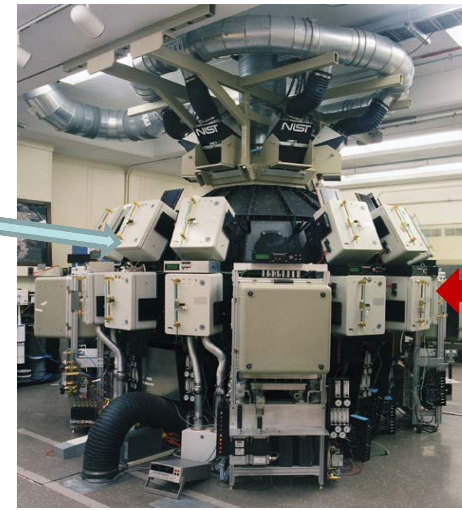


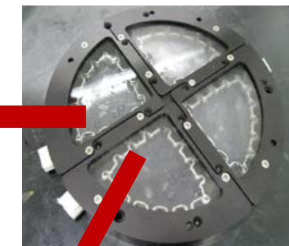
1. Characterize abraded surfaces (LSCM, SEM, EDX)
2. Remove Particles from Abraded Surface (TEM grid pressed against the surface or using an Adhesive Tape)
3. Collect residues from abrasion wheels

2 & 3→ Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), SEM/EDX

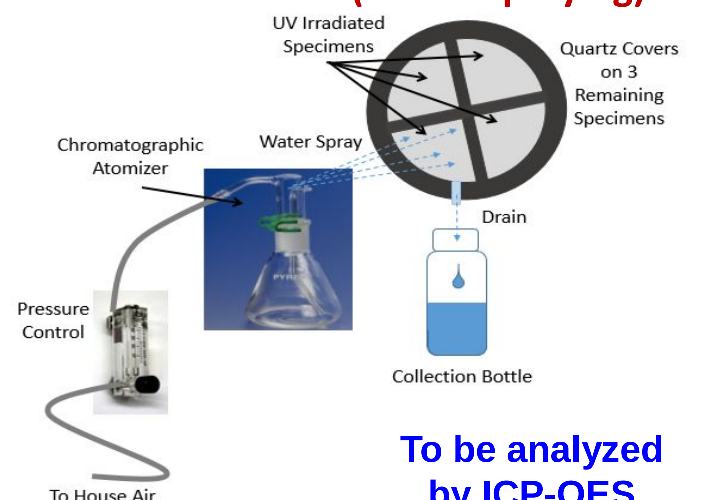
Matrix Degradation via UV

NIST SPHERE High Throughput, High Intensity UV Chamber





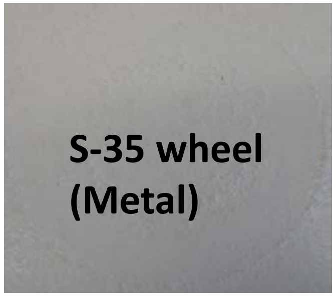
Simulated Rain Test (Water Spraying)



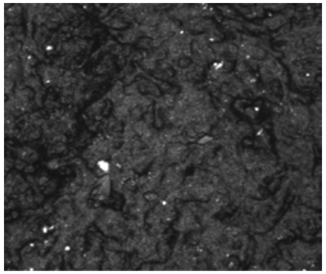
To be analyzed by ICP-OES

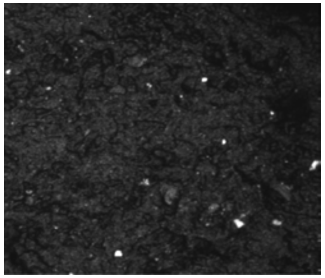
Lesson Learned- Abrasion Test

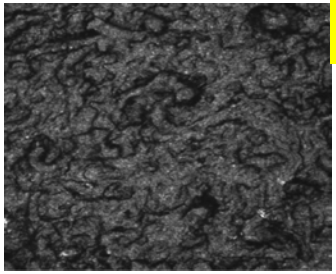
- Commercial rotary abraser can be used for nanoparticle release study, but commercial abrading wheels that are composed of a polymer binder and inorganic abrasives → release their own particles → **not suitable**



tungsten wheel





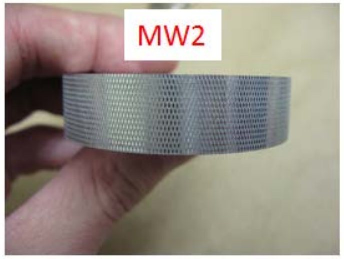


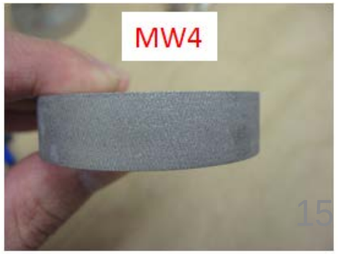
large grooves

Fewer particles

150 µm x 150 µm

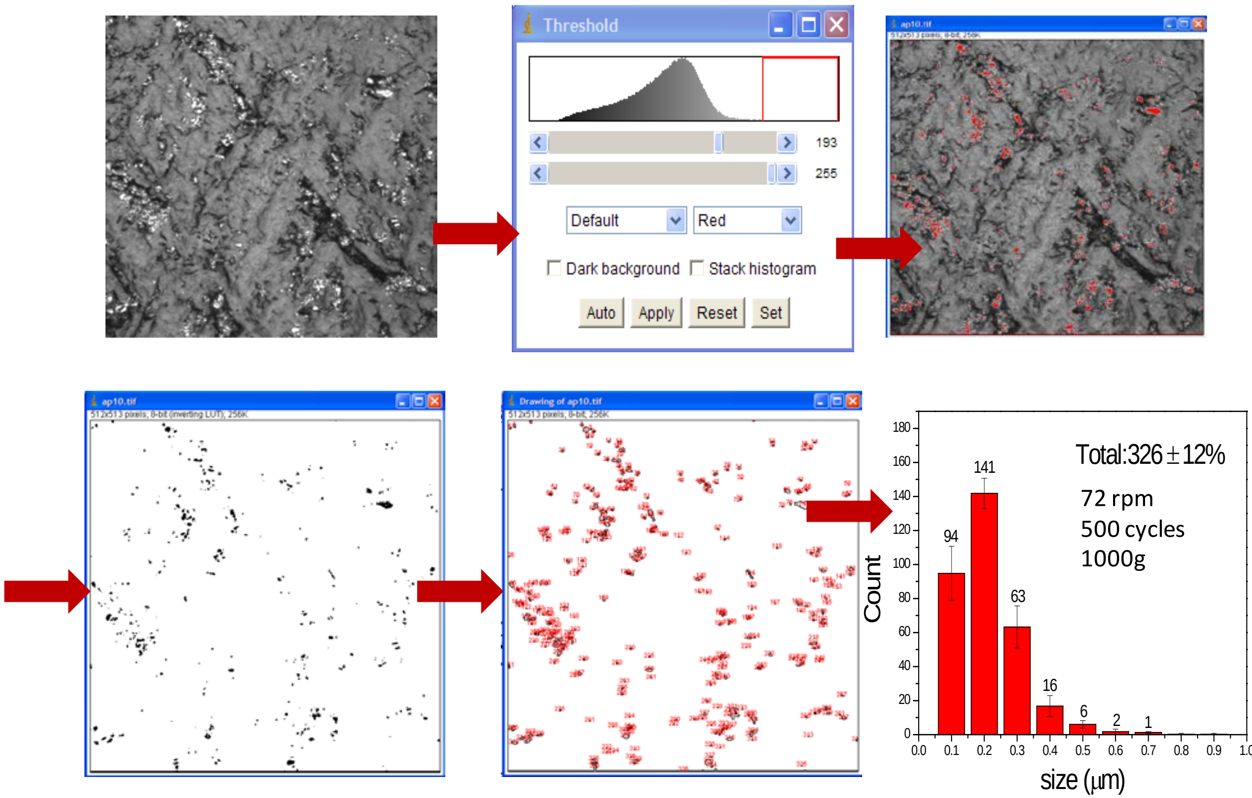
- NIST-made deep cross-patch (MW2) or sandblasted (MW4) noncorrosive stainless steel (e.g., 316 SS) wheels having a root mean square (RMS) surface roughness between 5 µm and 7 µm, are suitable for reproducibly abrading in water and in air for coatings and paints containing nanoparticles.



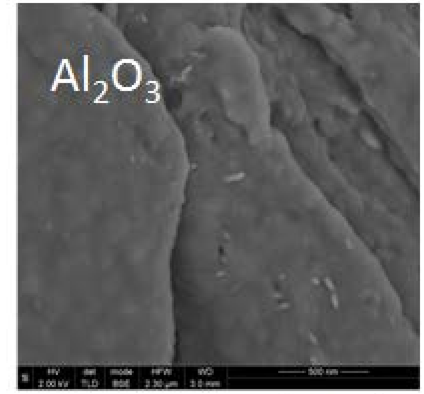


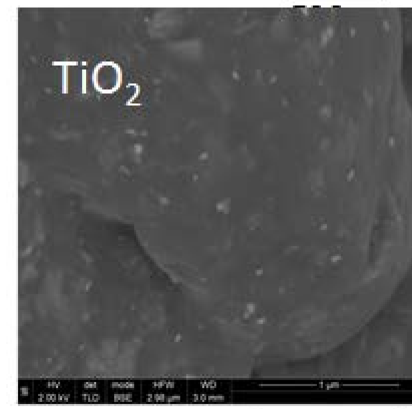
Lesson Learned- Abrasion Test

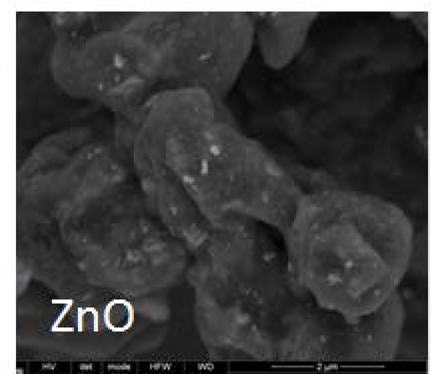
- Laser scanning confocal microscopy (LSCM) in combination with ima relatively fast method for quantifying the number and size distributio oxide/inorganic particles accumulated on abraded surfaces having pa than 100 nm (detection limit).



- LS scree detec
- Re nano nano in pol







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: $T_g = 40.4 \pm 3°$ C)

Release Pathways:

Polymer matrix degradation via UV exposure

→Simulated rain test

→Abrasion test

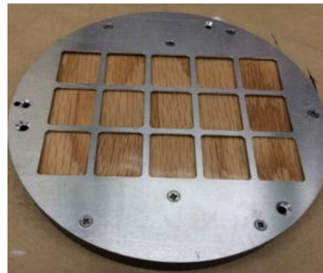
Characterization

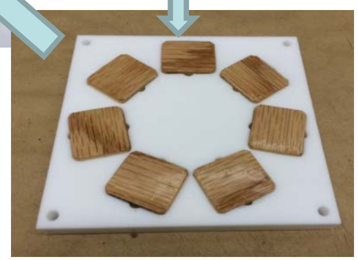
- Chemical Degradation (rates, mechanism)- FTIR, UV-vis, and XPS
- Surface Morphologies (AFM, SEM, EDXS)
- Release: amount & rate by ICP-OES

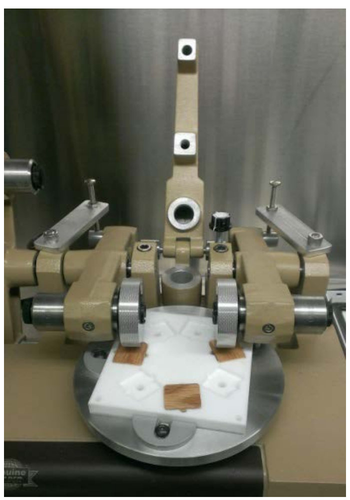
Nanoparticle Release Process and Collection

Mechanical abrasion

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





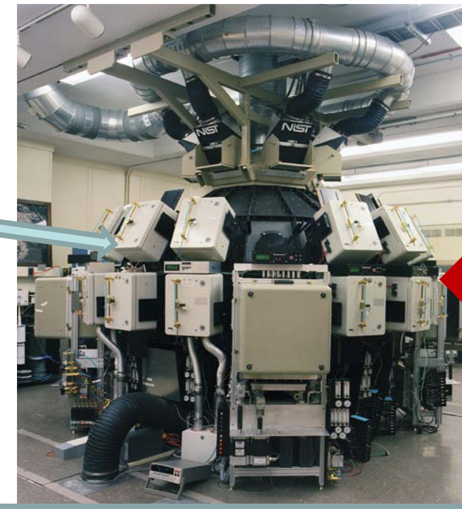


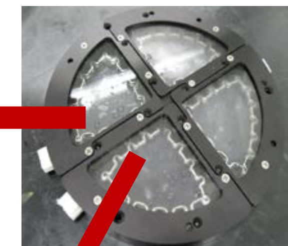
Abrasion parameters:

- MW2 metallic wheels
- Fixed loading
- 100 cycles

Matrix Degradation via UV

NIST SPHERE High Throughput, High Intensity UV Chamber





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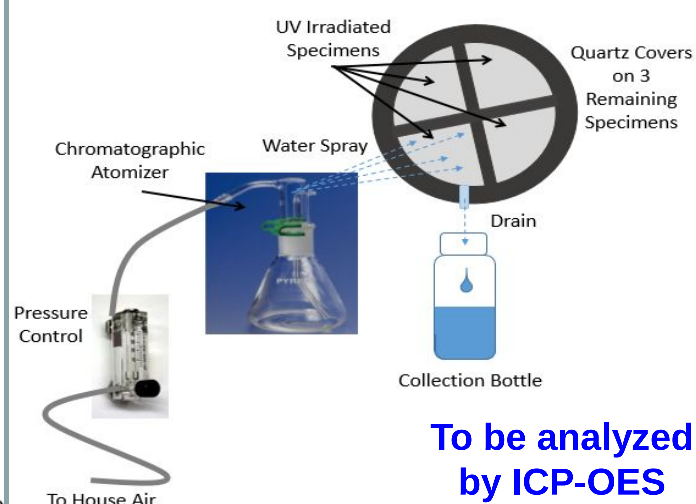
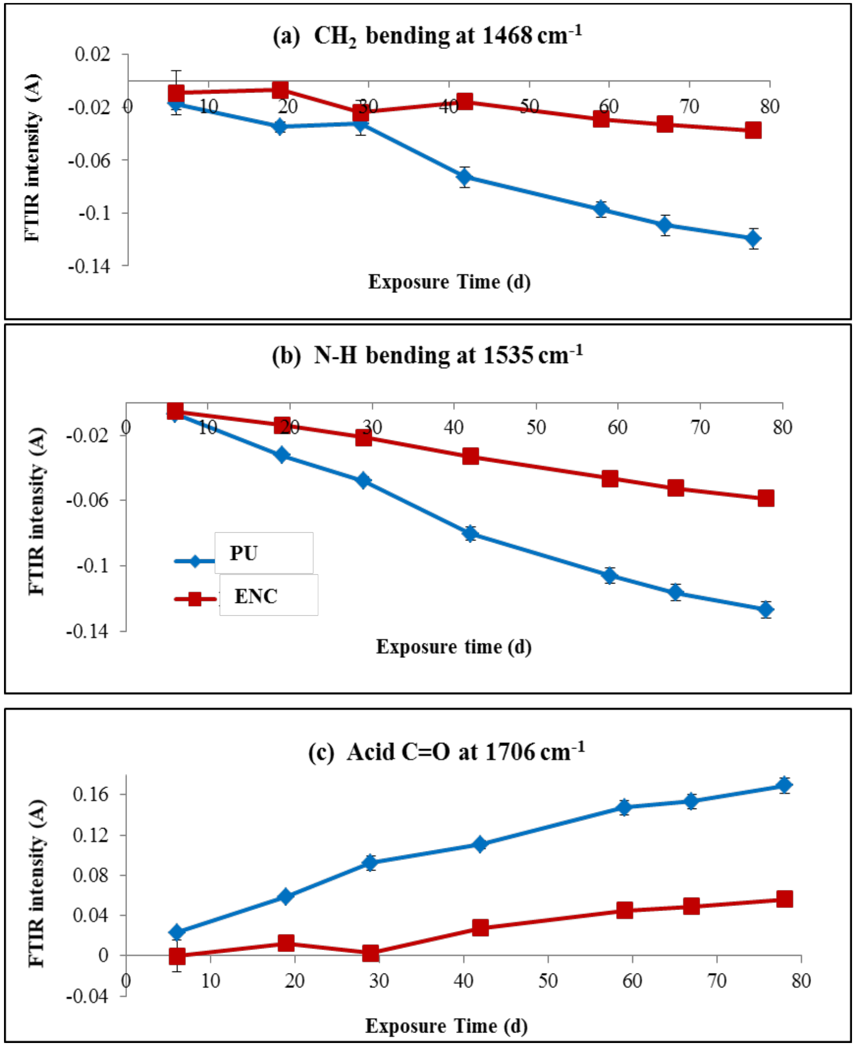


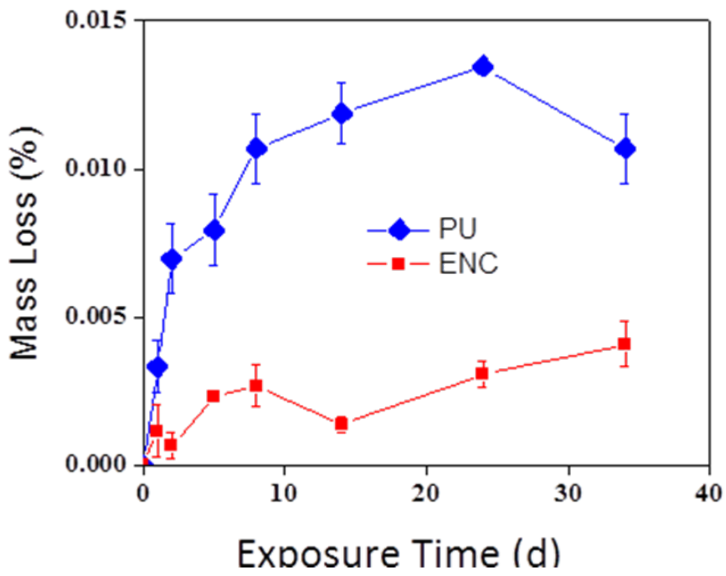
To be analyzed by ICP-OES

Chemical Changes and Moss Loss

FTIR – Intensity



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

Surface Morphological Changes

AFM

0 days 14 days 26 days 65 days

Hight

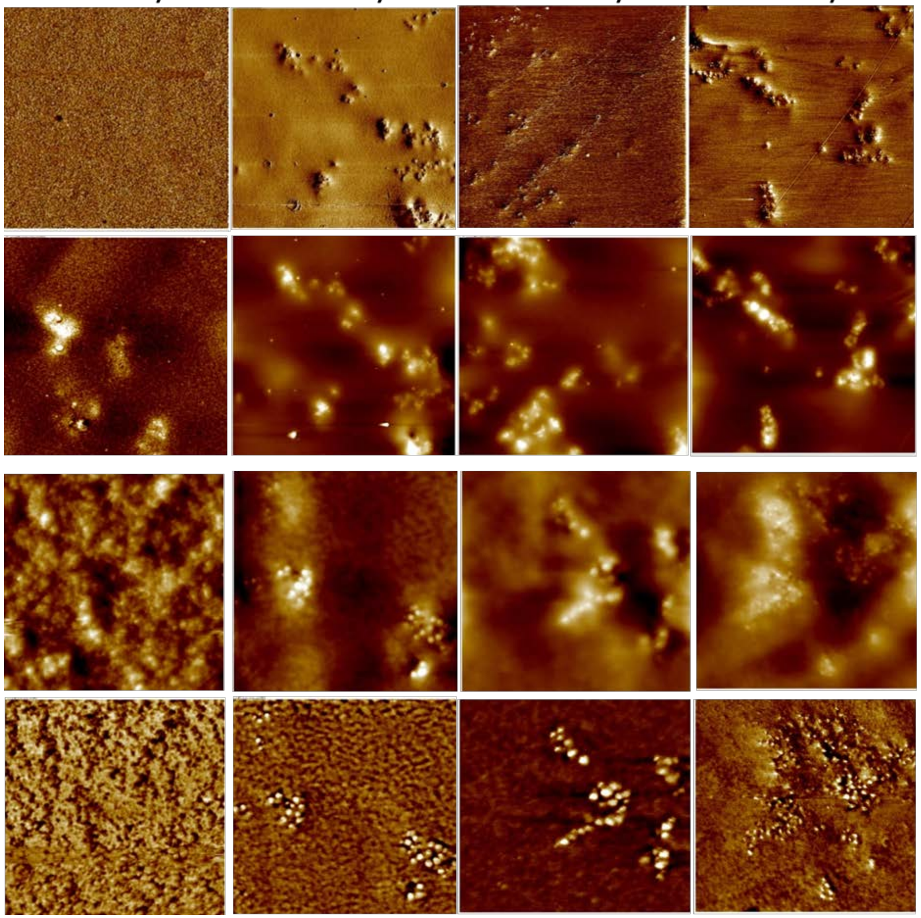
20 μm scan

Phase

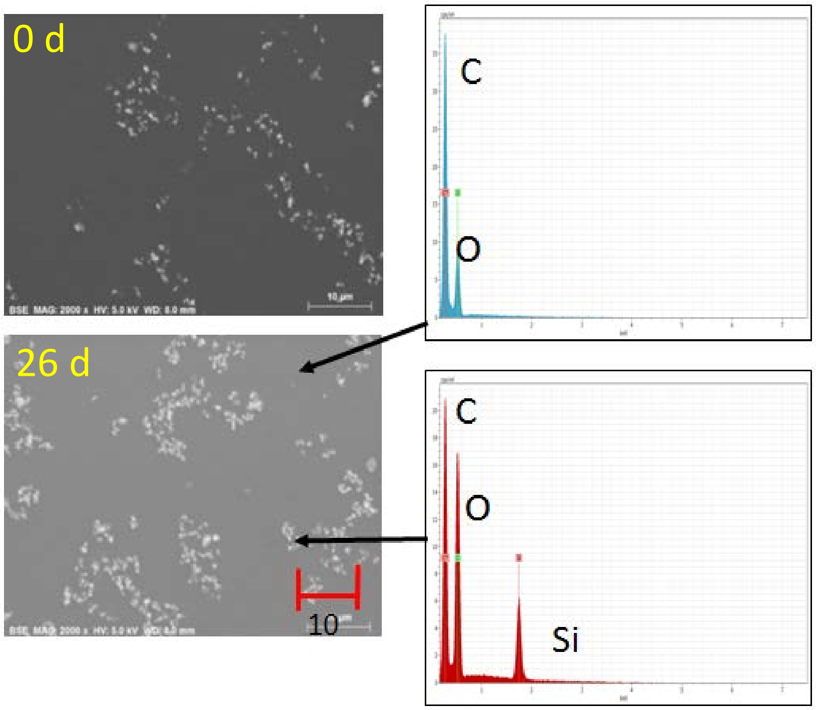
Hight

1 μm scan

Phase



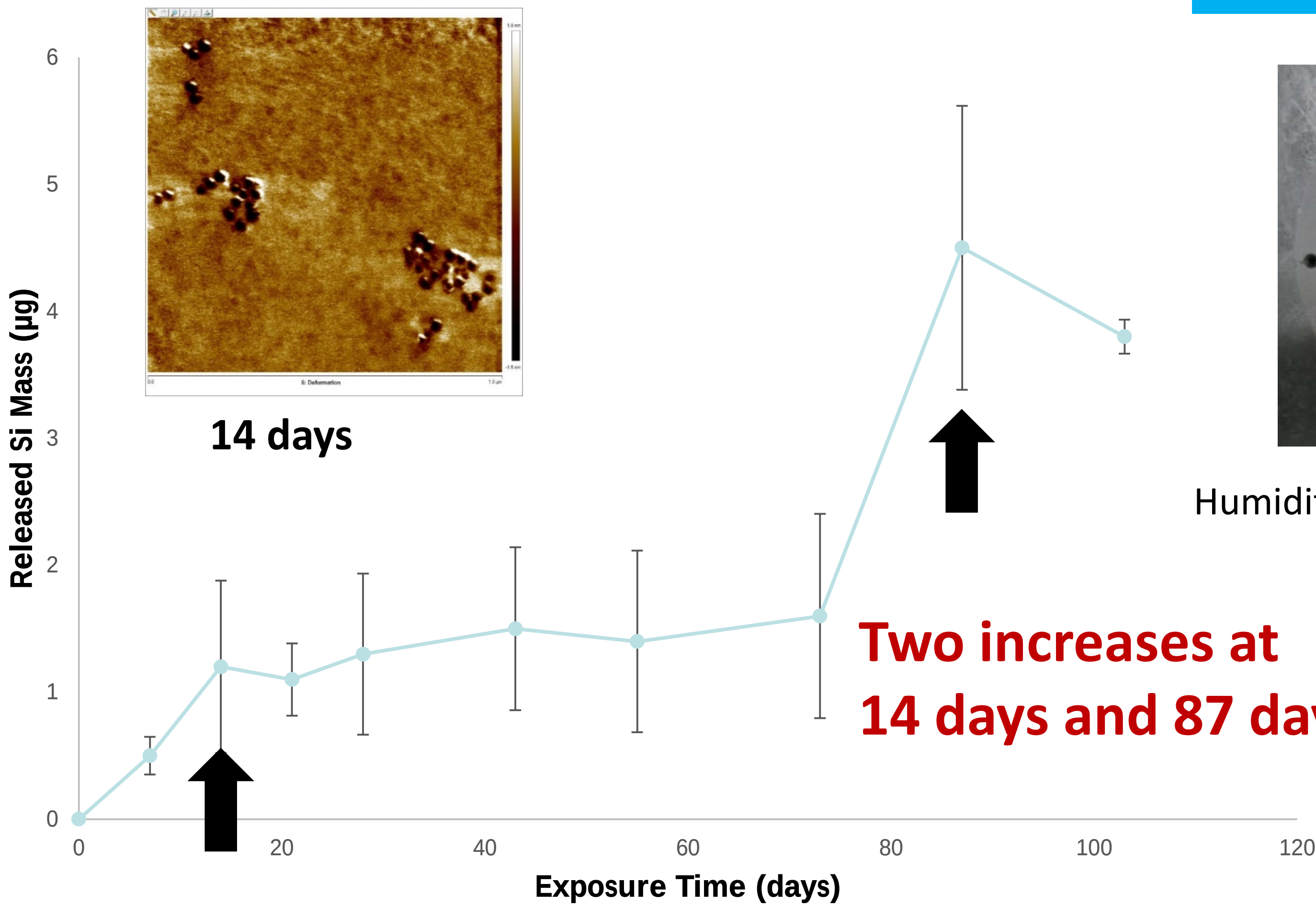
SEM/EDX



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

Released Si mass collected from simulated rain test

Savelas Rabb & Lee Yu, MML/NIST



Two increases at 14 days and 87 days

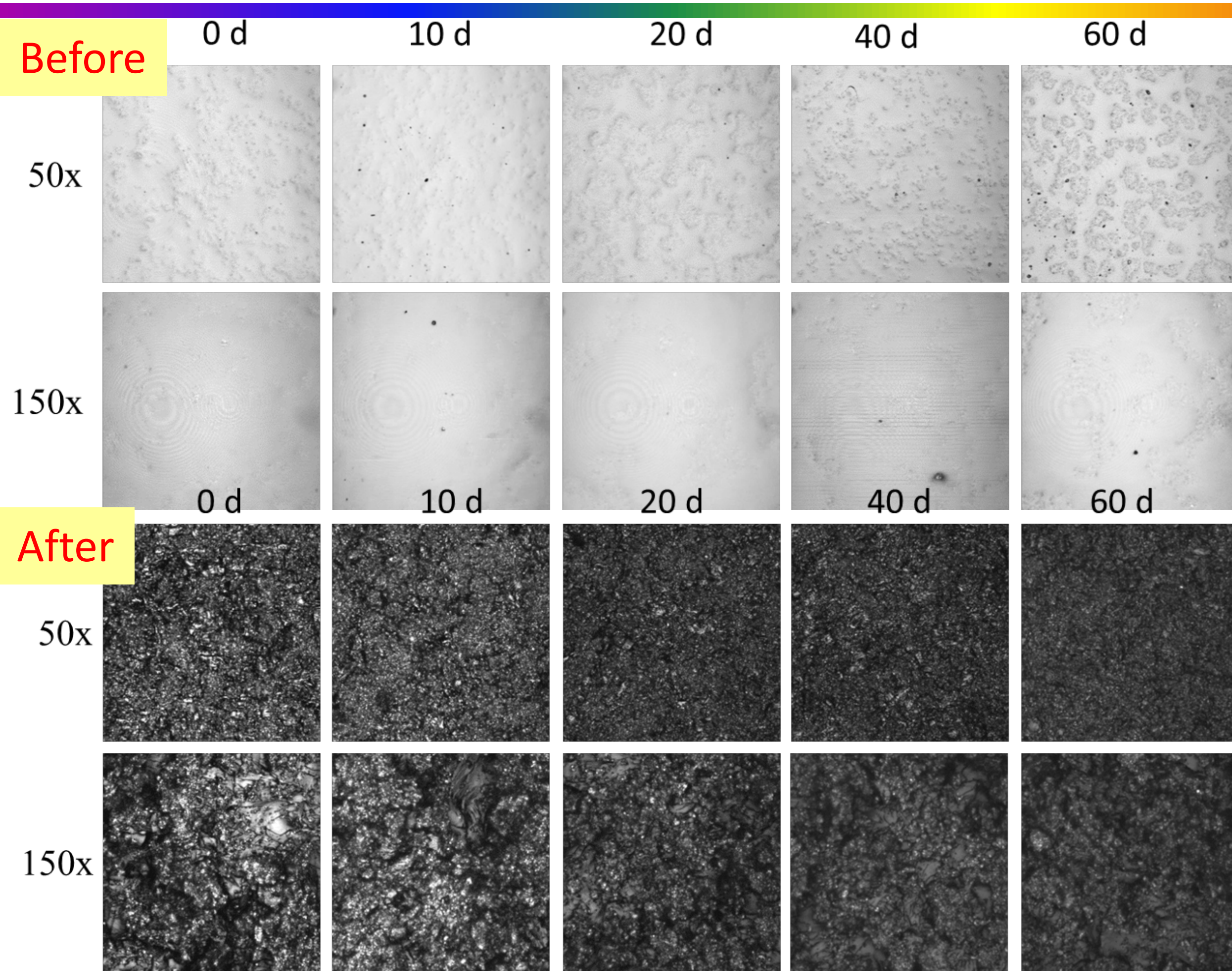
Humidity inside the cell~ 75% RH

Total Si collected:16.9 µg ± 0.5 µg

PU: 2.8 mg/m^2 ± 0.1 mg/m^2 after 103 days

Model epoxy: 83.1 mg/m^2 ± 0.2 mg/m^2 after 72 days

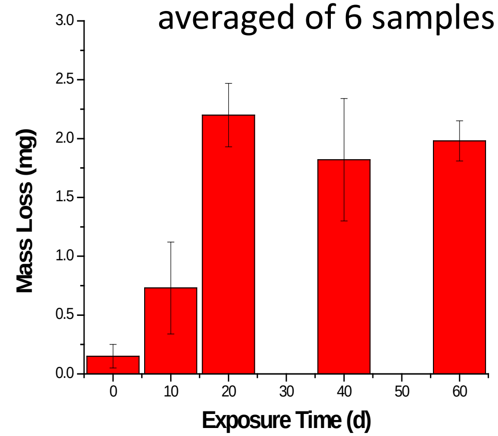
Surface morphology & mass loss before and after abrasion

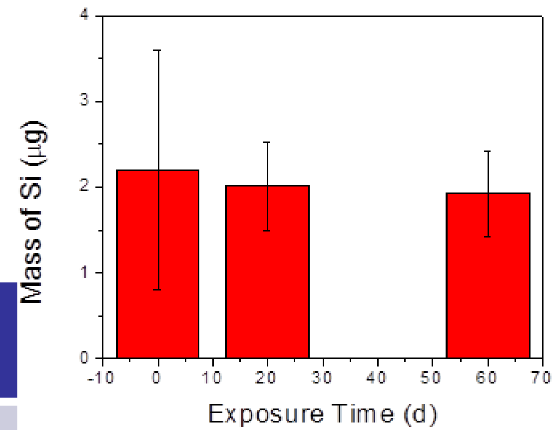


50 °C and dry (0%RH)

$M_{before\ abrasion}$-$M_{after\ abrasion}$ (mg)

averaged of 6 samples



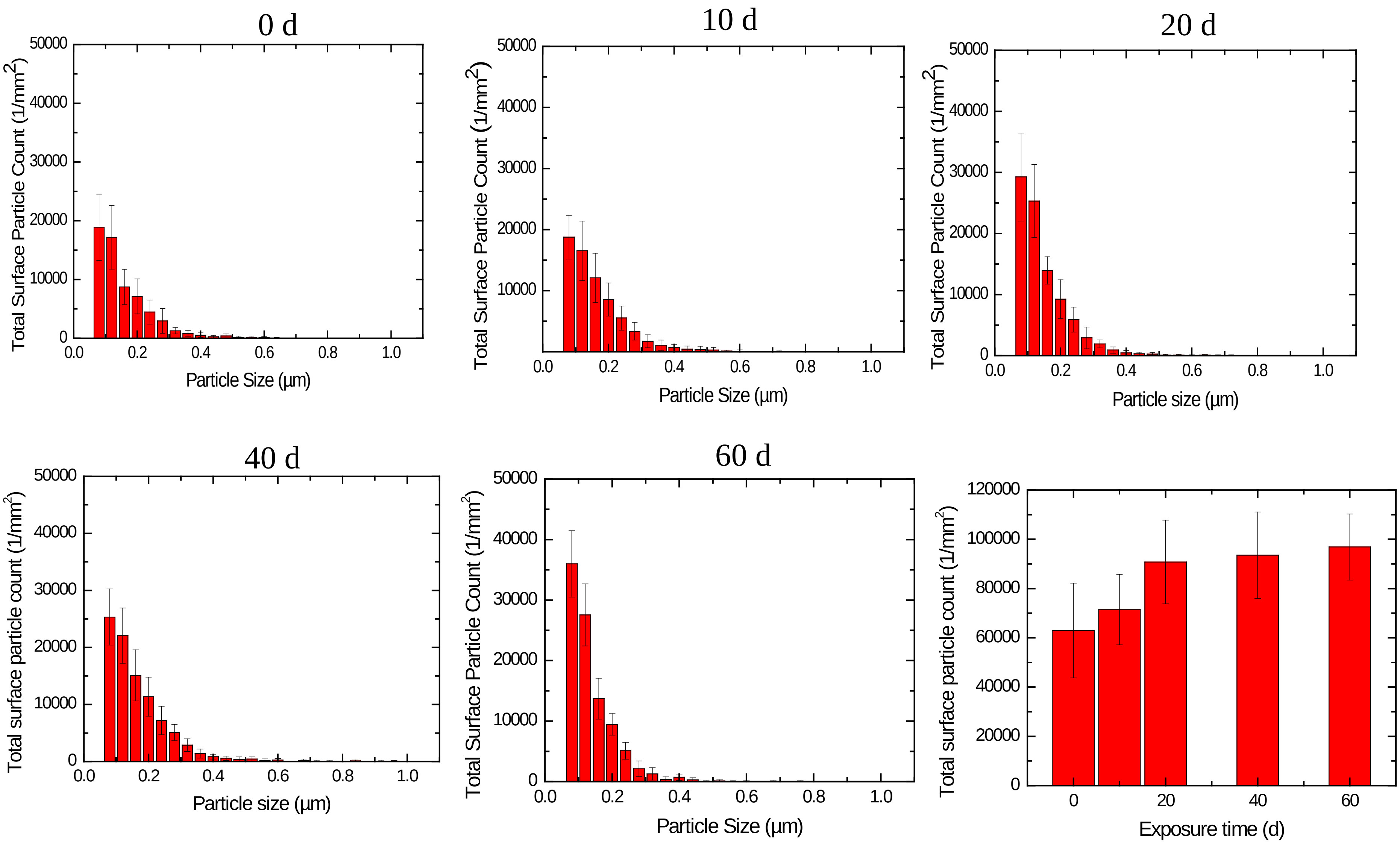


Exposure days	0	10	20	40	60
$M_{before\ abrasion}$-$M_{after\ abrasion}$ (mg)/samples	0.15 ± 0.10	0.73 ± 0.39	2.20 ± 0.27	1.82 ± 0.52	1.98 ± 0.17
Mass of Si (μg) by ICP*	2.2 ± 1.4		2.01 ± 0.51		1.92 ± 0.50

* Collected from abrasion wheels

averaged of 4 samples

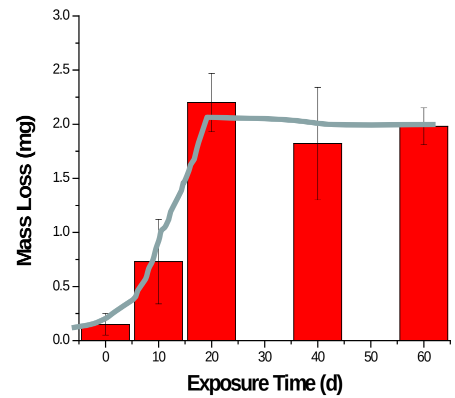
Surface morphology after abrasion – at different UV exposure times



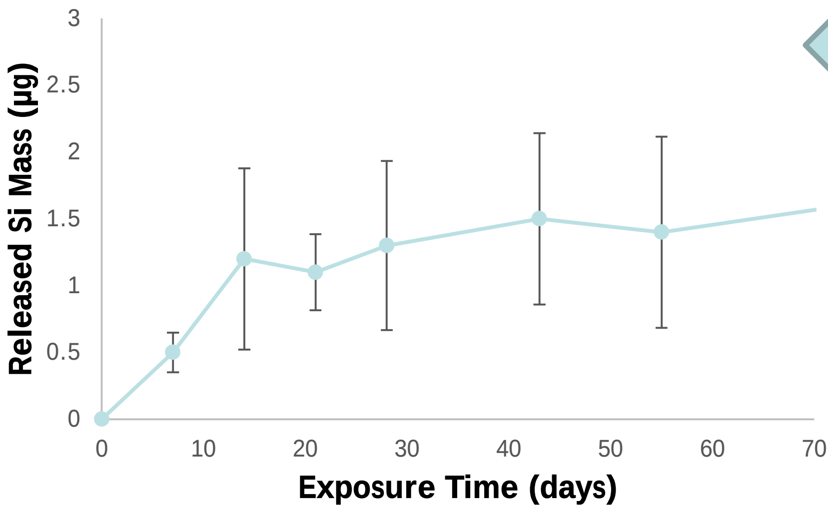
Summary

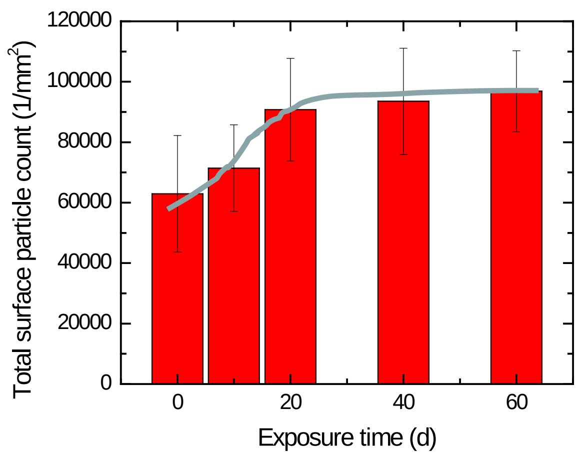
- Silica nanoparticles were observed to accumulate and cluster on the nanocoating surface with increasing UV exposure time and eventually release from the nanocoating.
- The trends (as a function of exposure time) of released Si mass collected from simulated rain process and the mass loss & total surface particle counts from abrasion process are similar.

Abrasion process



Simulated rain process





Current Issues – for discussion

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!