NanoRelease Consumer Products:
Developing measurement approaches for the analysis of release materials from nanocomposites

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NANOSAFE 2016

Outline

- NIST NanoEHS Activities
- ILSI NanoRelease Sanding
  - Sanding module overview
  - Sanding experiments
  - Analysis (real time & SEM)
  - Lessons learned

National Institute of Standards & Technology (NIST)

- **NIST** is a non-regulatory federal agency within the U.S. Department of Commerce
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- **NIST's mission** is to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life

NIST NanoEHS Activities

- Standard reference material development
  - Au NPs, SWCNTs, TiO2 NP, Ag NPs
- Support standard methods development by standards organization such as ISO, ASTM
- Metrology focused research activities
  - Nanotoxicity assay protocols
  - Imaging and visualization
- Collaborations with other US governmental agencies

Collaborative Activities

Development of testing protocols and analytical methods for assessing release from

- Consumer products such as sporting good, 3D printers, paints, etc. (U.S. Consumer Product Safety Commission, U.S. Department of Defense)
- Food contact materials such as cooking pots, baby bottles, food containers, and cutting boards (U.S. Food and Drug Administration)
  - ILSI Symposium on Food Packaging, Barcelona, Nov 16-18
- Nanocomposite materials (ILSI, CEA, IUTA, KIST, NRC Canada, CPSC, Nanocyl, BASF)

NanoRelease Consumer Products

Multi-stakeholder effort initiated to foster the safe development of nanomaterials by supporting development of methods to understand the release of nanomaterials used in products.

- Phase 1: Nanomaterial Selection
- Phase 2: Methods Evaluation
- Phase 3: Interlaboratory Studies
  - Weathering Module
  - Sanding Module

http://www.nanorelease.org/welcome-2/nanorelease-consumer-products-2/

Sanding Module

Goal

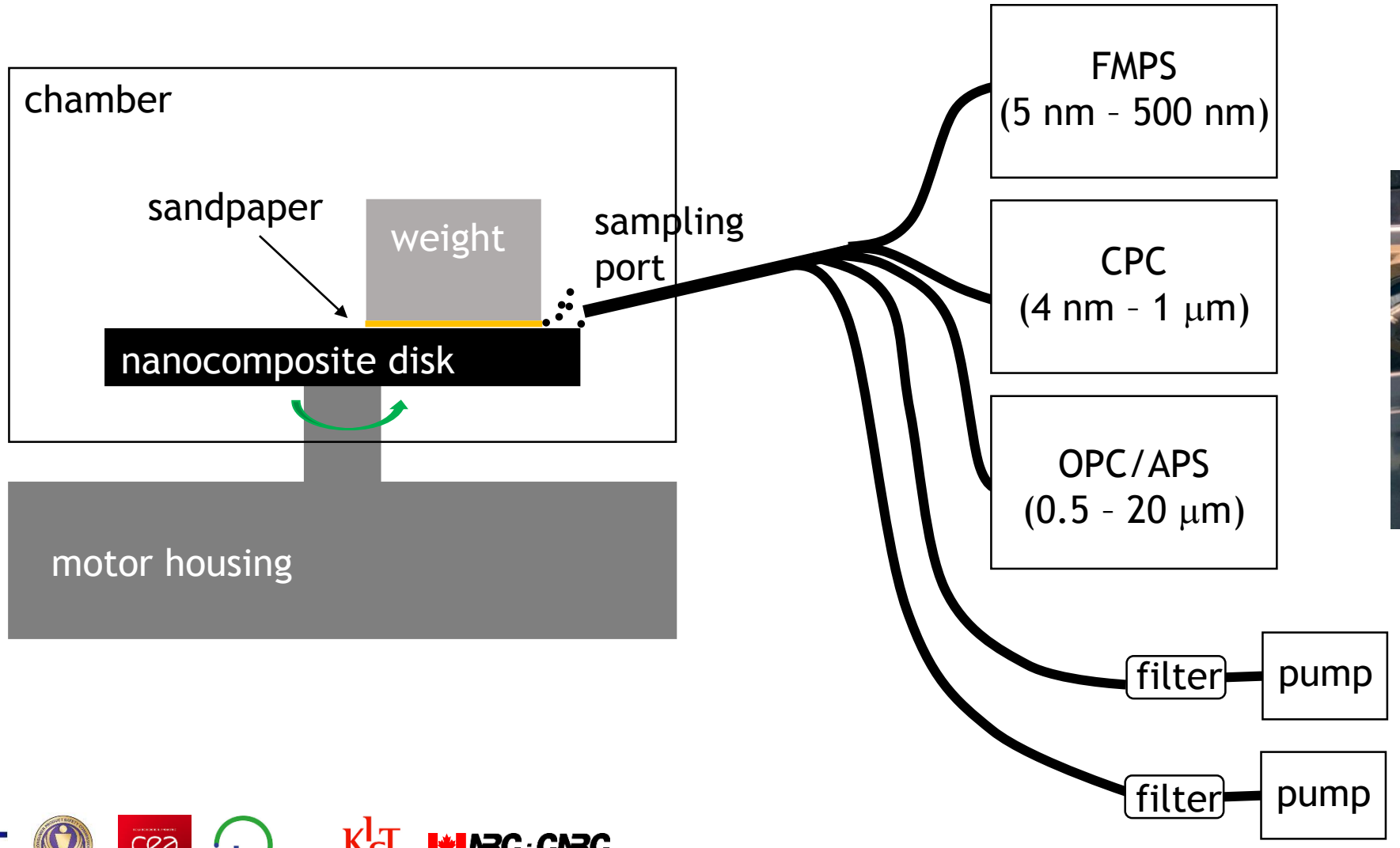
Develop a consensus protocol for generating and evaluating release particles from nanocomposite materials

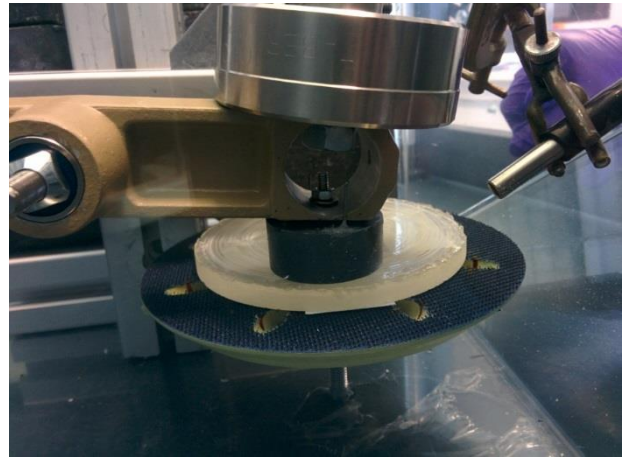
Approach

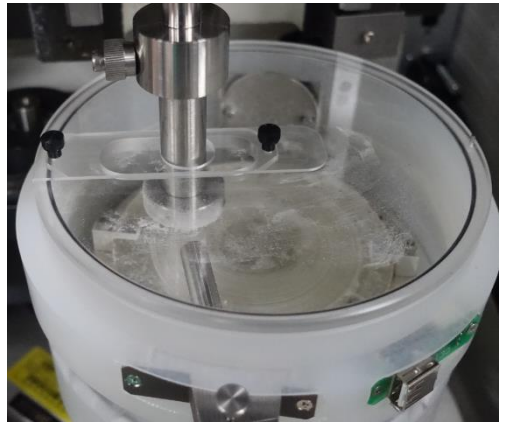
- Generate and sample release particles using three ‘equivalent’ processes using the same sample materials.
  - 3 sanding laboratories (L1, L2, L3)
  - Samples (neat epoxy, nanocomposite disks with mass fractions of 0.1 %, 0.25 % MWCNT)
  - Sandpaper (80 grit)

- Analyze release particles using real time particle analysis equipment and SEM imaging
  - FMPS, CPC, APS, OPC
  - 2 SEM analysis laboratories (A1, A2 plus self analysis by L3)

Sanding schematics

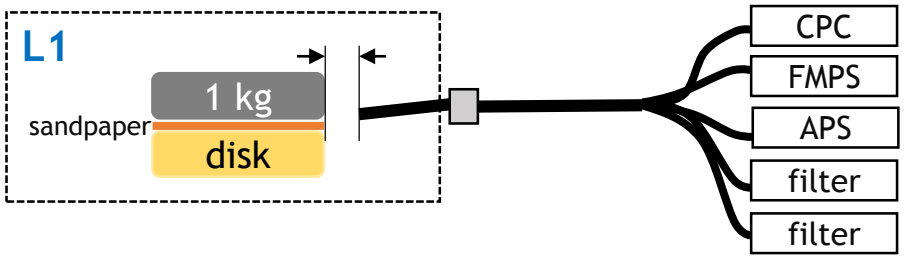


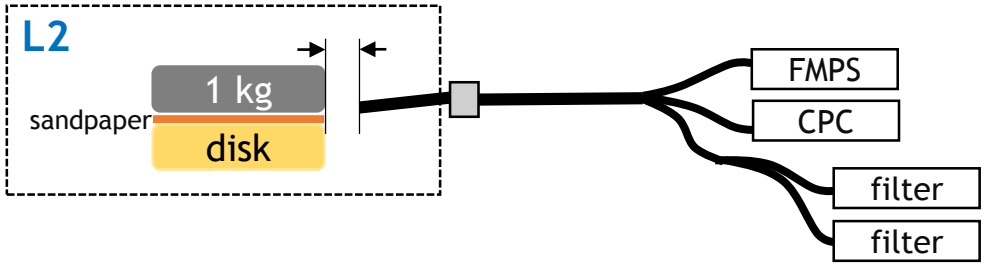


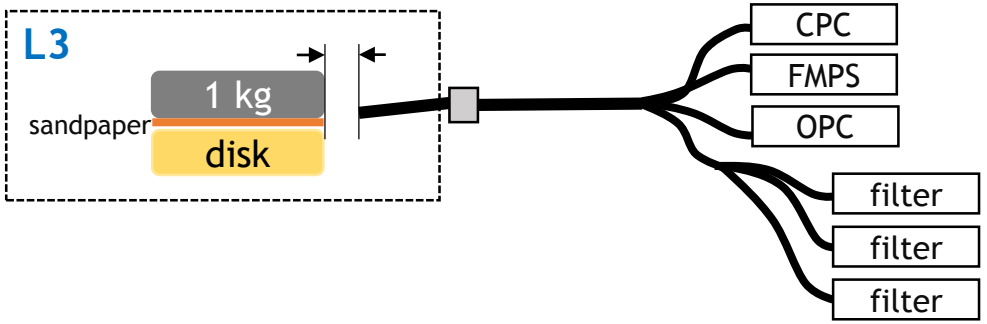


Sanding Setup

	L1	L2	L3
Chamber dimension	84,332.5 cm^3	27,000 cm^3	4,906.3 cm^3
Sampling Port Inner Diameter Sampling distance	Stainless Steel 6 mm 1 cm	Stainless Steel 6 mm 5 cm	Stainless Steel 9 mm 5 cm
Total tube length	***Varies!***		
Pre-separation (impactor)	Yes	Yes	No
CPC	0.3 L/min	0.3 L/min	1 L/min
FMPS	10 L/min	10 L/min	10 L/min
OPC/APS	APS, 1 L/min		OPC, 1.2 L/min
Filter	3 L/min	3 L/min	2 L/min





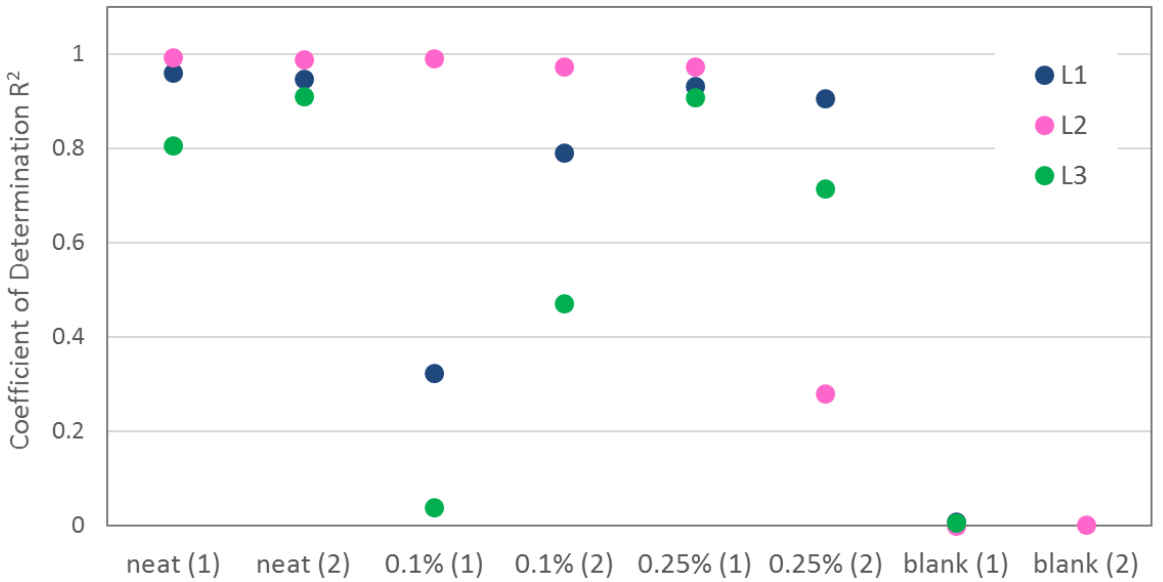


Temporal correlation of total concentration between FMPS and CPC

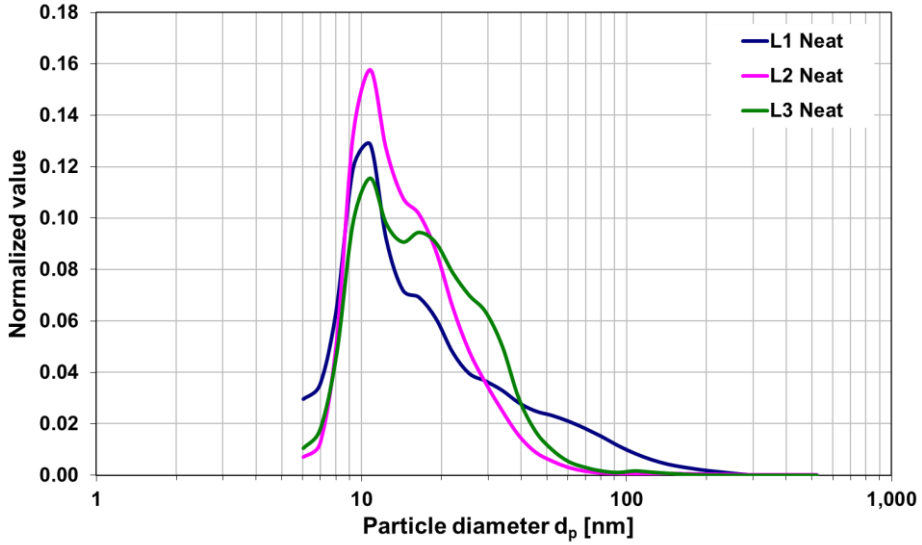
R^2	Neat epoxy rep 1	Neat epoxy rep 2	Epoxy 0.1% MWCNT rep 1	Epoxy 0.1% MWCNT rep 2	Epoxy 0.25% MWCNT rep 1	Epoxy 0.25% MWCNT rep 2	Method blank rep 1	Method blank rep 2	mean
L1	0.960	0.948	0.323	0.792	0.932	0.906	0.0077		0.810
L2	0.994	0.988	0.990	0.974	0.973	0.279	0.0003	0.0017	0.866
L3	0.806	0.911	0.040	0.472	0.909	0.715	0.0053		0.642

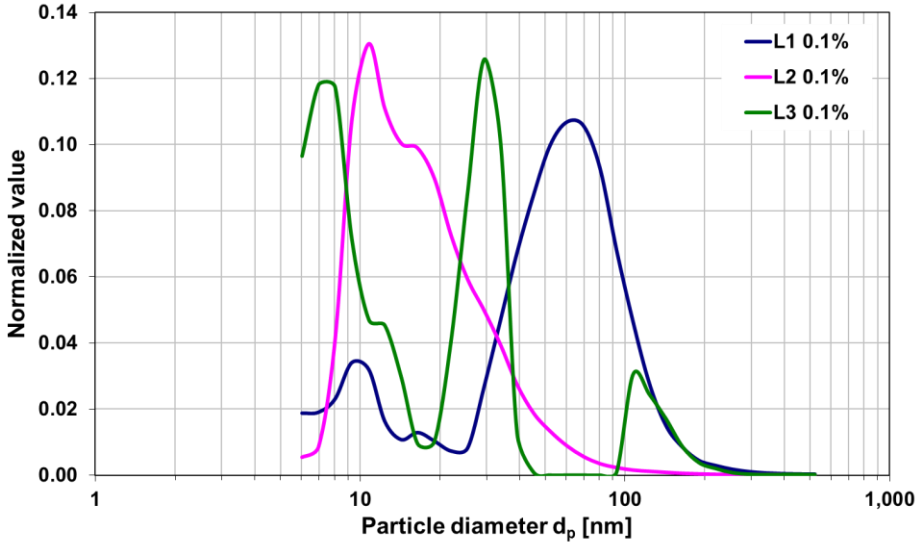
(mean without blanks)

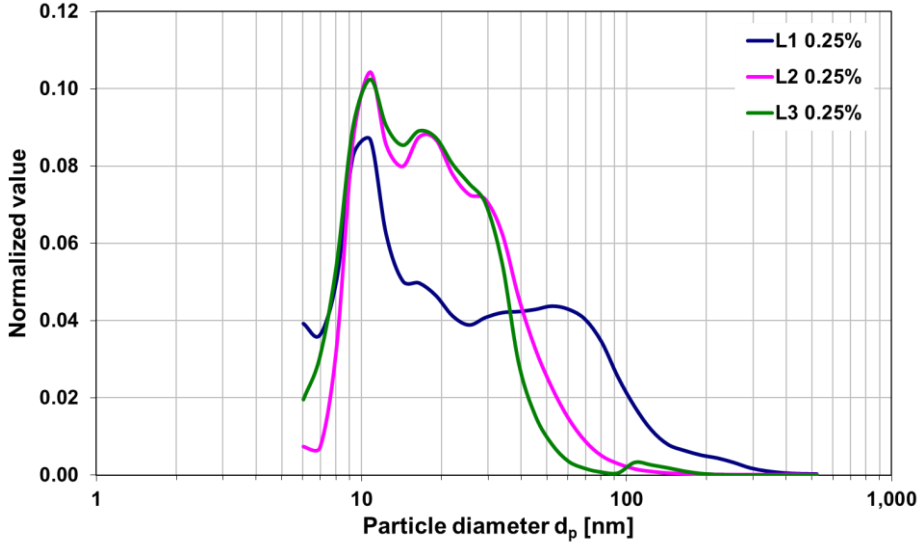
- Overall good FMPS & CPC temporal correlation for each run.
- Not expecting any correlation for blank runs.

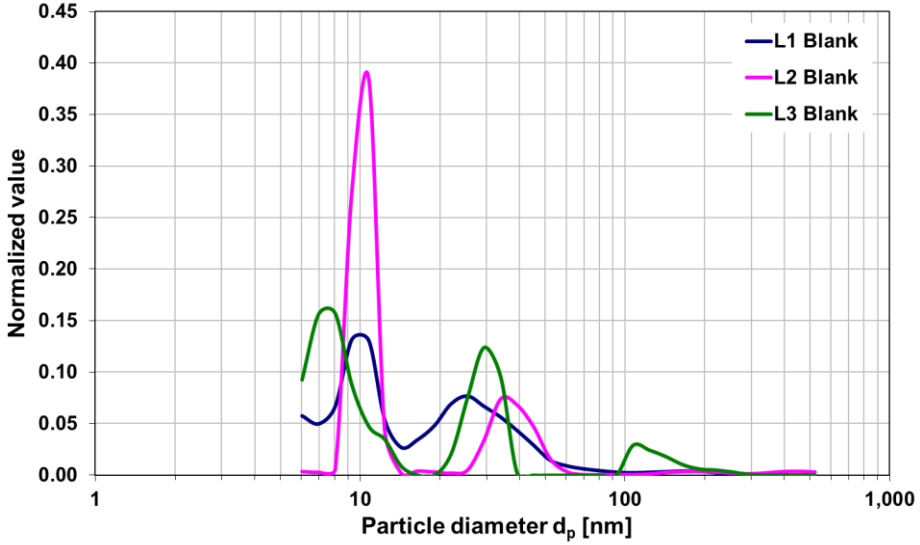


Normalized FMPS mean size distribution



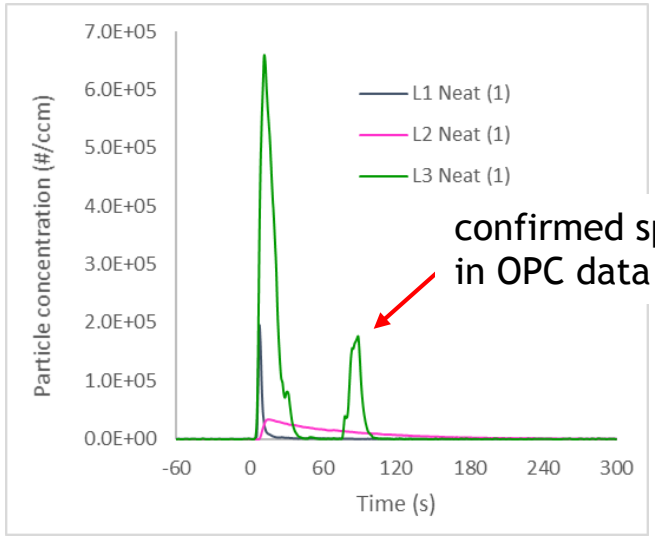


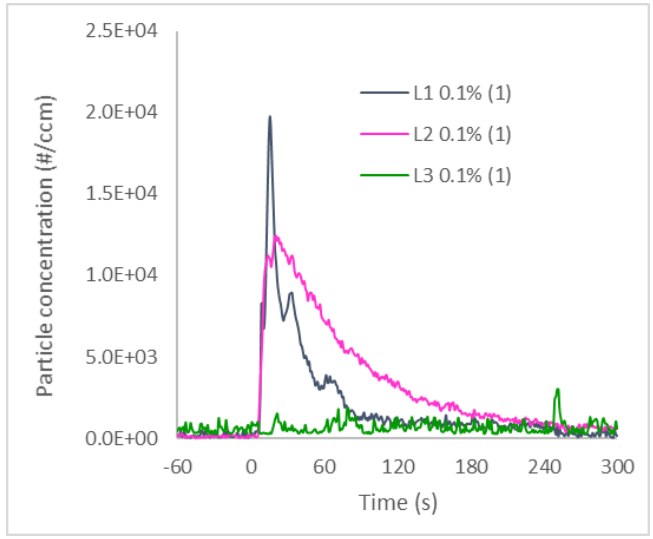


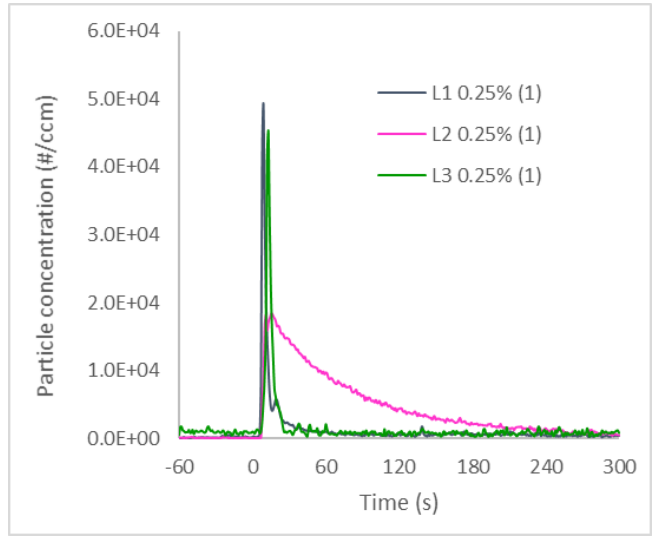


Time series FMPS total concentration

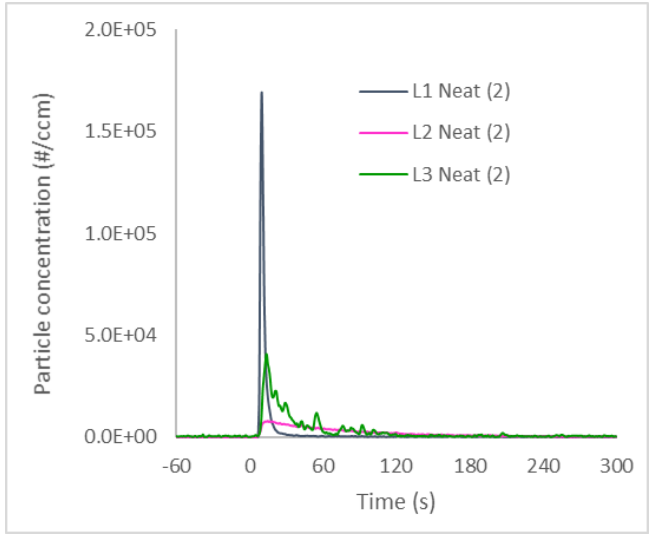
Replicate 1

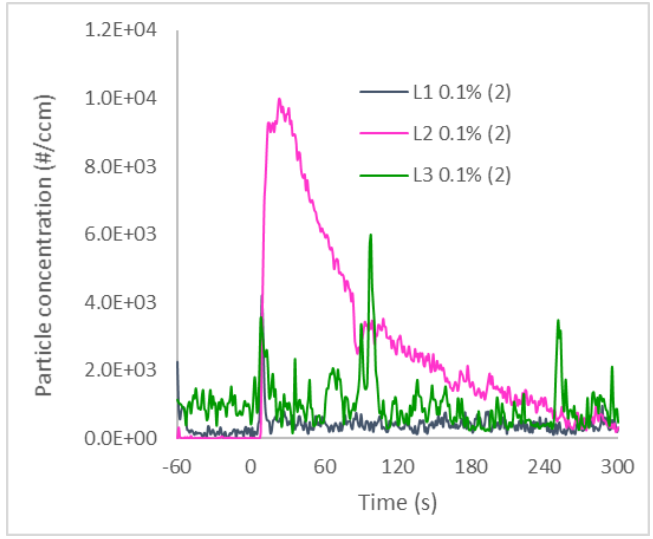


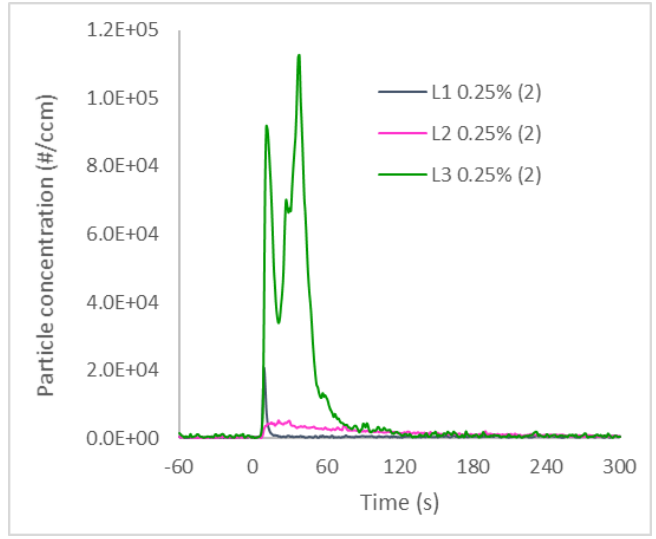




Replicate 2



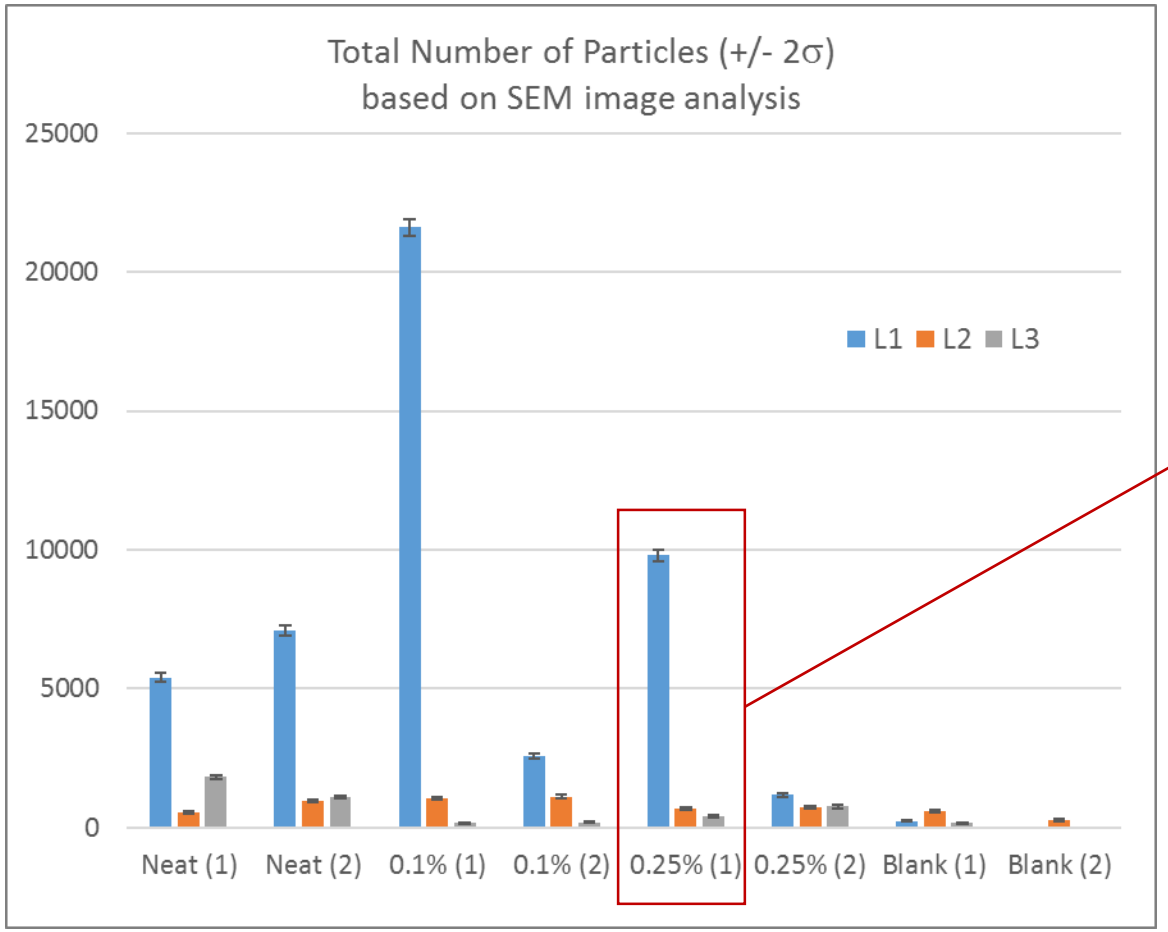




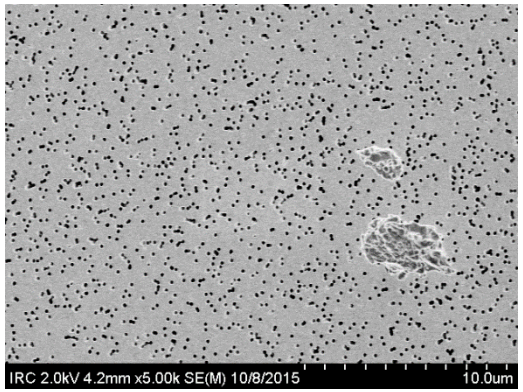
Data based on A1 Lab image dataset

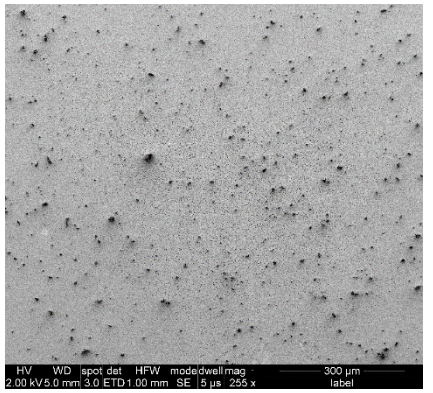
SEM analysis of filters

Limited to 500 nm to 20 μm
(comparable to OPC or APS measurement range)

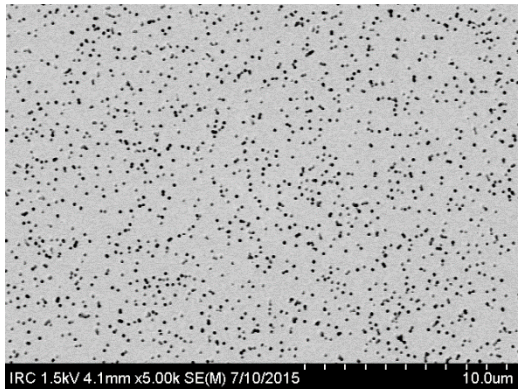


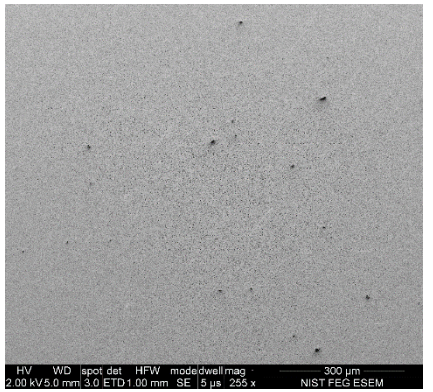
L1



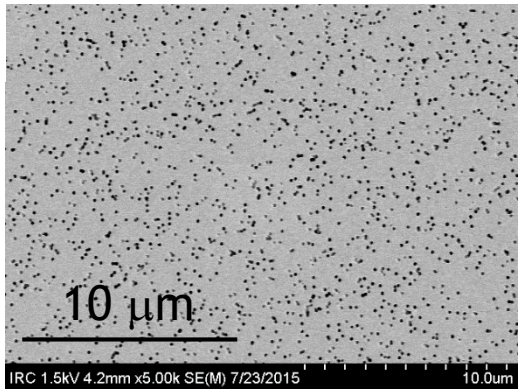


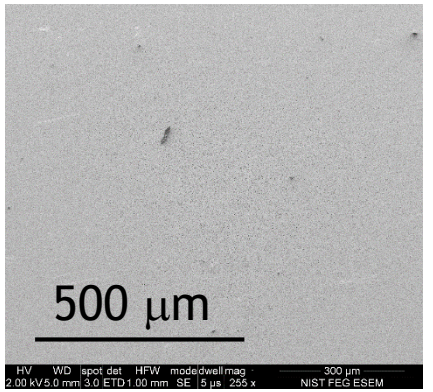
L2





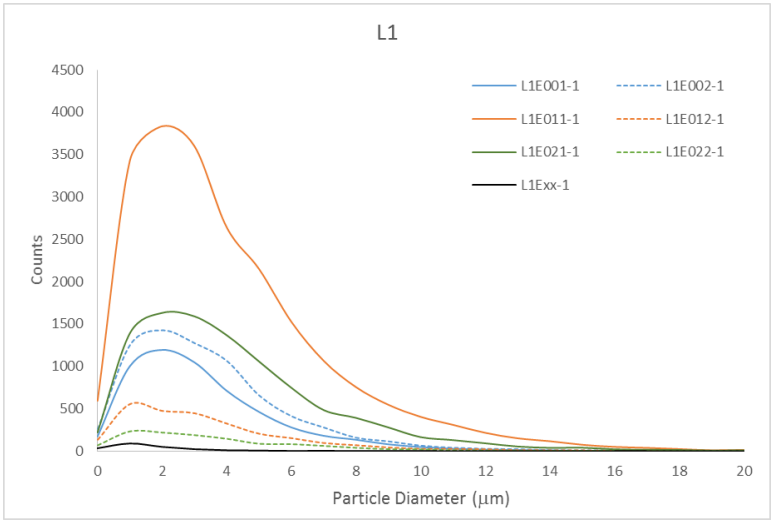
L3

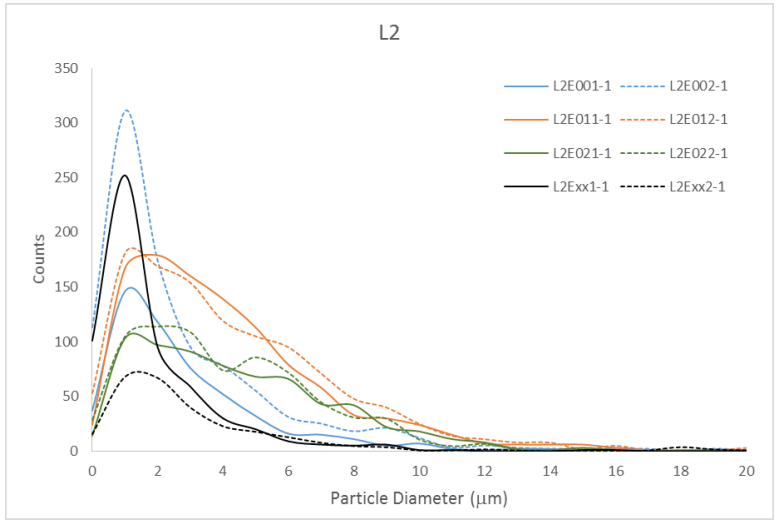


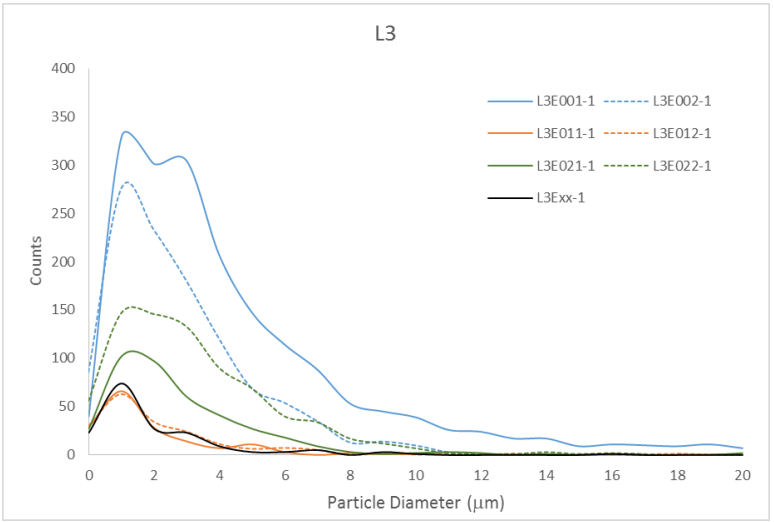


Particle size distributions from SEM image analysis: intra-lab

Particle diameter = equivalent area diameter





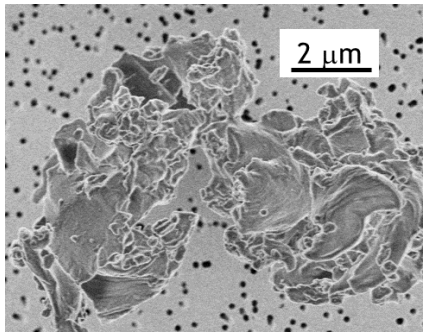


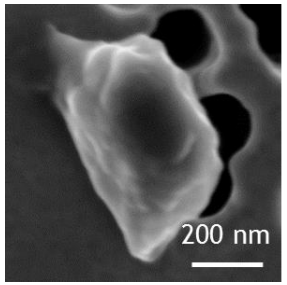
neat epoxy

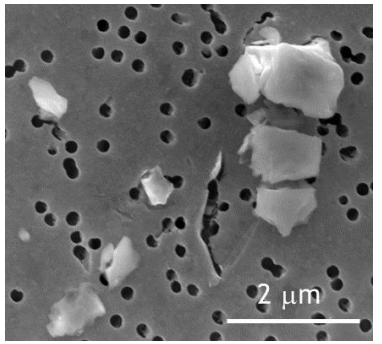
0.1 % MWCNT

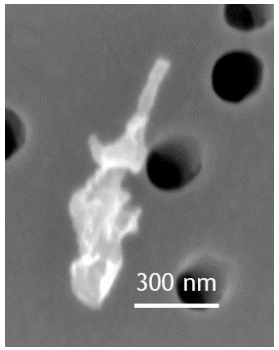
0.25 % MWCNT

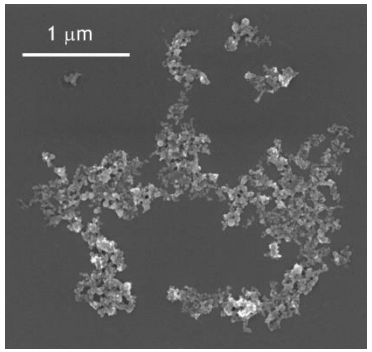
blank

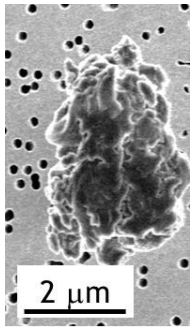






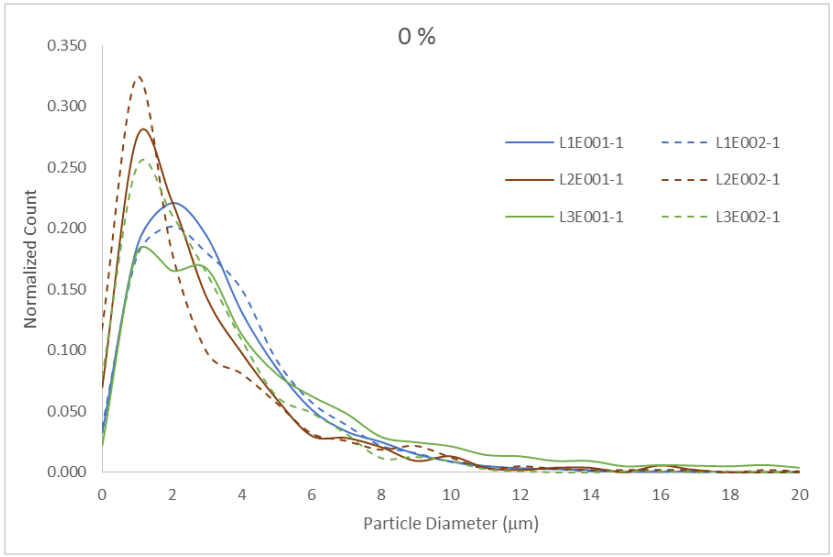


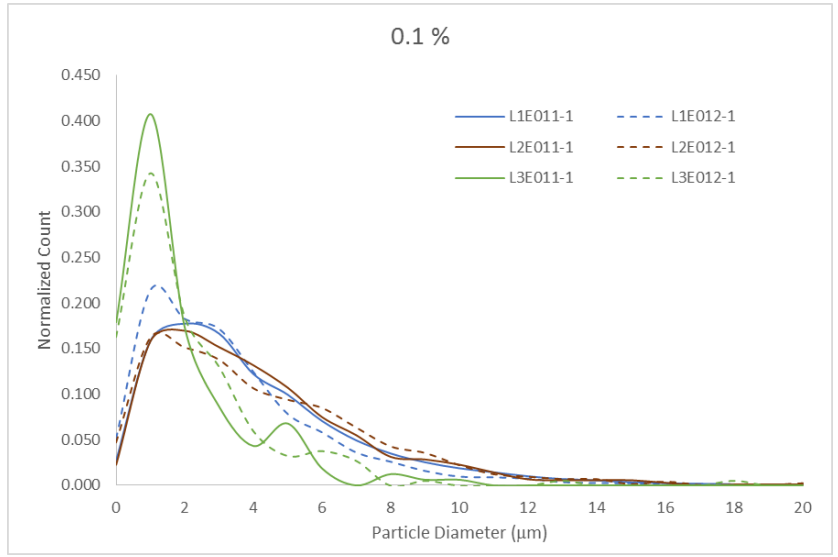


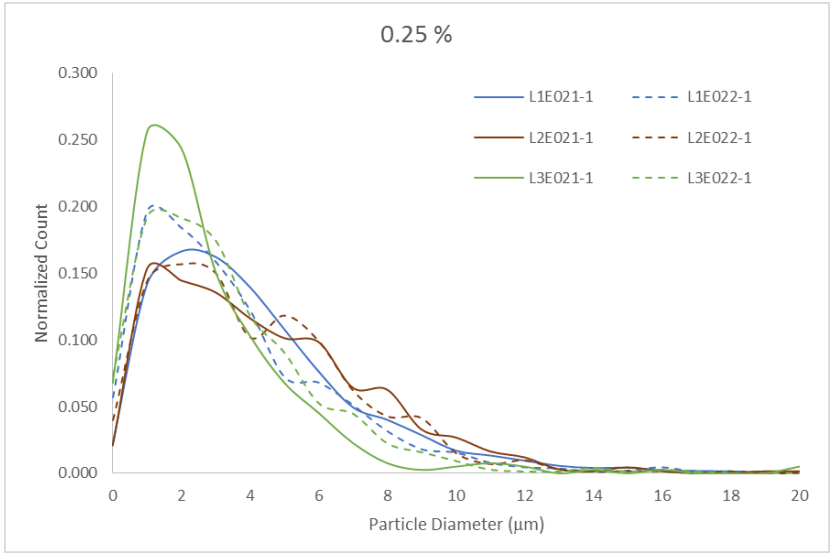


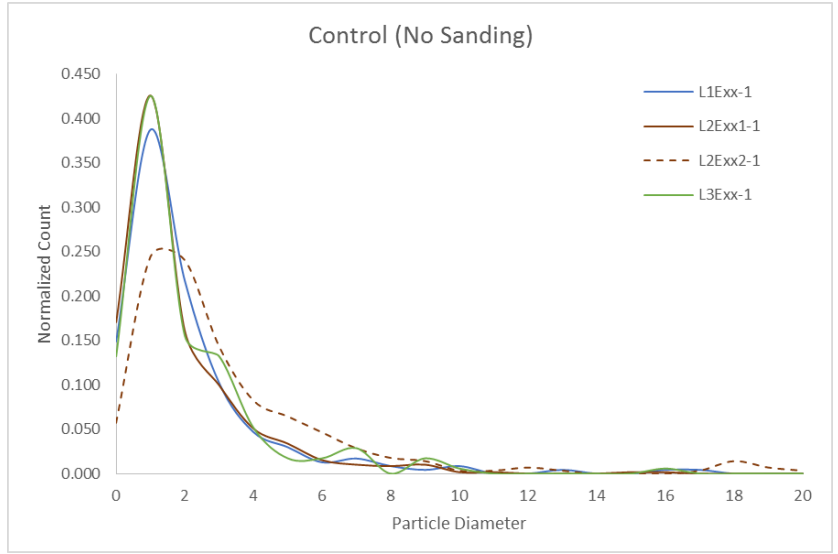
Particle size distributions from SEM image analysis: inter-lab

- Normalized counts for lab to lab size distribution comparison
- Most particles under 10 μm in diameter

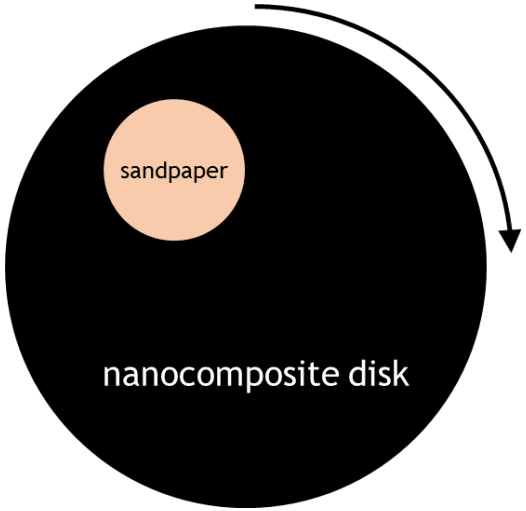


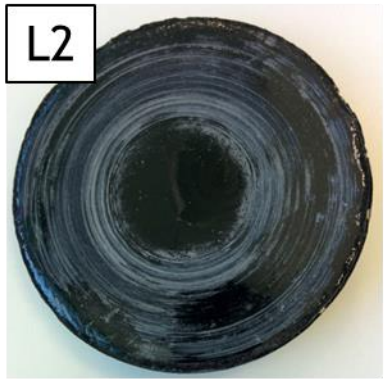


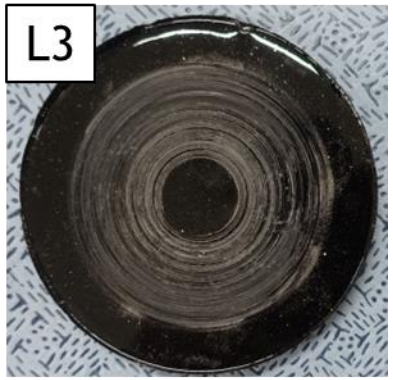




Summary of metadata







nanocomposite sample
0.1 % MWCNT

sand paper

- Sanding area and sand paper contact area vary from lab to lab.
- Intra-lab contact patterns are consistent.
- No clear correlation between sample and sand paper conditions and total particle concentration.

Summary (what worked & what didn't)

- Demonstrated successful organization and execution of a pilot nano-release study based on a "consensus protocol"
- Particle concentration data consistent across analytical methods
  - Ultrafine particles: 10 nm – 50 nm and most under 100 nm.
  - Fine/coarse particles: 500 nm to 10 μm.
- Good intra-lab temporal correlation between techniques
- Generated particle samples are consistent
- Instrumentations and test set-ups are generally applicable

- Inter-lab particle concentration and temporal correlation was poor
- Significant run to run variations in particle counts
- Relatively high blank filter particle count
- Poor filter collection efficiency for ultrafine particles
- Significant imaging and image processing challenges for ultrafine particles
- Sanding paper/sample photos show noticeable differences

Recommendations

Sanding testing is feasible & important

for risk assessment/safer-by-design approaches

but harmonization is urgently needed!

- a highly specified consensus sanding protocol based on a robust and statistically meaningful experimental design
- multiple analytical methods for consistency checks and method validation
- multiple substrates (e.g., filters & Si wafers) for particle sampling
- better experimental hygiene
- rigorous meta data collection

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BASF (sanding supplies)

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NIST Disclaimer

Certain commercial equipment, instruments, or materials are identified in this talk to foster understanding. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

CPSC Disclaimer

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NanoRelease

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- Health Canada
- US Environmental Protection Agency
- ILSI Research Foundation.
- American Cleaning Institute
- Society of Organic Chemical Manufacturers and Affiliates
- Adhesives and Sealant Council

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Terms & Abbreviations

APS: Aerodynamic Particle Sizer

CPC: Condensation Particle Counter

FMPS: Fast Mobility Particle Sizer

ILSI: International Life Sciences Institute

MWCNT: Multiwalled Carbon Nanotube

OPC: Optical Particle Counter

SEM: Scanning Electron Microscope

%: mass fraction of MWCNT