Exposures to Nanoparticles and Fibers during Manufacturing and Recycling of Polycarbonate Carbon Nanotube (PC-CNT) Composites

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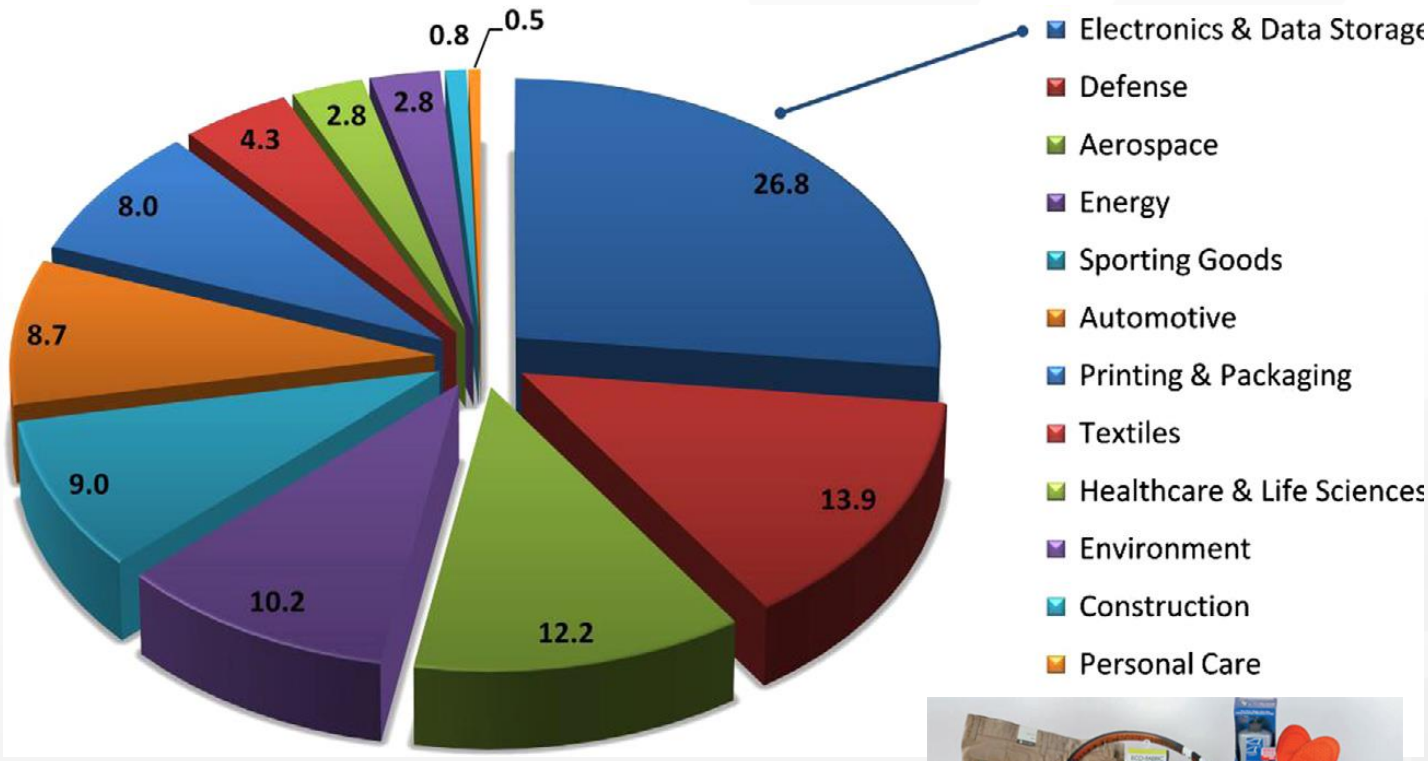
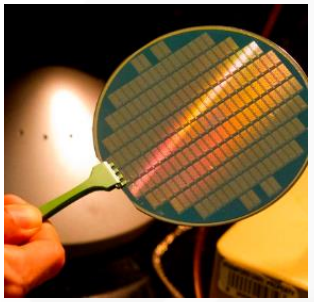
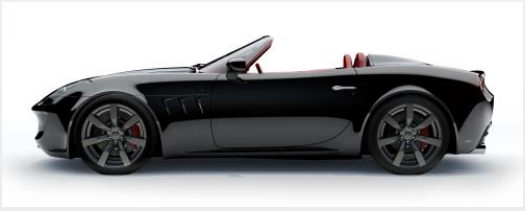
Global CNT demand by application





Ref. : Nanoposts.com. The global market for carbon nanotubes to 2015: a realistic assessment. Available from: http://www.reportbuyer.com/publishers/2961/nanoposts.html.



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Why we care about CNTs…

NIOSH REL:
1ug/m^3 as EC

BSI, 0.01 f/c

IARC
- MWCNT-7
- Others, C

CNTs are NOT a single entity. They represent a diverse class of materials with different physicochemical and morphological (PCM) and toxicological properties. Intentional or incidental modifications of such PCM properties may have a profound impact on their intrinsic hazard.

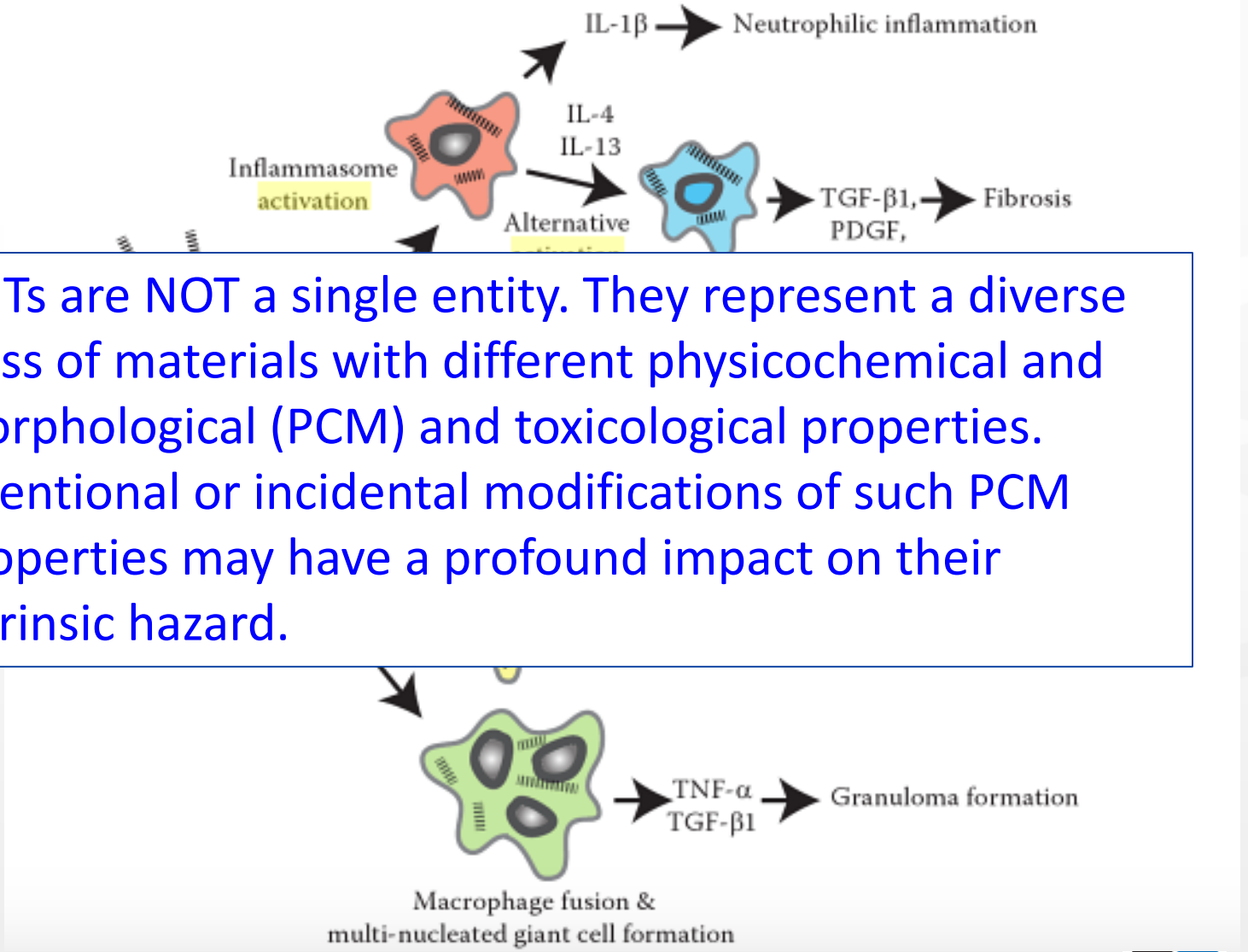
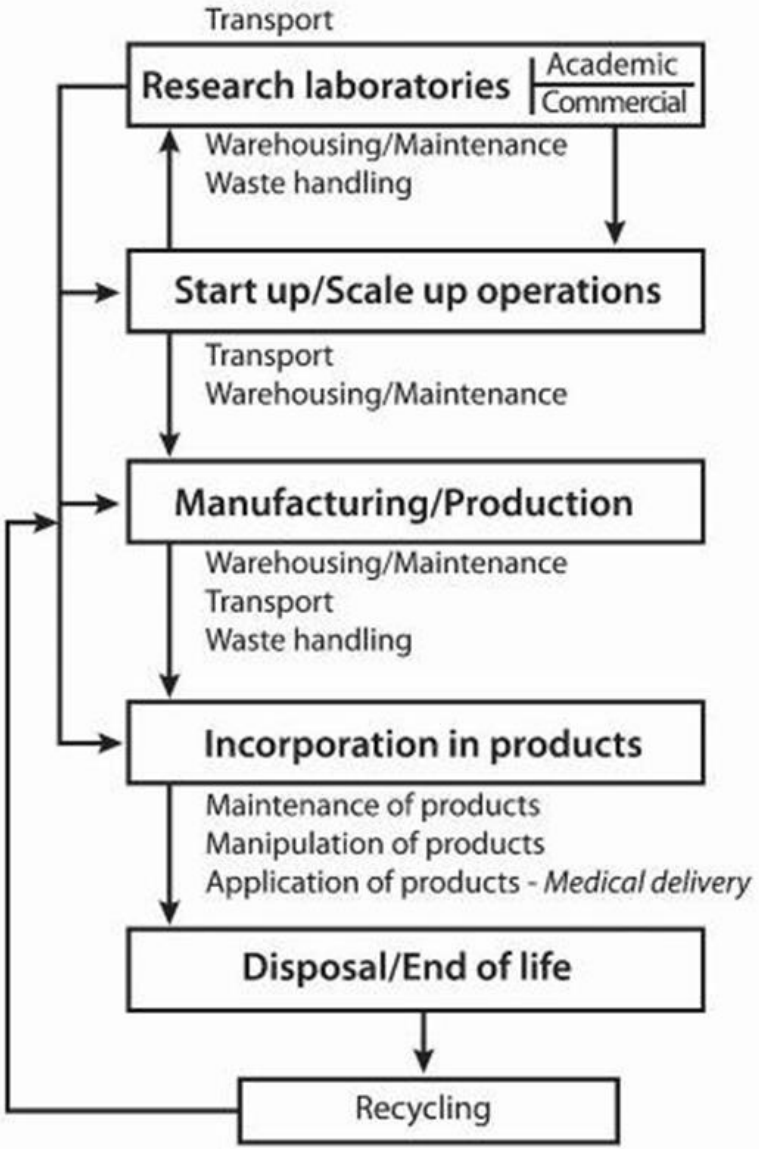
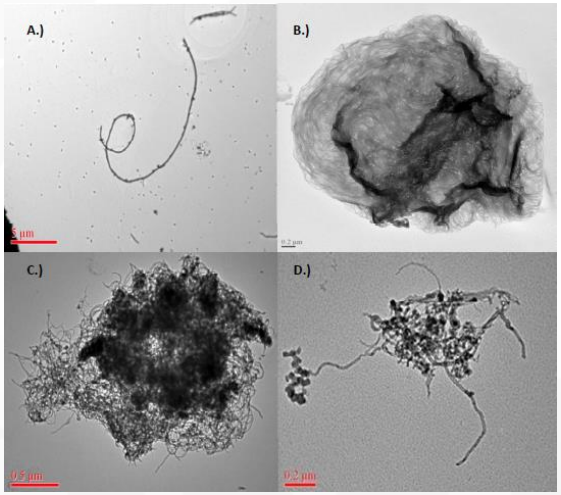


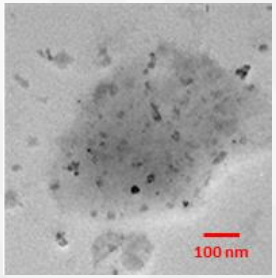
Figure 10.3 Bohner J. pg 218; In: Wohlleben et al edit's, 2015

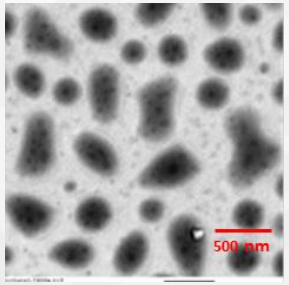
Where could exposures (to CNTs) occur?

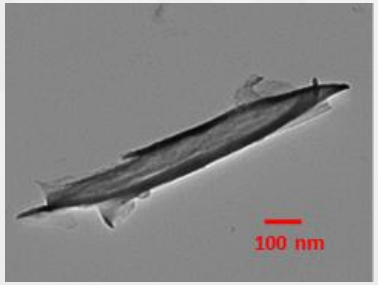


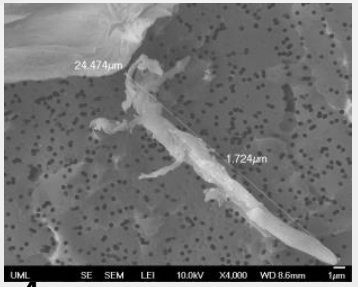


M. Dahm, NIOSH





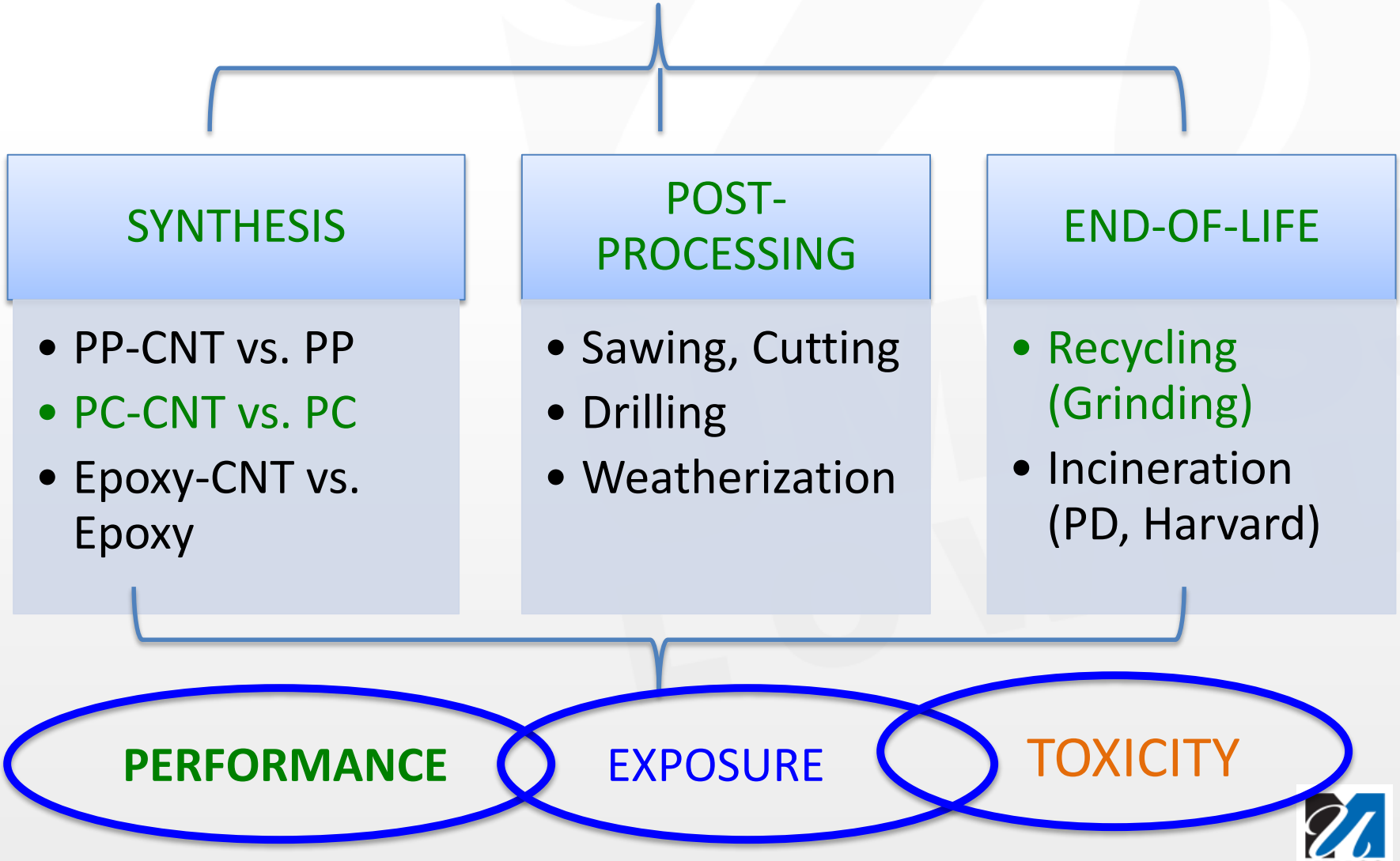




Schulte P et al., 2009: Occupational risk management of engineered nanoparticles.

Project Overview

CNT-COMPOSITES ALONG THEIR LIFE CYCLE



OBJECTIVES

- Assess Airborne NP and CNT exposures:
  - Injection molding (IM) of PC-CNT & PC Composites
  - Grinding (for recycling)

- Evaluate the impact of recycling on emissions

Process diagram and sampling locations

(A) Loading

(B) Melting

(C) Molding

(D) Grinding #1, 2

Masterbatch PC/CNT 15 wt %

PC

Base material PC/CNT 3 wt %

Injection/Molding Process

Sample parts + Scraps

Grinding #1 Coarse fragments

Grinding #2 Fine fragments

n=20

No

Yes

Stop

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Methods

Instrumentation

Real time Characterization

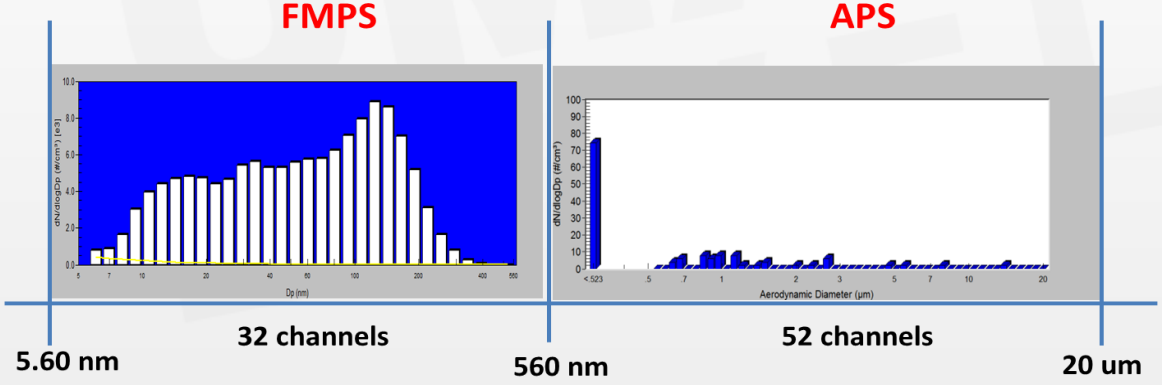
Integrated Sampling off-line Characterization

Number Concentration FMPS, APS (p/cm^3)

Size distribution FMPS, APS (dN/dLogDp, p/cm^3)

FMPS

APS



Learning with Purpose

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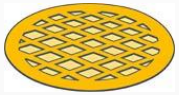
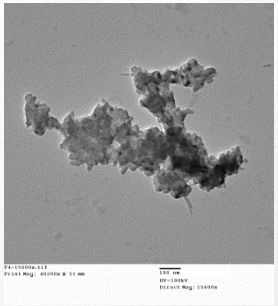
Methods

Instrumentation

- **Real time Characterization**
- **Integrated Sampling off-line Characterization**

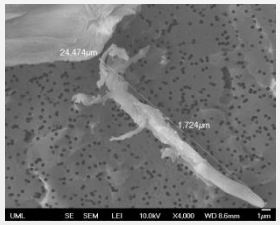


200-mesh Cu with C film



Morphology (source)
ESP → TEM

Nucleopore, 0.4 um



Morphology (BZ) and Fiber count
Filters → SEM

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TPNC Emissions: Injection Molding

Area / Task	n	Total particle (x 10^3 p/cm^3)[a]			P/B ratio[b]	Trend test (p-value)[c]
		GM	GSD	Max		
Loading						
PC/CNT-00R	300	12.6	1.02	43.5	1.1	
PC/CNT-05R	300	11.7	1.01	13.5	1.1	
PC/CNT-10R	300	4.7	1.01	5.7	1.1	
PC/CNT-15R	300	12.4	1.03	70.9	1.3	
PC/CNT-20R	300	7.8	1.01	9.4	1.2	0.1088
Melting						
PC/CNT-00R	900	19.7	1.05	941.0	1.7	
PC/CNT-05R	900	16.4	1.05	458.0	1.6	
PC/CNT-10R	900	5.0	1.02	90.1	1.1	
PC/CNT-15R	900	11.7	1.03	300.0	1.2	
PC/CNT-20R	900	11.9	1.02	69.9	1.9	0.3080
Molding						
PC/CNT-00R	900	12.5	1.01	48.7	1.1	
PC/CNT-05R	900	11.6	1.02	74.2	1.1	
PC/CNT-10R	900	5.0	1.01	11.2	1.1	
PC/CNT-15R	900	10.6	1.02	38.4	1.1	
PC/CNT-20R	900	9.1	1.01	29.8	1.4	0.2809

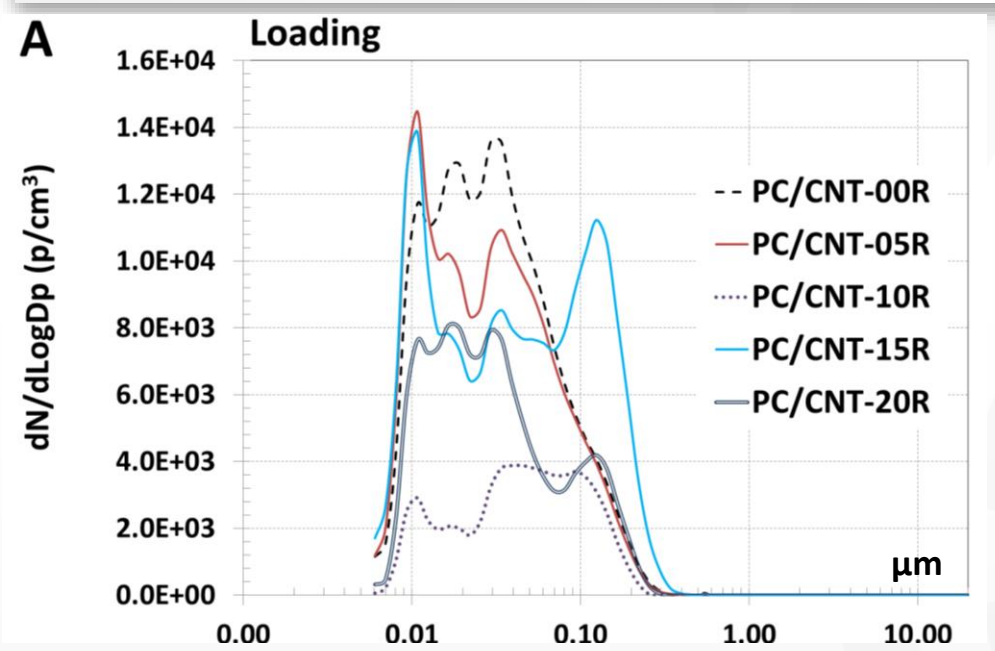
[a] Raw data (log transformed) for reporting GM, GSD; P/B ratio = Process/background ratio of (GM, particles/cm3); [b] Statistically significantly higher than background ($p < 0.05$), calculated from AUTOREG procedure in SAS; [c] p-value calculated from the linear trend weighted GM of background and S.E.

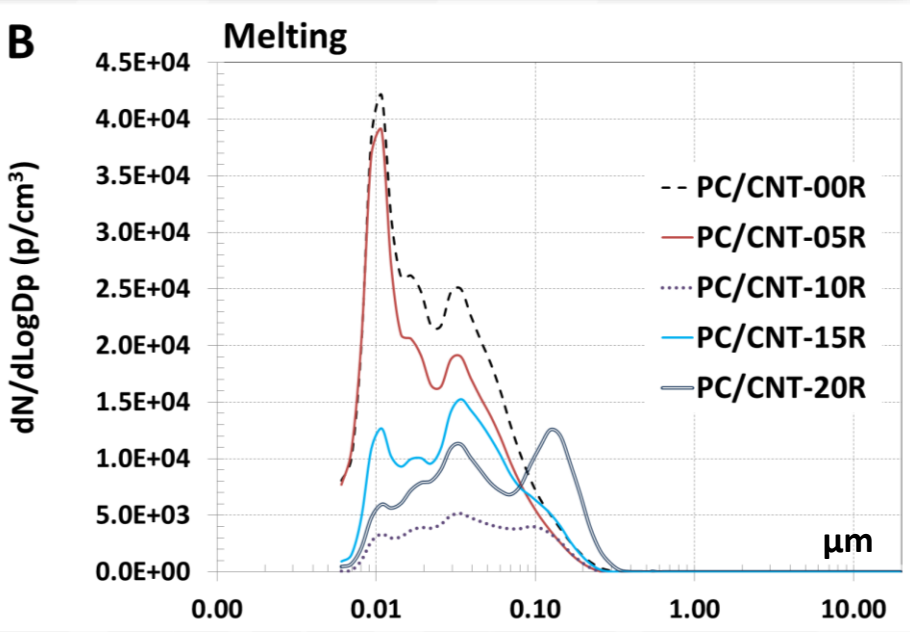
TPNC Emissions: Grinding

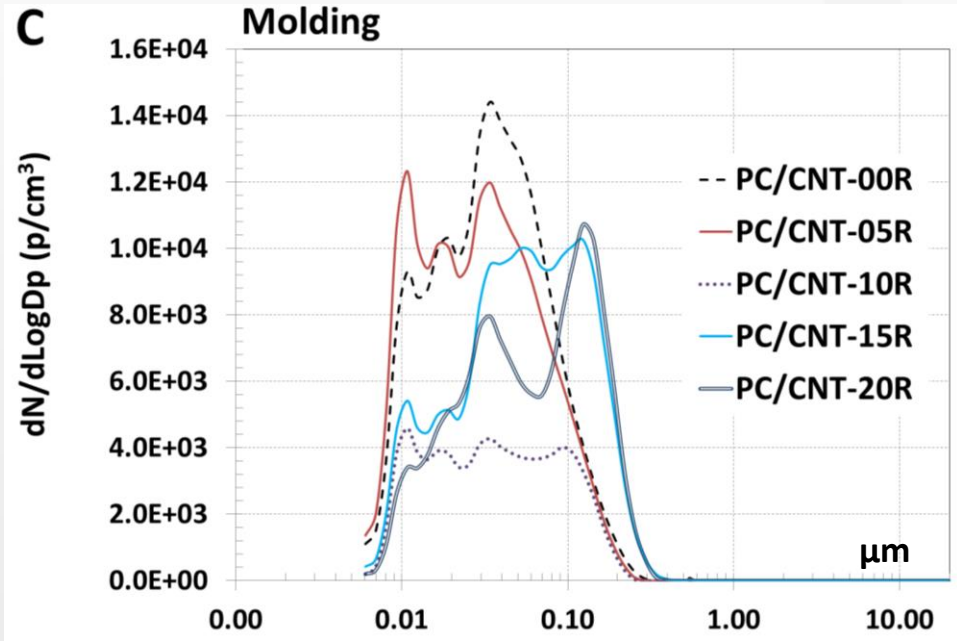
Area / Task	n	Total particle ($\times 10^3$ p/cm^3)[a]			P/B ratio[b]	Trend test (p-value)[c]
		GM	GSD	Max		
Grinding #1						
PC/CNT-00R	300	1665.6	1.09	5320	92.6	
PC/CNT-05R	300	477.9	1.20	8320	82.4	
PC/CNT-10R	300	194.7	1.22	6330	36.8	
PC/CNT-15R	300	290.5	1.22	5420	40.9	
PC/CNT-20R	300	92.9	1.18	4890	12.0	0.9381
Grinding #2						
PC/CNT-00R	900	1341.1	1.09	4380	74.6	
PC/CNT-05R	900	139.9	1.17	1630	24.1	
PC/CNT-10R	900	363.8	1.10	1640	68.7	
PC/CNT-15R	900	300.8	1.09	909	42.4	
PC/CNT-20R	900	142.9	1.08	1130	18.5	0.3088

[a] Raw data (log transformed) for reporting GM, GSD; P/B ratio = Process/background ratio of (GM, particles/cm3); [b] Statistically significantly higher than background ($p < 0.05$), calculated from AUTOREG procedure in SAS; [c] p-value calculated from the linear trend weighted GM of background and S.E.

Particle size distribution: Injection Molding (IM)

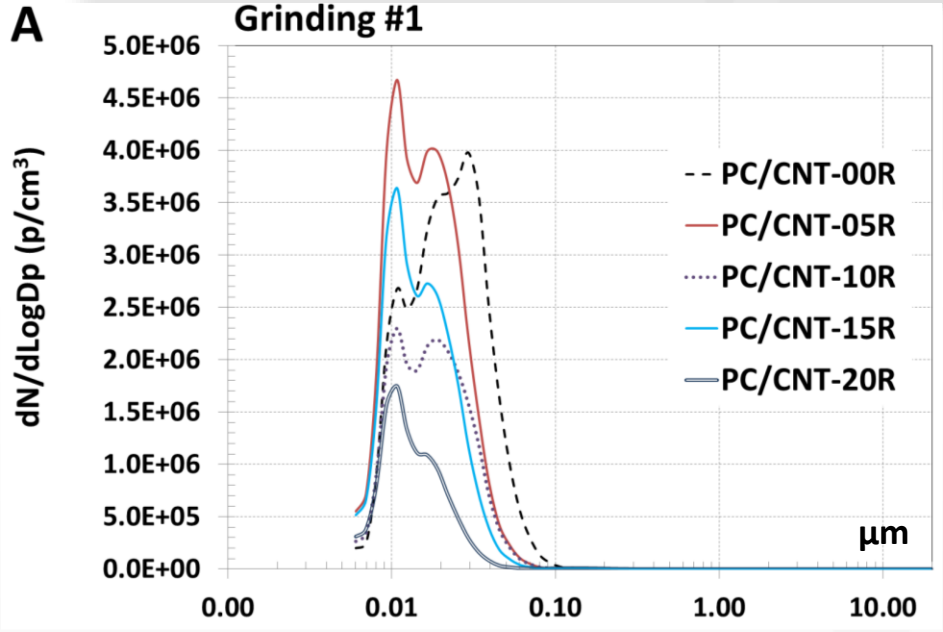


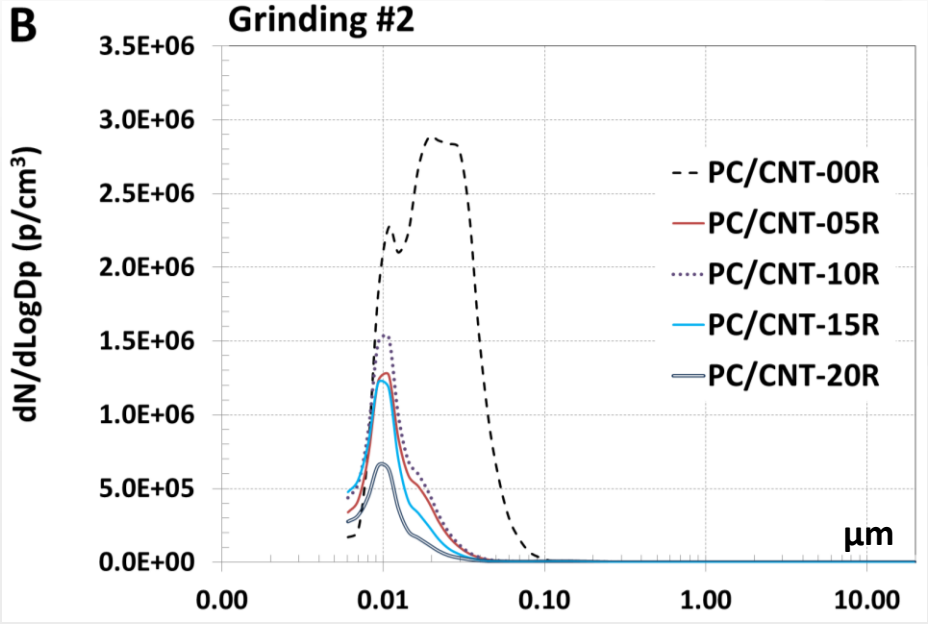




- Predominantly NPs (5.6 nm -0.56 µm)
- Multimodal - (coagulation + process differences)
- Limited influence by recycling #, R
- Fine PM fraction was negligeable
- SVOCs – condensation nano aerosols

Particle size distribution: Grinding





- Dominated by NPs (5.6 nm - 0.56 µm).
- Bimodal distributions – 10 nm and 30 nm
- Grinder influences SD (grinder #1 –coarse powder)
- Limited impact of recycling number R on SD
- Fine PM present, but low (~1 µm, <30 p/cm³)

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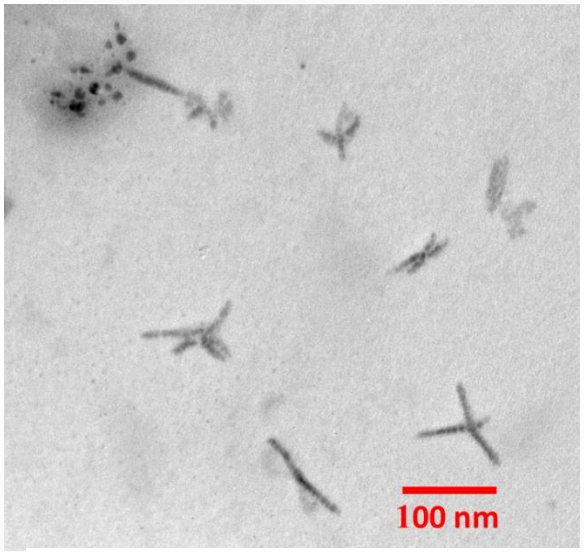
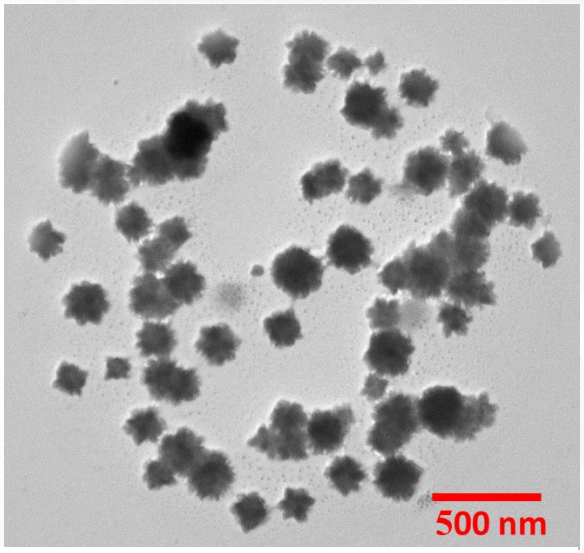
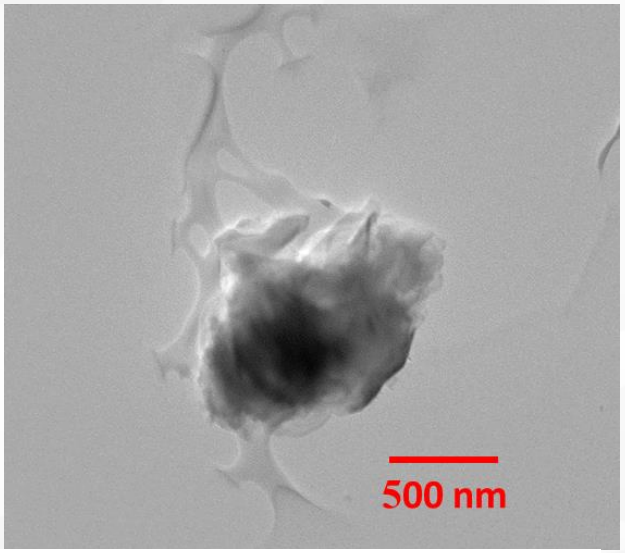
TEM Particle Morphology



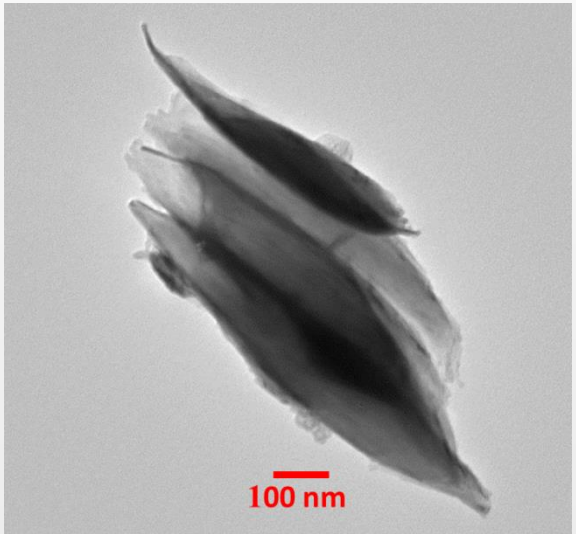
Loading

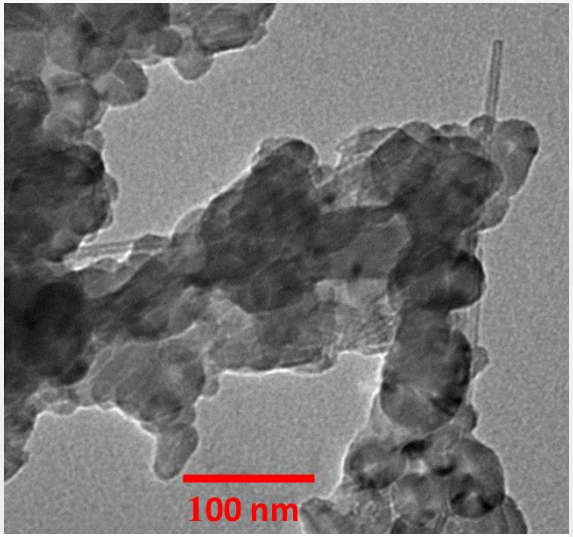


Melting

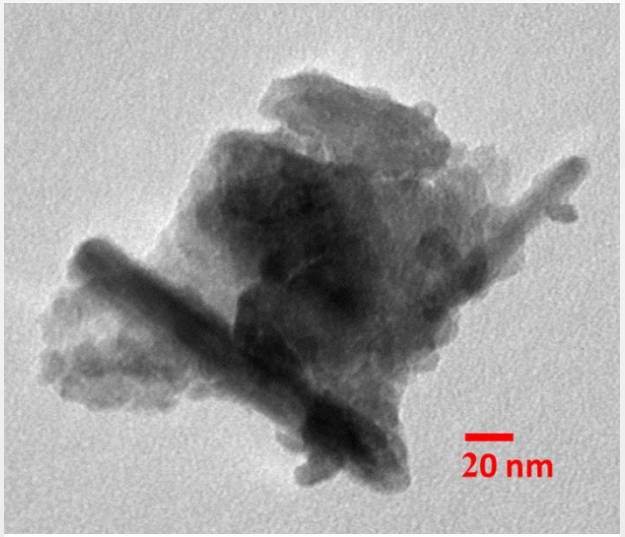


Molding



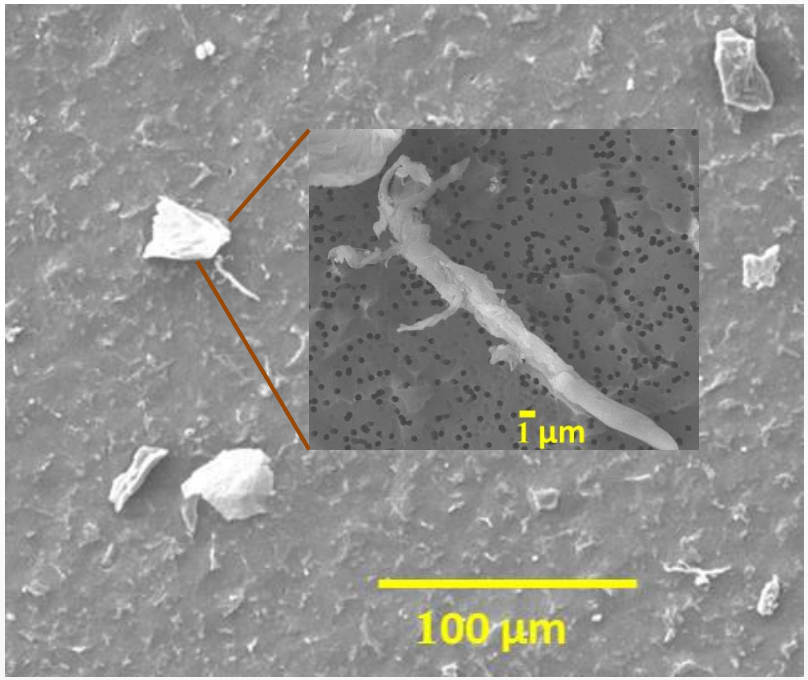


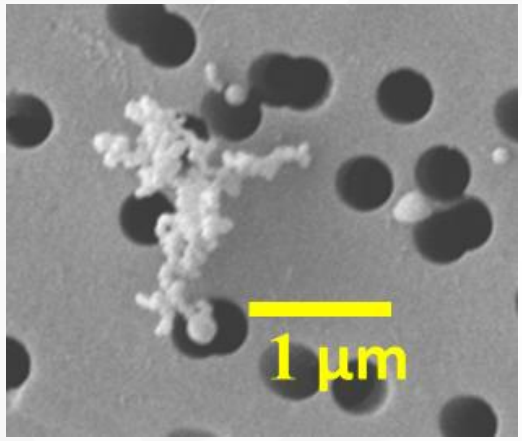
Grinding #1

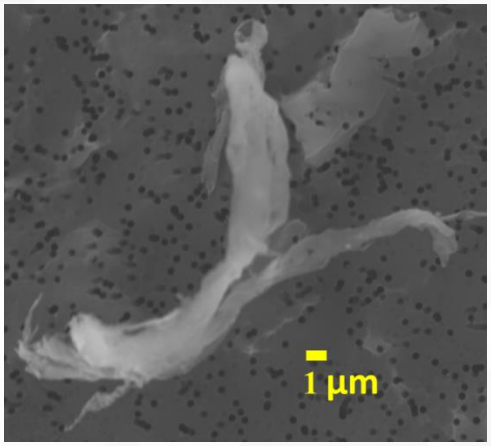


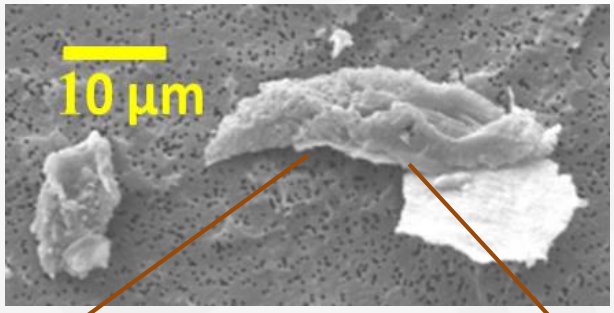
Grinding #2

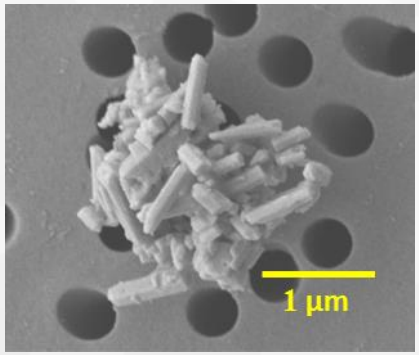
Particle morphology at PBZ during Grinding

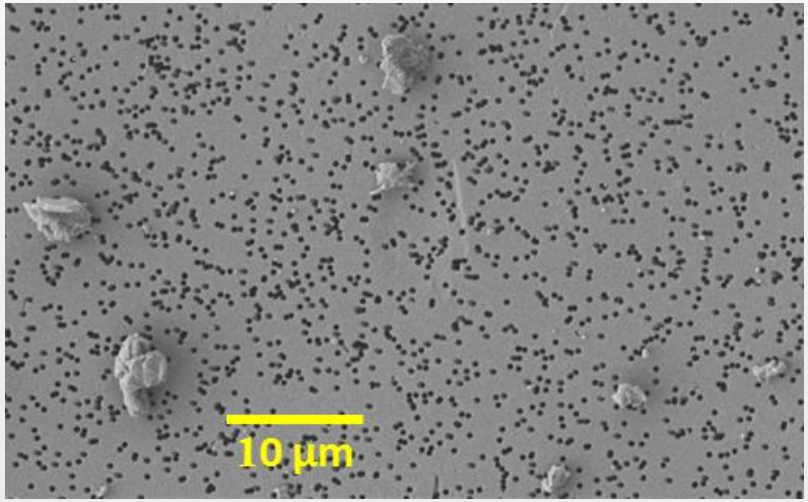


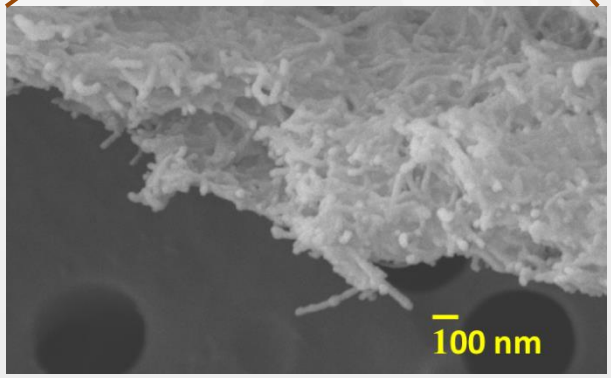


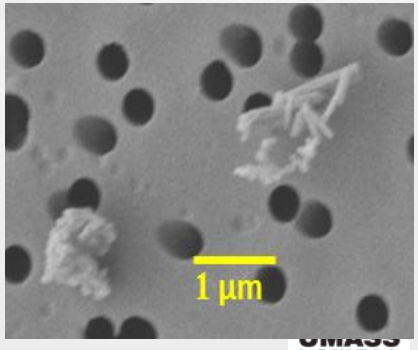




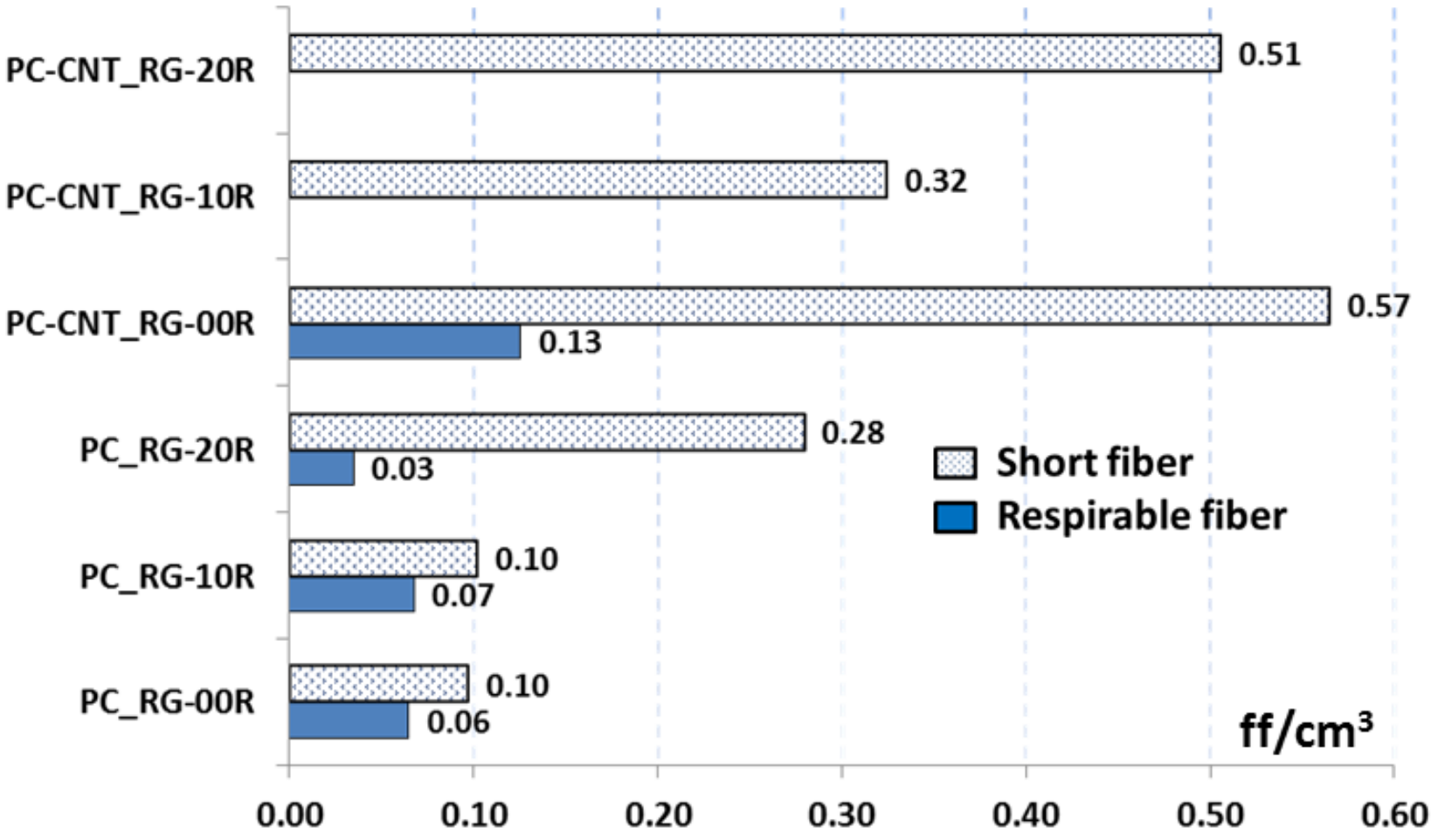








Respirable Fibers at the PBZ During Grinding



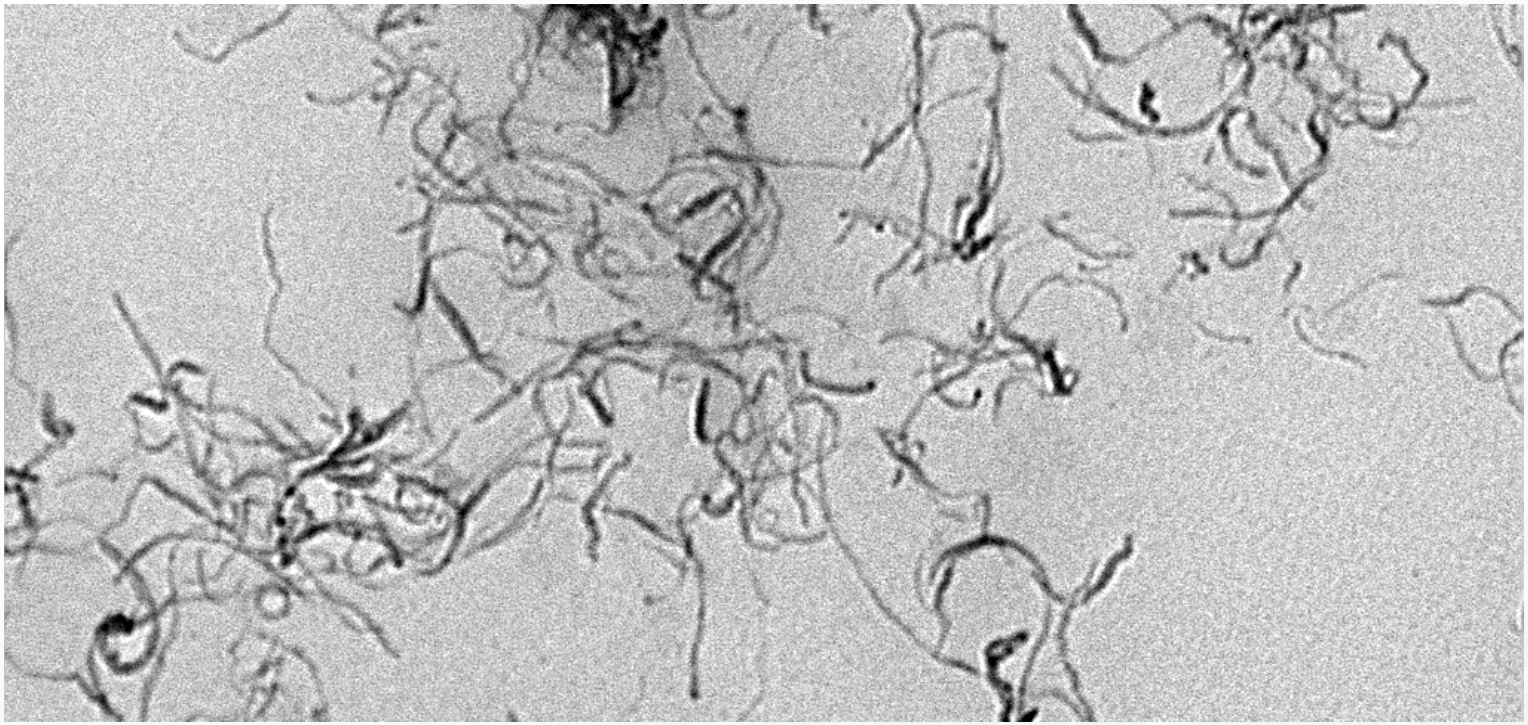
Respirable fibers are defined as having an aspect ratio ≥3:1, a diameter < 3 µm, and length > 5 µm; Short fibers are defined as having an aspect ratio ≥3:1, a diameter < 3 µm, and a length ≤ 5 µm.

Conclusions

- Processing and grinding of PC/CNT composite generate significant airborne NPs, up 100x above background (Grinding)
- No free CNTs were released
- Respirable fibers (0.13 ff/ cm^3) & CNT protrusions
- R (# recycling cycles) did not appear to significantly influence NPs exposures – understandable
- Exposure controls should be instituted during synthesis and processing of PC/CNT
- Further research is needed to elucidate the chemical composition of NPs, CNT content encapsulated in airborne particle and their toxicological properties

Acknowledgement

- NSF grants 120329 and 0425826
- Dr. Arthur Miller, NIOSH
  for the ESP
- Dr. Earl Ada of UML
  material Characterization laboratory
  for the supervisions of TEM and SEM
  analysis



Thank You for Your Attention!

Questions?

Dhimiter_Bello@uml.edu

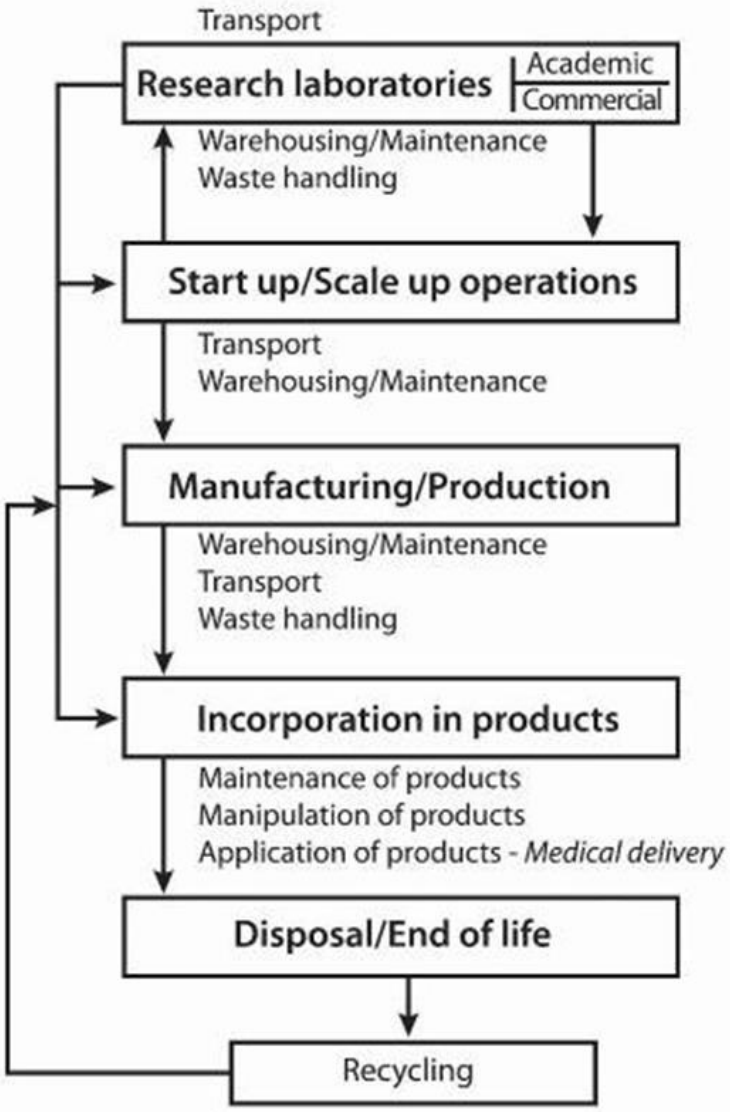
CNTs and Health Concerns

- Critical effects of CNT include:
  - pulmonary inflammation, pulmonary fibrosis and granulomas (high respect ratio)
  - Genotoxicity (mutations and DNA damage)
  - Carcinogenicity (mesothelioma, needle-like shape)
  - Oxidative stress

  (Lam et al., 2006; Aschberger et al, 2010; Liu et al., 2012)

- Changing parameters of CNTs such as shape, charge, solubility, surface chemistry, aggregation results in very different toxicologic response (Wick et al., 2007; Warheit et al., 2007; Hsieh et al, 2012, 2013)

Workplaces that could involve exposures to CNTs



- Workers are involved with CNTs throughout their lifecycle.
- More chances to be exposed to CNTs, if control measures are inappropriate.
- Limited research on NPs and CNTs emission during commercial manufacturing process, as well as recycling process.

Schulte P et al., 2009: Occupational risk management of engineered nanoparticles.

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