Characterizing Particle Emissions from Burning Polymer Nanocomposites

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Introduction

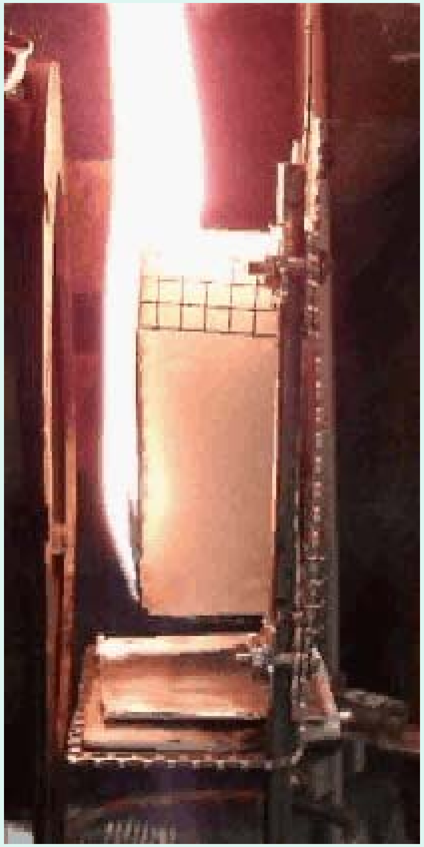
Engineered nanoparticles are increasingly being used as fire retardants and performance additives in polymeric materials. However, because of their small size and ability to interact with biological molecules, these nanoadditives may pose significant health and environmental risks if they are released into the enviroment.

In an effort to gain a better understanding of the potential hazards associated with the commercialization of polymer nanocomposites, we have undertaken an investigation into the nature of the particles released when these materials are burned. Some of the questions we hope to answer are:

1) Do nanocomposite materials release significant amounts of nanoparticles (in addition to soot, which is a ubiquitous byproduct of gas phase combustion) when they are burned? 2) If so, under what circumstances are these nanoparticles emitted and 3) Are the size distributions, morphologies, and chemistries of the released nanoparticles different from what they were in the nanocomposite?

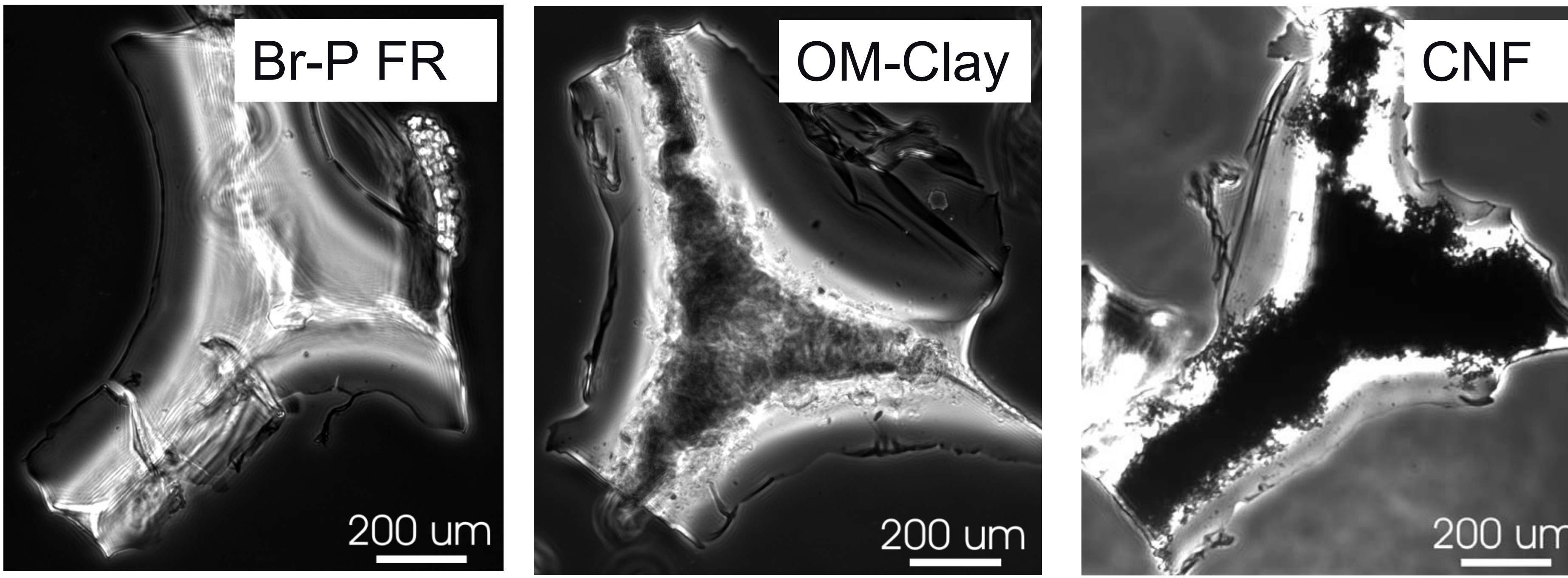
Flammability of Foam

- The special flammability characteristics of foamed polymers have been recognized for more than 25 years
- Due to:
- low density (ρ)
- low thermal conductivity (k)
- high surface area (SA)



CNF Network Formation in PUF

Strut structure of the foams with various fillers

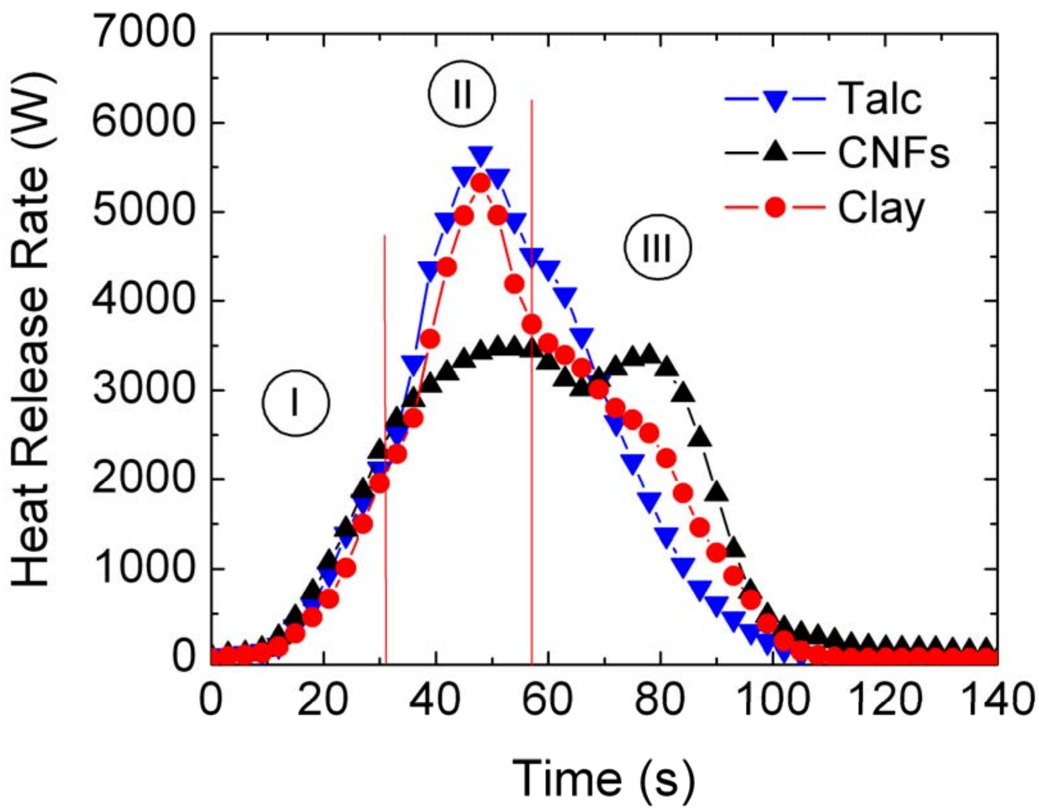


Both OM-Clay and CNFs generate a continuous network of nanoparticle in the core of the strut. <u>Only CNFs generate a thermally stable network during combustion</u>

Solid-like *vs.* Liquid-like behaviour

CNFs dispersion (left) and OM-clay (right) in polyol after annealing 10 min at 350˚C

HRR by "Melt-Dripping Cone"



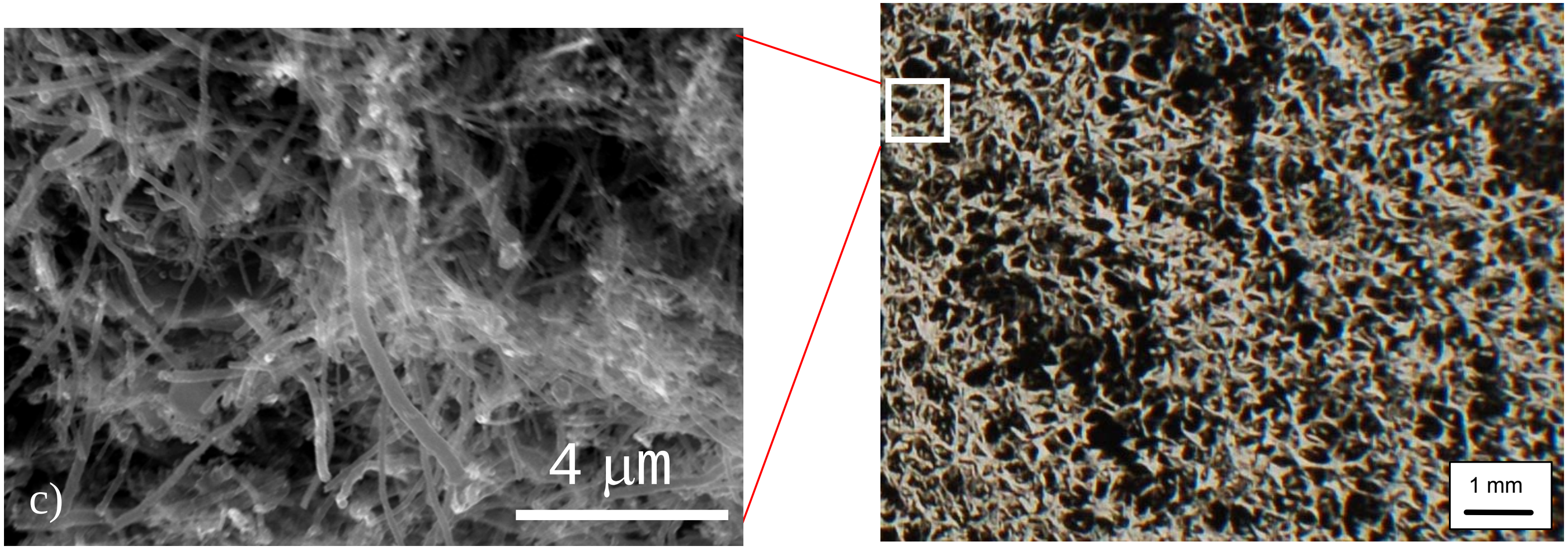
External Heat Flux: 11 kW/m^2

35% reduction in PHRR with CNF

Flame Retardant Mechanism of CNF

- Inhibition of dripping (solid like behavior)
- Heat shield effect of network structured protective layer

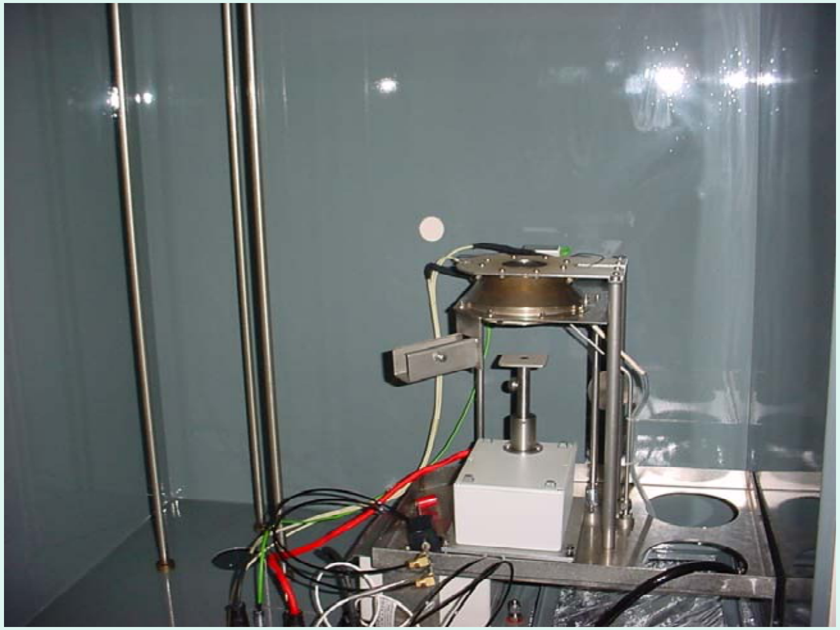
Residue of CNF foam after Cone test



Highly entangled CNFs → Thermally stable network

Fate of CNFs after CNF-PUFs are Burned

Polyurethane foam (PUF) with and without (3.9 %) oxidized CNFs was prepared as described in reference 4. Specimens measuring approximately 76 mm x 76 mm x 10 mm thick were burned in an NBS smoke density chamber in the horizontal orientation under an incident heat flux of 50 kW/m2; in accordance with the procedure specified by NFPA 270 (or equivalently, ISO 5659-2). Particulate emissions were collected by re-circulating at 1 L/min the smoke generated from the burning PUFs through an assembly containing a 2.0 µm teflon membrane filter. Samples of the emitted particulates were suspended in de-ionized water (by sonicating for 30 minutes in a Branson 2210 sonicator) and deposited on glass slides, which were examined by optical microscopy. Samples of the non-volatilized particulates (char) were similarly suspended in de-ionized water and subjected to microscopic study.



Optical Microscopy of Smoke from Nano-foam

Figure 1a is an optical micrograph of the char left behind after the CNF-containing foam was burned. The CNFs are clearly visible appearing more elongated than the spherical structures, which are typical of soot formed during gas phase combustion. These elongated structures are not apparent in the optical micrographs obtained from the smoke generated during the burning of CNF-containing (figure 1b) and CNF-free (figure 1c) foams. In fact, the micrographs of the volatilized component (smoke) from both foams look similar in that they are dominated by spherical structures which we attribute to soot. The fact that the CNFs decompose at temperatures attained in the flames was verified by heating slides prepared with the char of the CNF-containing foam. The elongated structures disappeared after heating about a minute at a temperature of about 650 ^{0}C (in air), which is far below the temperatures attained in the flames above the sample, which are probably in excess of 1200 ^{0}C.

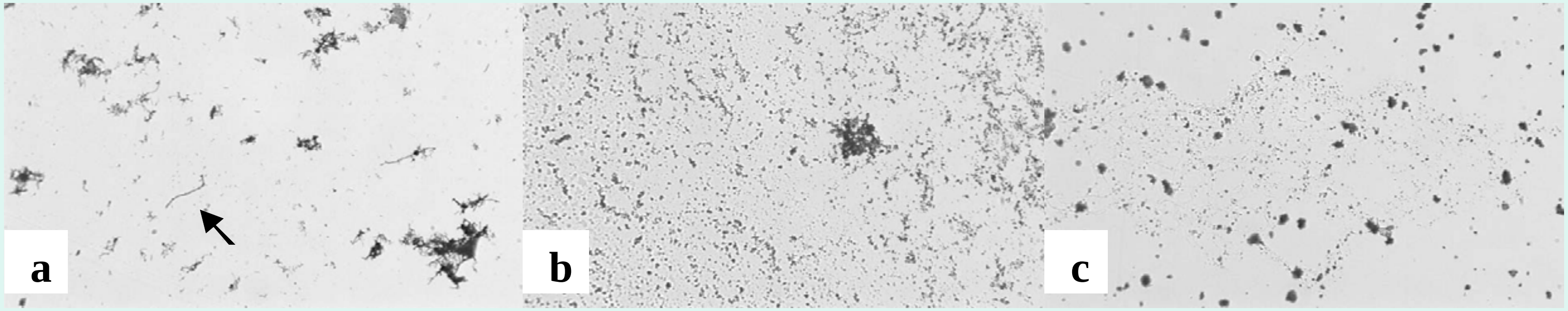
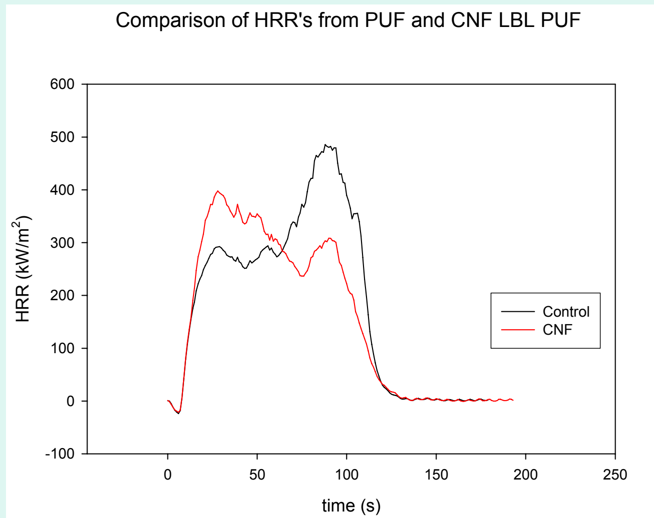
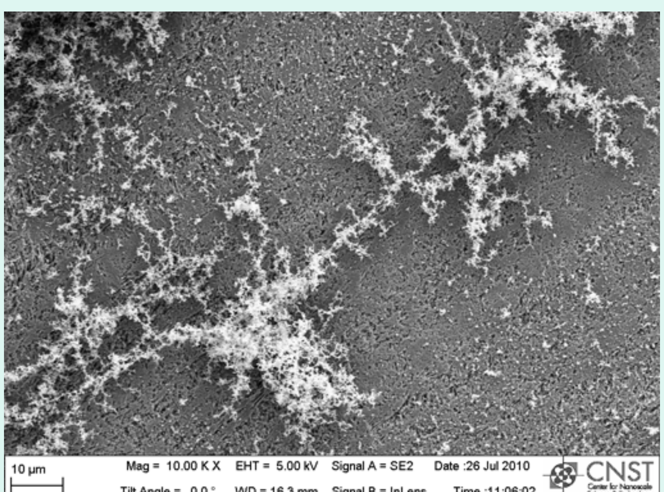


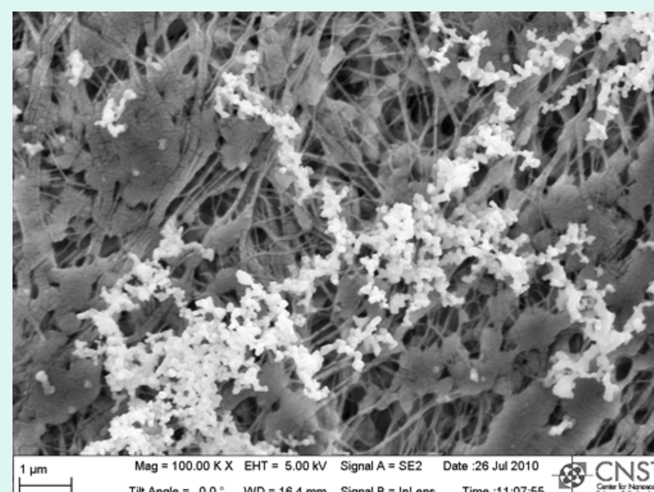
Figure 1. Optical micrographs of the nonvolatized char from the CNF-containing foam (a) and smoke from the CNF-containing (b) and CNF-free PUFs (c). Note the presence of the fibers in micrograph a and the absence of these structures in b and c.

SEM Microscopy of Smoke from Nano-foam

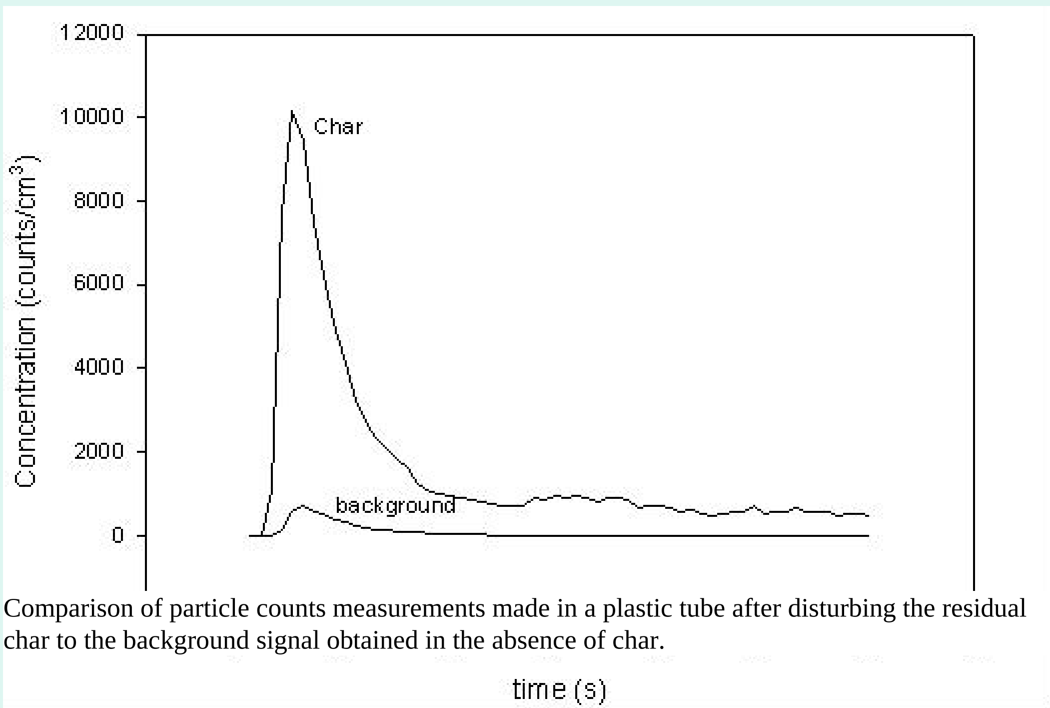
We also conducted cone calorimeter measurements on nano-foams. Smoke samples collected from a port in the stack did not show evidence of any CNFs.







Monitoring Nanoparticle Release from Chars

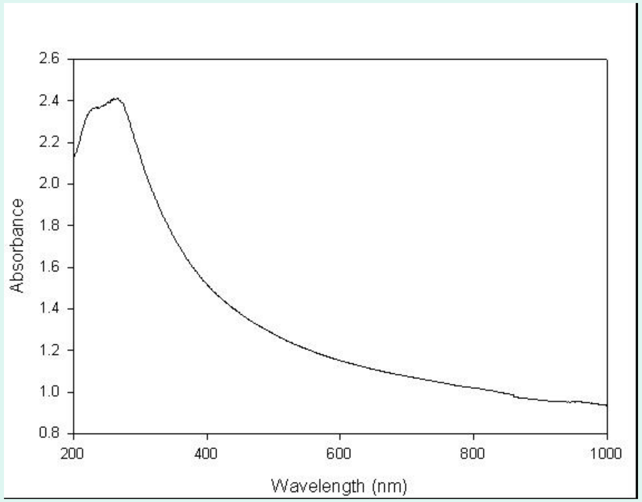


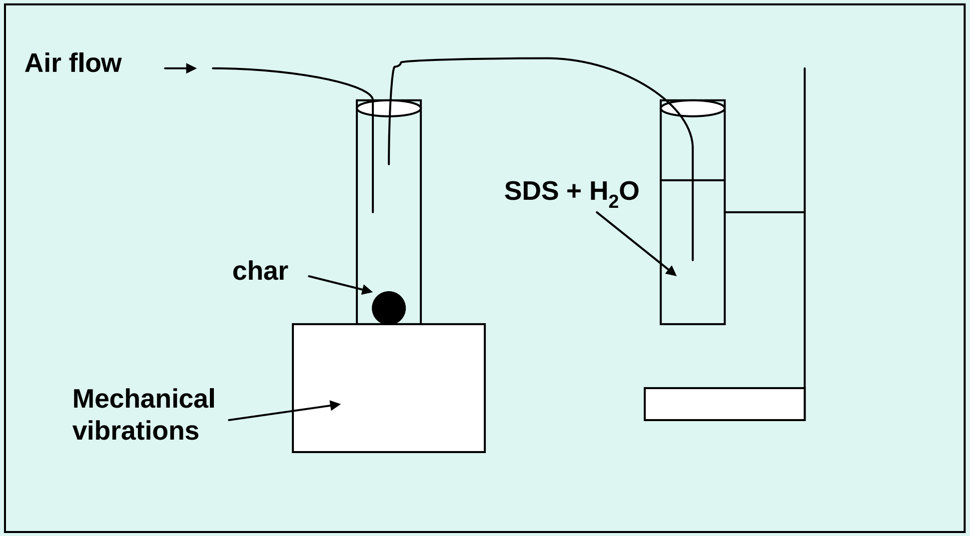
Comparison of particle counts measurements made in a plastic tube after disturbing the residual char to the background signal obtained in the absence of char.

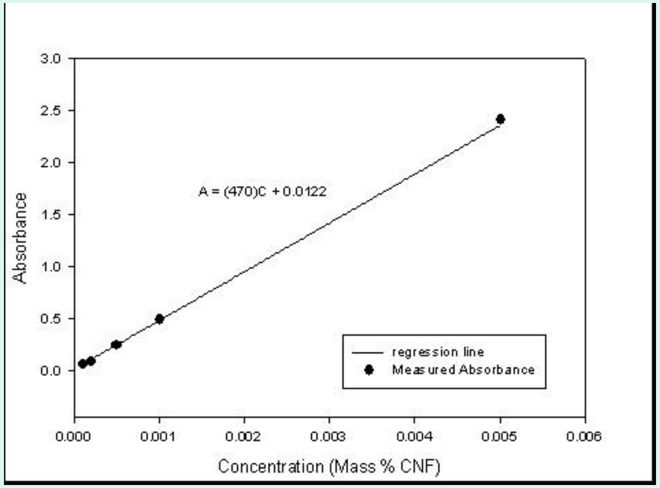
The possibility that CNFs might be released when chars left behind after burning CNF-containing PUF are mechanically disturbed was also investigated.

Particle count measurements of the aerosolized nanoparticles were made using a TSI 3007 condensation particle counter. The values obtained during agitation of a representative char sample are compared to the background obtained in the absence of char in the figure. The maximum peak count from agitation of the char is an order of magnitude larger than the background signal (due to particles already present in the laboratory air), suggesting that significant amounts of sub-micron particles are released in this way.

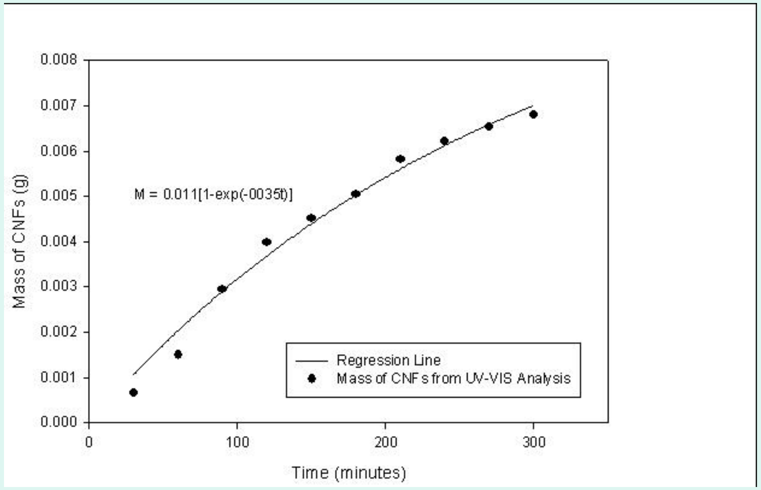
Nanoparticle Release from Chars





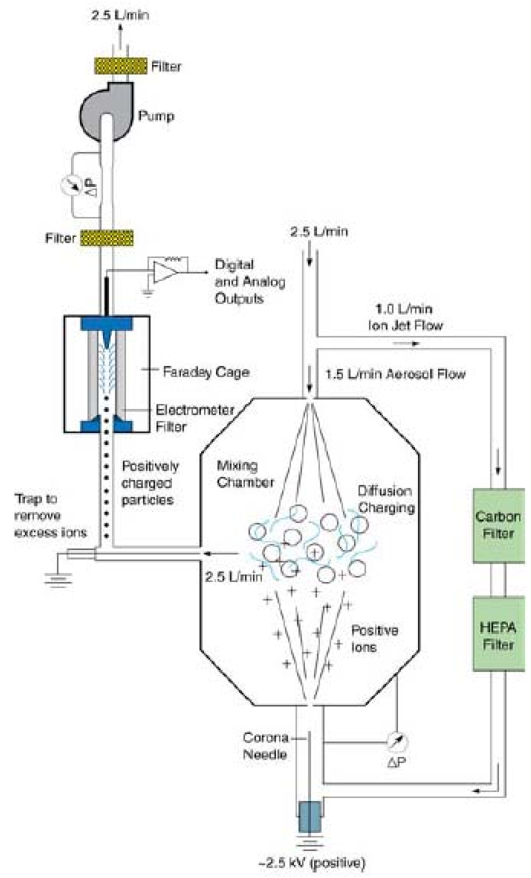


The measured absorbance at 267 nm (position of the peak maximum) for a series of CNF suspensions with known concentrations.



The mass of aerosolized CNFs was determined from analyses of UV-VIS absorbance measurements.

Nanoparticle Release from Chars



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The surface area (per unit volume) of the aerosolized nanoparticles was measured using a TSI AeroTrak 9000 nanoparticle aerosol monitor. Depending on the severity of the mechanical disturbance to the char, we obtained values ranging from about 6000 $\mu m^2/cm^3$ to more than 14000 $\mu m^2/cm^3$ in tracheobronchial (TB) deposition mode. These measurements should give an indication of the surface areas of the particles that have the right aerodynamic properties to be deposited in the tracheobronchial region of the lungs. While we do not have a metric for assessing the degree of hazard associated with these values, the fact that they are at least three orders of magnitude higher than the background measurements (~3 $\mu m^2/cm^3$), suggests that they may pose a severe threat to human health and safety.

Conclusions

Measurements were conducted to determine whether carbon nanofibers (CNFs) are released into the environment when polyurethane foam containing these nanoadditives are burned under well ventilated conditions. Microscopic analyses of particulates in the fire smoke indicated that the CNFs present in the foam were effectively destroyed in the flames. However, high levels of nanoparticles were detected when the residual char was disturbed by air currents or mechanical forces. Thus, it appears that the major hazard for CNF exposure during well-ventilated burning arises from agitation of the residual char, rather than from the fire smoke.

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