

Characterization of Nanoparticle Release from Polymer Nanocomposites Due to Fire¹

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Engineered nanoparticles, such as carbon nanotubes (CNTs) and nanofibers (CNFs) 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 environment [1,2]. Although it is unlikely that encapsulated nanostructures will be released when the materials containing them are used in protected, indoor environments, this risk becomes more significant when these materials are exposed to fire (either unintended or during incineration) or other forms of intense energy (e.g., sunlight) when they are disposed of in landfills. The nanoparticulate morphologies generated in this way may be vastly different than those adopted by the pristine nanostructures due to agglomeration and interactions with other decomposition products and may pose significant new health risks [3].

Studies are being conducted to understand the potential hazards associated with burning materials containing carbon nanotubes (CNTs) and nanofibers (CNFs) either in the process of incineration or in accidental fires. Some of the important questions that need to be answered are: 1) are significant amounts of CNTs and CNFs released into the environment (in addition to soot, which is a ubiquitous byproduct of gas phase combustion) when nanocomposite materials are burned? 2) if so, under what conditions are these nanoparticles emitted and 3) what are the size distributions, morphologies, and chemistries of the released nanoparticles?

Initial measurements were conducted to determine whether CNFs are released into the environment when polyurethane foam (PUF) containing these nanoadditives are burned under well ventilated conditions. Specimens of PUF foam (with and without CNFs) 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) [4]. 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 sonication 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. Although CNFs were clearly visible in the microscopic images obtained from suspensions of these chars, no CNFs could be identified in the images of the suspensions obtained from the filtrates of the fire smoke generated during the combustion of the CNF-PUF foams (see figure 1). In fact, the micrographs of the suspended fire smoke from both the CNF-PUF and CNF-free PUF are dominated by spherical structures that are characteristic of soot [5].

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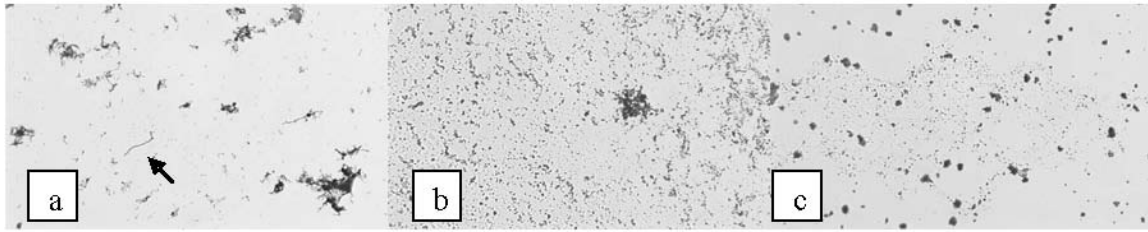


Figure 1. Optical micrographs of the nonvolatilized char from CNF-containing foam (a) and smoke from CNF-containing (b), and CNF-free PUFs (c). Note the presence of the fibers in micrograph (a) and the absence of these structures in (b) and (c).

Additional experiments were performed on PUF foams that were coated with CNFs using the layer-by-layer (LBL) assembly process described in reference [6]. Specimens were burned in a cone calorimeter [7] under an incident heat flux of 50 kW/m^2 . Particulates present in the fire smoke were collected on teflon filters situated in the exhaust port. Micrographs obtained using scanning tunneling microscopy (at resolutions between 10 KX and 100 KX) also failed to reveal the presence of any CNFs in the fire smoke. These observations suggest that the CNFs, which are present in both the foam and nonvolatilized char, are destroyed in the flames or are entrapped in the CNF network that comprises the char. Presumably, soot is destroyed as well, but it is also generated in the gas phase combustion process.

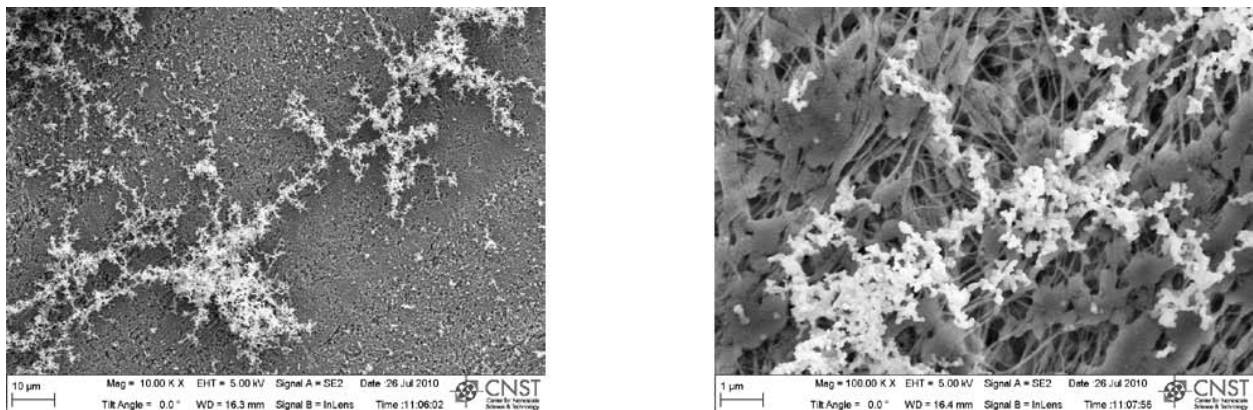


Figure 2. Electron micrographs of particulates present in fire smoke generated during cone calorimeter burns of PUF nanocomposites made by the LBL method. Higher magnification (right) reveals that of what looks like it might be a CNF at low magnification (left) is not, in fact, a continuous fiber.

The possibility that CNFs might be released when chars left behind after burning CNF-containing PUF are mechanically disturbed was also investigated. Samples of these CNF chars were placed in enclosed test tubes and agitated using a mechanical vibrator. The particle count measurements made by sampling the air above the char (using a TSI Model 3007 condensation particle counter) during agitation is compared to the background obtained in the absence of char in the figure 3. The maximum peak count after 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. Spectroscopic measurements of the chars indicated that they consisted of only about 50 % CNFs by mass fraction. Thus, it was speculated that the observed particle counts are probably due to CNF bundles partially encapsulated by a thin layer of charred PUF.

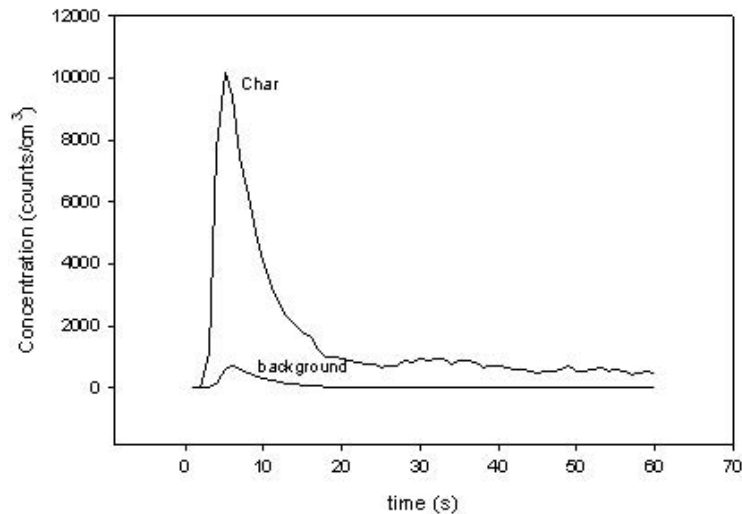


Figure 3. Comparison of particle count measurements made after agitation of the char to the background signal obtained in the absence of any char.

Preliminary measurements of the surface area of aerosolized nanoparticles were also made using a TSI AeroTrak 9000 nanoparticle surface area monitor. Depending on the severity of the mechanical disturbance to the char, values ranging from about $6000 \mu\text{m}^2/\text{cm}^3$ to more than $14000 \mu\text{m}^2/\text{cm}^3$ were obtained in tracheobronchial (TB) deposition mode. 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.

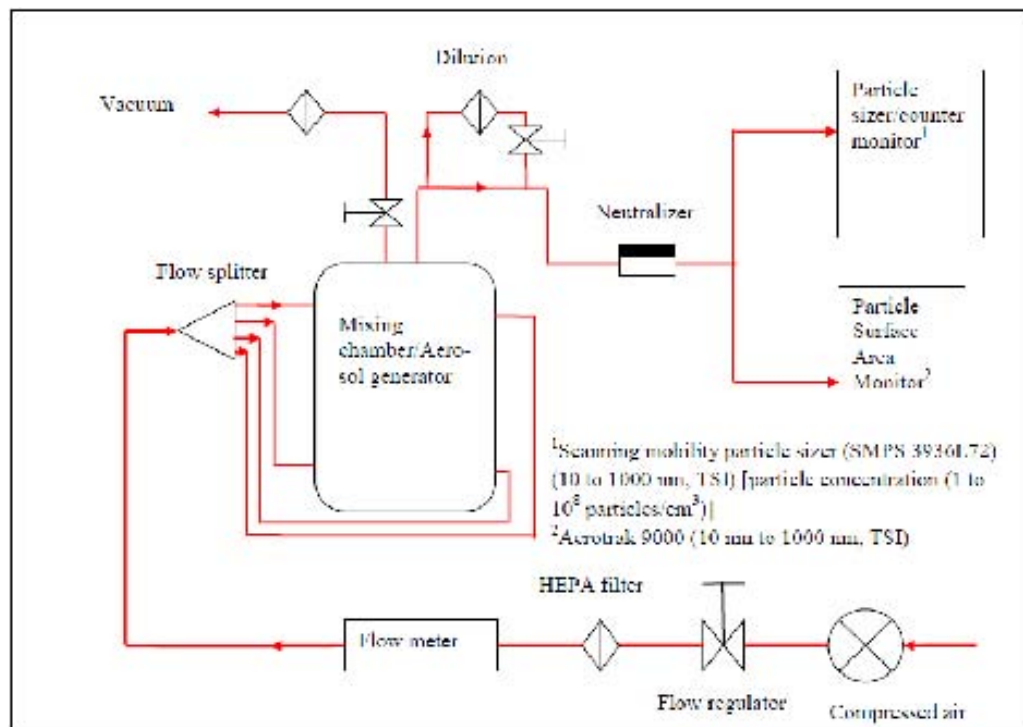


Figure 4. Diagram of the mixing chamber used in characterizing aerosolized effluents from nanocomposite chars.

An experimental setup was designed to further characterize the particle release from nanocomposite chars. A diagram showing the essential components is shown in Figure 1. Once it is operational, a poly-disperse nanoparticle aerosol will be generated in the mixing chamber by blowing compressed air at a specified flow rate over the nanocomposite char. The particle concentration will be kept constant by controlling the dilution of the aerosol. Time dependent values for the particle surface area and size distribution will be monitored using a nanoparticle surface area monitor and a scanning mobility particle spectrometer, respectively.

References

1. Nanoscience and Nanotechnologies: Opportunies and Uncertainties; The Royal Society & The Royal Academy of Engineering; July, 2004; http://www.nanotec.org.uk/report/Nano_report_2004_fin.pdf.
2. The National Nanotechnology Initiative Strategy for Nanotechnology-Related Environmental, Health, and Safety Research, Subcommittee on Nanoscale Science, Engineering, and Technology, Committee on Technology, National Science and Technology Council; Feb. 2008; http://www.nano.gov/NNI_EHS_Research_Strategy.pdf.
3. Günter Oberdörster, G., Maynard, A., Donaldson, K., Castranova, V., Fitzpatrick, J. Ausman, K., Carter, J., Karn, B., Kreyling, W., Lai, D., Olin, S., Monteiro-Riviere, N., Warheit, D., Yang, H.; Part. Fibre Toxicol. 2:8; doi:10.1186/1743-8977-2-8 [Online 6 October 2005].
4. NFPA 270: Standard Test Method for Measurement of Smoke Obscuration Using a Conical Radiant Source in a Single Closed Chamber.
5. Sorensen, C.M. and Feke, G.D.; Acrosol Science and Technology **2**; 328-337; 1996.
6. Davis, R and Kim, Y.S.; NIST Technical Note 1674; 2010.
7. ASTM E 1354-10a, Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter, 1999, ASTM International, West Conshohocken, Pennsylvania.

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