CHARACTERIZING PARTICLE EMISSIONS FROM BURNING POLYMER NANOCOMPOSITES[&]

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ABSTRACT

The use of nanoscale materials as performance additives in polymers may pose significant health and environmental risks. Although it is unlikely that nanoadditives encapsulated in polymers will be released during normal use, there is the potential for nanoparticle aerosolization when these materials are exposed to heat and fire (either accidentally or during incineration). Furthermore, the nanoparticle morphologies and chemical compositions generated during the combustion of nanocomposite materials may be vastly different than the structures of the pristine nanoadditives due to oxidation and/or interactions with other decomposition products. The potential health and environmental impact of these morphological transformations are unknown.

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. The first question we hope to answer is whether significant amounts of nanoscale additives are released (in addition to soot, which is a ubiquitous byproduct of gas phase combustion) when polymer nanocomposites are burned.

Keywords: carbon nanofibers, fire, polyurethane foam, nanocomposites.

1 INTRODUCTION

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].

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?

2 MATERIALS AND METHODS

2.1 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) [5]. 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.

2.2 Measurements were made to determine whether CNFs were released when the char left after burning the CNF-containing PUF was mechanically disturbed. Samples of CNF chars were placed in test tubes and agitated using a mechanical vibrator. The atmosphere above the char was sampled continuously with a TSI Model 3007 condensation particle counter.

2.3 The mass of CNFs released from the char was also quantified. Air was circulated through the test tube during mechanical agitation of the char and bubbled into a trap

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containing deionized water. The contents from the trap were transferred to separate containers at 30 minute intervals over a total of 3 hours. Each of these (10) time resolved suspensions was treated by adding deionized water and sodium dodecyl sulfate (SDS) to obtain a volume of 100 ml containing 0.23 % SDS by mass. These suspensions were then sonicated using a Sonics VCX 130 ultrasonic processor with a 13 mm probe for 1 hour at 50 W to exfoliate and suspend the aerosolized CNFs. Absorbance spectra of these suspensions were measured in the UV-VIS region extending from 185 nm to 1800 nm (over a 1 cm path length) using a Perkin Elmer Lambda 950 spectrometer. The concentration of CNFs in the time resolved suspensions were obtained by inversion of a linear fit (Beer's law) generated before hand from absorbance measurements made on a series of CNF suspensions of known concentration (figure 1).
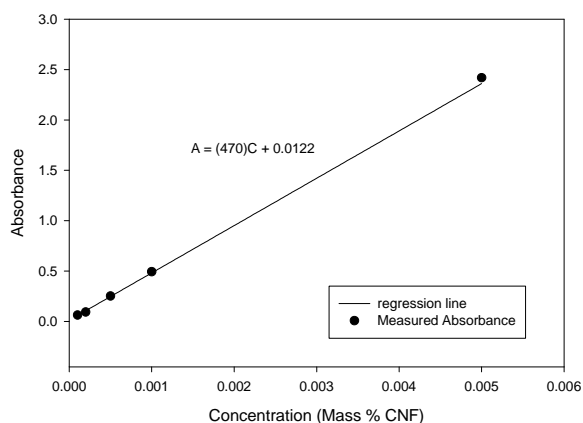

Figure 1. Plot of the measured absorbance (at 267 nm) versus concentration for a series of CNF suspensions of known concentrations.

3   RESULTS AND DISCUSSION

In the absence of added CNFs, PUF produces little if any char when it is burned. However, when the CNFs are well dispersed in PUF they form an entangled network that prevents the collapse of the foam during burning, thereby reducing dripping and flammability. This network of CNFs is left as char at the conclusion of the burn [4]. Figure 2a is an optical micrograph obtained by imaging a suspension of a representative sample of these chars. 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 2b) and CNF-free (figure 2c) 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. These observations suggest that the CNFs, which are present in the both the unburnt foam and nonvolatilized char, are destroyed in the flames (presumably, soot is destroyed as

well, but it is also generated in the gas phase combustion process). 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°C (in air), which is far below the temperatures attained in the flames above the sample, which are probably in excess of 1200 ^{O}C. The next step will be to investigate the effects of changing the combustion conditions from well-ventilated to under-ventilated, which should reduce the destructive efficiency of the flames thereby increasing the likelihood that CNFs will be released into the environment.
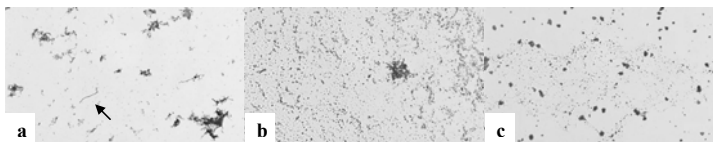

Figure 2. Optical micrographs of the nonvolatized char from the CNF-containing foam (a) and smoke from the CNF-containing (b) and CNF-free PUFs (c). Note the presence of the fibers in micrograph a and the absence of these structures in b and c.

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 plastic test tubes and agitated using a mechanical vibrator. UV-VIS analysis of the suspensions obtained from the trap indicated that the rate of aersolization of the CNFs was approximately 1.4 mg/hour. The particle count measurements made during agitation of a representative char sample is compared to the background obtained in the absence of char in figure 3. The maximum peak count from agitation of the char (~10,000 counts/cm3) is an order of magnitude larger than the background signal (due to particles already present in the air), suggesting that significant amounts of sub-micron particles are released in this way. Since these chars are comprised almost exclusively of CNFs, we assume that they are responsible for the observed particle counts. However, we have not yet determined the state of aggregation of the emitted CNFs in time to include results in this report. We expect to complete our investigation of the size distributions and morphologies of the emitted CNFs in time for presentation at the meeting in June. 2010.
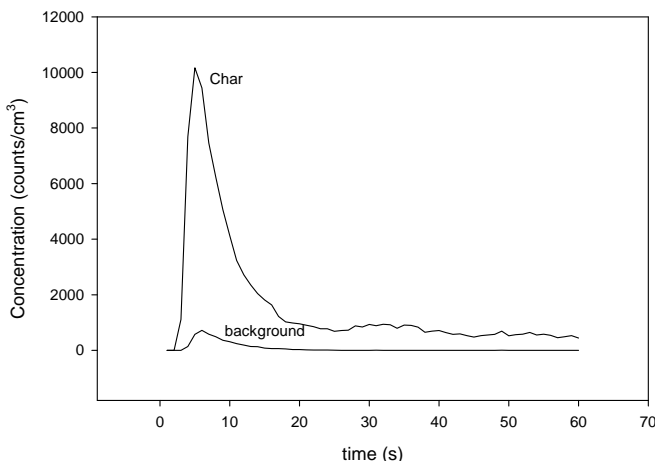

Figure 3. Comparison of particle counts measurements made in a plastic tube after disturbing the residual char to the background signal obtained in the absence of char.

4 CONCLUSIONS

Microscopic analyses of the particulate emissions produced in burning CNF containing PUF under well-ventilated conditions indicates that the CNFs 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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