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Research paper

Generation and characterization of aerosols released from sanding composite nanomaterials containing carbon nanotubes

J. Kang [a], A. Erdely [a,b], A. Afshari [b], G. Casuccio [c], K. Bunker [c], T. Lersch [c], M.M. Dahm [d], D. Farcas [b], L. Cena [b,e,*]

[a] West Virginia University, Morgantown, WV, United States
[b] National Institute for Occupational Safety and Health, Morgantown, WV, United States
[c] RJ Lee Group, Monroeville, PA, United States
[d] National Institute for Occupational Safety and Health, Cincinnati, OH, United States
[e] West Chester University, West Chester, PA, United States

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ABSTRACT

An adaptable system was developed to generate and characterize particles released from composite materials containing carbon nanotubes (CNTs). The system was tested with a belt sander by sanding 1) glass fiber/epoxy resin, 2) acrylonitrile butadiene styrene (ABS), and 3) ABS with carbon black. Each material was tested with fine and coarse sandpaper in its neat form and with CNT additives. Total number concentrations, respirable mass concentrations, and particle number/mass distributions of the released particles were measured with a combination of direct-read instruments. Airborne particle samples for electron microscopy analysis were collected on polycarbonate filters, and onto a transmission electron microscopy grid supported carbon film using a thermophoretic sampler. Using automated microscopy analysis and a newly developed method, over 200 particles from each filter sample were analyzed for chemical composition, size, and the presence of CNT protrusions. Direct-read instruments revealed that the highest number and mass concentrations were generated with Material 1 (6×10^4 particles/cm^3 and 0.5 mg/m^3 with coarse sandpaper) and that the addition of C'NTs decreased number concentrations (4.5×10^4 particles/cm^3 with coarse sandpaper). Respirable concentrations of the materials containing CNTs were higher than the respective base materials without additives with the exception of Material 1 with coarse sandpaper. Microscopy analysis results indicated that particles were primarily micrometer-sized and some particles had protruding features. From the chemical analysis, the percentages of particles generated during sanding that were attributable to the deterioration of sandpaper were 59–83% for Material 1 and 6–27% for Materials 2 and 3. The highest number of protrusions were found in Material 3 with CNT additive and fine sandpaper (3.71 average protrusions per particle) while the lowest number or protrusions were found in Material 2 with short CNTs and fine sandpaper (0.66 average protrusions per particle). No free-standing CNTs were observed in the samples. The combination of direct-read instruments and automated electron microscopy provides greater insights in particle chemistry, size measurements and CNT associations.

1. Introduction

Carbon nanotubes (CNTs), have unique physical and chemical properties, such as thermal/electrical conductivity and mechanical strength, that allow them to be used in a wide range of industrial applications (Thostenson et al., 2001). CNTs can be used to strengthen structural composites made of carbon or glass fiber by enhancing the properties of the baseline material (Zhang et al., 2013). Products that utilize CNT composites range from materials and devices for use in medical applications, electronics, energy production, cosmetics, packaging, food manufacturing, automotive, and many other fields (De Volder et al., 2013). The increase of CNT use in industrial applications leads to the potential for increased exposure of CNTs to workers and consumers (Mackevica and Foss Hansen, 2015; Wohlleben and Neubauer, 2016). The life-cycle of CNTs involves production of the raw nanotubes, incorporation in composite matrices and finite products, distribution to consumer, and finally disposal or recycling.

Ongoing exposure assessment studies at facilities that produce or handle CNTs and/or nanocomposite materials have shown the potential for inhalation exposure at various levels of the production process (Bello et al., 2008, 2009, 2013; Han et al., 2008; Tsai et al., 2009; Lee et al., 2010; Mazzuckelli et al., 2007; Methner et al., 2010; Evans et al., 2010; Birch et al., 2011; Dahm et al., 2012, 2015). Potential for exposure are highest during the production and handling of as-produced CNTs and the incorporation and manipulation of composite materials. Several

* Corresponding author at: 855 South New Street, West Chester, PA, United States.
E-mail address: LCena@wcupa.edu (L. Cena).

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studies have shown that exposure to CNTs poses health risks and adverse toxicological effects including pulmonary inflammation, granulomas, oxidative stress, fibrosis, (Lam et al., 2006; Mercer et al., 2008; Shvedova et al., 2008) cardiovascular inflammation, (Duffin et al., 2007; Erdely et al., 2008) immunological effects, (Kunzmann et al., 2011; Mitchell et al., 2009) systemic exposure, (Erdely et al., 2008; Riviere, 2009; Simeonova and Erdely, 2009) genotoxicity and mitotic spindle abnormalities (Sargent et al., 2009, 2012).

Sanding of composite materials is a common practice in manufacturing facilities to polish surfaces or decrease the thickness of the composites to the desired dimensions. Studies have been carried out to measure exposure during sanding of composites nanomaterials. Gohler et al. used a hand-held tool to simulate the sanding of different coatings containing nanomaterials including zinc oxide and iron oxide nanoparticles (Göhler et al., 2010). They reported that particle emission rates depended on the coating material rather than the incorporation of nanoparticles. Electron microscopy (EM) analysis showed that both zinc oxide and iron oxide particles remained embedded within the released particles, while no free dissociated nanomaterial was observed. Wohlleben et al. measured the release of particles from polyoxymethylene/CNT nanocomposite being abraded by a Taber Abraser in an enclosed chamber (Wohlleben et al., 2011). They observed the release of nanosized particles regardless of the addition of CNTs. No CNTs dissociated from the composite matrix were observed under EM analysis. When Wohlleben et al. later applied the same method to a polyurethane/CNT nanocomposite, they again observed no release of free CNTs (Wohlleben et al., 2013). Schlagenhauf et al. performed a similar Taber Abraser study with epoxy resin containing CNTs, however, they observed the release of free-standing CNTs as well as CNT agglomerates (Schlagenhauf et al., 2012). Methner et al. did not detect nanoscale debris from epoxy-based nanocomposites during sanding but EM analyses found free-standing and matrix-bound carbon nanofibers during machine sanding, while hand sanding exclusively produced matrix -bound carbon nanofibers (Methner et al., 2012).

Cena and Peters compared background to process particle emissions from CNT-epoxy nanocomposites during a manual sanding process (Cena and Peters, 2011). The process to background ratio showed that sanding had a significant impact on particle emission. EM analysis revealed that the sanding process generated micron sized particles with CNT protrusions. Hellmann et al. investigated particle release from CNT-epoxy nanocomposites during a sanding task and reported protrusion of CNTs, but no free standing CNTs from EM analysis (Hellmann et al., 2012). Huang et al. used a disk sander to evaluate particle emission from epoxy resin samples with different CNT levels (Huang et al., 2012). The epoxy resin was sanded with three different grit sizes and three disk sander speeds. The highest number concentrations were produced by the coarse sandpaper and medium disk sander speed, while the fine sandpaper produced the highest respirable mass concentrations at medium disk sander speed. Particles around 100 nm were recorded on the size distributions for the materials. Micrometer-sized particles with CNT protrusions were observed by EM analysis. Free-standing CNTs were only found with the epoxy resin samples containing the highest CNT concentration (4%). Furthermore, the 4% CNT samples produced the highest number and respirable mass concentrations. The authors speculated that the addition of CNTs made the materials more brittle, and in turn increased particle emission.

Release of free CNTs from the matrix has been inconsistent. Kohler et al. suggest that the release of CNTs is determined by the method used to incorporate them into the material (Köhler et al., 2008). Mackevica and Foss Hansen performed a review of studies pertaining to engineered nanomaterial release, and suggest that future studies should focus on improving analytical methods for determining nanomaterial release rates from particle products (Mackevica and Foss Hansen, 2015). Direct-read instruments provide real-time particle concentrations and distributions by size but do not differentiate between particles released from the degrading material and those from other sources such as the mechanical tools used. Traditional EM methods provide the ability to differentiate particles by their chemical composition, however, the instrumentation is expensive, the analysis can be time consuming, and the results are often considered qualitative.

Computer-controlled scanning electron microscopy (CCSEM) techniques have been developed and used to provide statistical information on individual particles in a more time efficient manner (Coz et al., 2010; Huffman et al., 2012; Sawvel et al., 2015; Peters et al., 2016). Casuccio et al. characterized ambient particulate matter shortly after CCSEM was developed (Casuccio et al., 1983). Mamane et al. performed a statistical evaluation of CCSEM as applied to an ambient urban aerosol sample (Mamane et al., 2001). Laskin et al. provided an overview of the analysis of individual environmental particles using EM and x-ray microanalysis techniques, including CCSEM and Edgerton et al. evaluated analysis of carbonaceous particles using CCSEM methods (Laskin et al., 2006; Edgerton et al., 2009). Presently, CCSEM is capable of providing size/morphology, elemental composition and an image of individual particles in a very rapid manner (<1 s/particle). The technology has evolved into a standard practice in numerous applications including steel research (Story et al., 2006) and criminal forensics gunshot residue analysis (White and Owens, 1987). However, CCSEM has primarily been used to characterize particles larger than 0.2 μm and has not been documented to be a viable method for nano-size particles as of yet. Further, images acquired in an automated manner may not be of sufficient quality to assist in the evaluation of nano-sized particles. Thus, improvements to CCSEM techniques and/or new methods need to be developed to obtain a better understanding of particle release from degrading composite materials.

The objective of this study was twofold. The first objective was to develop and test an adaptable system designed to generate particles during lifecycle events of composite materials. The second objective was to develop methods for the differentiation and characterization of the particles released during the sanding process. To achieve these goals, an adaptable system was developed and tested to simulate a sanding process. The system was tested with composite materials containing CNTs and the particles generated were analyzed by direct-read instruments and a combination of manual EM and automated EM techniques, including a newly developed nano-computer controlled scanning electron microscopy (nanoCCSEM) method.

2. Methods

2.1. Particle generation

The experimental setup to generate sanding particles is shown in Fig. 1. The generation chamber measured 1.2 m (Width) by 0.5 m

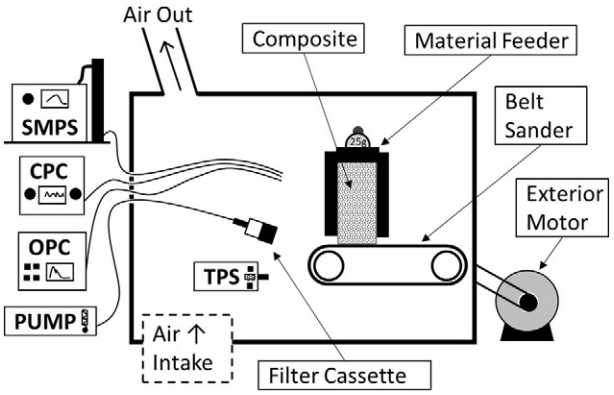

Fig. 1. Experimental setup. SMPS = scanning mobility particle spectrometer; CPC = condensation particle counter; OPC = optical particle counter; TPS = thermophoretic sampler; HEPA = high efficiency particulate air filter.