Published in final edited form as:

J Nanopart Res. 2012 October 1; 14(11): . doi:10.1007/s11051-012-1231-8.

Evaluation of Airborne Particle Emissions from Commercial Products Containing Carbon Nanotubes

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Abstract

The emission of the airborne particles from epoxy resin test sticks with different CNT loadings and two commercial products were characterized while sanding with three grit sizes and three disc sander speeds. The total number concentrations, respirable mass concentrations, and particle size number/mass distributions of the emitted particles were measured using a condensation particle counter, an optical particle counter, and a scanning mobility particle sizer. The emitted particles were sampled on a polycarbonate filter and analyzed using electron microscopy. The highest number concentrations (arithmetic mean = 4670 particles/cm³) were produced with coarse sandpaper, 2% (by weight) CNT test sticks and medium disc sander speed, whereas the lowest number concentrations (arithmetic mean = 92 particles/cm³) were produced with medium sandpaper, 2% CNT test sticks and slow disc sander speed. Respirable mass concentrations were highest (arithmetic mean = 1.01 mg/m³) for fine sandpaper, 2% CNT test sticks and medium disc sander speed and lowest (arithmetic mean = 0.20 mg/m³) for medium sandpaper, 0% CNT test sticks and medium disc sander speed. For CNT-epoxy samples, airborne particles were primarily micrometer-sized epoxy cores with CNT protrusions. No free CNTs were observed in airborne samples, except for tests conducted with 4% CNT epoxy. The number concentration, mass concentration, and size distribution of airborne particles generated when products containing CNTs are sanded depends on the conditions of sanding and the characteristics of the material being sanded.

Keywords

Airborne particles; Carbon nanotubes; Number concentration; Particle size distribution; Respirable mass concentration; Sanding

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Introduction

The unique physicochemical and mechanical properties of carbon nanotubes (CNTs)—nanoscale cylinders of carbon sized 1–100 nm—are used extensively to enhance commercial products, such as airplane frame parts (Ajayan and Zhou 2001). The increase in their commercial interest and mass production gives rise to the potential for increased interactions of CNTs with humans and the environment (Lewinski et al. 2008). The risk, especially inhalation risk, posed by these interactions can be characterized by the severity of exposure (i.e., the toxicity) and the probability of exposure (Shatkin 2008). Adverse toxicological effects including acute inflammation, granuloma, and lung fibrosis have been observed in animals exposed to CNTs (Shvedova et al. 2005b, 2007, 2008; Muller et al. 2005, 2008; Ma-Hock et al. 2009). Sargent et al. (2011) observed mitotic spindle aberrations in human epithelial cells after exposure to CNTs at concentrations equal to the Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for particles not otherwise regulated (PNOR) respirable fraction of 5 mg/m³.

Inhalation exposure to aerosols containing CNTs may occur as products undergo various life cycle events from manufacturing to recycling (FERA 2009). Exposure to CNTs may occur in manufacturing processes that involve handling bulk nanomaterial, such as pre-mixing and polymer compounding. Numerous studies that have characterized exposures when handling nanomaterials were summarized by Kuhlbusch et al. (2011). Exposure may also occur when CNTs embedded in a matrix (e.g., CNT-epoxy nanocomposite) are mechanically disrupted, such as in sanding (Cena and Peters 2011). These processes include mechanical manipulation of nanocomposites in manufacturing, product use, and recycling (FERA 2009).

There have been conflicting results in laboratory studies that have characterized airborne particles generation when products containing CNTs go through various mechanical processes. For weak shear forces, an increase in nanoparticle number concentration above background was found when composites with CNTs were scraped with a rubber knife (Hsu and Chein 2007) and underwent simulated wear with a Taber Abraser (Guiot et al. 2009; Schlagenhauf et al. 2012; Golanski et al. 2012). However, no significant particle release compared to background was observed in another Taber Abraser study (Vorbau et al. 2009). For strong forces applied to nanocomposites and surface coating materials, dry cutting with a band-saw and a rotary cutting wheel (Bello et al. 2008), shredding (Raynor et al. 2012) and sanding with a miniature sander (Göhler et al. 2010) have been observed to substantially increase airborne particle number concentrations. In contrast, manual sanding of CNT-epoxy nanocomposite increased mass but not number concentrations compared to background in a field study (Cena and Peters 2011).

Several studies focused on identifying the determinants of airborne particle emissions in the sanding processes. Regarding the effect of nanocomposites on particle emission, Bello et al. (2008) and Wohlleben et al. (2011) found no significant difference in airborne concentrations compared to their nanoparticle-free counterparts during dry cutting of CNT-composites. In addition, Wohlleben et al. (2011) simulated a do-it-yourself sanding process with matrix materials containing nanofillers and concluded that rigidity of matrix, rather than the presence of nanofillers, played a dominant role in determining the particle mass and size distribution of released aerosols. This finding was in agreement with Göhler et al. (2010), who identified that the nanoparticle emissions from surface coating via a miniature sander depended largely on the coating material rather than the presence of nanomaterial. Koponen et al. (2009) found that sub-50-nm particles dominated the number distribution, whereas the nano-sized particles only played a minor role on the mass and surface area distributions. This finding was supported by another study by the same group (Koponen et al. 2011), which revealed that nano-sized particles accounted for most of the number

concentration and micrometer-sized particles dominated the mass and surface area distributions. Koponen et al. (2009) attributed nano-sized particles to the abrasion of the sandpaper rather than that of the material being sanded, and the sandpaper grit size and the sander speed were identified as the major determinants of the number concentration modes. In electron microscopy (EM) analyses, individual CNTs free from matrix were not found in most studies (Wohlleben et al. 2011; Cena and Peters 2011; Bello et al. 2009), although Schlagenhauf et al. (2012) identified free CNTs released as airborne particles when a CNT-epoxy matrix was sanded.

The objectives of this study were: (1) to develop a method to characterize the emission of airborne particles when products containing CNTs are sanded; and (2) to compare the particle number concentrations, mass concentrations, particle size distributions, and airborne particle morphology under different sanding conditions such as various sanding speed, sandpaper grit, and test samples used.

Materials and Methods

Experimental setup

As shown in Fig. 1, the experimental setup consisted of a system to simulate sanding and a system for sampling and monitoring airborne particles. A commercial lathe (L1015, Taig Tools, Chandler, AZ, US) was placed inside a sand blasting cabinet (Item 93608, Central Pneumatic, Byron Center, MI, US), which was housed in a secondary clear plastic enclosure (1 m × 0.7 m × 1 m). The clean air from a high-efficiency particulate air (HEPA)-filtered air blower (#1 in Fig. 1; CM3000; Fantech, Lexena, KS, US) was supplied to the plastic enclosure at a flow rate of 0.14 m³/s (300 ft³/min) to maintain a low background concentration outside the cabinet. The clean air from an identical HEPA-filtered air blower (#2 in Fig. 1) was supplied to the cabinet at a flow rate of 0.12 m³/s (250 ft³/min). A slightly negative pressure (−25 Pa) was maintained in the cabinet by pulling air with a valve-controlled local exhaust system. A terminal exhaust pump (Air Sampling Pump, 6P-280; Air Diagnostics and Engineering Inc., Naples, ME, US) was used to extract a portion of the cabinet exhaust through a sampling manifold at 22.5 L/min.

The lathe in the cabinet was used to simulate a sanding life-cycle event. A disc plate (10.4-cm diameter) was fixed to the spindle of the lathe. An electric motor (Marathon Electric Motor, JVD48S17D2042NK; Marathon Electric, Wausau, WI, US) used to rotate the disc plate was positioned outside the cabinet to avoid particle contamination in the cabinet. The rotational speed of the disc plate was controlled by adjusting a pulley outside the cabinet. Adhesive-backed sandpaper made of aluminum oxide (Al₂O₃) as abrasive material was affixed to the surface of the disc plate. Three levels of sandpaper roughness were used (ADALOX A290 P80, P150, and P320; Norton Abrasive, Worcester, Mass., US). Test objects were fed by a carriage, which was driven towards the sanding disc by a turning screw beneath the lathe. In this project, the carriage speed was kept low (0.0025 cm/s) and constant to prevent the disc sander from dysfunction, which may occur when the test material is fed at a rate faster than the rate at which the sand paper can abrade material.

Sampling and monitoring system

The sampling and monitoring system consisted of a manifold from which airborne particles concentrations were measured with direct reading instruments (DRIs) and collected with a filter sampler. The total number concentration of particles from 10 nm to 1 μm in diameter was measured with a handheld condensation particle counter (CPC; 3007; TSI, Shoreview, MN, US). An optical particle counter (OPC; PDM-1108; Grimm, Ainring, Germany) was used to measure the particle number concentration in 15 channels from 0.35 μm to 25 μm in

optical diameter and a scanning mobility particle sizer (SMPS; 5.400; Grimm, Ainring, Germany) was used to measure particle number concentration in 44 channels from 9.8 nm to 850 nm. The sampling flow rates were 0.7 L/min for the handheld CPC, 1.2 L/min for the OPC, and 0.3 L/min for the SMPS.

The number concentrations measured by the CPC and the OPC were used to calculate the respirable mass concentration, M_R , using the following equation (Peters et al. 2006):

$$M_R = \frac{\pi}{6} d_{CPC}^3 \rho N S_R d_{CPC} + \sum_{i=1}^{15} \frac{\pi}{6} d_{OPC,i}^3 \rho N_{OPC,i} S_R d_{OPC} \quad \text{Eq. (1)}$$

where d_{CPC} is the assumed midpoint diameter of the CPC channel (150 nm), ρ is the particle density (assumed to be 1190 kg/m³, the density of neat epoxy), N is the number concentration indicated by the CPC, S_R is a function for the fraction of respirable mass, $d_{OPC,i}$ is the midpoint diameter of the OPC channel, i , $N_{OPC,i}$ is the number concentration indicated by the OPC for a given size channel, i . The size distribution of the particles was derived by merging data from the SMPS and the OPC.

Airborne particles in the sampling manifold were collected on a 0.4- μ m-pore polycarbonate filter (E0413-MB; Structure Probe Inc., West Chester, PA, US) using a sampling pump (Universal Sample Pump, 224-PCXR4; SKC Inc., Eighty Four, PA, US) operated at 1 L/min. The morphology of a representative subset of collected airborne particles was characterized by transmission electron microscopy (TEM; JEM-1230; JEOL USA Inc., Peabody, Mass., US) and scanning electron microscopy (SEM; Hitachi S-4800; Tokyo, Japan). For TEM samples, the airborne particles were dispersed in acetone and then the TEM grid was dipped in the solution. The grid was air-dried and analyzed by TEM. For SEM analysis, the filter was put on a carbon tape, coated with carbon using a sputter coater.

Protocol and testing matrix

The protocol for characterizing the particles emitted during sanding is depicted in Fig. 2. Before each test, the disc speed and carriage speed were set. A test object was then mounted on the carriage and positioned perpendicular to the face of disc sander 2.16 cm from the outer edge. Then the air blowers and the DRIs were turned on. Number and mass concentrations were measured with the DRIs every 6 seconds continuously throughout the test. The sanding process was then started by simultaneously activating the disc sander and the carriage feed, and the system was allowed to operate for five minutes to ensure stability of the airborne particle emissions. The sampling pump was then turned on to collect airborne particles onto the filter, and the particle size distribution was measured by the SMPS (one SMPS measurement took 6.5 minutes). As soon as an SMPS measurement was completed, the test was ended by turning off the disc sander, the carriage feed, and the sampling pump simultaneously.

Using the test protocol, twelve tests were conducted as summarized in Table 1. Epoxy test sticks were prepared by adding multi-walled CNTs (10–50 nm in outer diameter and 1–20 μ m in length; Baytubes, Bayer Material Science, LLC, Pittsburgh, PA) to epoxy resin, pouring the mixture into a mold, and baking it in an oven. Tests were conducted with test sticks having five CNT levels (0% - neat epoxy; 1, 2, 3 and 4% by weight of CNTs in epoxy). The test samples composed of neat epoxy were light yellow, whereas adding CNTs turned the samples black. Tests were also conducted with two commercially available products that contained epoxy mixed with CNTs (< 1% by weight) and carbon fiber. These products were cut into a similar size and shape as the test sticks and then identified as Sample 1 and Sample 2. Sample 2 was more brittle than Sample 1. Tests were conducted for

three sandpaper grit levels (fine, P320, grit sized 46.1 μm in average; medium, P150, grit sized 100 μm on average; and coarse, P80, grit sized 201 μm on average) and three disc sander speeds (slow, 586 revolutions per minute (RPM); medium, 1425 RPM; and fast, 2167 RPM). When one variable (i.e., CNT percentage, sandpaper level, disc sander speed) was changed, the other two variables were kept constant. An additional test was performed to investigate the particle emissions when the disc sander was spinning at the speed of 1425 RPM with P150 sandpaper but the test sample was not fed to the disc sander. All the tests were performed in triplicate.

Data analysis

Data obtained during the SMPS measurement were analyzed (Minitab 16 Statistical Software, Minitab Inc., State College, PA, US) by means of the ANOVA multivariate analyses followed by the Tukey's test as post hoc multiple comparison (number concentration and respirable mass concentration mean between one test condition and other test conditions) at the significance level of 0.05. A total of four ANOVA analyses were performed: analysis of five test samples with different CNTs percentage, analysis of 2% CNTs samples sanded with three different sandpaper grit, analysis of 2% CNTs samples under three different disc sander speeds, and analysis of three different types of test samples (i.e., 2% CNT stick, Sample 1, and Sample 2).

Results

The results for each test condition are summarized in Figs. 3–6 by boxplots and particle size distributions. For boxplots, the upper and lower boundary of the boxes indicates the 75th and 25th percentiles, respectively, the central line indicates the median, and the whiskers indicate maximum and minimum concentrations. The arithmetic means of the number and respirable mass concentrations as well as statistical results are presented in Table 2 and Table 3, respectively.

For the test conducted with the disc sander spinning but with the carriage feed off (i.e., no sanding), the particle number concentrations decreased from approximately 100 particles/ cm^3 at the beginning of the test to lower than 80 particles/ cm^3 after 5 minutes. Similarly, the respirable mass concentrations decreased from 0.2 mg/m^3 when the tests started to lower than 0.005 mg/m^3 after 5 minutes. Number concentrations were low throughout the size distribution (<30 particles/ cm^3). These results indicated that airborne particle emissions with the disc spinning but with no sanding were comparable to background measurements.

Percentage of CNT loading

Results of sanding test sticks with different CNT loadings are shown in Fig. 3. In all tests, number concentrations were lower than 650 particles/ cm^3 (Fig. 3a) and the respirable mass concentrations were lower than 0.8 mg/m^3 (Fig. 3b). With the exception of the neat epoxy test sticks (0% CNT), the number concentrations became slightly higher while increasing the CNT loading (Fig. 3a; Table 2a). The number concentration for 4% CNT test sticks was statistically different from that of 1% CNT, 2% CNT, and 3% CNT test sticks ($p < 0.001$). The respirable mass concentrations also increased with the percentage of CNT loading (Fig. 3b). The mean respirable concentration for 4% CNT test sticks was significantly different ($p < 0.001$) and more than three times higher than tests conducted with the lowest percentage CNT loadings (Table 3a).

Two size modes were observed in the number size distribution: one associated with particles smaller than 100 nm and the other associated with particles between 500 nm and 5 μm (Fig. 3c). Number concentrations by size were similar for all the test sticks, except for the fact

that more particles across all particle sizes were generated for tests conducted with 4% CNT test sticks than test sticks with lower CNT loadings, which was in accordance with the number concentration boxplots. The particle mass size distributions were dominated by a single mode with the peak mass concentration associated with particles approximately 5 μm in diameter. Particles larger than 1 μm accounted for most of the mass concentration (Fig. 3d). The mode in the mass concentration was shifted to a smaller diameter for 4% CNT test sticks and to larger diameter for 0% CNT test sticks compared to other percentages.

Disc sander speed

The results from test runs at three disc sander speeds are shown in Fig. 4. The speed greatly determined both the number concentrations (Fig. 4a; Table 2b) and the respirable mass concentrations (Fig. 4b; Table 3b). The mean number concentration of generated particles with high disc sander speed was 3100 particles/cm³, which was 30 times higher than that of the slow speed and 10 times higher than that of the medium speed. The variability in particle number concentrations at the fast speed was also the highest with values ranging from 2190 particles/cm³ to 4400 particles/cm³. Similarly, respirable mass concentrations were highest for the test conducted at the fast speed (mean = 0.58 mg/m³) and lowest for the test conducted at the slow speed (mean = 0.21 mg/m³). The difference in the mean of the number concentration and respirable mass concentration from the three speeds were statistically significant ($p < 0.001$), as illustrated in Table 2b and Table 3b.

The number concentration by size for the slow and medium speeds was low with no obvious peaks (Fig. 4c). However, a substantial quantity of sub-50-nm particles were generated at the fast speed. The particle mass size distribution in Fig. 4d illustrates a peak at the particle diameter between 1 μm and 10 μm for all three speeds. This peak for the fast speed was higher compared to the other speeds.

Sandpaper grit

Tests conducted with different sandpaper grit are summarized in Fig. 5. The highest particle number concentrations were produced by the coarse sandpaper (Fig. 5a), whereas the highest respirable mass concentrations were produced by the fine sandpaper (Fig. 5b). Coarse sandpaper produced significantly different number concentration ($p < 0.001$) from medium sandpaper and fine sandpaper (Table 2c), and fine sandpaper produced significantly different respirable mass concentration ($p < 0.001$), as illustrated in Table 3c.

The number concentration in sub-50-nm size range was substantially higher for the coarse sandpaper compared to medium and fine sandpaper, whereas in other size ranges there was no significant difference between sandpaper types (Fig. 5c). The mass size distributions were similar for all three sandpaper types with a single mode peaking at 7 μm .

Commercial samples compared to test sticks

The concentrations and size distributions of emitted particles from sanding the two commercial samples were comparable to those from sanding 2% CNT test sticks (Fig. 6). Respirable mass concentrations (Fig. 6b) were similar for 2% CNT test sticks compared to the commercial products, although the mean concentrations were statistically different (Table 3d). The number concentrations produced by Sample 2 (mean = 2320 particles/cm³) was substantially and statistically higher than those of Sample 1 (mean = 332 particles/cm³) and 2% CNT test sticks (mean = 454 particles/cm³; Table 2d). The ranges of number concentrations for both Sample 1 and Sample 2 were larger than 2% CNT test sticks. The higher number concentration for Sample 2 was attributed to sub-100-nm particles. The mass distributions for the three test samples were similar except for the fact that distribution for

the 2% CNT was wider and the magnitude at the peak was higher than that for either commercial sample.

Microscopy analysis results

Emitted particles from sanding the 2% CNT test stick with medium grit sandpaper at medium speed were sampled with the filter for TEM analysis. Images of the most frequent particle type found when sanding test sticks composed of CNT-epoxy are shown in Fig. 7. These particles consisted of an epoxy core with CNT protrusions (outer diameter of 25 nm) on the particle surface. Shown in Fig. S1 of Supplementary Information (SI), sub-50-nm particles were observed in TEM images for samples conducted at fast sanding speeds. No free CNTs were found in the samples, except for tests conducted with test sticks with 4% CNT by weight (SI Fig. S2).

Discussion

The composition of the material being sanded and the conditions under which sanding occurs influences the number concentrations, respirable mass concentrations, and size distributions of airborne particles released. Regardless of test conditions, the overall shape of the particle mass distribution remained similar with only one size mode present that was associated with coarse particles (1 to 20 μm). This coarse particle mode was shifted to slightly smaller particles for the highest CNT loading (4%, Fig. 3d) and for the commercial products (Sample 1 and Sample 2, Fig. 6d) compared to samples without CNT present (0%, Fig. 3d). Respirable mass concentrations were a reflection of the extent to which the size distribution was shifted to smaller diameter particles and the magnitude of the coarse particle size mode. Accordingly, respirable mass concentrations produced with the 4% CNT test samples were three times higher than the concentrations produced by 0% and 1% CNT test samples.

The finding of a single size mode in the mass concentration distribution is consistent with Wohlleben et al. (2011). These results are also consistent with the idea that the presence of the nanomaterial at higher weight percentage increases the brittleness of the material and allows the sanding process to break the test object into small particles. This notion is similar to that proposed by Göhler et al. (2010) and Wohlleben et al. (2011), who suggested that the rigidity of the test samples rather than the presence of nano-additives determined the particle concentration.

The conditions under which CNT-containing materials are sanded also influences the emission of airborne particles. For all particle mass size distribution, the magnitude of the coarse particle mode varied depending on mechanical energy (fast speed > medium speed > slow speed) and sandpaper grit (coarse > medium and fine). The finding that increased respirable mass concentrations are produced by increases in sanding speed was expected and is consistent with the findings of Golanski et al. (2010). This fact may be explained by the increased abrasion energy available to break up the test samples induced by increased disc sander speed. The finding that respirable mass concentrations were highest with the fine grit sandpaper and lowest for the coarse grit sandpaper may be attributed to the ability of the fine grit sandpaper to break the test object into more respirable-sized particles than with the coarse grit sandpaper. However, this finding is in contradiction with the work of Chung et al. (2000), who found that the finer grit sandpaper generated less airborne particle mass than coarse grit sandpaper when sanding medium density fibreboard.

The interpretation of number size distributions is more complicated because there were two size modes present. The mode in the number distribution associated with particles larger than 500 nm is the same coarse-particle mode described above for the mass distribution. The

magnitude of this large-particle mode followed the same trends as that described for the coarse-particle mode of the mass distribution. A second mode, present in the number distribution for particles smaller than 200 nm, was dramatically different for some tests. Compared to background, the number concentrations of sub-50-nm particles were substantially higher for tests conducted with fast sanding (Fig. 4c) and for tests conducted with coarse sandpaper roughness (Fig. 5c). From microscopy, the morphology of these particles was spherical (SI, Fig. S1), not rod shaped like CNTs. This morphology is consistent with a secondary source of particles from thermal decomposition. The background test showed that the motor or the spinning of the disc did not generate sub-50-nm particles, thus, leaving only thermal decomposition of the paper portion of the sandpaper or its adhesive backing and subsequent condensation after cooling as the potential source for these particles. These particles may originate from the friction of test samples as they abrade on the sandpaper, which increased with disc sander speed. Koponen et al. (2009) also found particles smaller than 50 nm in the number distribution when sanding nanocomposites that they attributed to sparks generated from the electrical motor, which is not the case in our tests.

No free CNTs were observed by TEM or SEM for test sticks composed of less than 4% by weight CNT. This result is consistent with field observations made by Cena and Peters (2011) and laboratory tests made by Vorbau et al. (2009) and Göhler et al. (2010). For tests conducted with the test sticks composed of 4% CNT, we did observe particles on air filters by SEM with features consistent with free CNTs (SI, Fig. S2). Schlagenhauf et al. (2012) also observed free CNTs in liberated by abrasion of 1% CNT nanocomposite material. Our microscopy work was focused on samples collected during tests with high number concentrations of sub-50-nm particles, which are thought to be particles from thermal decomposition. Consequently, we may have unintentionally biased our ability to detect free CNTs in samples with less than 4% CNTs.

Most particles observed in electron microscopy were larger than 500 nm with morphology consistent with an epoxy core surrounded by protruding CNTs. The tensile strength of CNTs is substantially greater than epoxy. Thus, an explanation of the protrusions is that the CNTs pull out from the adjacent epoxy material as they are ripped into particle form. This idea is consistent with the work of Song and Youn (2005), who found that the tensile strength of the composite with well dispersed CNTs increases as the percentage of CNTs increases. Some of the micron-sized particles may also be sandpaper grit because the sandpaper was observed to be worn after completion of each of the 12-minute sanding tests, which is in contradiction with Gohler et al. (2010) who did not find abrasive removed from the sandpaper. Wohlleben et al. (2011) also considered sandpaper as a source of particles.

Results obtained for tests conducted with commercial objects with embedded CNTs were similar to those conducted on CNT-epoxy test sticks. Similar to the test sticks, a single coarse-particle mode was observed in the mass distributions for the commercial samples, whereas two modes were observed in the number distributions. The respirable mass concentrations produced by sanding the commercial samples was similar to that produced by sanding the test sticks, ranging from 0.13 mg/m³ to around 0.22 mg/m³. However, Sample 2 produced a mean number concentration of 1500 particles/cm³, three times higher than that of 2% CNTs and Sample 1, which could be attributed to the highest brittleness of Sample 2. Noticeably, the two commercial products contain CNTs less than 1% by weight, but produce particle number concentration higher than test sticks with higher CNTs percentage under the same test condition, which could be attributed to different composition of the products. These tests show the ability of our sanding method to examine subtle differences in the production of airborne particles as a function of test object and sanding conditions.

From a regulatory perspective, the respirable mass concentrations produced by all the test samples were considerably lower than the OSHA PEL for PNOR total dust of 15 mg/m³ and respirable fraction of 5 mg/m³ (OSHA 2011) and ACGIH respirable particle PNOS TLV of 3000 µg/m³ (ACGIH 2011). However, one should keep in mind that there is no specific standard regulating neat CNT or CNT-epoxy nanomaterials.

There are several limitations of this study. The combination of the OPC data and the SMPS data might not accurately reflect the particle size distribution since the two measurements are based on different principles. Moreover, the refractive index of particles was assumed to be uniform across test samples, although the fact that the test samples have different colors may lead to an inconsistency in refractive index across tests and some inaccuracies in particle sizing with the OPC. Our manual microscopy was qualitative, which may be biased from operator selection of representative particles. Future efforts would benefit from quantitative microscopy, perhaps through computer-controlled microscopy, to determine the relative fraction of particles that contain protuberances, for example.

Conclusions

The quantity and size distribution of airborne particles emitted when CNT-containing materials are sanded depend on characteristics of the material being sanded and the conditions under which sanding occurs. The determinants of particle concentration include the brittleness of test samples, which is a function of the loading of nanomaterial, and the abrasion energy, which is associated with sandpaper grit and disc sander speed during the sanding process. In addition to the abrasion, the friction originated by the contact of test samples and sandpaper may cause the sandpaper or adhesive backing to thermally decompose and produce sub-50-nm particles. No free CNTs were observed on air filters, except for tests conducted with 4% by weight CNT test sticks.

This study presented a well-defined test method to characterize the particle emission during sanding process, and a high repeatability was achieved with both CNT-composites and selected commercial products. Also the methodologies established could be modified for other nanocomposite products and extended to other life cycle events such as shredding, and can include degradation factors such as UV exposure. Future studies on the inhalation toxicity of environmentally-relevant aerosols could be accomplished with the combination of the test apparatus and a toxicological test chamber.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Authors would like to acknowledge National Institute of Environmental Health Sciences (NIEHS) (Award No. 1R41ES019384-01).

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Fig. 1.
Experimental setup

Fig. 2.
The timeline of the test protocol

Fig. 3. Boxplots of **(a)** number and **(b)** respirable mass concentrations and particle size distributions by **(c)** number and **(d)** mass for test sticks with varying percentages of CNTs (medium disc sander speed and medium sandpaper grit)

Fig. 4. Boxplots of **(a)** number and **(b)** respirable mass concentrations and particle size distributions by **(c)** number and **(d)** mass for different disc sander speeds (2% CNTs test stick and medium sandpaper grit)

Fig. 5. Boxplots of **(a)** number and **(b)** respirable mass concentrations and particle size distributions by **(c)** number and **(d)** mass for different roughness of sandpaper (2% CNTs test stick and medium disc sander speed)

Fig. 6. Boxplots of **(a)** number and **(b)** respirable mass concentrations and particle size distributions by **(c)** number and **(d)** mass for different test objects (medium disc sander speed and medium sandpaper grit)

Fig. 7.
Airborne particle with detail of protruding carbon nanotube (TEM image).

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Table 1

Test conditions

Test Object	Sandpaper Type			Disc Sander Speed	
Test Stick CNTs Percentage	Roughness	Grit Level	Presenting Grit Size, μm	Speed	RPM
0%, neat	Mediu	P150	100	Mediu	1425
1%	Mediu	P150	100	Mediu	1425
2%	Mediu	P150	100	Mediu	1425
3%	Mediu	P150	100	Mediu	1425
4%	Mediu	P150	100	Mediu	1425
Sample 1	Mediu	P150	100	Mediu	1425
Sample 2	Mediu	P150	100	Mediu	1425
2%	Coarse	P80	201	Mediu	1425
2%	Fine	P320	46.1	Mediu	1425
2%	Mediu	P150	100	Fast	2167
2%	Mediu	P150	100	Slow	586
No Object	Mediu	P150	100	Mediu	1425

Table 2

Comparison of number concentration mean differences between test conditions using one-way ANOVA and multiple comparison with Tukey's test at $\alpha=0.05$. Significant differences were observed in all cases ($p<0.001$).

Test Condition	Number of Samples	Number Concentration Mean (SD), particles/cm ³	Grouping
(a) CNTs Percentage (%)			
4	3	455 (99)	A
0	3	361 (80)	A B
3	3	340 (91)	B C
2	3	332 (55)	C
1	3	200 (82)	D
(b) Disc Sander Speed			
Fast	3	3140 (581)	A
Medium	3	332 (55)	B
Slow	3	92 (18)	C
(c) Sandpaper Roughness			
Coarse	3	4670 (1220)	A
Medium	3	332 (55)	B
Fine	3	214 (124)	B
(d) Commercial Sample Compared to Test Sticks			
Sample 2	3	1470 (397)	A
Sample 1	3	454 (204)	B
2% CNTs	3	332 (55)	C

Table 3

Comparison of respirable mass concentration mean differences between test conditions using one-way ANOVA and multiple comparison with Tukey's test at $\alpha=0.05$. Significant differences were observed in all cases ($p<0.001$).

Test Condition	Number of Samples	Respirable Mass Concentration Mean (SD),	Grouping
(a) CNTs Percentage (%)			
4	3	0.690 (0.10)	A
2	3	0.324 (0.03)	B
3	3	0.248 (0.05)	C
1	3	0.220 (0.04)	D
0	3	0.200 (0.04)	D
(b) Disc Sander Speed			
Fast	3	0.580 (0.05)	A
Medium	3	0.324 (0.03)	B
Slow	3	0.208 (0.03)	C
(c) Sandpaper Roughness			
Fine	3	1.011 (0.08)	A
Coarse	3	0.401 (0.06)	B
Medium	3	0.324 (0.03)	C
(d) Commercial Samples Compared to Test Sticks			
Sample 1	3	0.367 (0.03)	A
Sample 2	3	0.356 (0.04)	B
2% CNTs	3	0.324 (0.03)	C