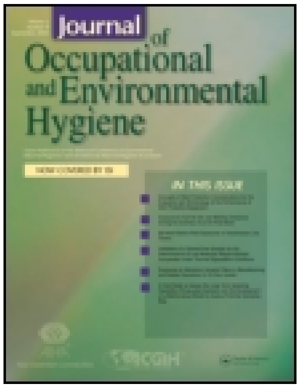

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Evaluation of the Potential Airborne Release of Carbon Nanofibers During the Preparation, Grinding, and Cutting of Epoxy-Based Nanocomposite Material

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The National Institute for Occupational Safety and Health conducted an initial, task-based comparative assessment to determine the potential for release of carbon nanofibers (CNFs) during dry material handling, wet cutting, grinding, and sanding (by machine and hand) of plastic composite material containing CNFs. Using a combination of direct-reading instruments and filter-based air sampling methods for airborne mass and transmission electron microscopy (TEM), concentrations were measured and characterized near sources of particle generation, in the breathing zone of the workers, and in the general work area. Tasks such as surface grinding of composite material and manually transferring dry CNFs produced substantial increases in particle number concentration (range = 20,000–490,000 1-cm^{-3}). Concomitant increases in mass concentration were also associated with most tasks. Nearly 90% of all samples examined via TEM indicated that releases of CNFs do occur and that the potential for exposure exists. These findings also indicate that improperly designed, maintained, or installed engineering controls may not be completely effective in controlling releases. Unprotected skin exposure to CNFs was noted in two instances and indicated the need for educating workers on the need for personal protective equipment.

[Supplementary materials are available for this article. Go to the publisher's online edition of Journal of Occupational and Environmental Hygiene for the following free supplemental resource: a PDF file containing information on materials, evaluated processes, personal protective equipment, and existing ventilation/engineering controls.]

Keywords carbon nanofiber, composite, cutting, exposure, grinding, nanomaterials, release, sanding

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INTRODUCTION

Although adverse health effects have not yet been linked with worker exposure to carbon nanotubes (CNTs) or carbon nanofibers (CNFs), early animal studies have shown an increase in lung effects such as pulmonary fibrosis and inflammation[1–5] as well as the ability for CNTs to migrate across the pleura in a manner similar to asbestos fibers.[6] These recent studies and others designed to evaluate the adverse health effects associated with exposure to nanomaterials in general have amplified concerns about such exposure.[7]

In recent years, there has been an increase in research on the uses and application of composite materials containing CNTs and CNFs.[8,9] Polymeric composite materials containing CNTs/CNFs are becoming more popular in the aerospace, defense, and ground transportation industries. As these materials are incorporated into structural components of larger pieces of equipment (e.g., aircraft parts), the need to drill, cut, sand, and grind the materials is inevitable. With such manipulations come questions regarding the potential for worker exposure during such tasks.

Few data exist on the potential for release of CNTs/CNFs and subsequent exposure during machining of CNT-containing composite material. One study examined mechanical sanding of such material inside a glove box,[10] and another characterized airborne exposure during the processing of CNT-containing hybrid composites in a research laboratory.[11] Although the extent of knowledge about worker exposure to CNTs and CNFs is limited, workplace measurements indicate the potential for exposure.[12–19] However, without validated exposure assessment and analytical methods and legally enforceable occupational exposure limits, data collected during such studies (including this one) can be used only for the purposes of comparing processes, tasks, work practices, and engineering controls.

The evaluated facility conducts a variety of research, development, and technical service projects on polymeric materials. Concerns about the potential exposure of workers involved in the handling of CNFs during the preparation of epoxy-based CNF composite nanomaterials—in addition to cutting, sanding, and grinding the materials—provided the impetus for the field research study described here. To address these concerns, the goals of this study were to (1) determine whether CNFs are released and the magnitude of such releases during a variety of tasks or processes that in turn may result in potential worker exposure; (2) determine whether the CNF material migrates to the personal breathing zone (PBZ) of the worker; (3) evaluate the effectiveness of existing engineering control devices in reducing or eliminating potential exposure during the processing and handling of CNFs, and (4) observe work practices to identify factors that may contribute to exposure via other routes (e.g., dermal).

METHODS

Information on materials, task descriptions, and existing engineering controls appear in a supplemental online file. Photographs of some workers engaged in some tasks as well as the equipment and personal protective equipment (PPE) used appear in Figures 1 and 2.

Sampling

Over a period of 4 days, an assessment of potential sources of CNF exposure was conducted on a task-by-task basis using a combination of direct-reading instrumentation and filter-based air sampling techniques. Filter-based air samples analyzed for mass of elemental carbon (EC) and qualitative transmission electron microscopy (TEM) were collected. Personal breathing zone and process area (PA) air samples were collected during specific tasks/processes to determine the possible presence and quantity of CNF concentrations. PBZ samples were collected as close as possible to each subject's face (e.g., the lapel of the Tyvek suit), whereas PA samples were collected as close as possible to the suspected source (e.g., just above a receptacle during product transfer). In addition, some PA samples were collected outside specific controls (e.g., ventilated booths) to determine whether CNFs migrated outside such controls. Finally, general area (GA) samples were collected in some rooms for the duration of CNF handling activity to determine the overall background concentration of the material of interest. In general, this sampling strategy was used to determine whether CNFs are released during a variety of tasks/processes, the relative magnitude of concentrations that could result in potential worker exposure, and the extent to which the material migrated to the PBZ of the worker.

While the time necessary to complete most tasks (weighing, transferring, cutting composite material, and so on) was of short duration (e.g., 5 min), the staff engaged in the tasks were asked to repeat the process for multiple cycles to increase the volume of air sampled, create a worst-case scenario, and to simulate production activities on a larger scale. Also, the longer sampling time and larger air volume sampled increased the probability of capturing released CNFs. If sampling times had been limited to the normal duration of each task (a few minutes), then the low volume of sampled air would likely result in samples being reported (with regard to CNF content) as ND. Therefore, the results obtained during these extended tasks may not be indicative of the true magnitude of short duration potential exposure. Likewise, because the design of this initial assessment was to identify task(s) that resulted in releases of material and potential exposure, it was decided that a full-shift integrated sample would not be collected for each worker; there would have been no direct way to identify which task(s) were contributors to the overall potential worker exposure. Therefore, the task-based sampling approach, as it is applied here, should not be interpreted as representative of full-shift worker exposure.

All filter-based air samples were collected with Leland Legacy pumps (SKC Inc., Eighty Four, Pa.) operating at a sampling rate of 7.0 L/min. All pumps were calibrated before and after each day of sampling. Air samples to determine the airborne mass concentration of CNFs (using EC as an indicator of CNFs) were collected on 37-mm-diameter open face quartz fiber filters (QFFs) and analyzed according to Method 5040 of the *NIOSH Manual of Analytical Methods* (NMAM).[20]

Alongside each mass-based air sample, an additional air sample was collected simultaneously on a 37-mm-diameter, open face, mixed cellulose ester (MCE) filter and examined qualitatively via TEM to determine the presence or absence of CNFs. The rationale behind conducting a qualitative examination is that no validated microscopy method for quantitatively analyzing air sampling media for CNFs exists. Each MCE filter was analyzed using TEM in a manner similar to NMAM Method 7402,[20] whereby a small portion of the filter was placed on a 3-mm carbon-coated copper TEM grid and collapsed onto the grid structure using acetone vapor inside a covered petri dish. Each TEM grid was allowed to dry overnight prior to examination.

A slight modification of Method 7402 was used where the analyst examined the TEM grid and attempted to identify any CNFs present in 40 grid openings. To ensure consistency in identifying the CNF material of interest, the analyst prepared a TEM grid containing the bulk CNF material supplied by the facility (Figure 3) and used images of the material for visual identification purposes. In general, TEM provides an indication of the relative abundance of particles across a wide size range (including those in the nanometer size range), as well as other characteristics such as size, shape, and degree of agglomeration. Sampling times for all filter-based air samples ranged from 21 min to 428 min (volume of air sampled ranged from 147 L to 2996 L) and was dependent on the time necessary to complete the task.

Direct-Reading Instrumentation

Three direct-reading instruments were used to characterize task-based releases by determining the number concentration and approximate size ranges of airborne particulate, as well as the aerosol mass concentration. The first instrument used was a TSI P-Trak (TSI, Inc., Shoreview, Minn.) hand-held condensation particle counter (CPC). The P-Trak measures particles in the size range of 20 nm to 1000 nm and expresses the data output as total number of particles per cubic centimeter of air (1-cm^{-3}), with an upper range limit of approximately 500,000 1-cm^{-3}. The value of this instrument for evaluating

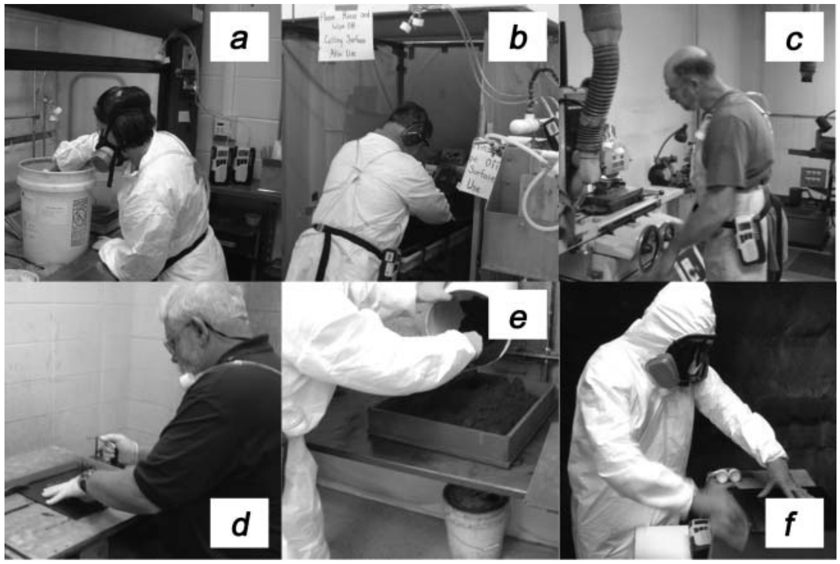

FIGURE 1. Photos of workers engaged in some tasks. (a) Weighing CNF's inside lab hood with sash in operating position; (b) Wet saw cutting composite inside canopy ventilated booth; (c) Surface grinding composite containing CNFs with LEV; (d) Table saw with wet diamond blade cutting composite (no controls); (e) Transferring CNF's to tray inside ventilated booth; (f) Hand sanding composite laminate material inside ventilated booth.

nanoparticle emissions is its ability to detect particles in the range of 20 to 100 nm, even though it will respond to the presence of larger particles up to 1000 nm.

The second instrument, an HHPC-6 (ART Instruments, Grants Pass, Ore.), was used to determine the number concentration of particles, based on optical counting principles using laser light scattering. This instrument measures the total number of particles per liter of air (1-L^{-1}) within the following size channels: 300–500 nm, 500–1000 nm, 1000–3000 nm, 3000–5000 nm, and 5000–10,000 nm. This instrument was operated in differential mode whereby the count data include all particles that are larger than or equal to the particle size selected but smaller than the next greatest particle size.

The third instrument, the DustTrak DRX Aerosol Monitor (Model 8533; TSI, Inc.), can simultaneously measure both mass and size fraction of airborne particulate using laser light scattering. This instrument was used to estimate the aerosol mass concentration of particulate less than 15,000 nm in aerodynamic diameter. Aerosol photometers provide estimates based on assumed density and particle size distributions produced by the instrument manufacturer. The instrument will respond to particles in the size range of 100 to 15,000 nm and aerosol mass concentrations ranging from 10 to 150,000 μg-m^{-3}. However, the detector's sensitivity to particles below a 250 nm diameter cutpoint drops dramatically, and its efficiency in measuring fiber-like aerosols is less than that obtained when sampling an aerosol composed of spherical particulate. Therefore, data collected using this instrument should not be interpreted as specific to CNFs.

To estimate the magnitude of source releases during each task, the sampling inlet of each instrument was positioned simultaneously within the airspace closest to the source (e.g., opening of container during transfer of CNFs). To estimate PBZ number and mass concentrations, the inlet was positioned within the airspace of the head/neck region, forward of the shoulder area.

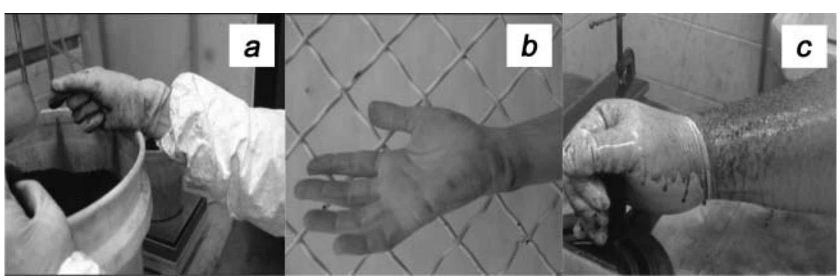

FIGURE 2. Tasks with potential dermal exposure. (a) Glove/elastic wrist closure separation; (b) Dermal exposure due to separation between glove and wrist closure; (c) Aerosol plume deposition onto unprotected skin during cutting of composite (no controls).

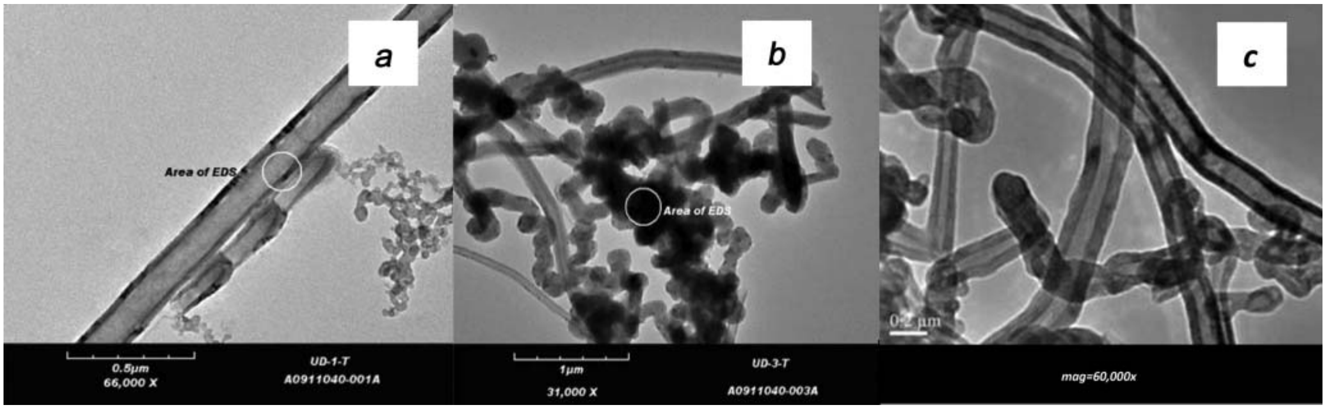

FIGURE 3. TEM images of filters collected during CNF weighing task inside hood. (a) PBZ during weighing of CNF's inside lab hood; (b) PA (above balance) during weighing of CNFs inside lab hood; (c) Bulk CNF material

Because the size range of CNFs existing as single or agglomerated masses was unknown at the time of this evaluation, it was determined that using these particle sizing and counting instruments would provide a semiquantitative indication of the nature and magnitude of potential releases for each task. The two sizing and counting instruments used simultaneously provided an approximate differential evaluation of the aerosol being sampled. For example, particle number concentration between 20–300 nm can be estimated by subtracting the HHPC-6 counts in the 300–1000 nm size range from the counts obtained using the P-Trak (20–1000 nm). All of the direct-reading measurements were evaluated relative to background concentration values. The background number concentration and aerosol mass concentration measurements were made before and after each task. An average of the two measurements was calculated and used to adjust, via subtraction, each task-based measurement.

Because the direct-reading instruments are not material-specific (e.g., detect CNFs only) and cannot identify the chemical composition of the particles detected, one cannot definitively conclude that increases in particle number concentration for a specific operation are due to a release of particulate material from that process. Differences in operation, counting efficiency, calibration materials, and the relative influence of refractive index make direct comparison of data across instruments difficult.[(21)] Also, non-spherical particles and agglomeration state may cause variability in the precision and accuracy of optical-based counting instruments.[(22)] However, trends involving increases in particle number concentration or aerosol mass concentration associated with specific tasks can be identified.

RESULTS

Of the task-based air samples analyzed for EC, 79% had airborne concentrations above the analytical limit of detection of 0.6 μg/sample (Table I). For all samples collected, air concentrations of EC ranged from non-detectable (ND) to 1900 μg/m^3. PBZ samples ranged from ND to 1000 μg/m^3, with 90% of the samples having detectable amounts of EC. Of the 11 PA samples collected, 80% had detectable amounts of EC, ranging from ND to 1900 μg/m^3. Of the three GA samples collected, EC was detected on only one—the room where the wet saw cutting occurred with ventilation controls (3.7 μg/m^3). The lowest measureable PBZ air sample was collected during the weighing of CNFs inside a laboratory hood, whereas the highest measured PBZ sample occurred during wet saw cutting of composite without controls. For the PA air samples, the lowest values obtained (ND) were for those collected during the transfer of CNFs to graphite trays inside the ventilated booth and also outside the laboratory hood during the weighing of CNFs. The highest value PA sample was collected inside the ventilated enclosure during wet saw cutting of composite material.

Images produced during the TEM analysis of the bulk material and air sampling filters appear in Figures 3–8. Of the filter-based air samples examined, nearly all PBZ and PA samples (89%) showed evidence of CNFs (Table I). The majority of samples contained mostly nonagglomerated CNFs, whereas a smaller subset of samples contained a larger amount of loosely agglomerated CNFs.

The data presented in Table I also illustrate the changes in particle number concentration and aerosol mass concentration, as measured by the direct-reading instruments. Similar to the results of the filter-based analyses, specific tasks were found to release particulate. The largest increase in particle number concentration in the PBZ and also close to the source (PA) occurred during three different tasks: surface grinding, wet saw cutting, and transfer of CNFs to trays. When measuring the task-based airborne mass concentration, values ranged from 10 to 18,500 μg/m^3. The highest value was measured during belt sanding of CNF composite, whereas the lowest value (10 μg/m^3) occurred in the PBZ during weighing of CNFs inside the hood. Other processes that emitted a substantial aerosol mass concentration were wet saw cutting, transfer of CNFs to trays, and hand sanding of composite material with no ventilation.

TABLE I. Task-Based EC Concentration, Number Concentration, Mass Concentration, and Evidence of CNFs Detected with TEM

Task Description	Location of Sample	20–300 nm Number Concentration (1-cm^{-3})	EC Concentration (μg-m^{-3})	Photometer (300–10,000 nm) (μg-m^{-3})	TEM: CNFs Present?
Weighing CNFs inside lab hood	PBZ	1697	2	10	Yes (Figure 3a)
Weighing CNFs inside lab hood (above balance)	PA	1476	15	870	Yes (Figure 3b)
Weighing CNFs inside lab hood (outside hood)	PA	0	ND	N/A	No
Wet saw cutting of CNF composite inside ventilated booth	PBZ	2605	910	1130	Yes (Figure 4a)
Wet saw cutting of CNF composite inside ventilated booth (inside booth)	PA	N/A	1,900	N/A	Yes (Figure 4b)
Wet saw cutting of CNF composite inside ventilated booth (outside booth)	PA	N/A	480	N/A	Yes (Figure 4c)
Wet saw cutting of CNF composite (no controls)	PBZ	1934	1,000	N/A	Yes (Figure 4d)
Wet saw cutting of CNF composite (no controls)	PA	N/A	390	5750	Yes (Figure 4g)
Surface grinding of CNF composite with LEV	PBZ	42,088	14	500	Yes (Figure 5a)
Surface grinding of CNF composite with LEV (at edge of LEV inlet)	PA	491,599	45	900	Yes (Figure 5b)
Belt sanding of CNF composite with LEV	PBZ	0	8	N/A	No (Figure 6b)
Belt sanding of CNF composite (at edge of LEV inlet)	PA	0	76	18,500	Yes (Figure 6a)
Transfer of CNFs to trays inside ventilated booth	PBZ	20,866	44	1840	Yes (Figure 7a)
Transfer of CNFs to trays inside ventilated booth (inside booth)	PA	N/A	ND	N/A	Yes (Figure 7b)
Transfer of CNFs to trays inside ventilated booth (outside booth)	PA	N/A	ND	N/A	Yes (Figure 7c)
Hand sanding of CNF composite inside ventilated booth (vent on)	PBZ	N/A	7	N/A	Yes (Figure 8a)
Hand sanding of CNF composite inside ventilated booth (vent off)	PBZ	N/A	ND	N/A	Yes (Figure 8b)
Hand sanding of CNF composite inside ventilated booth (vent on)	PA	0	11	160	Yes (Figure 8c)
Hand sanding of CNF composite inside ventilated booth (vent off)	PA	0	79	3090	Yes (Figure 8d)

Notes: PA = process area; PBZ = personal breathing zone; μg-m^{-3} = micrograms per cubic meter of air; ND = none detected (analytical limit of detection = 0.6 μg/sample); LEV = local exhaust ventilation; N/A = Not applicable, due to potential interference with the worker engaged in the task, measurement not made. Photometer limit of detection = 10 μg-m^{-3}.

DISCUSSION AND CONCLUSIONS

The design of this initial assessment was to be range-finding, with the primary goal of determining tasks that release particulate that could migrate to the PBZ. A secondary goal was to determine whether existing engineering controls are effective in controlling emissions. The rationale behind collecting PA samples inside a ventilated enclosure was to estimate the magnitude of a release that could potentially result in exposure, while those collected outside the enclosure

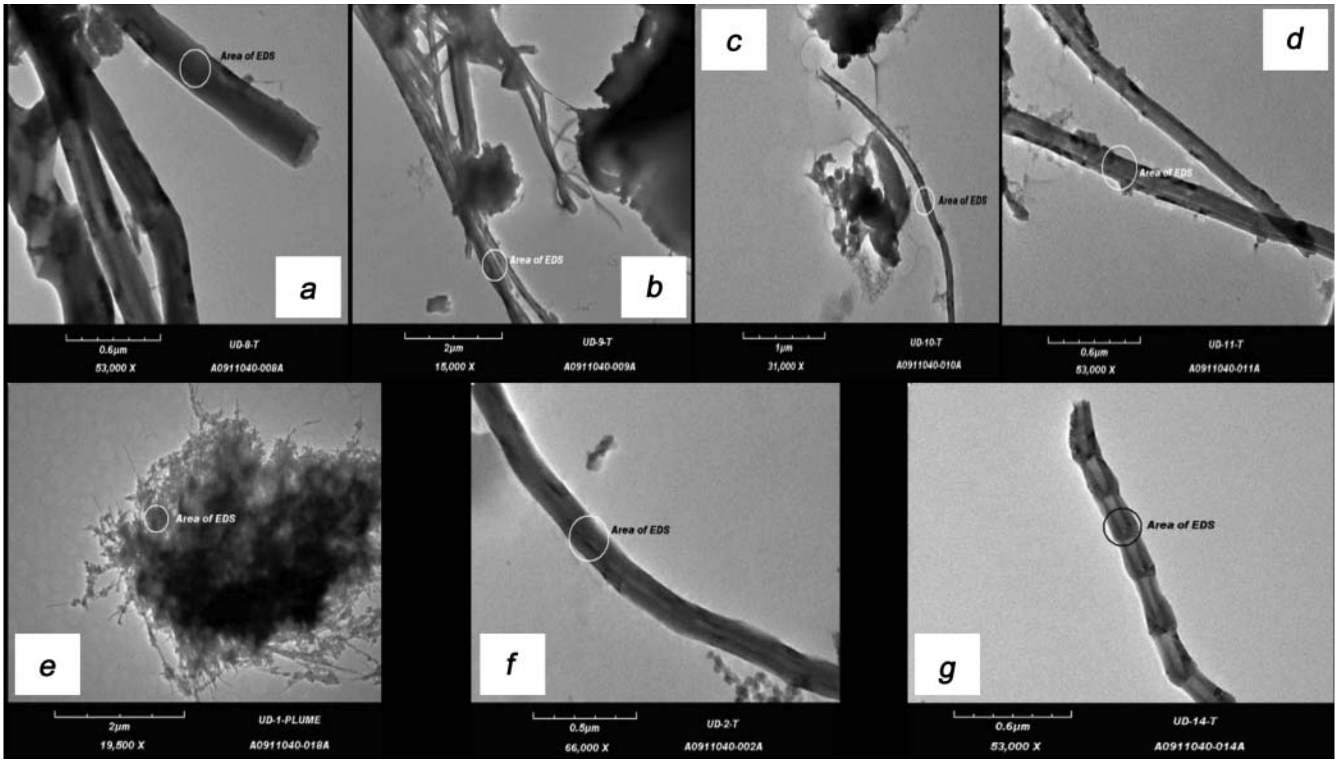

FIGURE 4. Wet saw cutting of composite. (a) PBZ during wet saw cutting of composite in ventilated enclosure; (b) PA inside ventilated enclosure; (c) PA outside ventilated enclosure; (d) PBZ during wet saw cutting (no controls); (e) Aerosol plume spun off blade; (f) GA sample in center of laboratory (with controls); (g) PA sample near wet saw (no controls)

could serve as an indicator of the effectiveness of the exhaust ventilation system in capturing the released particulate. The PBZ samples provide an indication (relative to the PA samples) of the amount and physical state of the CNFs reaching the workers' breathing zone.

On the basis of the TEM images, air concentrations of EC, and direct-reading instrument data, it is apparent that CNF material is released to the workplace atmosphere in both bound forms (within or attached to the composite matrix) and unbound forms (free fibers, bundles, or agglomerates). With respect to the effectiveness of existing engineering controls, the data show that releases are not completely controlled. Considering the results (Table I) along with the TEM images (Figures 3–8), one can determine which tasks resulted in a release. Because the particle number concentrations in the lower size ranges are higher than the average background (e.g., surface grinding), and the results of the TEM analysis yielded evidence of CNFs, one can conclude that a release occurred and the potential for exposure exists. In general, the results presented here are in agreement with those observed in a similar study using similar materials, instrumentation, and sampling strategies.[23]

Given the lack of a validated method specific for the analysis of CNFs in composite material, it was decided to analyze the filter samples via NIOSH Method 5040[20] and use the EC data as an indicator of the airborne mass concentration of CNFs. However, a limitation of the method involves the specificity related to the identification and contribution of different sources of EC that are collected on the filter. In addition, Method 5040 is unable to distinguish free CNFs from those embedded in the composite matrix, which may contain other source(s) of EC (e.g., carbon black). If there is a substantial fraction of the composite material that contains EC from a source other than CNFs (e.g., carbon black), this would result in an overestimation of the airborne mass concentration of CNFs. Therefore, the airborne EC mass concentration data should be interpreted with caution, and not all mass should be considered indicative of free CNFs. However, if the parent material remains consistent in its chemical constituents, then the airborne mass data can be used on a relative basis to identify tasks that generate the most particulate. Such issues further support the need for the collection and analysis of filter samples via electron microscopy.

Some observations of work practices, PPE, and existing engineering controls yielded unexpected results. For example, there was evidence of a release of CNFs and potential exposure in the PBZ of the worker engaged in weighing CNFs inside a laboratory hood (Figures 1a, 3a, 3b). This may be because the hood sash was fully open and the worker leaned inside the hood to execute the transfer of CNFs from the bucket to the electronic balance. If the worker was not wearing a respirator, such a work practice would position the PBZ closer to the

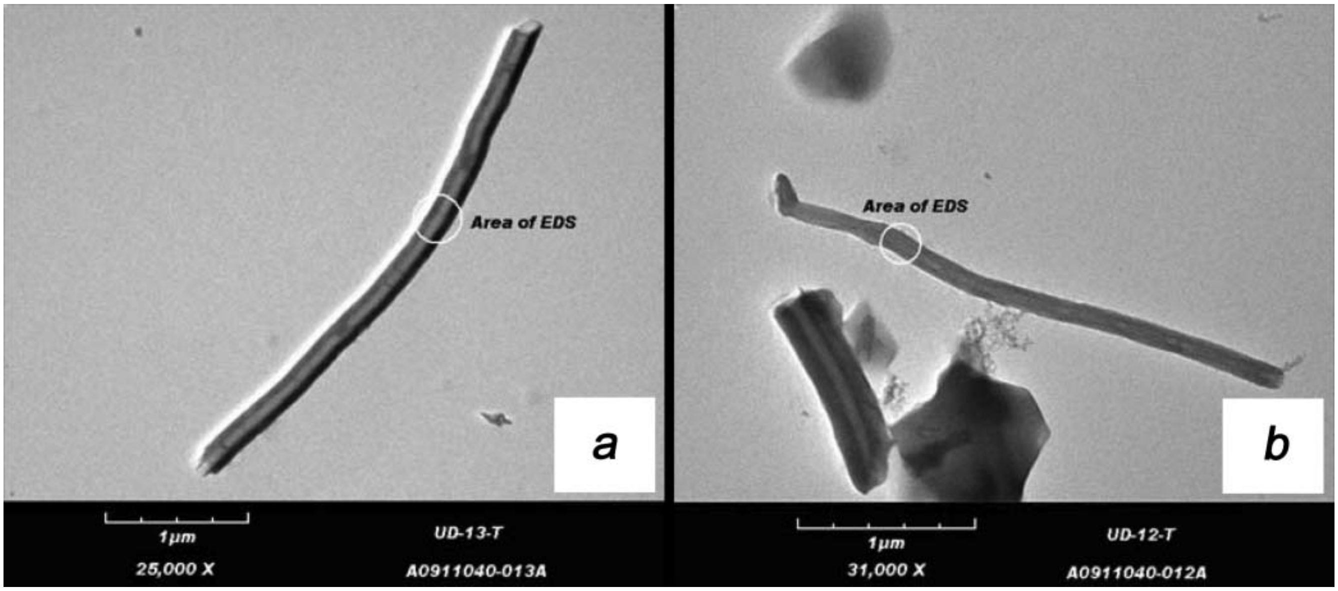

FIGURE 5. Horizontal surface grinding of composite. (a) PBZ; (b) PA above grinding wheel (adjacent to inlet of LEV)

source of exposure and may also reduce the effectiveness of the laboratory hood in capturing emitted CNFs. Also observed during this task was the potential for dermal exposure to CNFs. During the weighing operation, the sleeve of the PPE garment tended to ride up at the wrist/glove junction, thereby exposing the skin and enabling the deposition of CNFs onto bare skin (Figures 2a, 2b).

Two different wet saw operations that involved the cutting of CNF composite materials were evaluated during this study. In one operation, all cutting was done with a diamond blade table saw inside a three-sided ventilated enclosure fabricated out of vinyl sheets positioned below a canopy exhaust hood (Figure 1b). The average face velocity ($n = 9$ measurements) at the opening of the enclosure was very low (3 m/min). Filter-based air samples collected inside and outside the enclosure (PA) as well as in the PBZ, all yielded substantial amounts of EC, with TEM analysis indicating that single and bundled CNFs, in addition to fractal particles of composite material, were released (Figures 4a, 4b) and not well controlled (Figure 4c). In fact, CNF-containing aerosol escaping the enclosure could result in bystander worker exposure and gross contamination of the laboratory workspace (Figure 4f).

In another room, wet sawing of CNF composite material was done with a diamond blade table saw without any controls (Figure 1d). Again, both PBZ and PA filter-based samples contained substantial amounts of EC (Table I; Figures 4d,

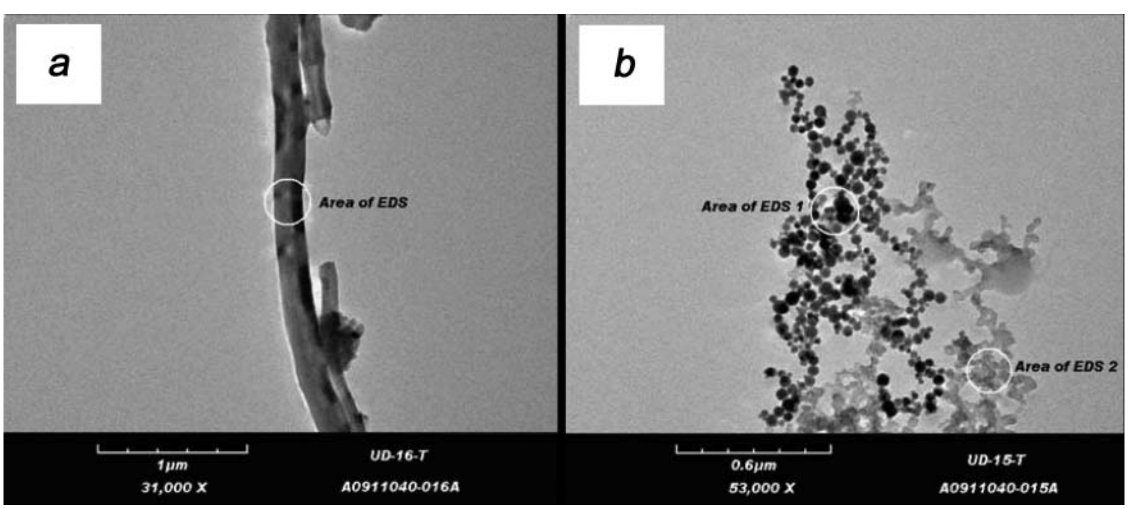

FIGURE 6. Belt sanding composite. (a) PA near inlet of LEV; (b) PBZ

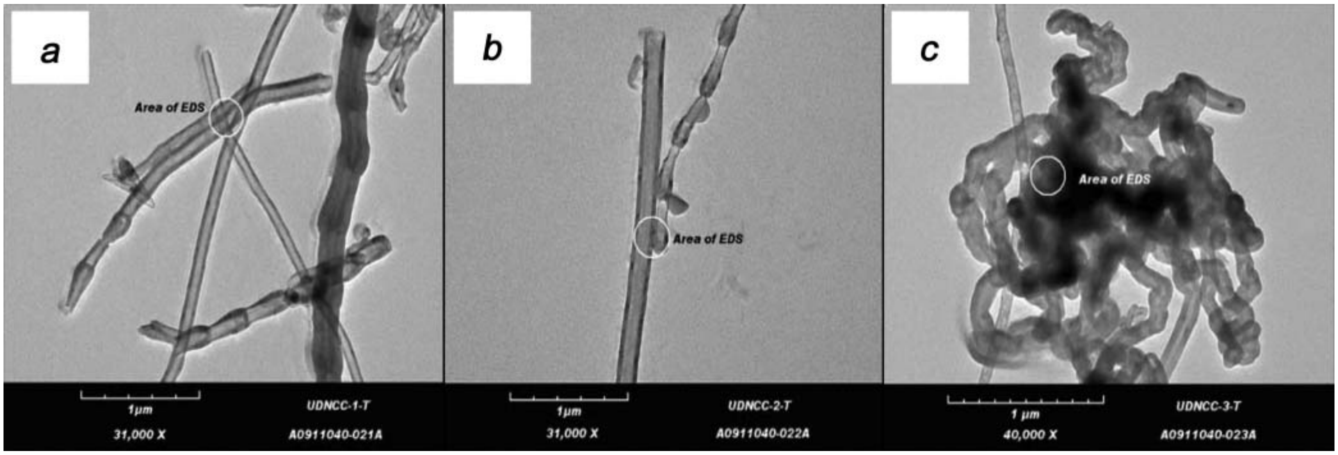

FIGURE 7. Transfer of CNF inside ventilated booth. (a) PBZ; (b) PA on work table inside booth. (c) PA outside booth

4g). During this operation, an attempt at capturing the droplet plume was made whereby an open MCE filter cassette was placed in front of the plume and allowed to collect the aerosol via impingement. TEM analysis of this sample (Figure 4e) indicated that the droplets contained structures of nested CNFs, in agreement with the observations by Johnson et. al.,[24] who noted agglomerates of nested CNTs in droplets released into the workplace atmosphere via sonication of an aqueous solution containing CNTs. This finding, along with visual evidence of uncontrolled plume impaction on the wall behind the wet saw, supports the indication that the aerosol plume could be dispersed and result in gross contamination of the entire room. In addition, there is the potential for dermal exposure during this operation (Figure 2c). Even though the worker was wearing latex gloves, the unprotected skin of the wrist and forearm area became saturated with the aerosol plume spun off from the rotating diamond blade.

In another room, dry surface grinding of CNF composite material was conducted with a horizontal surface grinder equipped with an LEV exhaust duct inlet oriented 90° to the direction of the particulate plume spun off the grinding wheel (Figure 1c). Both PBZ and PA samples had measureable amounts of EC and the highest particle number concentration of any task evaluated. Clearly, the dust generated by this operation was not well controlled. The aerosol mass concentration data obtained during this operation followed the same trend (Table I). TEM analysis of both PBZ and PA filter samples indicated that single CNFs and fractal particles of composite were emitted during this operation (Figures 5a, 5b). The lack of control appears to be due to the perpendicular orientation of the exhaust LEV inlet, relative to the direction of the plume spun off from the wheel (Figure 1c). Because of its direction and velocity, the plume appears to bypass the inlet of the LEV duct installed to capture the particulate emitted from the grinding wheel.

For sanding edges of composite material containing CNFs, a tabletop belt sander with LEV was used. A partial plastic enclosure was fabricated by the worker, attached to the LEV duct system, and positioned at the belt spindle in an effort to capture any particulate emitted during this task. The LEV air velocity was measured at the inlet opening and was found to be 76 m/min. The PA sample obtained near the point of contact between the material and the sanding belt was analyzed by TEM and showed evidence of CNFs (Figure 6a) and an EC

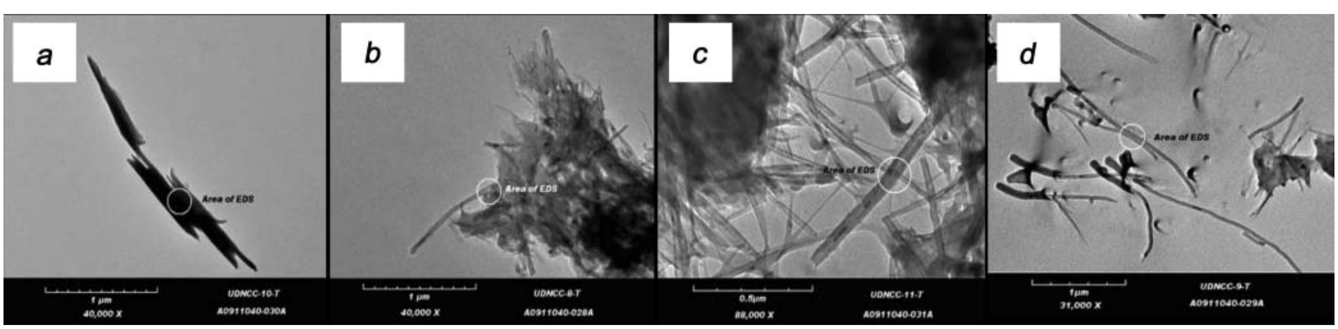

FIGURE 8. Hand sanding composite laminate inside booth. (a) PBZ (ventilation on); (b) PBZ (no ventilation); (c) PA (ventilation on); (d) PA (no ventilation)

concentration of 76 μg/m^3 (Table I) and an aerosol mass concentration of 18,500 μg/m^3, which was the highest measurement made with the photometer during this assessment (Table I). However, the particle number concentration in the PBZ and PA indicated no release of material in the 20–300 nm size range occurred. Such a finding indicates that the particulate generated by this operation is of a size larger than 300 nm. In addition, the EC concentration for the PBZ sample collected during this operation was approximately 10 times less than the PA sample.

Furthermore, the PBZ sample analyzed via TEM did not show tubular structures but clusters of spherical carbon particles (Figure 6b). This finding may be the result of an insufficiency of CNFs present on the TEM grid (which represents a very small fraction [approximately 1%] of the total filter surface area) or extremely light loading of the filter, or it may indicate that the particulate plume is spun off and directed away from instead of toward the LEV inlet.

During CNF tray loading activities inside a ventilated booth, the PBZ air sample had detectable amounts of EC and an increase in particle number concentration, and there was visual evidence of CNFs on filters analyzed via TEM (Table I; Figures 1e, 7a). However, the PA samples collected inside and outside the booth did not have detectable amounts of EC, yet TEM analysis indicated CNFs were present (Figures 7b, 7c). This finding may be due to the location of the PA sampling, which was farther away from the trays than the PBZ of the operator loading the trays. Also, TEM is a sensitive analysis by which one can visually detect CNFs on a filter sample yet find no detectable amount of EC mass, which may be attributed to CNFs having little mass. The TEM analysis proved useful in confirming the observation that not all CNFs released during the tray loading process were captured by the ventilated booth and can migrate outside the booth and potentially contaminate the air and surfaces throughout the room (Figure 7c). Another possible explanation of this finding may be that the CNFs are bypassing the edges of the HEPA filtration media and are discharged back into the room via recirculated air currents.

The last operation evaluated during this assessment occurred inside a walk-in paint spray booth, where CNF composite material was hand sanded with the booth ventilation on and off (Figure 1f). Analysis of the PA samples collected with the ventilation system off revealed EC levels that were approximately seven times higher than for the PA samples collected with the ventilation on (Table I). However, the EC level in the PBZ sample collected with the ventilation off was somewhat lower than in the sample collected with the ventilation on (Table I). This finding was unexpected and may be due to air turbulence around the worker while the ventilation was on, which could direct particulate, via air eddies, into the PBZ.[25] Similar to the belt sanding task, the particle number concentration in the 20–300 nm size range near the source during the hand sanding task was no different from the average background, regardless of the presence of ventilation. This finding seems to indicate that the sanding task produces particles greater than 300 nm. However, according to the photometer, there was a 19-fold difference in aerosol mass concentration with ventilation on vs. ventilation off. The TEM analysis of all filter-based samples showed evidence of CNFs, regardless of the ventilation condition (Figures 8a–d).

RECOMMENDATIONS

Currently, there are no legally enforceable quantitative regulatory exposure limits specific to CNFs. However, it is good occupational safety and health practice to keep exposures to new and uncharacterized materials as low as possible. The filter-based air sampling data and the direct-reading instrumentation data indicate that releases of CNFs to the workplace atmosphere occur during the tasks performed at this facility. Evidence from the TEM analysis of the air sampling filters confirm that there are loosely bundled and agglomerated CNFs as well as singular fiber releases occurring, which could result in worker exposure. Given these findings, the following recommendations are aimed at reducing or eliminating the potential for exposure to CNFs during the tasks described here:

1. Lower the sash on the laboratory hood to the proper operating height while weighing CNFs so that a hood face velocity of 24–32 m/min is achieved. However, given the relatively low density of the CNFs/CNTs, such a face velocity may result in the loss of the CNFs/CNTs during the transfer of material to the weighing apparatus. Move all materials (bucket, lid, and so on) away from the hood opening and conduct all operations at or exceeding a source-to-sash working distance of approximately 15 cm, and avoid leaning inside hood during this operation. If possible, use a shorter bucket to transfer CNFs. Avoid swift arm and body movements in front of or inside the hood. Keep the slots in the hood baffle free of obstruction by apparatus or containers. If possible, conduct all weighing inside a ventilated balance enclosure equipped with HEPA filtration. Remove all unnecessary items from inside the hood to reduce the amount of turbulence because release of nanoparticles to the laboratory environment has been shown to occur under turbulent conditions.[26] Conduct follow-up air sampling to determine the effect, if any, of such changes.
2. All wet sawing, dry grinding, and belt sanding operations should be placed inside a properly ventilated enclosure equipped with HEPA filtration to prevent fugitive releases from grossly contaminating the work area. Panels can be designed to allow the worker access to machine controls while maintaining control over the generated aerosol. Additional studies need to be performed not only on the design of such enclosures but also to measure the minimum air velocity necessary to achieve effective control of releases. HEPA-filtered local exhaust ventilation has been shown to be highly effective

in controlling nanoparticles, provided the system is designed properly and maintained [27,28]

3. The potential for dermal exposure to CNFs was observed during some of the operations studied. Studies have indicated that certain particles smaller than 1000 nm may penetrate skin.[29] Therefore, it is prudent to avoid having unprotected skin in contact with the nanomaterials. For example, the scenario involving the separation between the protective glove and the Tyvek laboratory coat elastic wrist enclosure could have been avoided if the juncture was sealed with tape. Another possible solution to such a problem would be to use gauntlet-style gloves that extend to the elbow and wear them over the sleeve of the laboratory coat.
4. The room and booth used to conduct CNF tray loading should have a source of fresh supply air and a dedicated exhaust with HEPA filtration directed outdoors. Use of a HEPA-filtered vacuum to clean up spilled CNFs is important to reduce general room contamination. Installing a "sticky mat" inside and outside doors leading to and from the room should substantially reduce the migration of CNF material present on the soles of footwear. Disposable footwear covers may also be an option for reducing contamination outside the handling room. Disposal of contaminated mats and footwear covers should be in accordance with facility waste management procedures.
5. Conduct all hand sanding of CNF composite inside an enclosed ventilated work station or use a ventilated sanding block attached to a HEPA-filtered vacuum source.
6. A variety of types of respiratory protection was observed at the facility and did not appear to be selected based on a specific task. At a minimum, and based on the absence of a legally enforceable occupational exposure limit for CNFs, an N95 filtering facepiece respirator should be worn during tasks shown to emit particulate based on guidance provided by NIOSH. [30]

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