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Workplace Monitoring of Airborne Carbon Nanomaterials by HRTEM

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Growing production and use of carbon nanomaterials may pose health risks for exposed workers. The National Institute for Occupational Safety and Health (NIOSH) set a recommended exposure limit (REL) for carbon nanotubes and nanofibers (CNT and CNF): an 8-hr time weighted average (TWA) of 1 μg/m^3 as respirable elemental carbon (EC) [1]. As other EC sources may interfere, complementary techniques (e.g., metals, organics, and microscopy analyses) have been used to better characterize exposure [1-4]. High resolution transmission electron microscopy (HRTEM) is especially useful because it provides visualization of particle size, shape, structure, and agglomeration state.

A TEM method for counting CNT and CNF particles was applied to air samples collected at 14 U.S. worksites [3,4]. Personal breathing zone (PBZ) samples were collected using open-faced, 25-mm cassettes with mixed cellulose ester filters (0.8 μm pore size; SKC, Inc.). Filters were analyzed on a JEOL 2100F TEM using a modified NIOSH Method 7402: asbestos by TEM [1]. Unlike asbestos fibers, CNT/CNF particles are typically entangled, complex agglomerates. Therefore, a counting method that considers the structural differences was needed for particle classification. Modifications to Method 7402 mainly relate to eliminating counting rules specific to asbestos (e.g., fiber diameters > 0.25 μm, aspect ratios ≥ 3:1, lengths > 5 μm).

In the modified method, any particle with associated CNT/CNF is counted as a 'structure,' ranging from single fibers to agglomerates of varying size and composition (Figure 1). In our studies [3,4], CNT agglomerates were roughly spherical (i.e., the longest crosswise dimension was no more than twice the orthogonal dimension). Therefore, the maximum crosswise dimension was used to classify agglomerates into the following five size bins: < 1 μm, 1-2 μm, 2-5 μm, 5-10 μm, and > 10 μm. A count of individual fibers also was made, though these were less common. Unlike asbestos, no minimum structure size cutoffs have been used due to a current lack of knowledge on respiratory deposition and health effects.
Also, the counting approach applies to free (unbound) CNT/CNF, but representative images and information on composite particles can be obtained. Polymer composite dusts (e.g., from drilling, cutting, sanding) contain respirable particles with CNT/CNF in the polymer matrix. Our analyses have shown little evidence of individual fiber release, but respirable matrix particles with protruding CNT/CNF have been observed (Figure 2). Because the CNT/CNF are embedded in a polymer matrix, the toxicity of these dusts may differ substantially from unbound CNT/CNF.

Based on the structure count, filter area, and sampled air volume, an air concentration (structures/cm^3) can be calculated. For comparison with the structure concentrations, EC samples (respirable and inhalable size fractions) also were collected [3,4]. Respirable EC (PBZ) ranged from 0.02 to 2.94 μg/m^3 (geometric mean [GM] = 0.34 μg/m^3), while the inhalable fraction ranged from 0.01 to about 80 μg/m^3 (GM = 1.21 μg/m^3). The corresponding (PBZ) structure counts ranged from 0.0001 to 1.613 structures/cm^3 (GM = 0.008) [4]. The most common CNT agglomerate sizes were 2-5 μm, and larger. A significant positive correlation was found between inhalable EC and structure counts [4], though with considerable data scatter. Given method limitations, structure counts should be considered semi-quantitative indicators of airborne CNT/CNF powders.

Until the health effects of CNT and CNF are better understood, monitoring of respirable and inhalable EC fractions should be conducted [2-4]. The complexity and variety of structures makes CNT and CNF particle counting a challenge, but unlike EC or other less selective measures, TEM (and SEM) can confirm the presence of CNT/CNF. However, with respect to quantification, it is important to recognize the limitations of a TEM counting method. Because of the heterogeneity of CNT/CNF, particles in the same size bin can vary greatly in their properties, such as mass, density, shape, and composition (e.g., amorphous carbon, catalyst residue). And these dissimilar particles may have different toxicological effects. Thus, even for a given material, particle envelope size may not be an adequate risk indicator. Given the heterogeneity, variety, and unknown toxicity of CNT/CNF products, it is important to apply several methods to assess exposure.

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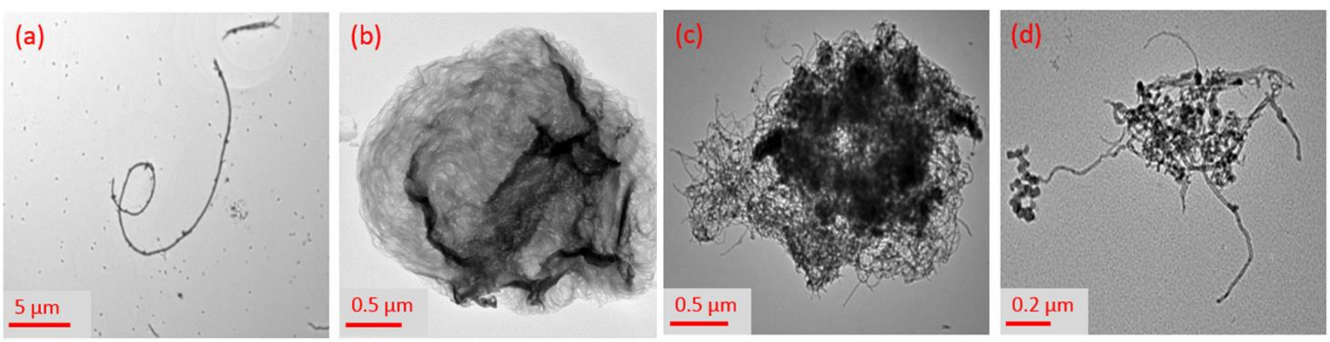

Figure 1. CNT in personal breathing zone samples from worksites: (a) MWCNT (polymer composite site), (b) SWCNT (agglomerate) aerosolized from aqueous suspension (electronics applications), (c) MWCNT (composites/thermoplastics applications), and (d) MWCNT (primary manufacturer).

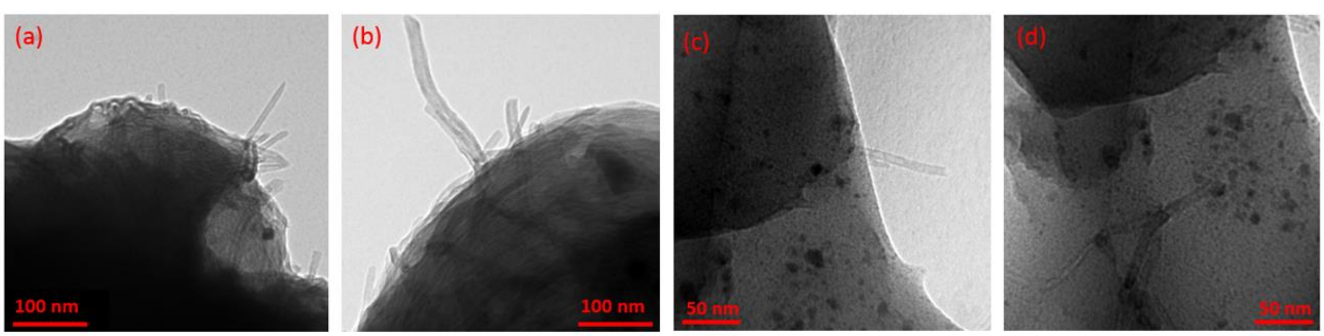

Figure 2. Example TEM images of CNT in a polymer composite (a-d).

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