Potential release of carbon nanotubes from their composites during grinding

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Abstract. We investigated the particle release caused by the grinding of polystyrene-based composites with and without single-wall carbon nanotubes (CNTs). In the results of real-time aerosol monitoring, considerable increases in the number concentration of nano-sized aerosol particles were observed during the grinding of both CNT-containing and CNT-free polystyrene. When a thermodenuder was used, the number of released nanoparticles was reduced by over 99.9%, indicating that the nanoparticles were presumably volatile particles released by the friction heat produced by grinding the composite. In an electron microscopic analysis of the aerosol particles, micron-sized particles with protruding fibers (probably CNTs) were observed, whereas free-standing CNTs were not observed.

1. Introduction
Carbon nanotubes (CNTs) have unique properties that make them an interesting prospect as a filler material in composites. CNT composites are expected to be used in a wide range of industrial applications and consumer products. However, there is still a concern about the potential impact of CNTs on health. To perform a risk assessment of CNT composites, it is important to know the potential release of CNTs throughout the life cycle.

The potential release of multi-wall CNTs and carbon nanofibers (CNFs) from composite materials as a result of cutting, drilling, sanding, grinding, and UV-light weathering has been investigated [1-9]. However, few studies have investigated composites with single-wall CNTs.

In this study, we investigated the particle release caused by the machining of polystyrene-based composites with and without single-wall CNTs (i.e., CNT-containing and CNT-free).

2. Methods
We utilized polystyrene-based composites containing single-wall CNTs at 0 and 5 wt%. These CNTs had a tube diameter of approximately 3 nm and were synthesized using a water-assisted chemical vapor deposition (CVD) method [10]. The composites were ground using a microgrinder in a conductive/antistatic plastic box that had an air supply opening with a high efficiency particulate air (HEPA) filter (see figure 1). Before the test, purified air was passed through the box to eliminate background particles. The aerosol particles released into the box by the grinding process were measured using real-time aerosol monitoring instruments such as a scanning mobility particle sizer.
(SMPS, model 3936L72, TSI Inc., USA) and a condensation particle counter (CPC, model 3007, TSI Inc., USA). Moreover, a thermodenuder [11], which was designed to remove volatile and semivolatile compounds from sample aerosol particles by heating the sample aerosol and adsorbing the volatile compounds in active charcoal, was used to distinguish the CNT-containing particles released by the grinding process from volatile particles potentially released by the friction heat produced by grinding the composite.

In addition, aerosol particles were collected on Nuclepore membrane filters (25-mm diameter, 0.080-µm pore size, Nomura Micro Science Co., Ltd., Japan). The particles collected on the Nuclepore membrane filters and those deposited on the inner surface of the box were observed using a field-emission scanning electron microscope (SEM, S-4300, Hitachi High-Technologies Corporation, Japan) under an accelerating voltage of 3 kV. Prior to the SEM observations, the samples mounted on SEM grids were coated with platinum-palladium (approximately 2 nm) to avoid image charging. Conductive silicone tubing was used to transmit the particles to the measuring instruments.

3. Results and discussion
In the results for the real-time aerosol monitoring, considerable increases in the number concentration of nano-sized aerosol particles were observed during the grinding of the CNT-containing polystyrene (figure 2). However, similar increases were also observed when CNT-free polystyrene was ground (figure 2). When the thermodenuder was used, the number of released nanoparticles was reduced by over 99.9% (figure 3), indicating that the nanoparticles were presumably volatile particles released by the friction heat produced by grinding the composite.

SEM images of the particles released into the air and those deposited on the inner surface of the box when the CNT-containing and CNT-free polystyrene were ground are shown in figures 4–7.

Figure 1. Schematic of experimental setup.
respectively. For the aerosol particles collected during the grinding of the CNT-containing polystyrene, micron-sized aerosol particles with protruding fibers (probably CNTs) were observed (see figure 4), whereas free-standing CNTs were not observed. The particles deposited during the grinding of the CNT-containing polystyrene had a fluffy, fibrous surface (see figure 6).

**Figure 2.** Number-based particle size distributions of released particles when CNT-containing and CNT-free polystyrene were ground. The particle sizes are expressed in terms of the electrical mobility diameter.

**Figure 3.** Number-based particle size distributions of released particles measured by SMPS with/without thermodenuder when CNT-containing polystyrene was ground. The particle sizes are expressed in terms of the electrical mobility diameter.
Figure 4. SEM images of particles released into air when CNT-containing polystyrene was ground.

Figure 5. SEM images of particles released into air when CNT-free polystyrene was ground.
Figure 6. SEM images of particles deposited on inner surface of box when CNT-containing polystyrene was ground.

Figure 7. SEM images of particles deposited on inner surface of box when CNT-free polystyrene was ground.
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