Airborne particles released by crushing CNT composites

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Abstract. We investigated airborne particles released as a result of crushing carbon nanotube (CNT) composites using a laboratory scale crusher with rotor blades. For each crushing test, five pellets (approximately 0.1 g) of a polymer (polystyrene, polyamide, or polycarbonate) containing multiwall CNTs (Nanocyl NC7000 or CNano Flotube9000) or no CNTs were placed in the container of the crusher. The airborne particles released by the crushing of the samples were measured. The real-time aerosol measurements showed increases in the concentration of nanometer- and micrometer-sized particles, regardless of the sample type, even when CNT-free polymers were crushed. The masses of the airborne particles collected on filters were below the detection limit, which indicated that the mass ratios of the airborne particles to the crushed pellets were lower than 0.02%. In the electron microscopic analysis, particles with protruding CNTs were observed. However, free-standing CNTs were not found, except for a poorly dispersed CNT-polystyrene composite. This study demonstrated that the crushing test using a laboratory scale crusher is capable of evaluating the potential release of CNTs as a result of crushing CNT composites. The advantage of this method is that only a small amount of sample (several pieces of pellets) is required.

1. Introduction
Carbon nanotubes (CNTs) exhibit unique properties, due to which they are promising candidates as filler materials in composites. Although CNT composites are expected to be used in a wide range of industrial applications, the potential impact of CNTs on human health remains a concern. In order to control the exposure to CNTs, collecting information on the potential release of CNTs throughout their life cycle is important.

In our previous study [1,2], we investigated particle release during the grinding of CNT composites. Many studies have investigated particle release by mechanical processes, such as grinding, drilling, cutting, and sanding [3–12]. However, limited study has been carried out regarding particle release by the crushing/shredding of CNT composites [13], which are related to waste treatment processes.

In this study, we investigated airborne particles released as a result of crushing CNT composites. Since commercially available shredding machines for waste treatment are too large to be used for a simulation test, in addition to requiring a large amount of test samples, we developed a crushing test using a laboratory scale crusher.
2. Methods

2.1. Test samples
The samples tested in this study are summarized in table 1. Polystyrene (PS) and polycarbonate (PC) composites containing multiwall CNTs (Nanocyl NC7000) were provided by a company where CNT composites are manufactured. The CNT-PS composite sample was manufactured in a worse condition intentionally, so that the CNTs would disperse poorly in PS (as a peculiar case). PC and polyamide 12 (PA12) composites containing another type of multiwall CNTs (CNano Flotube9000) were purchased from Marubeni Information Systems Co., Ltd., which is a sales agency for CNano Technology, Ltd. Nanocyl NC7000 has an average tube diameter of 9.5 nm, an average tube length of 1.5 μm, and a carbon purity of 90%, while CNano Flotube9000 has an average tube diameter of 10–15 nm, an average tube length of 10 μm, and a carbon purity of 95–97.5%, as provided by the manufacturers.

| Sample name      | Matrix | CNT type         | CNT content                  |
|------------------|--------|------------------|------------------------------|
| PS               | PS     | -                | 0%                           |
| Nanocyl-PS       | PS     | Nanocyl NC7000   | A few% (poorly dispersed)    |
| PC               | PC     | -                | 0%                           |
| Nanocyl-PC       | PC     | Nanocyl NC7000   | A few%                       |
| CNano-PC         | PC     | CNano Flotube9000| 3%                           |
| PA               | PA12   | -                | 0%                           |
| CNano(4%)-PA     | PA12   | CNano Flotube9000| 4%                          |
| CNano(10%)-PA    | PA12   | CNano Flotube9000| 10%                       |

2.2. Test methods
Figure 1 shows the schematic diagram of the experimental setup. The crushing test was conducted using a laboratory scale crusher with rotor blades (Wonder Crusher WC-3, Osaka Chemical Co., Ltd., Japan). The container (108 mmΦ × 51 mm) of the crusher was modified by providing air intake and exhaust ports for sampling the airborne particles. The crushing power was set to level 3 or level 7 (of 10), at which the samples were roughly and finely crushed, respectively. In these cases, the rotation speed in a steady state was 7,900 and 18,750 r/min, respectively. Considering that the maximum running time for the maximum crushing power (level 10 of 10) recommended by the manufacturer was 60 seconds, the crushing time was set to 120 and 57 s, respectively; so that the total number of rotations reached 14,000 in both conditions. For each crushing test, five pellets (approximately 0.1 g in total; the typical pellet size was 3–4 mm) of the test sample were placed in the container (see figure 2).

Prior to the test, purified air was passed through the container to eliminate background particles. The airborne particles released in the container by the crushing process were then measured using real-time aerosol measuring instruments: a scanning mobility particle sizer (SMPS, model 3936L75, TSI Inc., USA), an optical particle sizer (OPS, model 3330, TSI Inc., USA), and a condensation particle counter (CPC, model 3776, TSI Inc., USA).

In addition, the airborne particles released in the container were collected on (1) polytetrafluoroethylene (PTFE) membrane filters (37 mm diameter, 2 μm pore size, P/N R2PJ037, Pall Corporation, USA) set in the OPS for gravimetric analysis, (2) Nuclepore membrane filters (25 mm diameter, 0.2 μm pore size, GE Healthcare UK) with a stainless holder (1209, Pall Corporation, USA) [14] for scanning electron microscope (SEM) observation, and (3) holey carbon film-coated transmission electron microscope (TEM) grids (Quantifoil R1.2/1.3 on 200 mesh Cu, Agar Scientific, UK) with a TEM grid holder (Mini Particle Sampler, MPS, Ecomesure, France) [15,16] for TEM observation.
2.3. Gravimetric analysis

The masses of the airborne particles collected on the PTFE filters were determined by weighing the filters before and after sampling, using an ultra-microbalance (SE2-F ultra-microbalance, Sartorius AG, Germany). The limit of detection (LOD, 4.6 µg/filter) was defined as three times the standard deviation of the weight differences of the unused filters prepared and stored along with the filters used ($n=10$).

2.4. Electron microscope observation

The airborne particles collected on Nuclepore filters were observed using a field-emission SEM (Quanta 250 FEG, FEI Company, USA), under an accelerating voltage of 10 kV. Prior to the SEM observation, the Nuclepore filters were coated with osmium to prevent image charging. The aerosol particles collected on TEM grids were observed using a TEM (JEM-2100F, JEOL Ltd., Japan).
3. Results and discussion

3.1. Real-time aerosol measurements

Figure 3 shows the particle size distributions of the cumulative number of released airborne particles normalized by the mass of the crushed pellets. Compared with the particle concentrations during idle running (i.e., the running of a machine with no pellet), increases in the concentration of nanometer- and micrometer-sized particles were recorded, regardless of the sample type. However, similar increases were also observed when CNT-free polymers were crushed.

![Particle size distributions](image)

**Figure 3.** Particle size distributions of the cumulative number of released airborne particles normalized by the mass of crushed pellets. L and H represent low and high rotation speeds (7,900 and 18,750 r/min), respectively.

3.2. Mass ratio of airborne particles to crushed pellets

For all the samples, the masses of airborne particles collected on PTFE filters were below the LOD, which indicated that the mass ratios of the airborne particles to the crushed pellets were lower than 0.02%.
3.3. Electron microscopic observation

Figures 4 and 5 show respectively SEM and TEM images of airborne particles released as a result of crushing CNT composites at a rotation speed of 18,750 r/min. Particles with protruding CNTs were observed for all the CNT composites. On the other hand, free-standing CNTs (isolated or agglomerated CNTs) were found only for the Nanocyl-PS composite. As stated in the ‘Methods’ section, the dispersion of CNTs in the Nanocyl-PS composite was poor. Figure 6 shows SEM images of the fracture surface of the Nanocyl-PS composite strand (from which pellets were obtained) after tensile breaking. As shown in the areas enclosed by the circles in the image on the left side in figure 6, the CNTs were not uniformly dispersed, partly existing in the form of agglomerates. Thus, the release of free-standing CNTs could be related to the poor dispersion of CNTs in the polymer. Similar results were found in our previous study, in which agglomerated CNTs were found when poorly dispersed CNT-PS composites were ground [2].

![Figure 4](image-url)  
**Figure 4.** SEM images of airborne particles released as a result of crushing the CNT composites. Arrows indicate protruding CNTs.
Figure 4. (continued)
Figure 5. TEM images of airborne particles released as a result of crushing the CNT composites.
Figure 6. SEM images of the fracture surface of Nanocyl-PS composite strand after tensile breaking. The image on the right is the enlarged image of the area enclosed by the box in the image on the left. CNTs are not uniformly dispersed in PS and partly exist in the form of agglomerates in the areas enclosed by circles in the image on the left.

The percentages of the particle types detected by the electron microscopic observation are summarized in figure 7 for all particles (the graph on the left), as well as particles with a projected area-equivalent diameter less than 300 nm (the graph on the right). The percentages of the particles with protruding CNTs (categorized as Type C in figure 7) were several to several tens of percent and decreased as the particle size decreased. Comparing the CNano (4%)-PA composite with the CNano (10%)-PA composite, the percentages of the particles with protruding CNTs were higher for the CNano (10%)-PA composite than for the CNano (4%)-PA composite.

Figure 7. Types of airborne particles detected by electron microscopic observation. A, B, C, and D represent isolated CNTs, agglomerated CNTs, particles with protruding CNTs, and others, respectively.

*Projected area-equivalent diameter.
4. Conclusions

We investigated airborne particles released as a result of crushing CNT composites, using a laboratory scale crusher with rotor blades. The real-time aerosol measurements showed increases in the concentration of nanometer- and micrometer-sized particles, regardless of the sample type, even when CNT-free polymers were crushed. The mass ratios of the airborne particles to the crushed pellets were lower than 0.02%. In the electron microscopic analysis, particles with protruding CNTs were observed for all the tested CNT composites. On the other hand, free-standing CNTs were found only for a poorly-dispersed CNT composite. This study demonstrated that the crushing test using the laboratory scale crusher is capable of evaluating the potential release of CNTs as a result of the crushing of CNT composites. The advantage of this method is that only a small amount of sample (several pieces of pellets) is required.

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