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Exposure assessment method for products containing carbon nanotubes inside a test chamber with a Taber abrasion machine

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Abstract. Polymer/carbon nanotube (CNT) composites exhibit distinguished properties, but more quantitative risk assessments on CNTs are necessary as research and development advances. One method to assess the exact risk is to evaluate the characteristics of nanoparticles generated from CNT composites during sanding or Taber abrasion tests. Some researchers have applied loads to CNT composites using Taber machines and analysed the particles using aerosol-measuring instruments and electron microscopes. However, employing aerosol-measuring instruments is challenging due to the small amount of generated particles. Additionally, the presence of abundant background nanoparticles in testing environments creates issues in quantitative measurements. Our research strives to develop an examination method to measure even very small amounts of nanoparticles generated by Taber abrasion. In this study, a Taber abrasion machine is miniaturised so that it fits inside a small chamber. A high-efficiency particulate air filter is attached to the chamber to eliminate background nanoparticles. Then CNT composites are abraded with the miniaturised Taber abrasion machine inside the chamber and the generated particles are analysed.

1. Introduction
Due to their outstanding properties, products containing CNTs are actively being researched and developed. Although many studies have focused on composite materials of multiwall carbon nanotubes (MWCNTs) and epoxy resins, more quantitative risk assessments on CNTs, including hazard and exposure assessments, are required. Some researchers have reported hazard assessments of the MWCNT itself. Takagi et al. reported that MWCNT (MITSUI MWCNT-7, Lot NO. 060125-01k) induced mesothelioma upon injecting a 1 ml solution containing of 1.0×10⁹ of the MWCNT particles intraperitoneally to p53 heterozygous male mice (age of 9 to 11 weeks) [1]. Other works have measured the released particles from CNT products by sanding, Taber abrasing, shredding, and grinding. Using aerosol measuring instruments and electron microscopes to analyse nanoparticles generated from epoxy/MWCNTs via a hand-held sander, Gupta et al. detected CNT protrusions from the particles [2].

However, a standardised exposure assessment method for products containing CNTs has yet to be established. In general, a Taber abrasion test is a common wear assessment, which uses a Taber
abraded with an abrasive machine to perform accelerated wear testing. It is the global standard for evaluating abrasion resistance. A Taber abrasion machine can evaluate weight loss, the Taber wear index, wear cycles per mil, the depth of wear, the residual breaking force, average breaking strength, and percentage loss in breaking strength. Although the Taber test has been applied to evaluate exposure during abrasion of CNT products, it is designed to assess the abrasion resistance and not the generated particles from the products.

This study verifies whether inhalation dust is generated from products containing carbon nanotubes (CNTs) by accelerated tests using a Taber abrasion machine inside a chamber. Since our research strives to analyse particles generated by wear in this test, a load larger than that used in a general Taber test was prepared.

2. Methods

The experiment consisted of a Taber abrasion machine inside a chamber. Eight samples were used to measure and analyse the particles released by sanding. A Taber abrasion machine, which can evaluate the wear resistance of plane materials by abrasion rings, has been used to examine plastic, rubber, construction materials, smooth-planed board, leather, paper, cloth, and coatings. A general Taber abrasion machine is based on JIS K6264-2, but some aspects of our machine differ. Similar to a general Taber abrasion machine, our machine used the same abrasion rings: CS10 for soft rubber samples and H10 for hard rubber sample. However, the sample size (a square with sides of 50 mm and 1 mm thick) differed from that based on JIS K6264-2 (a circle with 120-mm diameter and from 1 to 5 mm thick). Although the rotation speed of our machine was the same as a general machine (72 r/min), a heavier load (19.6 N) than the general one (2.45 N, 4.9 N or 9.8 N) was applied because we wanted to verify if the samples released nanoparticles. In addition, we examined the released particles using a general Taber abrasion machine.

To control the background nanoparticles in the testing environment, we created a stainless steel chamber with an attached high efficiency particulate air (HEPA) filter to eliminate background nanoparticles. The chamber measured 30 cm deep, 30 cm wide, and 30 cm high. The Taber abrasion machine was placed in the chamber. This setup generated nanoparticle samples, which were barely deposited inside the chamber, allowing the released particles to be precisely measured. Furthermore, the drive part of the Taber abrasion machine was outside the chamber in order to control the particles generated from the drive part. Table 1 lists the samples used in the experiment.

Table 1. Samples used in the experiment.

| No. | Corporation | Matrix                  | Nanomaterial    | %  |
|-----|-------------|-------------------------|-----------------|----|
| 1   | A           | Polyamide12             | CNT_3           | 4  |
| 2   |             | Polycarbonate           |                 | 3  |
| 3   |             | Polybutylene terephthalate |                 | 4  |

2.1. Generation and sampling of nanoparticles

The Taber abrasion machine inside the chamber was operated at a rotation speed of 72 r/min until the total number of rotations reached 1,000 revolutions. Table 2 shows the instruments used to measure the released particles. Figure 1 depicts the system used to analyse the released particles.
Table 2. Instruments used in the experiments.

| Item                                | Instrument          | Application                                      |
|-------------------------------------|---------------------|-------------------------------------------------|
| Number of particles and size distribution | FMPS, SMPS, OPS    | 5.6–560 nm, 10–420 nm, 0.3–10 µm               |
| Morphology observations             | SEM                 | Particles on the filter, abrasion powder, matrix |

Three aerosol measurement instruments were used. The fast mobility particle sizer (FMPS, model 3091, Tokyo Dylec Co.), which can classify 32 total channels at a flow rate of 10 L/min, measured particles between 5.6–560 nm. The scanning mobility particle sizer (SMPS, model 3910, Tokyo Dylec Co.), which can classify 13 channels at a flow rate of 1.0 L/min, had a range of 10–420 nm. The optical particle sizer (OPS, model 3330, Tokyo Dylec Co.), which can classify 16 channels at a flow rate of 1.0 L/min, measured the sub-micron and micron-sized particles with a size distribution between 0.3–10 µm. We also conducted morphological observations of the particles sampled on a Nuclepore filter (PC MB 25 mm 0.2 µm, GE Healthcare Japan Co.), the abrasion powder, and the surface of the samples using a Scanning Electron Microscope (SEM). For the sample on the filter, we used a pump with a flow rate of 1.0 L/min.

2.2. Analysis of the particles
Prior to the actual experiment, particles were eliminated in the chamber using clean air. Then the Taber abrasion machine was used to release particles from the samples. We measured the number of particles released and the size distribution while sanding as well as conducted morphological observations.

2.2.1. Measurements of the number of released particles and their size distribution
Using the aerosol-measuring instruments, we measured the number of particles in the chamber prior to running the machine. The particles were assessed for five minutes to determine the particle background (BG). In addition, we measured the particles in the chamber while the machine was running without sanding a sample for five minutes. Finally, we measured the samples while sanding for about 14 minutes.

2.2.2. Morphology observations
We collected the released airborne particles on the filters while sanding the samples. After the experiment, we collected the abrasion powder using carbon tape. SEM was used to observe the filters, powder, and sample surface after abrasion.

3. Results

3.1. Results of the aerosol measuring instruments

Figure 2 shows the number of particles present in the laboratory as well as in the chamber where the particles in the air are controlled. Using FMPS, we measured the total number of particles for both conditions (ambient air and the chamber) for five minutes. The vertical axis represents the average value of the total number of particles per second. The error bars denote the standard deviation.

![Figure 2. Total number of particles in the laboratory (room) and the chamber.](image)

The chamber can control the number of particles present. Figures 3 and 4 show the measurement results for the number of particles and the size distribution during abrasion using different aerosol measuring instruments. The vertical axis represents the average number of particles (dN/dlogDp) while the horizontal axis represents the diameter (nm). The error bars represent the standard while sanding for about 14 minutes.
Figure 3. Size distribution of BG and released particles during abrasion (FMPS).

The number of particles is represented by the average size distribution measured by FMPS. In all samples, the concentration near 100 nm is high, but the concentration during abrasion is similar to the detection limit.

Figure 4. Size distribution of BG and released particles during abrasion (SMPS and OPS).

The number of released particles was also determined by SMPS and OPS. In all samples, the number of particles near 10 nm is very high, and the numbers of particles are high near 40, 100, and 400 nm. However, both the size distribution and concentrations are similar to the BG concentration. Bello et al. reported that drilling composite materials generates smoke with a particle diameter around 10 nm [3].
Thus, the high particle concentration near 10 nm may be due to thermal decomposition during abrasion. Because the BG concentration at 10 nm is higher than that during abrasion, the origin of the high concentration near 10 nm is unclear.

There are possible three reasons why BG is high. 1) Particles are generated from the driving part of the Taber abrasion machine. 2) The HEPA filter used to introduce air into the chamber does not sufficiently control the particles. 3) Ambient air outside of the chamber enters the chamber due to a negative chamber pressure. Regarding 1), we measured the concentration near the drive section, but the number of particles is very low. Regarding 2), the concentration measured when the HEPA filter was connected to FMPS indicates that the filter sufficiently controls the particles. Regarding 3), in this study, the total flow rate evacuated from the chamber to the instruments is extremely high at 20 L/min, causing a negative pressure inside the chamber. This pressure difference may result in contamination from the general environment. In the future, it is necessary to repeat the experiment while measuring the pressure difference inside and outside of the chamber with the pressure gauge. If the chamber has a negative pressure, the pressure difference should be reduced by introducing clean air using a pump.

In Figs. 3 and 4, there is an inversion of the curves, which may be due to the measurement principles of FMPS, SMPS, and OPS. Each device charges the particles and then classifies the particles using a high voltage rod. However, the particle detection method varies between FMPS and SMPS·OPS. In the former, the current value of the charged particles is measured and converted into the concentration. Consequently, a high temporal resolution is possible. Thus, FMPS is suitable for measurements requiring high time decomposition. In the latter, particles are detected using a condensation particle counter (CPC). Thus, SMPS·OPS can accurately measure the particle size distribution. Therefore, the inversion of the curve is due to these differences.

3.2. Result of morphological observations

We attempted to confirm the CNT release by observing the shape of the collected particles. Figure 5 shows the SEM results of the collected particles on the Nuclepore filters.

![Figure 5](image)

**Figure 5.** Morphological observations of the released particles collected on the filters.

None of the samples have confirmed protrusions. Although all the samples have high aspect ratios, they are much larger in size than the CNT raw materials. Scattering with CNT alone cannot be confirmed, but it is likely that CNTs are packed in the collected particles. The size of the released particles in No. 2 is smaller than those of No.1 and 3. We can discuss the shape and size of the released particles, but it is difficult to discuss the CNT release as a function of the matrix using only morphological observations. To discuss the scattering of CNTs from the composites, we have to identify whether CNTs are in the released particles simultaneously with the morphological observation.

Figure 6 shows the SEM results of the abrasion powders, while Fig. 7 shows the sample surfaces after abrasion. The abrasion powder and protrusions are confirmed from the surface of the sample, but CNTs cannot be identified.
4. Conclusion
The chamber can control the BG concentration to some extent compared to ambient air. We were unable to measure the change in the concentration in the chamber before and after abrasion due to particle contamination. If the chamber setup is improved, it may be possible to confirm particle generation under the load of the Taber test. Thus, we should measure the pressure differential inside and outside the chamber.

The SEM images confirm scattering of the abrasion powder and particles, but not whether CNTs are packed in the abrasion powder or released particles. Elemental analysis of the released particles is necessary to confirm the presence of CNTs. Depending on the production method, a metal catalyst is terminated in the CNTs, and it may be possible to confirm the presence of CNTs by following that metal element. A method combining Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and a Gas Exchange Device (GED) and a method using FE-SEM are options to trace the metal element. Using a GED, the released particles can be introduced directly into an ICP-MS, which identifies and determines the quantities of metals in the released particles. By examining the proportion of catalytic metal in the CNT, we can convert the trace metal amount into the amount of CNT.

We also considered collecting the generated particles by a filter and measuring the weight with an electronic balance. Because the collected particles include the particles derived from the sample and those from the abrasive ring, it is possible that the CNT weight is not accurately measured. Ultimately, the analysis should separate and analyse the released particles because particles are also generated from the abrasion ring of the Taber abrasion instruments. Consequently, we want to further control the number of particles in the chamber and conduct simultaneous analysis of GED-ICP-MS, aerosol measurement equipment, and SEM observations by filter collection in the future in order to verify and quantify the released particles of CNT decisively.
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