

Original

Exposure assessment of carbon nanotubes at pilot factory focusing on quantitative determination of catalytic metals

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Abstract: Objectives: The application of multiwall carbon nanotubes (MWCNTs) currently extends to various fields. However, it has been reported that exposure to CNT causes hazardous effects on animals and cells. The purpose of this study was to quantify the exposure to MWCNT in MWCNT/polymer composites for exposure assessment. We focused on catalytic metals included in the MWCNT and the diameter of dust released during the working processes. Although the Co in MWCNTs is not a common catalyst, it was used as a tracer in this study. **Methods:** A field survey was conducted in a MWCNT / polymer composite pilot factory. Airborne MWCNTs were monitored using black carbon monitors (BCMs) and optical particle sizers (OPSs) and collected on a filter. The MWCNT powder, all polymer resins used during the working processes, and the filter were analyzed in our lab using inductively coupled plasma mass spectrometry (ICP-MS) and electron microscopic observation. **Results:** The mean concentration of airborne MWCNT contained in the collected dust was 0.92 $\mu\text{g}/\text{m}^3$ a few meters away from the extruder during the working processes (using elemental analysis). The maximum concentration measured using BCMS was shown to be seven times higher than the base concentration during the pelletizing process of polycarbonate (PC) and MWCNT composites. However, free, isolated, and unbound agglomerated MWCNTs were not detected using scanning electron microscopic (SEM) observation. **Conclusions:** The result obtained by elemental analysis indicated it was possible to quantify MWCNT in composites. The mean concentration at this factory was lower than the rec-

ommended exposure limit. However, additional studies during the pelletizing process are required in the future.

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Key words: Carbon nanotube, Catalytic metals, Elemental analysis, Exposure assessment, Polymer composite

Introduction

The application of multiwall carbon nanotubes (MWCNTs) currently extends to various fields. MWCNTs typically have a diameter in the range of 10-100 nm and lengths of 100-10,000 nm. MWCNTs possess superior mechanical, electrical, and thermal properties. However, it has been confirmed by several reports that exposure to carbon nanotubes (CNTs) causes hazardous effects on animals and cells¹⁻⁴. This indicates a potential hazard for workers handling MWCNTs. CNTs released in workplaces are often determined using thermal carbon analysis methods, such as National Institute for Occupational Safety and Health (NIOSH) method 5040⁵⁻¹⁰ or the IMPROVE protocol¹¹, also used for quantifying CNTs¹²⁻¹⁵. In addition, by measuring respirable-sized MWCNT dust using both a black carbon monitor (BCM) and thermal carbon analysis, a relationship between the analytical methods was detected¹⁶. However, it is difficult to identify whether or not some CNTs are released during the working process when elemental carbon exists in the background atmosphere. Also, it is difficult to distinguish some CNTs from some types of polymer resins.

A number of CNTs distributed in the market are produced using the chemical vapor deposition method. Many of these CNTs incorporate metal impurities as a catalyst. Therefore, it has also been reported that elemental analysis of CNT in workplaces could be conducted using these

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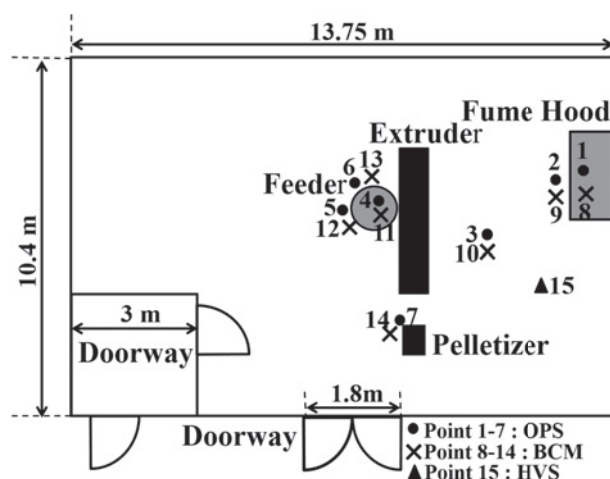


Fig. 1. Outline of the pilot factory showing measurement points.

catalysts as airborne tracers^{9,17-19}). Currently, few studies have been carried out to distinguish MWCNTs from polymer mixed MWCNT composites as well as to quantify exposure to MWCNTs in a factory manufacturing MWCNT/polymer composites. The exposure to MWCNT released from MWCNT/polymer composite during the pelletizing process has not yet been thoroughly researched.

The purpose of this study was to consider the exposure assessment method by quantification of the exposure to MWCNTs included in MWCNT/polymer composites using elemental analysis of a catalytic metal (Co) as a tracer in a pilot factory and qualitative analysis of airborne dust using electron microscopic observation. In addition, the exposure is focused on each working process using BCMs and optical particle sizers (OPSs). These instruments are real-time monitoring instruments. By using these analyses, we reveal whether the airborne MWCNTs are included in polymer composites or not during the manufacture of MWCNT/polymer composites.

Methods

A field survey was conducted in a CNT/polymer composite pilot factory. This survey was carried out by focusing on the handling of MWCNT processes throughout the day. MWCNTs, with an average diameter of 9.5 nm, an average length of 1.5 μm , and a carbon purity of 90%, as stated by the manufacturer, were used as a filler for MWCNT/polymer composites. The MWCNT content of the composites was a few wt%. Polymer matrices used for the composites were polystyrene (PS), polypropylene (PP) and polycarbonate (PC). The temperature in the workplace was 20-27°C and the relative humidity was 23-26%. Two doorways were closed during the field survey.

Filter samples and all the materials used during the process were brought back to the lab for elemental analysis.

Sampling design

The outline of the factory and measurement points are shown in Fig. 1. Real-time aerosol monitoring and filter sampling for electron microscopic observation and elemental analysis were conducted at fifteen points (points 1-15). OPSs were operated at points 1 to 7, and BCMs were operated at points 8 to 14. Points 1 and 8, and 2 and 9 were in and outside a fume hood in which MWCNT powder in a big bag was subdivided into six small bags using a ladle while sitting (repacking). Points 3 and 10 were at the middle position among the fume hood, extruder, and pelletizer. Each point was in a parallel position. Points 4 to 6 and points 11 to 13 were in and outside a feeder enclosure, respectively, in which the MWCNT powder in the six small plastic bags was fed into the feeder of the extruder using local exhaust ventilation down the ceiling (feeding). Points 7 and 14 were next to the pelletizer. Raw materials and resin were extruded using twin screws; plus, they were pelletized using the pelletizer after cooling (Extruding and pelletizing). These instruments were attached to the tube at the inlet, and on the fume hood and feeder. The measurement was conducted by inserting the attached tube into the inside of the devices. For elemental analysis, the filter sampling that was in the middle position between the fume hood, extruder and pelletizer, was conducted at point 15. For elemental analysis and electron microscopic analysis, the airborne dust was collected on a glass fiber filter (GB100R, ADVANTEC) using a high-volume air sampler (HVS; HVC-500N, SIBATA) throughout the period of all processes. The sampling flow rate was set at 500 l/min. It ran for 390 min in total. It was predicted that the respirable con-

centration at a fixed point away from the working devices would be difficult to estimate using the very small amount of catalytic metal. Therefore, we measured the total dust without a separator.

Real-time aerosol monitoring and filter sampling

Mass concentrations of black carbon were measured using BCMs (Model AE51, Aeth Labs). The BCMs were run at a flow rate of 0.1 l/min and time interval of 60 s. The OPSs (Model 3330, TSI Inc, size range 0.3 to 10 μm) measured particle concentrations at a rate of 10 s/scan. Three OPSs were used to simultaneously measure the airborne dust at the three measurement points (points 1 to 3 during repacking, points 3 to 5 during feeding, and point 3 and points 6 to 7 during extruding and pelletizing). In addition, mass concentrations during each process were measured close to the processes at the measurement points (points 8 to 10 during repacking, points 10 to 12 during feeding, and point 10 and points 13 to 14 during extruding and pelletizing) using three BCMs.

Electron microscopic observation

The sample filters were cut into approximately 5 \times 5 mm pieces and fixed onto sample stages with carbon tape. The aerosol particles collected on the glass fiber filter were observed using a field-emission SEM (JSM-7401, JEOL) under an accelerating voltage of 3.0 kV. To avoid charging of the filters, the samples were sputtered with platinum-palladium.

X-ray fluorescence analysis

Prior to elemental analysis of the filter samples collected at the pilot factory, in order to find the most adequate tracers for the identification of MWCNTs, the catalytic metals included in three types of MWCNT/polymer composites (PS, PP, and PC) and MWCNT powder were analyzed using total reflection X-ray fluorescence spectroscopy (XRF; NANO HUNTER2, Rigaku). A few dozen mg of each sample were placed on the sample stage and measured.

Elemental analysis by inductively coupled plasma mass spectrometry

Elemental analysis of the filter samples collected at the pilot factory was carried out using inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific X series 2). The sampled filter was cut into three pieces at equal intervals (sample A: 54.7 mg, sample B: 85.5 mg, sample C: 77.2 mg). In addition to the filter samples, a blank sample of a solution of nitric acid, three pieces of filter blank samples, the PP (3 samples, mean weight 59.3 \pm 0.9 mg), the PS (3 samples: mean weight 58.4 \pm 1.4 mg), the PC (3 samples, mean weight 65.4 \pm 1.7 mg), and the MWCNT powders (all three samples, 5.2 mg) were analyzed. A Mars 6 microwave oven (CEM Corporation) was

used for the microwave digestion of the samples. Each sample was mixed with 10.00 ml of nitric acid solution (3.75 ml concentrated HNO_3 (60%) + 3.75 ml Mill Q water + 2.50 ml H_2O_2 (30 %)). The samples were digested in the next method. The sample solutions were heated at 180–200 $^\circ\text{C}$ for 1.5 h. The samples were diluted 50 times (filter samples), 5000 times (all polymer resins), or 500 times (MWCNT powders) with nitric acid solution. Before introducing the samples into the ICP-MS, the samples were filtered through pure PTFE membrane filters (pore size: 0.45 μm). The calibration samples were prepared using 10.00 ml of the nitric acid solution (1.00 mol/l) containing a standard solution of Co, Fe, and internal standard Y in the ranges (Co, Fe 0.01–10.00 μg). Note that Co and Fe were found to be the most adequate tracers for the identification of the MWCNTs using XRF analysis (see Results section).

Results

Monitoring with BCM and OPS

Fig. 2 shows real-time monitoring with BCMs and with OPSs. Table 1 shows the mean and standard deviation (SD) of mass concentration at each measurement point obtained with BCMs during the working processes and the base concentration before operations. The differences were not statistically significant. However, the trend of changing concentrations had been confirmed using real-time monitoring. The repacking process (Fig. 2a–c and Fig. 2j) indicated that the concentration of point 8 was the highest value in the fume hood. The maximum concentration at point 8 during the repacking process was twice the base concentration. The feeding process (Fig. 2d–f and Fig. 2k) indicated that the measured value of point 11 increased at the feeding action. Each concentration measured on the outside was approximately the same as the base concentration. Next, the extruding and pelletizing processes (Fig. 2g–i and Fig. 2l) showed the highest concentration among the processes. Among all the composites, the concentration of pelletizing PC increased most sharply during the pelletizing process. Especially, the maximum value was approximately seven times the base concentration at point 14. The mean concentration measured using BCMs throughout all working processes was 1.0 $\mu\text{g}/\text{m}^3$ (SD = 1.57).

Focusing on results measured using OPSs, Fig. 2a and Fig. 2b show tiny increase in the mean particle number concentrations under 3.3 μm in diameter during the repacking process. However, Fig. 2j shows approximately twice as much concentration as the base concentrations measured at point 8 using BCM. Therefore, it is estimated that suspended MWCNT powders had the diameter above micron meter. Next, Fig. 2d shows very few concentration fluctuations at any of the measurement points. Fig. 2e and Fig. 2f show increase in the concentration only in the

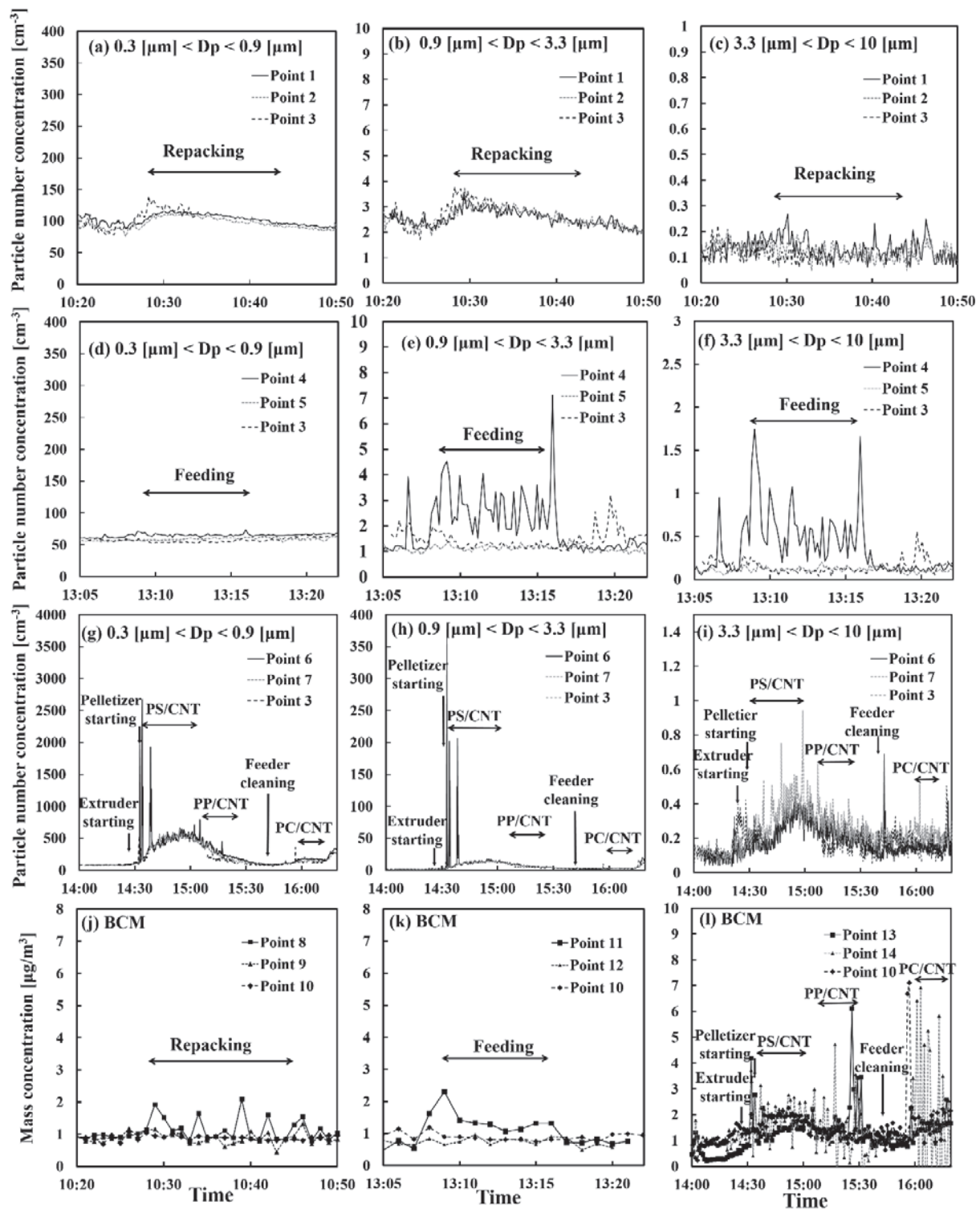


Fig. 2. Real-time measurements of mass concentrations and particle number concentrations by diameter at each of three measurement points using BCMs and OPSs in each process: (a)-(i) the particle number concentrations measured using OPSs and (j)-(l) the mass concentrations measured using BCMs during each process.

feeder during the feeding process. However, the peaks of concentration at point 3 were detected after the feeding process. Since the concentration measured using BCM showed no fluctuation at point 10, there is a possibility

that the peak showed other particles without black carbon (Fig. 2k). Finally, during extruding and pelletizing processes, the particle number concentrations measured using OPSs show the increase in Fig. 2g, Fig. 2h and Fig. 2i. In

Table 1. The mean mass concentrations at measurement points using BCMs in each process.

| | Point 8 | Point 9 | Point 10 | Point 11 | Point 12 | Point 13 | Point 14 |
|---------------------------|---------|---------|----------|----------|----------|----------|----------|
| Before operation | 0.9±0.1 | 0.9±0.1 | 0.9±0.1 | – | – | – | – |
| Repacking | 1.2±0.4 | 0.9±0.2 | 0.9±0.1 | – | – | – | – |
| Feeding | – | – | 0.9±0.1 | 1.3±0.4 | 0.8±0.1 | – | – |
| Extruding and pelletizing | – | – | 1.6±0.8 | – | – | 1.4±0.8 | 1.6±1.2 |

Values ($\mu\text{g}/\text{m}^3$) are mean \pm SD of 1-min interval data in working process: Before operation (n=15), Repacking (n=18), Feeding (n=11), Extruding and pelletizing (n=124).

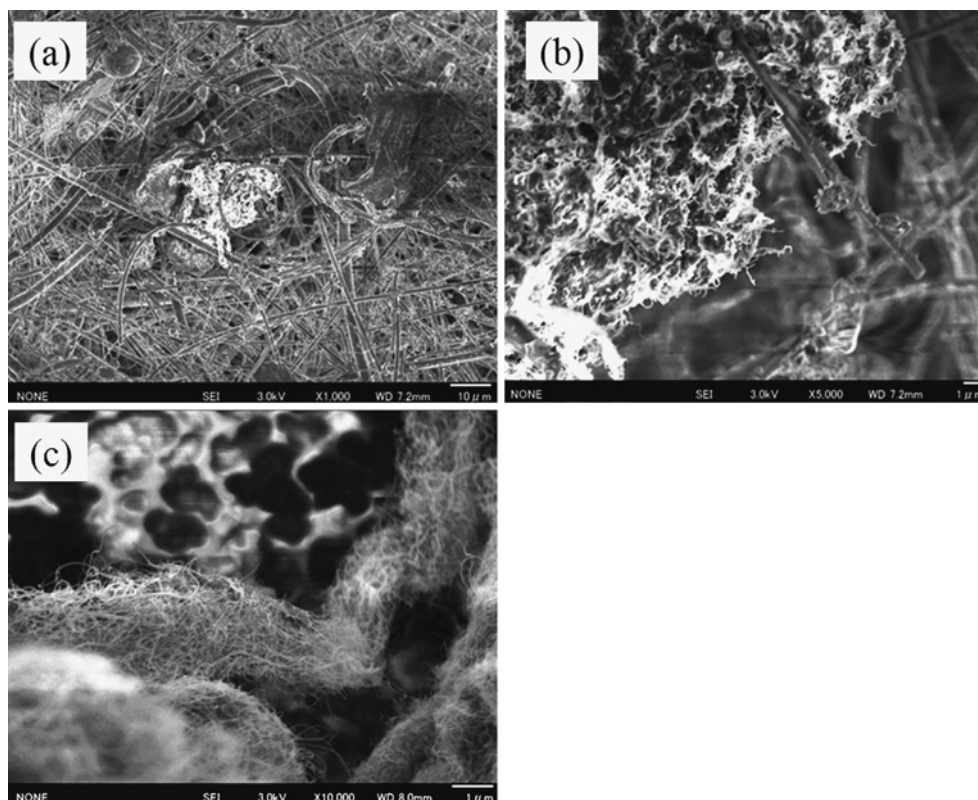


Fig. 3. SEM images of suspended dust collected using an HVS and MWCNT powder used in the pilot factory: (a) Suspended dust, magnification $\times 1000$, (b) Expansion of the circle in (a) magnification $\times 5000$; and (c) MWCNT powders used in the facility.

addition, the mass concentrations measured using BCMs show the increase in Fig. 21. In conclusion, there is a possibility that MWCNTs in the composite may be released as the dust of various sizes during the pelletizing process.

Electron microscopic observation

Fig. 3 shows representative particles found through SEM observation of airborne dust collected on the filter with an HVS and MWCNT powders used in the pilot factory (Fig. 3c). The airborne dust shows particles $>10 \mu\text{m}$ long (Fig. 3a). MWCNTs included in the MWCNT/polymer composites were observed in the dust (Fig. 3b). However, there were no free, isolated, and unbound agglomerated MWCNTs.

XRF analysis

Fig. 4 shows the results of XRF analysis. The analytical results of transition elements contained in the MWCNT/polymer composites and the MWCNT powder using XRF indicated that all the samples showed sharp peaks for Co and Fe. Therefore, Fe and Co were found to be the most adequate tracers for the identification of MWCNTs.

Elemental analysis by ICP-MS

Good linear calibration curves were obtained (Co, $R^2 = 0.9997$; Fe, $R^2 = 0.9996$). The limit of detection was defined as three times the SD of the blank concentration. The limit of quantitation (LOQ) was defined as ten times

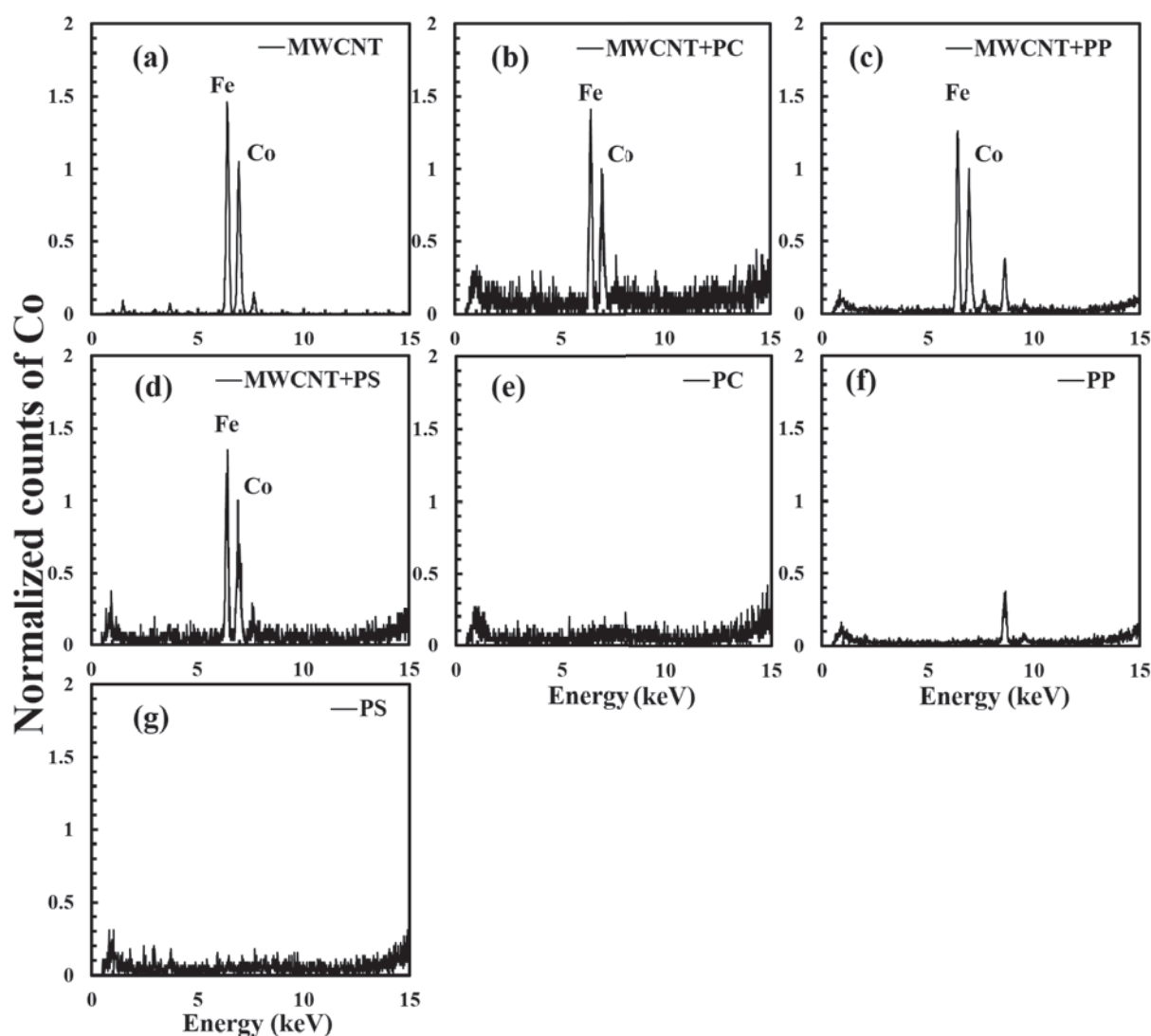


Fig. 4. Normalized counts of Co contained in the materials using total reflection XRF: (a) MWCNT powder; (b)-(d) three types of MWCNT/polymer composites; and (e)-(g) three types of polymer resin.

Table 2. Quantitative analytical results of airborne catalytic metals and MWCNT estimated by catalyst.

| | Co (μg) | Co ($\mu\text{g}/\text{m}^3$)* | Co ($\mu\text{g CNT}/\text{m}^3$)** |
|----------|-------------------------|-------------------------------------|--|
| Sample A | 0.47 | 0.0024 | 1.12 |
| Sample B | 0.32 | 0.0016 | 0.75 |
| Sample C | 0.38 | 0.0019 | 0.90 |
| Mean | 0.39 | 0.0020 | 0.92 |
| SD | 0.08 | 0.0004 | 0.19 |

*Total volume was of air sampled using the HVS was 195 m^3 . **Rate of Co contained in MWCNT was 0.22%.

the SD of the slope ($0.04 \mu\text{g Co/L}$, $0.56 \mu\text{g Fe/L}$). The Co and Fe contents of the MWCNT powder were above the LOQ ($0.043 \mu\text{g Co/mg}$). On the other hand, those of all polymer resins were below the LOQ. The Co and Fe concentrations in the MWCNT powder diluted 500 times were $2.2 \pm 0.1 \mu\text{g Co/L}$ and $4.2 \pm 0.7 \mu\text{g Fe/L}$ (mean \pm SD). On the other hand, the Co and Fe concentrations in the blank solution were $0.078 \pm 0.003 \mu\text{g Co/L}$ and $1.00 \pm 0.28 \mu\text{g Fe/L}$. Based on these concentrations, the Co and Fe contents of the MWCNT powder were calculated as $2.2 \pm 0.1 \mu\text{g Co/mg}$ and $3.3 \pm 0.7 \mu\text{g Fe/mg}$. The contents quantified by ICP-MS were similar to the count ratio on the surface obtained using XRF.

Table 2 shows the concentrations of Co in the filter samples. The Co and Fe concentrations in the filter samples diluted 50 times (500 ml total volume) were $0.079 \pm 0.007 \mu\text{g Co/L}$ and $49.0 \pm 10.9 \mu\text{g Fe/L}$. The Co and Fe

concentrations in the blank filter samples diluted 50 times were 0.26 ± 0.01 ng Co/L and 0.48 ± 0.02 μ g Fe/L. Based on these results, the Co and Fe contents of the filter were calculated as 0.39 ± 0.08 μ g Co/filter (Table 2) and 92 ± 25 μ g Fe/filter. Since the total flow of the HVS from start to end of the process was 195 m^3 , the mass concentrations of Co and Fe in the air at point 15 were estimated to be 2.0 ± 0.4 ng Co/ m^3 (Table 2) and 0.47 ± 0.13 μ g Fe/ m^3 . In conclusion, the airborne MWCNT included in collected dust was estimated to be $0.92 \mu\text{g}/\text{m}^3$ (Table 2) by using the Co content of the MWCNTs on the assumption that the content ratio was equal ($2.20 \mu\text{g Co}/\text{mg}$). This concentration was estimated to be $143 \mu\text{g}/\text{m}^3$ by using the Fe content ratio in MWCNTs ($3.30 \mu\text{g Fe}/\text{mg}$). Unlike the case of Co, a sub-microgram level of Fe/ m^3 exists in the atmospheric environment^{20,21}. Although this pilot factory has an exhaust ventilation system and the doors were closed, it was difficult to estimate the airborne MWCNT concentration by using the Fe content ratio.

Discussion

The mass concentration of airborne MWCNT included in collected dust obtained by Co tracer with ICP-MS was $0.92 \mu\text{g}/\text{m}^3$ at point 15. This result is based on the assumption that background Co is equal to or lower than the Co concentration in the atmospheric environment. This assumption is based on the following reasons. There was no source of Co except for handling MWCNT, and the doors were closed. The value was almost the same as the base concentration obtained using BCMs at points 8 to 10. Measurements using BCMs are performed using a very simple method. Moreover, point 15 was different from the measurement points using BCM. Although it should be noted that the results cannot be simply be compared, it is possible that the value measured using HVS was very close to the base concentration using BCMs because the HVS was operating during the break time in this study. It was reported that black carbon base concentrations were monitored continuously using an aethalometer for 24 h at four CNT workplaces located in rural, urban, and industrial areas²². Compared with the report, the base concentration was at low levels at the industrial workplace in this factory. As a result of real-time monitoring, it was discovered that the mass concentrations during the repacking and feeding processes, measured using BCMs on the outside, were approximately the same as the base concentration. Therefore, it is estimated that the probability of exposure during repacking and feeding processes was very low. In contrast, particle number concentrations by all diameter class, measured using OPSs during extruding and pelletizing processes, were linked with mass concentrations measured using BCMs. These particle number concentrations increased especially sharply near the working point during pelletizing PC. The

result of the repacking process using the fume hood was better controlled, compared with previous reports^{7,23}. However, the result of the pelletizing process was consistent with the increase in concentration of dust reported in previous findings²⁴. The results require further validation by increasing the number of sampling points near the pelletizer and conducting a detailed elemental analysis of nanoparticles.

Conclusions

The concentration of airborne MWCNTs obtained by elemental analysis of catalytic metal tracers was $0.92 \mu\text{g}/\text{m}^3$ at point 15. Since there is a possibility that the MWCNT concentration is less than this value due to background Co, this concentration was lower than the NIOSH recommended exposure limit (NIOSH REL, $1.0 \mu\text{g}/\text{m}^3$) of CNT. Moreover, the results obtained by conducting elemental analysis of all handled resins, SEM observations, and real-time measurements focusing on the diameter, are expected to be an effective method to measure MWCNT exposure in workplaces handling composites. Depending on the composite materials, it is important to select the right method (elemental analysis or thermal carbon analysis). In addition, additional studies during the pelletizing process are required in the future.

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Conflicts of interest: The authors declare that there are no conflicts of interest.

References

- 1) Brown DM, Wilson MR, MacNee W, et al. Size-dependent proinflammatory effects of ultrafine polystyrene particles: A role for surface area and oxidative stress in the enhanced activity of ultrafines. *Toxicol Appl Pharm* 2001; 175: 191-199.
- 2) Lam CW, James JT, McCluskey R, et al. Pulmonary toxicity of single-wall CNT in Mice 7 and 90 days after intratracheal instillation. *Toxicol Sci* 2004; 77: 126-134.
- 3) Takagi A, Hirose A, Nishimura T, et al. Induction of mesothelioma in p53±mouse by intraperitoneal application of multi-wall carbon nanotube. *J Toxicol Sci* 2008; 33: 105-116.
- 4) Poland CA, Duffin R, Kinloch I, et al. Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nat Nanotechnol* 2008; 3: 328-333.
- 5) NIOSH. current intelligence bulletin 65: occupational exposure to carbon nanotubes and nanofibers. Cincinnati, Ohio: US: Department of Health and Human Services Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health; 2013. Publication No. 2013-145.

- 6) Myojo T, Oyabu T, Nishi K, et al. Aerosol generation and measurement of multi-wall carbon nanotubes. *J Nanopart Res* 2009; 11: 91-99.
- 7) Methner M, Hodson L, Dames A, Geraci C. Nanoparticle emission assessment technique (NEAT) for the identification and measurement of potential inhalation exposure to engineered nanomaterials-part B: results from 12 field studies. *J Occup Environ Hyg* 2010; 7: 163-176.
- 8) Methner M, Beaucham C, Crawford C, Hodson L, Geraci C. Field application of the Nanoparticle Emission Assessment Technique (NEAT): task-based air monitoring during the processing of engineered nanomaterials (ENM) at four facilities. *J Occup Environ Hyg* 2012; 9: 543-555.
- 9) Birch ME, Ku BK, Evans DE, Ruda-Eberenz TA. Exposure and emissions monitoring during carbon nanofiber production-Part 1: elemental carbon and iron-soot aerocols. *Ann Occup Hyg* 2011; 55: 1016-1136.
- 10) Dahm MM, Evans DE, Schubauer-Berigan MK, Birch ME, Fernback JE. Occupational exposure assessment in carbon nanotube and nanofiber primary and secondary manufacturers. *Ann Occup Hyg* 2012; 56: 542-556.
- 11) Chow JC, Watson JG, Pritchett LC, et al. The DRI thermal/optical reflectance carbon analysis system. *Atmos Environ* 1993; 27A: 1185-1201.
- 12) Ono-Ogasawara M, Myojo T. A proposal of method for evaluating airborne MWCNT concentration. *Ind Health* 2011; 49: 726-734.
- 13) Takaya M, Ono-Ogasawara M, Shinohara Y, Kubota H, Tsuruoka S, Koda S. Evaluation of exposure risk on the weaving process of MWCNT-coated yarn with real-time particle concentration measurements and characterization of dust particles. *Ind Health* 2012; 50: 147-155.
- 14) Ono-Ogasawara M, Takaya M, Kubota H, et al. Approach to the exposure assessment of MWCNT by considering size distribution and oxidation temperature of elemental carbon. *J Phys Conf Ser* 2013; 429: 012004.
- 15) Ogura I, Kotake M, Hashimoto N, Gotoh K, Kishimoto A. Release characteristics of single-wall carbon nanotubes during manufacturing and handling. *J Phys Conf Ser* 2013; 429: 012057.
- 16) Hashimoto N, Ogura I, Kotake M, Kishimoto A, Honda K. Evaluating the capabilities of portable black carbon monitors and photometers for measuring airborne carbon nanotubes. *J Nanopart Res* 2013; 15: 2033.
- 17) Maynard AD, Baron PA, Foley M, Shvedova AA, Kisin ER, Castranova V. Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. *J Toxicol Environ Health* 2004; Part A 67: 87-107.
- 18) Rasmussen PE, Jayawardene I, Gardner HD, Chenier M, Levesque C, Niu J. Metal impurities provide useful tracers for identifying exposures to airborne single-wall carbon nanotube particles released from work-related processes. *J Phys Conf Ser* 2013; 429: 012007.
- 19) Reed RB, Goodwin DG, Marsh KL, et al. Detection of single walled carbon nanotubes by monitoring embedded metals. *Environ Sci Process Impacts* 2013; 15: 204-213.
- 20) Var F, Narita Y, Tanaka S. The concentration, trend and seasonal variation of metals in the atmosphere in 16 Japanese cities shown by the results of National Air Surveillance Network (NASN) from 1974 to 1996. *Atmos Environ* 2000; 34: 2755-2770.
- 21) Saito I, Onuki A, Hosaka M, Ogata A, Nakae D. Measurement of Size Distribution and Metal Content in Airborne Particle Matter. *Ann Rep Tokyo Metr Inst Pub Health* 2012a; 63: 255-265[in Japanese].
- 22) Kim JB, Kim KH, Yun ST, Bae GN. Detection of carbonaceous aerosols released in CNT workplaces using an aethalometer. *Ann Occup Hyg* 2016; 60: 717-730.
- 23) Kuhlbusch TA, Fissan H. Number size distribution, mass concentration, and particle composition of PM1, PM2.5 and PM10 in bag filling areas of carbon black production. *J Occup Environ Hyg* 2004; 1: 660-671.
- 24) Kuhlbusch TA, Fissan H. Particle characteristics in the reactor and pelletizing areas of carbon black production. *J Occup Environ Hyg* 2006; 3: 558-567.

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