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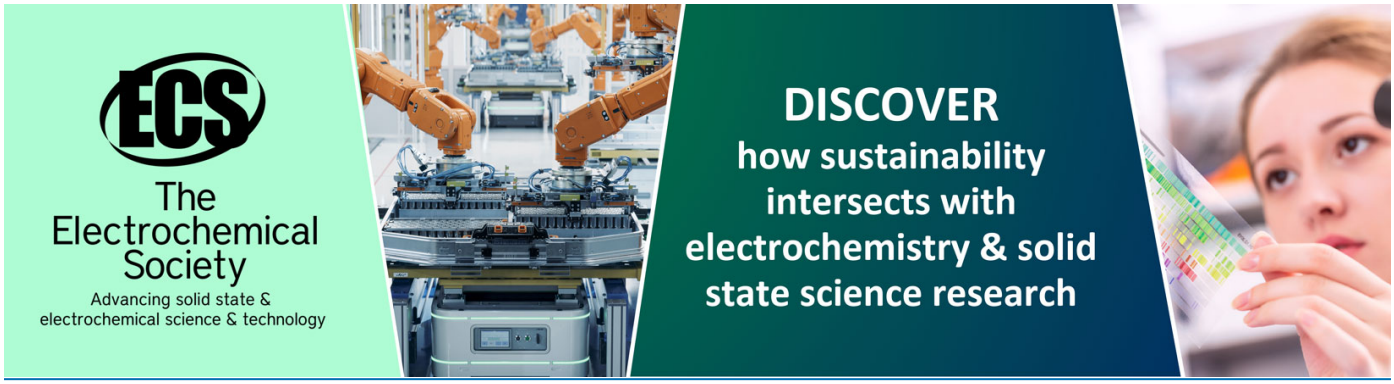

IOP Conf. Series: Journal of Physics: Conf. Series **838** (2017) 012014 doi:10.1088/1742-6596/838/1/012014

Quantitative measurement of carbon nanotubes released from their composites by thermal carbon analysis

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Abstract. The release of free carbon nanotubes (CNTs) and CNTs partly embedded in matrix debris into the air may occur during mechanical and abrasion processes involving CNT composites. Since the harmful effects of CNT-matrix mixtures have not yet been fully evaluated, it is considered that any exposure to CNTs, including CNT-matrix mixtures, should be measured and controlled. Thermal carbon analysis, such as Method 5040 of the National Institute for Occupational Safety and Health, is one of the most reliable quantitative methods for measuring CNTs in the air. However, when CNTs are released together with polymer matrices, this technique may be inapplicable. In this study, we evaluated the potential for using thermal carbon analysis to determine CNTs in the presence of polymer matrices. Our results showed that thermal carbon analysis was potentially capable of determining CNTs in distinction from polyamide 12, polybutylene terephthalate, polypropylene, and polyoxymethylene. However, it was difficult to determine CNTs in the presence of polyethylene terephthalate, polycarbonate, polyetheretherketone, or polyamide 6.

1. Introduction

Carbon nanotubes (CNTs) have unique properties, due to which their use as a filler material in composites is considered promising. However, the release of free CNTs and CNTs partly embedded in matrix debris into the air may occur during mechanical and abrasion processes involving CNT composites. Some studies have indicated that CNT-matrix mixtures are less harmful than free CNTs [1–4]. However, the harmful effects of CNT-matrix mixtures have not yet been fully evaluated. Under the present circumstances, it is considered that any exposure to CNTs, including CNT-matrix mixtures, should be measured and controlled.

Thermal carbon analysis, such as Method 5040 of the National Institute for Occupational Safety and Health (NIOSH) [5], is often used as a quantitative measurement of CNTs in the air [6–8]. This is a method to quantify organic carbon (OC) and elemental carbon (EC). It is one of the most reliable quantitative methods for measuring CNTs in the air. However, when CNTs are released together with polymer matrices, this technique may be inapplicable. In this study, we evaluated the potential for using thermal carbon analysis to determine CNTs in the presence of polymer matrices.

2. Methods

The samples tested in this study are summarized in table 1. Masses of OC and EC in each sample, placed in a boat made of Au foil or a quartz fiber filter, were measured using a thermal-carbon analyzer (CAA-202M-D, Sunset Laboratory Inc., USA). The results were compared with the carbon masses of the samples, calculated by their gravimetric masses—measured using an ultra-microbalance (SE2-F ultra-microbalance, Sartorius AG, Germany)—and carbon content. The temperature-step program was based on either the NIOSH method or the Interagency Monitoring of Protected Visual Environments (IMPROVE) method, with a slight modification (tables 2 and 3). The optical pyrolysis correction for pyrolytically generated carbon soot from OC during the analysis was not used.

Table 1. List of test samples.

CNTs	CNano Flotube9000 (average tube diameter: 10–15 nm, average tube length: 10 μm, carbon purity: 95–97.5%)
	Nanocyl NC7000 (average tube diameter: 9.5 nm, average tube length: 1.5 μm, carbon purity: 90%)
	AIST/TASC super-growth (SG) CNTs (average tube diameter: 3 nm, average tube length: >100 μm, carbon purity: 99.9%)
Polymers	Polyamide 12 (PA12)
	Polyamide 6 (PA6)
	Polybutylene terephthalate (PBT)
	Polypropylene (PP)
	Polyoxymethylene (POM)
	Polyethylene terephthalate (PET)
	Polycarbonate (PC)
	Polyetheretherketone (PEEK)
CNT composites	PA12-Flotube9000 (4%)
	PA12-Flotube9000 (10%)
	PA6-Flotube9000 (2%)
	PBT-Flotube9000 (4%)
	PBT-Flotube9000 (6%)
	PP-Flotube9000 (1%)
	PP-Flotube9000 (2%)
	POM-Flotube9000 (1%)
	PP-NC7000 (1%)
	PP-NC7000 (2%)
	POM-NC7000 (1%)
	PA6-SGCNT (1%)
	PA6-SGCNT (2%)
	PP-SGCNT (1%)
	PP-SGCNT (2%)
	POM-SGCNT (1%)

Table 2. NIOSH 5040 method-based protocol.

	Duration (s)	Temperature (°C)	Gas
OC1	80	310	He
OC2	80	475	He
OC3	80	615	He
OC4	300 (240*)	870	He
OC5	45	550	He
EC1	45	550	2%O_2/He
EC2	45	625	2%O_2/He
EC3	45	700	2%O_2/He
EC4	45	775	2%O_2/He
EC5	45 (300*)	850 (870*)	2%O_2/He
EC6	110 (120*)	870 (900*)	2%O_2/He

* When SGCNT was analyzed.

Table 3. IMPROVE method-based protocol

	Duration (s)	Temperature (°C)	Gas
OC1	300	250	He
OC2	600	450	He
OC3	600	500	He
OC4	300	550	He
EC1	300	550	2%O_2/He
EC2	120	600	2%O_2/He
EC3	120	650	2%O_2/He
EC4	240	700	2%O_2/He
EC5	180 (600*)	870	2%O_2/He

* When SGCNT was analyzed.

3. Results and discussion

First, the CNT powder samples were analyzed (figure 1). The amounts of total carbon (TC = OC + EC) detected were comparable to the carbon masses of the CNT powder, calculated by their gravimetric measured masses and carbon purity. The AIST/TASC super-growth (SG) CNT powder was detected mostly in the EC fraction in both cases of the NIOSH- and IMPROVE-based temperature-step protocols. In contrast, for Flotube9000 and NC7000, several tens of percent of the CNT powder was detected in the OC fraction when the NIOSH-based temperature-step protocol was used. When the IMPROVE-based temperature-step protocol was used, all the three types of CNTs were detected mostly in the EC2–5 fractions.

Subsequently, the grinding debris of the polymer samples (containing no CNTs) was analyzed using the IMPROVE-based protocol (figure 2). The amounts of TC detected were in good agreement with the carbon masses of the polymers, calculated by their gravimetric measured masses and carbon content (the percentage of carbon atoms). Polyamide 12 (PA12), polyamide 6 (PA6), polybutylene terephthalate (PBT), polypropylene (PP), and polyoxymethylene (POM) were detected mostly in the OC fraction and slightly in the EC1 fraction, indicating that they were potentially distinguishable from the CNTs. On the other hand, polyethylene terephthalate (PET), polycarbonate (PC), and polyetheretherketone (PEEK) were detected partly (or mostly) in the EC2–5 fractions, indicating that they were hardly distinguishable from CNTs. In a similar way, when the NIOSH-based protocol was

used, PET, PC, and PEEK were detected partly in the EC fraction (data not shown), indicating that they were hardly distinguishable from CNTs.

Finally, the grinding debris of the CNT composite samples was analyzed using the IMPROVE-based protocol. Although the amount of the grinding debris used for each analysis was only several hundred micrograms, judging from visual observation, the grinding debris seemed to have almost the same CNT content as the original CNT composite. For each sample, the analysis was repeated at least five times to increase the representativeness of the sample. The representative thermal-carbon analyzer thermograms are shown in figure 3. The CNTs in the composites tended to burn at a lower temperature than the CNT powder. The amounts of EC excluding EC1 were comparable to the carbon masses of the CNT composites, calculated by their gravimetric measured masses and CNT content, except for the PA6 composites (table 4). Because the ratio of the amount detected in the EC1 fraction to the TC was higher for the PA6 composites than for the pure PA6, the CNTs in the PA6 composites were probably detected partly in the EC1 fraction.

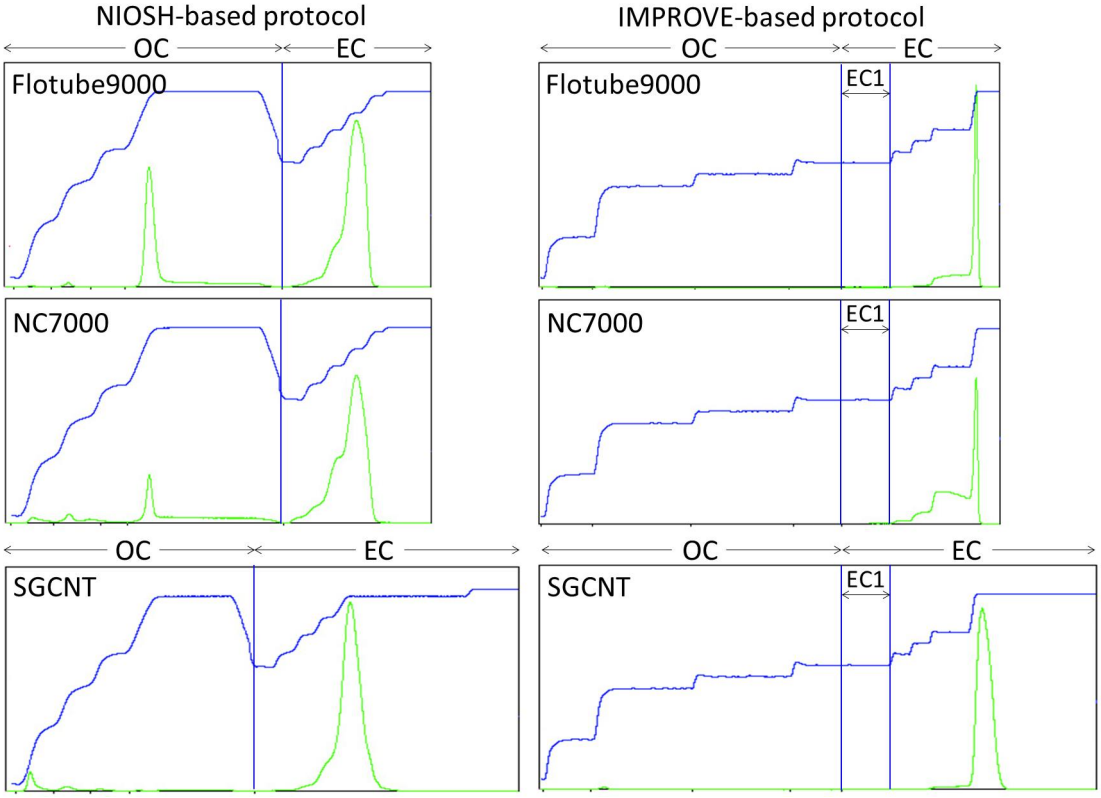

Figure 1. Thermal-carbon analyzer thermograms of CNT powder. Blue and green lines represent the temperature and detector response (arbitrary unit), respectively.

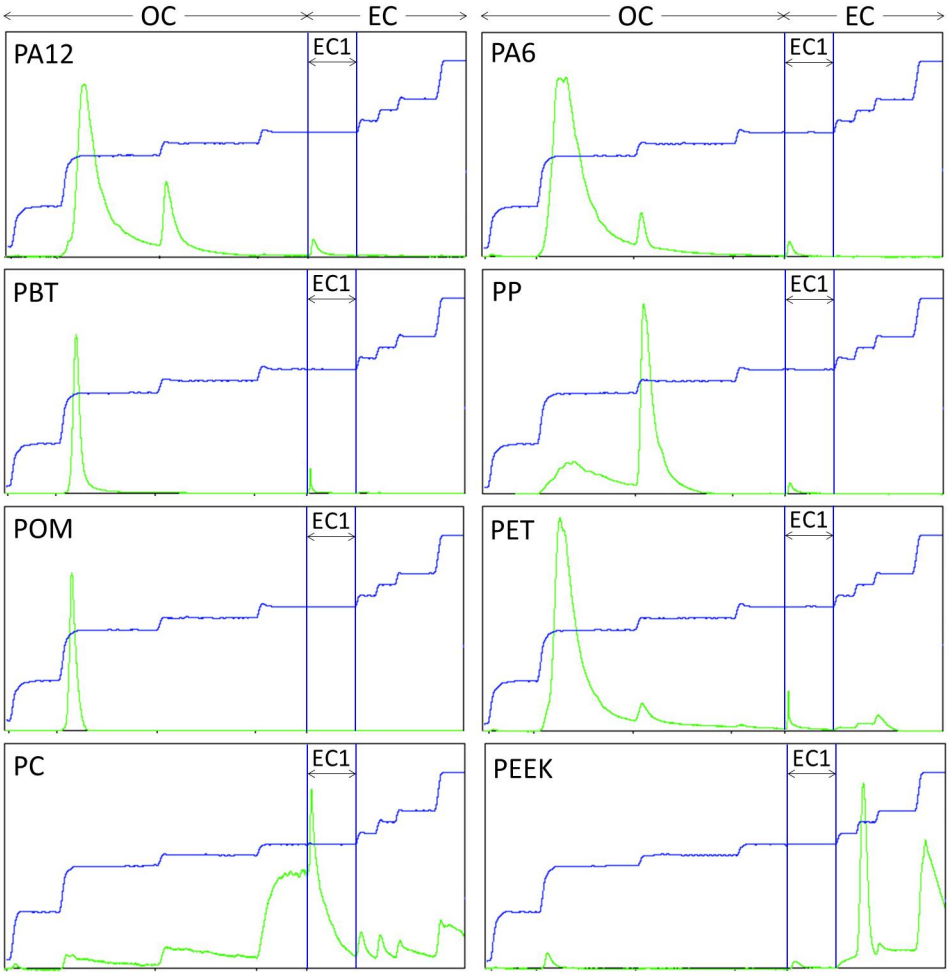

Figure 2. Thermal-carbon analyzer thermograms of polymer debris. Blue and green lines represent the temperature and detector response (arbitrary unit), respectively.

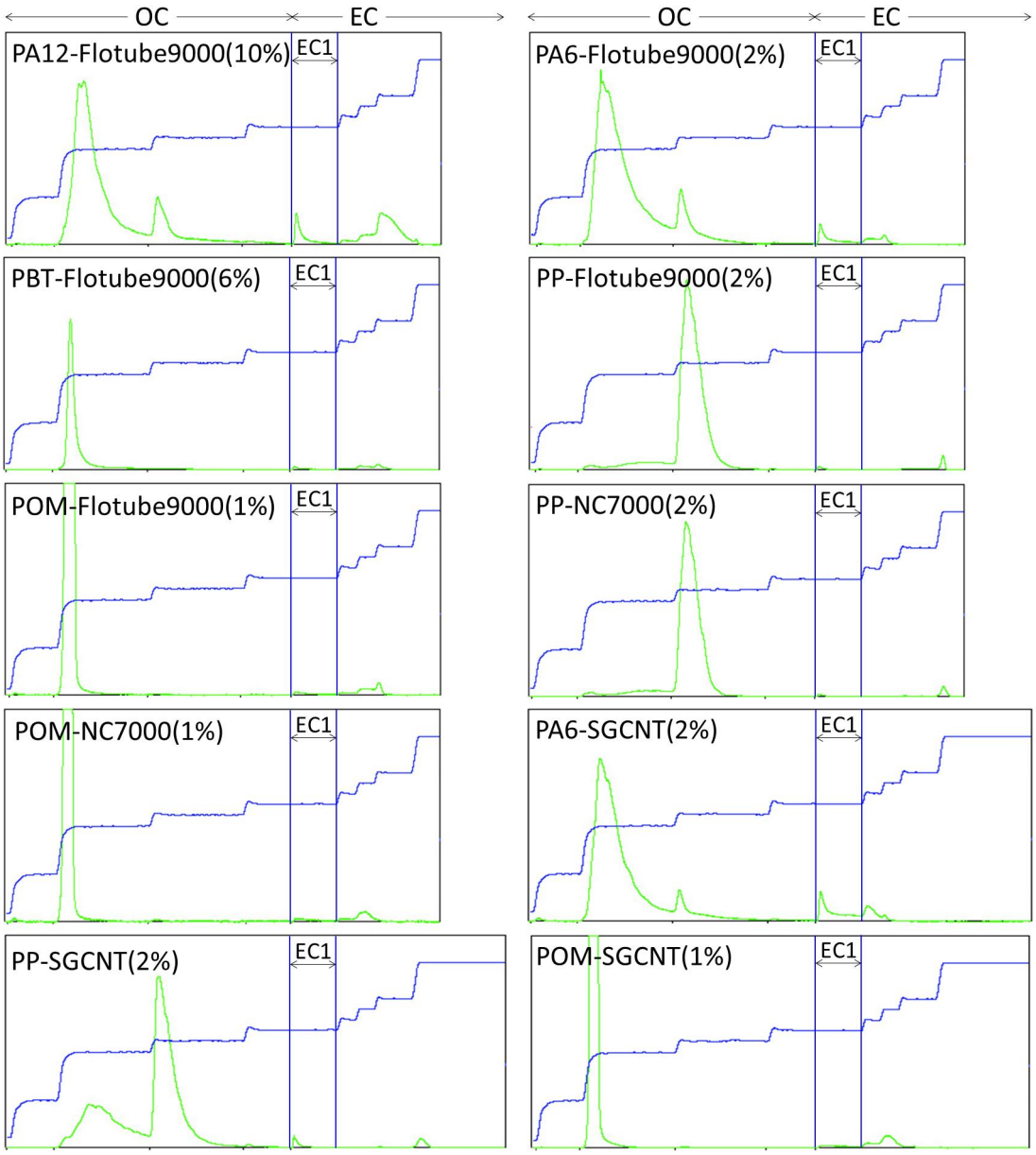

Figure 3. Thermal-carbon analyzer thermograms of CNT composites. Blue and green lines represent the temperature and detector response (arbitrary unit), respectively.

Table 4. Ratio of the amount of EC (excluding EC1) to the carbon mass of the sample (calculated by its gravimetric measured mass and CNT content).

Sample	Ratio
PA12-Flotube9000 (4%)	1.01±0.02
PA12-Flotube9000 (10%)	0.96±0.01
PA6-Flotube9000 (2%)	0.69±0.09
PBT-Flotube9000 (4%)	1.01±0.04
PBT-Flotube9000 (6%)	0.93±0.05
PP-Flotube9000 (1%)	1.09±0.05
PP-Flotube9000 (2%)	1.05±0.04
POM-Flotube9000 (1%)	0.98±0.04
PP-NC7000 (1%)	1.21±0.18
PP-NC7000 (2%)	1.05±0.08
POM-NC7000 (1%)	0.93±0.06
PA6-SGCNT (1%)	0.32±0.15
PA6-SGCNT (2%)	0.86±0.67
PP-SGCNT (1%)	1.09±0.06
PP-SGCNT (2%)	0.86±0.06
POM-SGCNT (1%)	1.10±0.06

n = 5–7

4. Conclusions

Our results showed that thermal carbon analysis was potentially capable of determining CNTs in distinction from PA12, PBT, PP, and POM when the CNT content was a few percent or higher. However, it was difficult to determine CNTs in the presence of PET, PC, PEEK, or PA6.

Acknowledgment

This work is based on results obtained from a project commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

References

[1] Wohlleben W, Brill S, Meier M W, Mertler M, Cox G, Hirth S, von Vacano B, Strauss V, Treumann S, Wiench K, Ma-Hock L and Landsiedel R 2011 On the lifecycle of nanocomposites: comparing released fragments and their in-vivo hazards from three release mechanisms and four nanocomposites *Small* **7** 2384–2395

[2] Wohlleben W, Meier MW, Vogel S, Landsiedel R, Cox G, Hirth S, Tomović Ž 2013 Elastic CNT-polyurethane nanocomposite: synthesis, performance and assessment of fragments released during use *Nanoscale* **5** 369–380

[3] Schlagenhauf L, Buerki-Thurnherr T, Kuo YY, Wichser A, Nüesch F, Wick P, Wang J 2015 Carbon Nanotubes Released from an Epoxy-Based Nanocomposite: Quantification and Particle Toxicity *Environ Sci. Technol.* **49** 10616–10623

[4] Schlagenhauf L, Kianfar B, Buerki-Thurnherr T, Kuo YY, Wichser A, Nüesch F, Wick P, Wang J 2015 Weathering of a carbon nanotube/epoxy nanocomposite under UV light and in water bath: impact on abraded particles *Nanoscale* **7** 18524–18536

[5] NIOSH (National Institute for Occupational Safety and Health) 2003 Method 5040 Issue 3, Diesel particulate matter (as Elemental Carbon). NIOSH Manual of Analytical Methods (NMAM; 4th ed.)

[6] NIOSH (National Institute for Occupational Safety and Health) 2013 NIOSH Current

intelligence bulletin 65: Occupational exposure to carbon nanotubes and nanofibers. http://www.cdc.gov/niosh/docs/2013-145/

[7] Ono-Ogasawara M, Takaya M, Kubota H, Shinohara Y, Koda S, Akiba E, Tsuruoka S and Myojo T 2013 Approach to the exposure assessment of MWCNT by considering size distribution and oxidation temperature of elemental carbon *J. Phys.: Conf. Ser.* **429** 012004

[8] Ogura (2013). Guide to measuring airborne carbon nanotubes in workplaces. https://en.aist-riss.jp/assessment/2571/