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

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Abstract. The ability of thermal carbon analysis to determine CNTs was evaluated in the presence of a polymer (Polystyrene, PS). Samples placed in an Au (Pt) foil boat were measured using a thermal-carbon analyzer, and the results were compared with gravimetric measurements of sample masses obtained using an ultra-microbalance. First, debris from the polymer without CNTs (i.e., PS debris) was analyzed. The amount of PS debris detected in the organic carbon (OC) fraction was found to be in good agreement with the gravimetrically measured mass of the PS debris, while the amount of pyrolytically generated carbon soot detected in the elemental carbon (EC) fraction was negligible. Next, single-wall CNT (AIST/TASC Super-Growth) powder was analyzed, and the amount of the CNT powder detected in the EC fraction was found to be 95–96% of the gravimetrically measured mass of the CNT powder. Subsequently, a mixture of the PS debris and the CNT powder was analyzed, and the amounts of detected OC and EC were found to be comparable to the gravimetrically measured masses of the PS debris and the CNT powder, respectively. Finally, debris from 5 wt% CNT–PS composites was analyzed, and amounts of OC and EC detected were found to be approximately comparable to the estimated masses of the PS and the CNTs in the debris of CNT–PS composite, respectively. The results therefore indicate thermal carbon analysis is capable of determining CNTs in the presence of PS.

1. Introduction

Carbon nanotubes (CNTs) have unique properties, and therefore, their use as a filler material in composites is considered promising. In the future, CNT composites are expected to be used in a wide range of industrial applications and consumer products. However, there are concerns regarding the potential impact of CNTs on the health of workers and users, and in this respect, the evaluation and control of CNT exposure is required.

Thermal carbon analysis, such as Method 5040 of the National Institute for Occupational Safety and Health (NIOSH), is often used as a quantitative measurement of CNTs in the air [1]. This is a method to determine the fractional content of organic carbon (OC) and elemental carbon (EC). The method used for analysis is as follows: a sample collected with a quartz-fiber filter is heated in stages in a helium atmosphere to vaporize OC, after which the EC is burned by heating in stages in the presence of oxygen. The vaporized or burned carbon is then completely oxidized to CO_2 with a catalyst. Furthermore, by reducing CO_2 to CH_4 with another catalyst, CH_4 is detected using a flame-ionization detector. Using this method, CNTs are detected within the EC fraction. This method is

currently one of the most reliable existing quantitative methods for measuring CNTs in the air. However, when a large quantity of other carbon material exists, this technique may be inapplicable.

When CNTs are used in a mixed state with a polymer as a composite material, particles of mixed CNTs and debris from the polymer itself can be released during mechanical and abrasive processing. Unattached (free) CNTs can also be released, but they may be in the minority. The harmful effects of mixed CNTs have not yet been fully evaluated, although Wohlleben et al. (2011) indicated that they are smaller than those of free CNTs [2]. However, it is considered that under the present circumstances, any exposure to mixed CNTs (as well as to free CNTs) should be measured and controlled.

In this study, we evaluated the capability of using thermal carbon analysis to determine CNTs in the presence of a polymer (Polystyrene, PS).

2. Methods

We prepared four test samples: **PS**: ground PS debris; **CNT**: CNT powder (AIST/TASC Super-growth single-wall CNTs with a tube diameter of approximately 3 nm and a carbon purity of 99.9%); **PS & CNT**: mixture of PS debris and CNT powder; and **CNT–PS composite**: ground debris of CNT–PS composites (approximately 5wt% CNTs).

Masses of OC, EC, and total carbon (TC) in each sample placed in an Au (or Pt) foil boat were measured using a thermal-carbon analyzer (CAA-202M-D, Sunset Laboratory Inc., USA), and the results were compared with the gravimetric measurement of the sample mass obtained using an ultra-microbalance. We used two different temperature-step protocols based on the NIOSH Method 5040 [3] and the IMPROVE (Interagency Monitoring of Protected Visual Environments) method [4], but with slight modifications (Tables 1 and 2). The optical pyrolysis correction for pyrolytically generated carbon soot from OC during analysis was not used.

Table 1. NIOSH 5040 method-based protocol.

	Duration (sec)	Temperature (°C)	Gas
OC	80	310	He
OC	80	475	He
OC	80	615	He
OC	*240*	870	He
OC	45	550	He
EC	45	550	$2\%O_2/He$
EC	45	625	$2\%O_2/He$
EC	45	700	$2\%O_2/He$
EC	45	775	$2\%O_2/He$
EC	*300*	870	$2\%O_2/He$
EC	*120*	*900*	$2\%O_2/He$

Table 2. IMPROVE method-based protocol.

	Duration (sec)	Temperature (°C)	Gas
OC	180	120	He
OC	180	250	He
OC	*540*	450	He
OC	*540*	550	He
EC	300	550	$2\%O_2/He$
EC	210	700	$2\%O_2/He$
EC	*540*	*870*	$2\%O_2/He$
EC	*120*	*900*	$2\%O_2/He$

3. Results and discussion

The thermograms of the samples obtained using the thermal-carbon analyzer with two different temperature-step protocols are shown in figure 1, and the results are summarized below.

3.1. PS debris (Table 3)

The amount of PS debris detected in the OC fraction was in good agreement with the gravimetrically measured mass of the PS debris, and the amount of pyrolytically generated carbon soot detected in the EC fraction was negligible.

3.2. CNT powder (Table 4)

The amount of CNT powder detected in the EC fraction was 95–96% of the gravimetrically measured mass of the CNT powder, while the amount of TC was in good agreement with the gravimetrically measured mass of the CNT powder. Thee detected OC could be derived from the volatile gas adsorbed on the surface of the CNTs.

### 3.3. PS debris & CNT powder (Table 5)

The amounts of detected OC and EC were comparable to the gravimetrically measured masses of the PS debris and the CNT powder, respectively. Thus, even when a mixture of the PS debris and the CNT powder was analyzed, the amounts were be distinct from each other.

3.4. CNT–PS composite (Table 6)

The amounts of detected OC and EC were approximately comparable to the estimated masses of the PS and the CNTs in the debris of CNT–PS composites, respectively. Although the thermogram (figure 1) indicated that CNTs in the composites were burned at a lower temperature than that of the as-produced CNT powder, it was considered that the PS and CNTs were distinct from each other.

4. Conclusions

Our results indicate that thermal carbon analysis can be used to determine CNTs in the presence of PS.
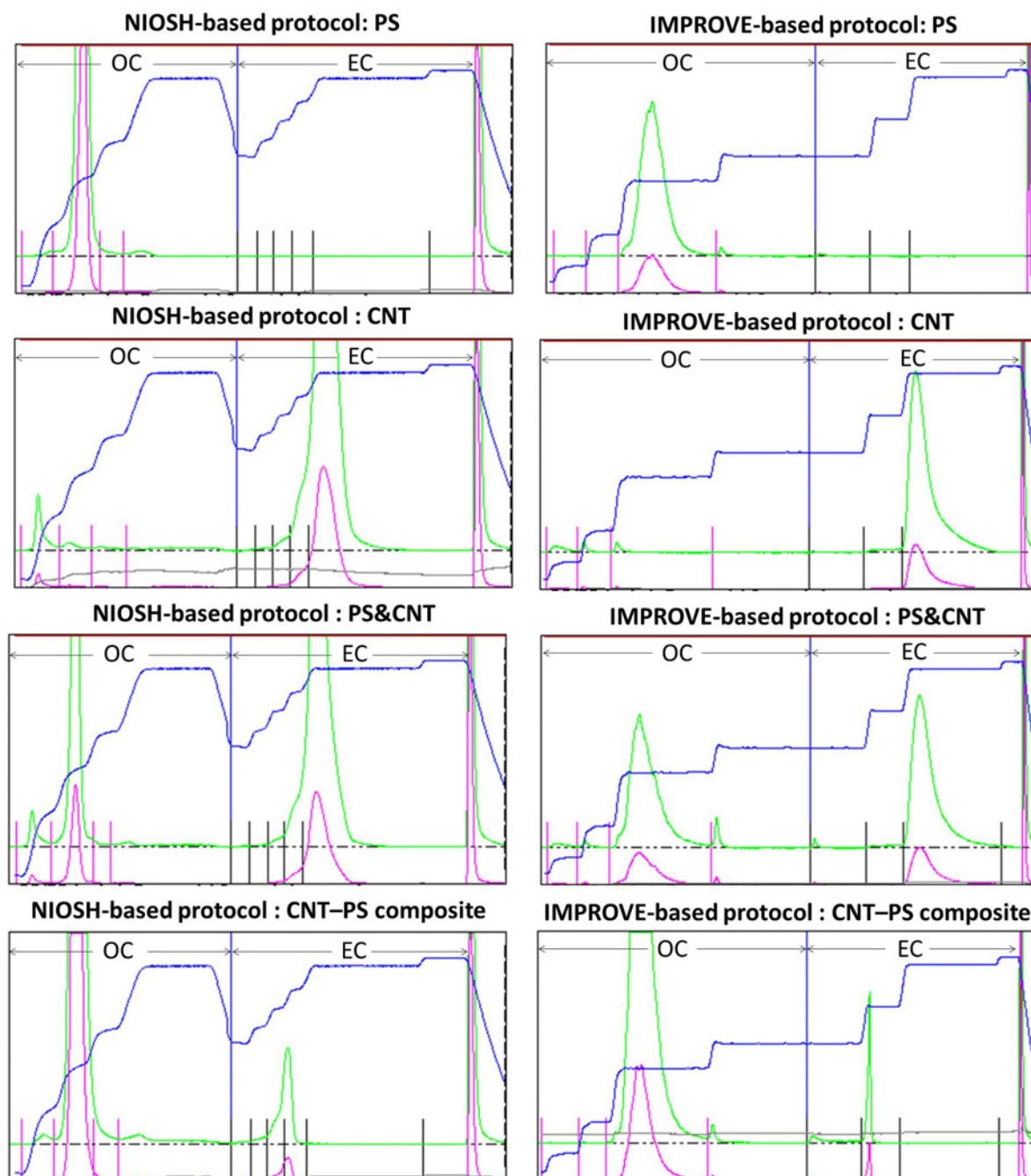
Figure 1. Thermograms produced using thermal-carbon analyzer.

Blue line: Temperature; green and purple lines: Flame ionization detector response

Table 3. Results of PS.

	n	OC $0.92 \times M_{PS}$	EC $0.92 \times M_{PS}$	TC $0.92 \times M_{PS}$
NIOSH-based protocol	8	1.02 ± 0.05	0.0014 ± 0.0009	1.02 ± 0.05
IMPROVE-based protocol	4	0.99 ± 0.04	0.0043 ± 0.0044	1.00 ± 0.04

M_{PS}: Mass of PS debris; **0.92**: Carbon content in PS

Table 4. Results of CNT.

	n	OC M_{CNT}	EC M_{CNT}	TC M_{CNT}
NIOSH-based protocol	9	0.073 ± 0.008	0.95 ± 0.02	1.02 ± 0.02
IMPROVE-based protocol	5	0.028 ± 0.016	0.96 ± 0.03	0.98 ± 0.02

M_{CNT}: Mass of CNT powder

Table 5. Results of PS & CNT.

	n	OC $0.92 \times M_{PS}$	EC M_{CNT}	TC $0.92 \times M_{PS} + M_{CNT}$
NIOSH-based protocol	9	1.06 ± 0.07	0.96 ± 0.02	1.00 ± 0.03
IMPROVE-based protocol	11	0.97 ± 0.03	0.97 ± 0.03	0.96 ± 0.01

M_{PS}: Mass of PS debris; M_{CNT}: Mass of CNT powder; **0.92**: Carbon content in PS

Table 6. Results of CNT–PS composite.

	n	OC $0.92 \times 0.95 \times M_{COMP}$	EC $0.05 \times M_{COMP}$	TC $(0.92 \times 0.95 + 0.05) \times M_{COMP}$
NIOSH-based protocol	12	1.09 ± 0.06	0.80 ± 0.08	1.07 ± 0.05
IMPROVE-based protocol	8	0.96 ± 0.03	0.93 ± 0.03	0.96 ± 0.03

M_{COMP}: Mass of CNT–PS composite; **0.92**: Carbon content in PS;
0.05: CNT content in composite (approximately); **0.95**: PS content in composite (approximately)

References

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