

Applications of TGA in quality control of SWCNTs

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Abstract Carbon nanotubes exhibit a range of chemistries, including mixtures of different nanotube diameters, lengths, and chiralities coupled with various concentrations of metallic and non-nanotube-carbon impurities. The performance of a given material for a specific application depends on the chemistry, which is dictated in large part by the manufacturing process. Here, thermogravimetric analysis is utilized as a bulk characterization method for determining nanotube quality after manufacturing. The application of thermogravimetric analysis for quantifying basic nanotube chemistry is described (e.g., carbon-to-metal content, homogeneity). In addition, extension of the method to analyze specific nanotube properties (i.e., length and diameter) is reported. Results indicate that thermogravimetric analysis is sufficiently sensitive to enable quality control at both the macro-scale (carbon-to-metal ratio) and nano-scale (single-walled to multi-walled) and can detect subtle modifications in manufacturing processes.

Keywords Thermogravimetric analysis · Quality control · Carbon nanotubes

Introduction

Carbon nanotubes are one of the most versatile nanomaterials available today, with applications ranging from bulk use for strengthening composites to use of individual nanotubes for medical and electrical applications [1]. The

properties of carbon nanotubes are diverse and structure-dependent. For example, carbon nanotubes are extremely strong [2] and their thermal conductivity surpasses that of isotopically pure diamond, a substance previously unsurpassed in conductivity [3]. The unique applications of carbon nanotubes are most pronounced for the single-walled form of nanotubes, the most expensive nanotube material because of the purification processes required and the associated low process yields [2].

The most common methods for single-walled carbon nanotube (SWCNT) synthesis are carbon-arc discharge, pulsed-laser vaporization, chemical vapor deposition, and high-pressure CO decomposition [3]. In all of these synthesis methods, a SWCNT sample consists of amorphous carbons, SWCNTs, other structured carbon materials (e.g., multi-walled carbon nanotubes (MWCNT), fullerenes), and metallic catalyst particles. After manufacturing, many vendors perform post-production purification steps on their materials, such as an acid rinse, to eliminate residual metal catalysts and attempt to isolate specific chiralities or diameters. The final product obtained after SWCNT synthesis and purification depends on each specific step in the process, and small changes to synthesis temperature, catalyst concentration, etc., can yield a substantially different product.

Despite the developments in uses for carbon nanotubes (CNTs), characterization of the material remains a difficult challenge for manufacturers, product developers, and scientists. Commercially available SWCNT samples can vary greatly in SWCNT content from 90% to 40%, with the remainder of the sample containing undesirable contamination from the manufacturing process (amorphous carbon, MWCNT, or other structured carbons and metal catalyst particles). Lengths, diameters, and chiralities of CNTs can also vary from sample to sample and can have a profound effect on the performance of the material for a given

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application. The level of purity desired for a given sample varies depending on application; many applications of SWCNTs require pure, well-characterized samples.

Recommendations for measuring single-walled carbon nanotubes have been published for the most common characterization techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, thermogravimetric analysis (TGA), near-infrared (NIR) spectroscopy, and atomic force microscopy (AFM) [4]. Taken together, these techniques can provide an in-depth profile of a given sample, but it can be both time- and labor-intensive to perform all of these measurements. SEM and TEM provide qualitative assessments of composition, and sample only a small fraction of a given specimen. AFM has been used in a quantitative manner to measure SWCNT length, but is not widely used because it is labor-intensive [5, 6]. Raman spectroscopy can be used to determine distributions of nanotube diameter and the fraction of amorphous carbon and electronic state (semiconducting or metallic) of the CNT, provided that the majority of the sample is SWCNTs [4]. NIR spectroscopy evaluates the relative purity of the sample and the fraction of semiconducting versus metallic SWCNTs present [4].

Thermogravimetric analysis is one of the most straightforward methods to characterize SWCNTs. TGA can be used to analyze the nanotube powder directly to give the percentage of amorphous carbon, catalytic metals, and graphitic structured carbons (SWCNT and MWCNT) within the bulk sample without requiring special sample preparation [4, 7]. The percentage of catalytic metals can be determined quantitatively, while the actual percentages of different carbon forms is only determined semi-quantitatively and secondary measurements are often used to confirm TGA results. TGA is a destructive technique that measures mass loss as a function of temperature for a 1 to 10 mg sample with the carbon materials decomposing on heating. The decomposition of amorphous carbon occurs from 200 to 400 °C, which is a lower temperature than that for the decomposition of SWCNTs in most cases, allowing for the quantitation of amorphous carbons within the sample [7, 8]. After CNT samples are heated to a temperature at or above 600 °C, all carbon-containing constituents are removed, and the residual mass is comprised of catalytic metals and their oxidation products [8]. In rare cases, MWCNTs can oxidize at higher temperatures. TGA has been used to (a) characterize as-produced SWCNT samples, (b) to track the effects of purification process [9], and (c) to monitor how changes in a manufacturing conditions affect the percentage of SWCNT within the sample. The method can be used for basic analysis of carbon nanotubes but is also under development for more advanced characterization. This paper will cover the current uses of TGA for determining SWCNT purity

and show how some of the thermogravimetric methods can be extended to characterize specific nanotube properties, such as length and diameter, as verified by recent advances in carbon nanotube sorting.

Experimental

Single-walled carbon nanotube comparison materials

Material A, as described by Manufacturer A, is an arc-produced [1] sample that contains 12+% SWCNT, 25% metal catalyst, and 20% other structured carbons by mass. Material B is produced by a high-pressure CO process (HiPCO) [10] and then purified by Manufacturer B. Material B is reported by the manufacturer to have 5.5% metal content and less than 15% ash content. Material C is produced by the cobalt–molybdenum process [11] and purified to contain greater than 50% (6,5) chirality nanotubes with 10% non-carbon impurities, according to the manufacturer (Manufacturer C). Length-sorted materials were obtained from an ultracentrifugation-based sorting of the NIST single-walled carbon nanotube reference material by a previously published procedure [5]. Diameter-sorted materials were purchased from Manufacturer D as a series of single-walled, double-walled, and multi-walled samples.

Dispersion and Mixture Preparation Suspensions of the length-sorted materials were obtained by dispersing SWCNT reference material into a sodium deoxycholate (DOC) solution. Through a process of ultracentrifugation and fraction collecting, length-sorted materials were obtained [5] in a 2% sodium deoxycholate solution with 0.08% sodium azide to prevent contamination. Deoxycholate/azide solutions were centrifuged in membrane tubes to exchange the buffer for a 0.25% sodium deoxycholate solution. For basic deoxycholate dispersions, Material A was dispersed in a solution of 0.25% DOC in water. The solution was sonicated for 15 min to yield a solution of dispersed carbon nanotubes. In all cases with dispersed materials, a small portion of the solution was deposited onto silicon wafers and dried to yield thin films of dispersed materials (more than 1 mg of dispersed material deposited).

Thermogravimetric analysis All sample runs were performed in 100- μ L ceramic pans. Sample masses were approximately 2 mg of material for Materials A and C and approximately 10 mg for Material B, as determined by the TGA instrument. For the materials studied here, sample masses within the given ranges were found to have little influence on oxidation temperature and residual mass. Pans were equilibrated to 40 °C in the TGA, and then heated at a rate of 10 °C/min to 800 °C unless otherwise noted. For the materials tested here, no oxidation was found above 800 °C

and heating rates of 10 °C/min yielded the most reproducible results. During the sample run, air was introduced to the samples at a rate of 25 mL/min unless otherwise noted to maintain an oxidizing environment around the sample. Air flow of 25 mL/min was found to be sufficient to remove oxidation products without introducing buoyancy effects.

Results and discussion

TGA of carbon nanotubes has become a relevant tool for purity analysis. The residual mass and the oxidation temperature data provide information on the material's decomposition. Figure 1a shows a typical plot for weight

percent versus temperature for three different types of material. From this curve, we can determine compositional differences in the material, which arise from the different manufacturing and post-production purification processes. First, we can identify the differences in residual mass at 650 °C. At this temperature, most carbon-based materials have decomposed (mass for Material A still shows a slight decrease), and the residual mass is attributed to the metal catalyst particles that remain. At 650 °C, the residual masses are $26.1 \pm 1.2\%$ for Material A, $8.8 \pm 0.4\%$ for Material B, and $6.3 \pm 0.3\%$ for Material C. For all three carbon nanotube materials, there is one major mass-loss event (Fig. 1a) that occurs, indicated by the drop of the weight percent of material from approximately 90% to the residual mass value at 650 °C. If the mass loss had occurred in a step-wise fashion, multiple plateaus in the weight-loss curve would be evident. Figure 1b shows the derivative weight curve with respect to temperature for the mass-loss curves seen in Fig. 1a. The derivative curve can be used to determine the oxidation temperature of the material, as well as defining the mass-loss event as a single decomposing species (e.g., single peak) or as multiple decomposition events (e.g., double peaks, shouldered peaks). The primary oxidation temperature for each material is defined as the temperature at the highest peak for the material on the derivative weight curve and can represent the thermal stability of the material. For the materials here, the oxidation temperatures are 411.4 ± 2.7 °C for Material A, 479.0 ± 1.3 °C for Material B, and 492.4 ± 0.7 °C for Material C. Material A exhibited the lowest oxidation temperature and has two peaks in the derivative curve (one apparent at 310 °C, as well as the major oxidation temperature of 390 °C), indicative of multiple types of carbons decomposing. The lower oxidation temperature of this material may also indicate the presence of amorphous carbons, which degrade at temperatures lower than those for the structured carbons (e.g., SWCNT and MWCNTs) [7]. Material B exhibits a fairly broad decomposition peak with multiple shoulders evident (~375 °C and ~650 °C), indicating that the material has many different species of carbons present (e.g., amorphous carbon, single-walled nanotubes). The higher temperature shoulder indicates that multi-walled carbon nanotubes or other structured carbon may also be present, as these tubes decompose at temperatures higher than those for single-walled carbon nanotubes. Material C decomposes at a higher temperature than Materials A and B, with a narrower distribution. The shoulder seen along the high-temperature edge of the peak indicates that there are multiple carbon species present.

It should be noted that specific measurement variables can have a significant effect on resulting TGA data. To ensure the ability to cross compare data, certain TGA parameters should be defined and standardized to avoid

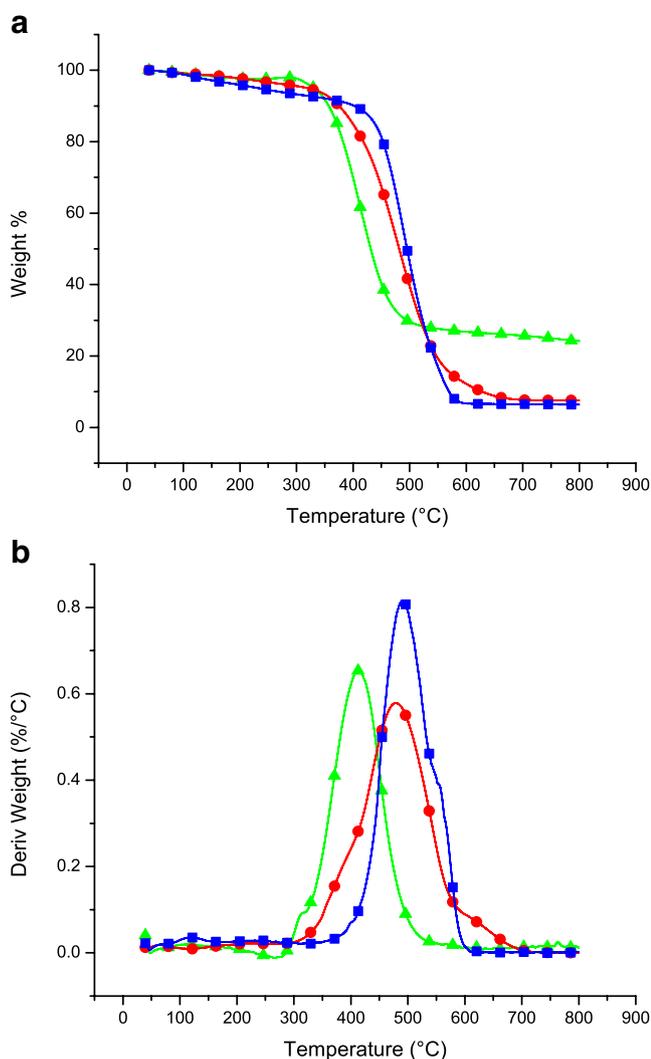


Fig. 1 Three different SWCNT materials. **a** Weight percent versus temperature curve for three manufactured SWCNT materials. **b** Derivative weight percent versus temperature curve for three manufactured materials. Material A (green, filled upright triangle), Material B (red, filled circle), and Material C (blue, filled square)

measurement-induced variability. For example, Fig. 2a shows the derivative weight-loss curves for the SWCNT materials as the heating rate is changed. Data acquired at rates of 5 °C/min, 10 °C/min, and 20 °C/min for Material A (i), Material B (ii) and Material C (iii) are shown. In all three materials, as the heating rate increases, the oxidation temperature of the material also increases. The general shapes of the derivative curves for Material A (Fig. 2a, i)

and Material C (Fig. 2a, iii) are maintained with the heating rate, but Material B (Fig. 2a, ii) shows a dramatic increase in peak width in conjunction with a decrease in peak height. For all materials, a change in the heating rate was determined to have a significant impact on the oxidation temperature. However, the morphology of Material B (i.e., greater extent of bundling) contributes to variations in peak shape which were not observed in the other materials.

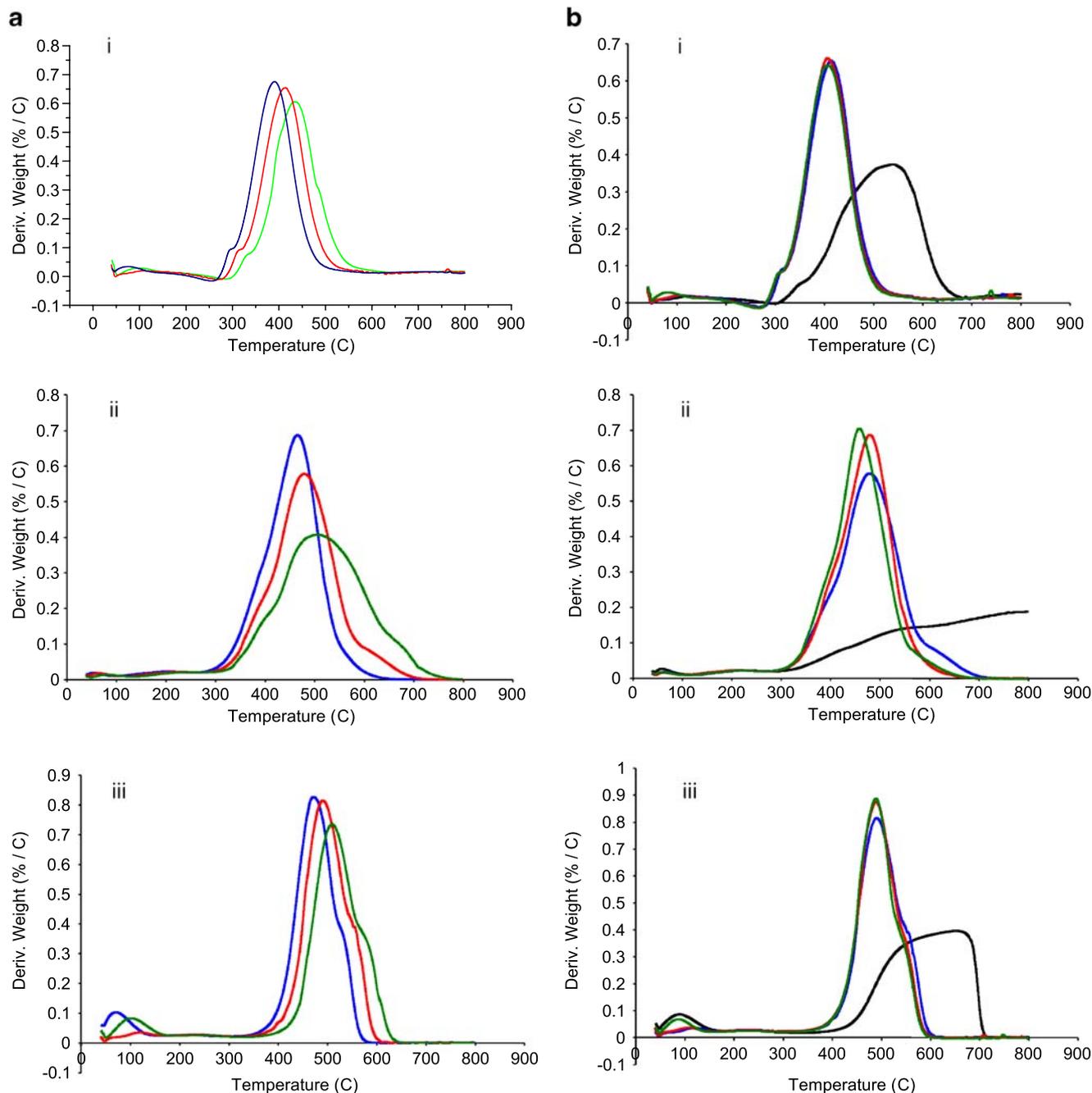


Fig. 2 Impact of heating and air flow rate on TGA. **a** Derivative weight percent versus temperature curve for Material A (i), Material B (ii), and Material C (iii) at three heating rates: 5 °C/min (blue), 10 °C/min (red),

and 20 °C/min (green). **b** Derivative weight percent versus temperature for different air flow rates: 0 mL/min (black), 25 mL/min (blue), 50 mL/min (red), and 100 mL/min (green)

In addition to heating rate, the effect of gaseous environment was also studied. The derivative weight-loss curves for each material (Material A (i), Material B (ii) and Material C (iii)) as the oxidizing environment changes within the system are shown in Fig. 2b. The different air flow rates evaluated were 0, 25, 50, and 100 mL/min. In a static environment, the oxidation temperature shifts to a much higher temperature for all three materials. This temperature is not within the tested range (to 800 °C) for Material B, so the complete decomposition profile is not available. For Material A, the oxidation temperature decreases by 1.3%, while the temperature decreases 3.4% in Material B once air flow is present. In both of these materials, the shift to lower temperature is consistent as the oxygen content increases. For Material C, the oxidation temperature shifts first to a lower temperature when air flow is introduced, then back to a higher temperature, with only a minor change of 0.1% in the oxidation temperature. The general peak shape was maintained for all materials from 25 to 100 mL/min for all materials. In general, within the range of 25 to 100 mL/min, it was determined that the flow rate had no impact on material decomposition. However, static environs provide to be problematic as insufficient flow was available to remove decomposition products. It should also be noted that differences in the manufacturing process can yield different SWCNT samples, which may be more or less dependent on the conditions in which the sample is analyzed, and so the sampling conditions should be chosen carefully, based on the type of material. For example, variations in amorphous carbon content, metallic content, or bundling of SWCNT can alter the thermodynamics of decomposition, which are affected by flow rate.

For quality control applications, repeatability of the measurement is important. When test parameters were fixed, the TGA method proved quite reproducible. Twenty-five samples of SWCNTs from a single manufacturer and batch were analyzed under identical TGA conditions and demonstrated less than 0.5% relative standard deviation (RSD) in oxidation temperature. The average oxidation temperature (\pm standard deviation) was determined to be $(384.1 \pm 1.7)^\circ\text{C}$. This result demonstrates that TGA can be used in a quality control setting for manufacturing, as it allows for quantitative characterization of a material. If greater variation was seen in the TGA curves (RSD $>2.0\%$), this would indicate the material, or the conditions in which it is sampled, are inhomogeneous. In comparison, sampling techniques such as SEM or TEM provide only qualitative assessments of the material.

Furthermore, the TGA method was demonstrated to be sensitive to minor varieties in material due to processing. For example, batch-to-batch differences were observed when four different batches were obtained from a single manufacturer (Fig. 3b). Each batch had slightly different

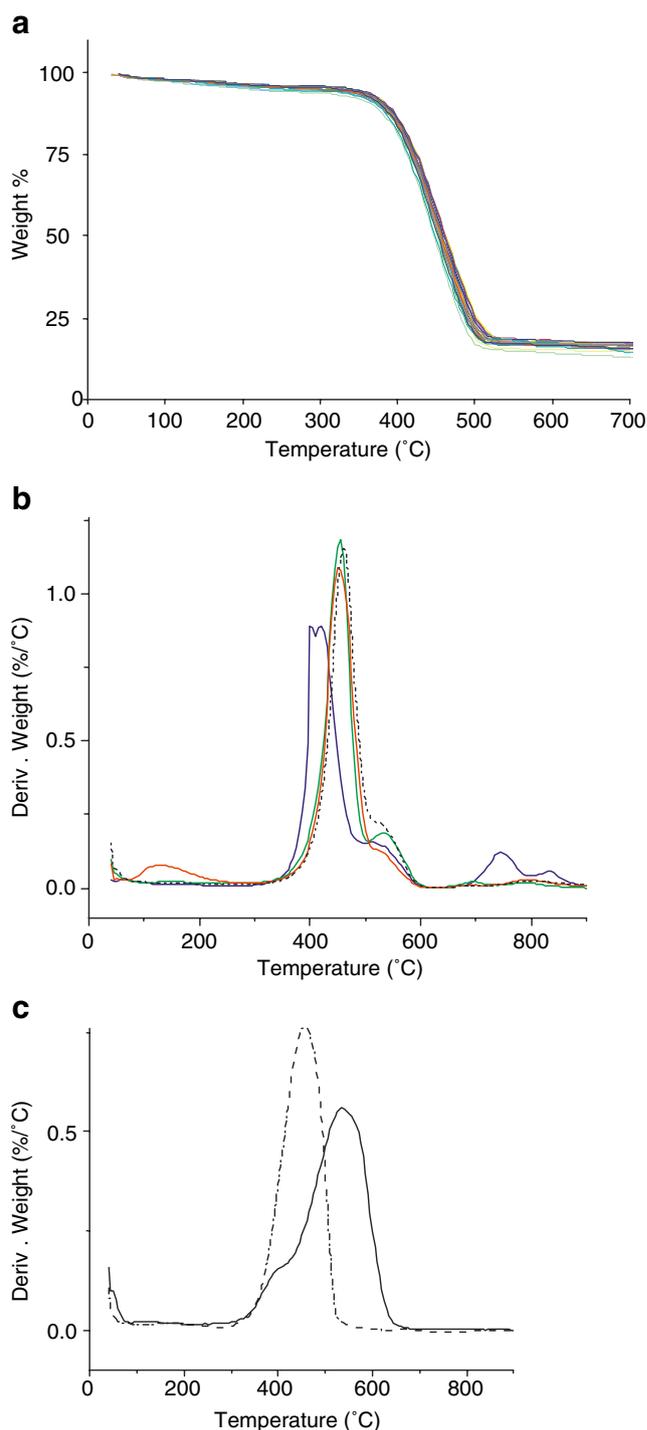


Fig. 3 Reproducibility of TGA with SWCNT. **a** Reproducibility of TGA technique is shown with 25 runs under the same conditions of one manufactured nanomaterial. **b** Four different batches of a material obtained from the same manufacturer. The *blue line* indicates a batch obtained from the company after the manufacturing scale-up occurred. **c** A HiPCO-processed material before (*solid line*) and after (*dotted line*) the material was chemically purified in the laboratory

decomposition profiles. For three batches, the main oxidation temperature was the same, even when extra peaks or shoulders on the main oxidation peak were seen. Before the fourth batch was obtained, the manufacturing process was scaled up with no intentional change in material composition. However, by qualitative examination of the TGA curve, it appears that the manufacturing change has led to a lower purity sample, as indicated by the shift to a lower oxidation temperature, the double peak at the main oxidation temperature, and the additional peaks seen at higher temperature.

In the laboratory setting, TGA can also be used to identify differences in material chemistry after modifications such as purification or functionalization. For example, the results for the carbon nanotube sample seen in Fig. 3c are shown as obtained from the manufacturer and post-purification. The purification process was able to eliminate the presence of a second carbon-containing species in the sample. The final oxidation peak is much narrower than the original peak, which indicates a sample of higher purity. Oxidation temperatures have also been observed to shift due to functionalization [12]. Wider or narrower peaks, multiple peaks, or a higher residual mass could all potentially be observed after functionalities are added to the carbon nanotube.

As purification processes improve for carbon nanotubes, quality control measurements will need to assess not only bulk chemistry, but also specific nanotube properties, such as diameter and length. Figure 4a illustrates how TGA can be extended from a bulk analysis method to a specific characterization instrument. Figure 4a shows the derivative weight percent curves for single-walled, double-walled (DWCNT), and multi-walled (MWCNT) carbon nanotubes illustrating the effect of diameter on the TGA curve. The SWCNT and MWCNT samples were reported to contain 98% carbon nanotubes. The double-walled carbon nanotube sample was reported as 50% DWCNT, 30% SWCNT, and 20% MWCNTs. The oxidation temperature (\pm standard deviation) shifts from $(598.1 \pm 1.3)^\circ\text{C}$ for SWCNT, $(606.3 \pm 0.7)^\circ\text{C}$ for DWCNT, to $(622.6 \pm 1.4)^\circ\text{C}$ for MWCNT. Multiple peaks were not seen in the DWCNT, as would be expected by the reported composition. The increase in oxidation temperature for the DWCNT sample indicates the presence of higher-walled CNTs, but does not indicate the extent of purity. Increased thermal stability is seen as more layers are added to the carbon nanotube structure, as previously seen in the literature [7].

Length dependency was also observed. Figure 4b shows how the derivative weight percent curve of a material changes as the single-walled carbon nanotube length increases from short (~ 80 nm) to medium (~ 320 nm) to long (~ 760 nm). During the length-sorting process, metallic catalyst particles and amorphous carbon are removed from

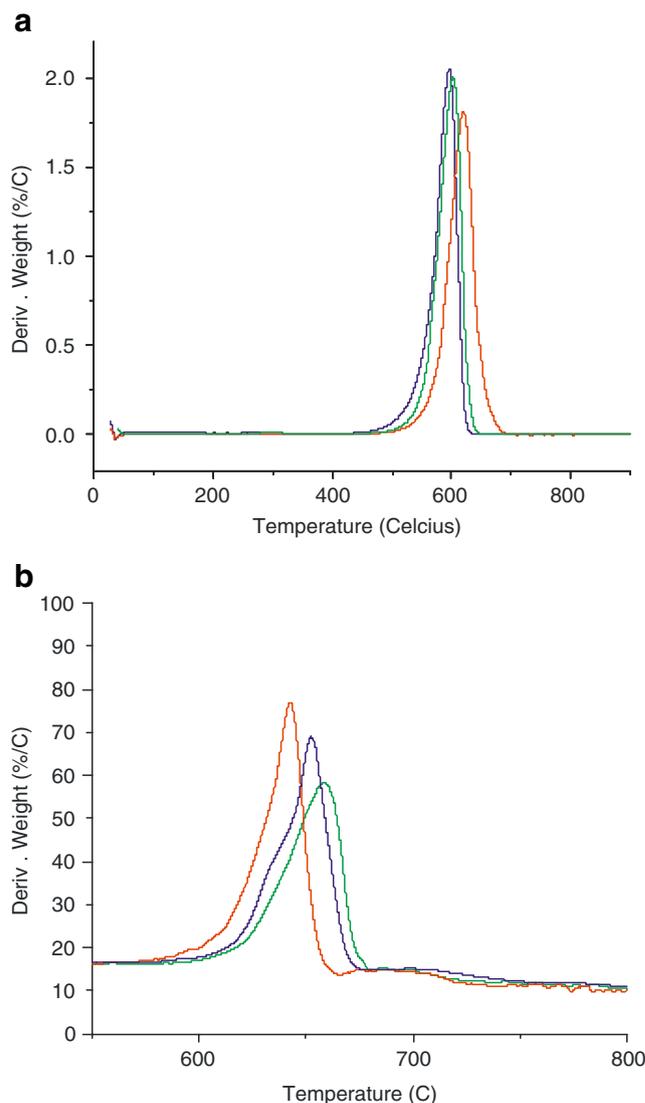


Fig. 4 Length and diameter effects in CNT TGA measurements. **a** Derivative weight percent vs. temperature for CNT with different diameter: single-walled (blue), double-walled (green), and multi-walled (red). **b** Derivative weight percent vs. temperature for length-sorted SWCNT material from 550 to 800 °C. The oxidation temperature shifts as the length progresses from short (green), to medium (blue), to long (red)

the sample, resulting in a very pure sample of length-sorted nanotubes [5]. Because of the purity of the sample, any effects seen in the TGA are assumed to be a result of the length of the material itself, not of contaminants within the sample. The long material decomposes at $644.5^\circ\text{C} \pm 2.4^\circ\text{C}$, the medium-length material decomposes at $651.6^\circ\text{C} \pm 1.4^\circ\text{C}$, and the short material decomposes at $657.8^\circ\text{C} \pm 0.8^\circ\text{C}$. The order of decomposition seems to be counterintuitive, as it would seem that longer tubes would be more stable than short carbon nanotubes. The early decomposition of long nanotubes may be a result of potential defects that occurred during the length-sorting process. The increased length could have

led to an increased probability of nanotube defect sites along the length and a lower oxidation temperature. The short SWCNT may not have experienced the same potential for defects during the length sorting, which gives way to increased thermal stability. The differences of the oxidation temperature seen with the diameter and length of the carbon nanotube illustrate potential uses of the method but also complicate TGA analysis of a manufactured sample. For example, Material C (Fig. 1b) has a high-temperature shoulder on the main oxidation peak. From the results in Fig. 4a and b, the peak at high temperature could represent the presence of MWCNTs or could indicate that two distinct lengths of carbon nanotubes are present within the sample. Peak fitting of SWCNT TGA curves is used to estimate the different populations present within the sample, but this method is not widely used in the TGA analysis of CNT samples [7]. To elucidate the cause of shoulders or multiple peaks within TGA samples, additional characterization techniques (i.e., scanning electron microscopy, Raman spectroscopy) may still be needed to support TGA results.

Conclusion

The utility of thermogravimetric analysis for analyzing the chemistry and homogeneity of carbon nanotube materials has been shown. The method has been used to (a) compare materials produced by different manufacturing processes, (b) identify variability within a single batch and from batch to batch, and (c) assess the effects of process modifications. Effects of specific test conditions, such as flow rate and heating rate, were observed, indicating that these variables should be fixed for all measurements to ensure maximum sensitivity to material inconsistencies. In particular, testing without air flow resulted in substantial modification of the data due to poor removal of decomposed species and slower kinetics because of reduced partial pressure of oxygen. The availability of well-characterized length- and diameter-sorted materials afforded the opportunity to

determine whether the TGA method could be extended to analyze more subtle variations in these materials. Results indicate that thermogravimetric analysis is sufficiently sensitive to enable quality control at both the macro- (carbon-to-metal ratio) and nano-scale (single-walled to multi-walled). As process control improves and manufacturing processes are scaled for higher volume production, the ability to detect these more subtle changes in material quality will become more critical. Taken together, these studies indicate that thermogravimetric analysis can be a powerful tool for comparing quality in batch-to-batch manufacturing of carbon nanotubes. When major changes in the manufacturing process occur, supporting techniques (i.e., Raman, TEM) may be necessary to fully understand TGA results.

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