2 Thermogravimetric Analysis (TGA)

2.1 General Description

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O_2 in N_2 or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis, or DTA) or the heat flow into the specimen pan compared to that of the reference pan (differential scanning calorimetry, or DSC). The latter can be used to monitor the energy released or absorbed via chemical reactions during the heating process. In the particular case of carbon nanotubes, the weight change in an air atmosphere is typically a superposition of the weight loss due to oxidation of carbon into gaseous carbon dioxide and the weight gain due to oxidation of residual metal catalyst into solid oxides.

2.2 Types of TGA Instruments

TGA instruments can be divided into two general types: vertical and horizontal balance. Vertical balance instruments have a specimen pan hanging from the balance (TA Instruments, etc) or located above the balance on a sample stem (Netzsch). It is necessary to calibrate these instruments in order to compensate for buoyancy effects due to the variation in the density of the purge gas with temperature, as well as the type of gas. Vertical balance instruments generally do not have reference pan and are incapable of true DTA or DSC measurements (Netzsch being an exception). Horizontal balance instruments (TA, Perkin Elmer, etc.) normally have two pans (sample and reference) and can perform DTA and DSC measurements. They are considered free from buoyancy effects, but require calibration to compensate for differential thermal expansion of balance arms. One common instrument for general purpose use, the TA Instruments Model SDT 2790, is used as an example for the following description and discussion.

2.3 Operating Principle and Definitions

In most cases, TGA analysis is performed in an oxidative atmosphere (air or oxygen and inert gas mixtures) with a linear temperature ramp. The maximum temperature is selected so that the specimen weight is stable at the end of the experiment, implying that all chemical reactions are completed (i.e., all of the carbon is burnt off leaving behind metal oxides). This approach provides two important numerical pieces of information: ash content (residual mass, M_{res}) and oxidation temperature (T_o) (**Figure 1**). While the definition of ash content is unambiguous, oxidation
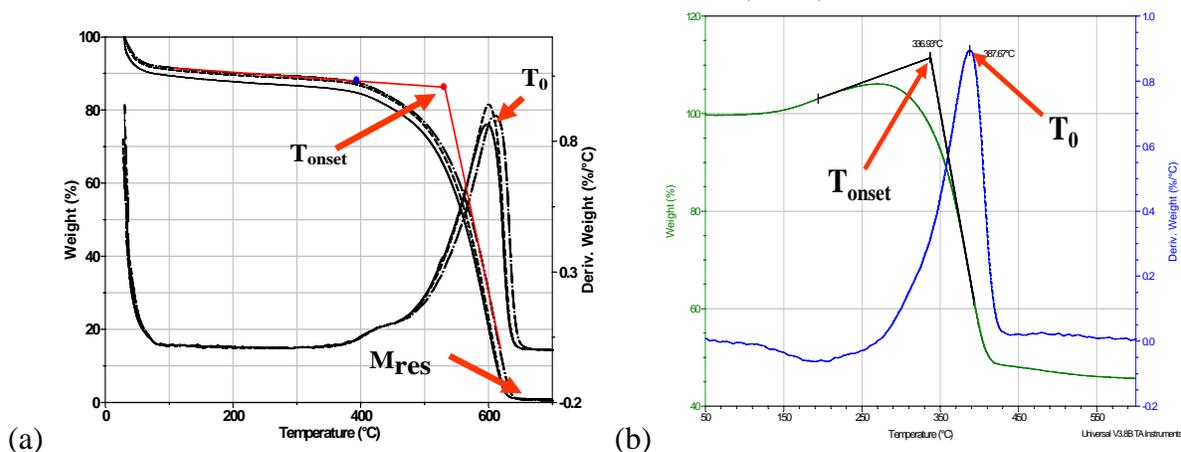
Figure 1: *(a) TGA of purified SWCNTs; 3 specimens sampled from the same batch. (b) Graph illustrating the ambiguity in determining T_{onset}.*

temperature can be defined in many ways, including the temperature of the maximum in the weight loss rate (dm/dT_{max}) and the weight loss onset temperature (T_{onset}). The former refers to the temperature of the maximum rate of oxidation, while the latter refers to the temperature when oxidation just begins. The use of the former definition, $T_o = dm/dT_{max}$, is preferred for two reasons. First, due to the gradual initiation of transition (sometimes up to 100 ^{o}C, Figure 1) it may be difficult to determine T_{onset} precisely. Gradual onset is believed to be due to nanotubes being contaminated with amorphous carbon and other types of carbonaceous impurities that oxidize at temperatures lower than that of nanotubes. In these cases, T_{onset} describes the properties of the impurities rather than the nanotubes. Second, weight loss due to carbon oxidation is often superimposed on the weight increase due to catalyst oxidation at low temperatures. In some cases this leads to an upward swing of the TGA curve prior to the bulk of the weight loss, which makes the definition of T_{onset} even more difficult and ambiguous. However, determining dm/dT_{max} is relatively straightforward. Therefore, oxidation temperature is herein defined as $T_o = dm/dT_{max}$.

TGA measurement of "as-produced" nanotube material in air usually produces only one peak in the dm/dT curve, as "fluffy" raw nanotubes oxidize rapidly in an oxygen-rich environment. However, analysis of purified nanotube material in air may produce more than one peak. These additional peaks are likely due to the fact that purified material contains a fraction of nanotubes with damage and/or with functional groups (i.e., the material is oxidized at lower temperatures) or because purified material is more compacted after drying. The position of each peak is also strongly affected by the amount and morphology of the metal catalyst particles and other carbon-based impurities, as well as their distribution within a specimen. A lean oxygen environment can be used to better separate these peaks. In addition, these peaks have also been attributed to various components in the nanotube material (amorphous carbon, nanotubes, graphitic particles), and it may be possible to quantify these components by deconvolution of peaks.

Oxidation temperature, T_o, is basically a measure of the thermal stability of nanotubes in air and depends on a number of parameters. For example, smaller diameter nanotubes are believed to oxidize at lower temperature due to a higher curvature strain. Defects and derivatization moiety in nanotube walls can also lower the thermal stability. Active metal particles present in the nanotube specimens may catalyze carbon oxidation, so the amount of metal impurity in the sample can have a considerable influence on the thermal stability. It is impossible to distinguish these contributions, but, nevertheless, thermal stability is a good measure of the overall quality of a given nanotube sample. Higher oxidation temperature is always associated with purer, less-defective samples.

2.4 Sources of Error

When performing TGA runs on especially clean nanotubes with minimal ash content (< 3 %), it should be noted that residual mass is sometimes negative. This happens even after fresh calibration of the instrument. The long-term stability of the instrument zero (over a 3-hour run) is within 20-40 μg, which constitutes 1-2 % of the initial 2-4 mg sample. For samples with very small ash content, this amounts to a fairly large error. It is therefore necessary to weigh each ash residue independently using a microbalance. This way ash content measurement accuracy is greatly improved. Other instruments may have better long-term zero stability, but it is still preferable to check ash content occasionally by independent measurement. Additionally, there may be a time lag in the sample temperature and the oven temperature which can be reduced by lowering the ramp rates. Finally, temperature calibration should be done periodically according to the instrument manufacturer's specifications.

2.5 Practical Concerns

2.5.1 Material Inhomogeneity

It has been noted that when TGA measurements are performed on several nanotube specimens sampled from the same batch, the TGA traces do not necessarily coincide (Figure 1, Figures 4-11 in Appendix). There is always some variation that exceeds the accuracy and repeatability of the instrument. This observation serves to emphasize that carbon nanotube batches are not pure chemicals and, therefore, are not as homogenous and uniform as is usually implied for pure chemicals. This means that values of M_r and T_0 produced in one TGA run are not necessarily representative of the whole batch. The only reasonable approach to this problem is to perform TGA on at least three (or more) specimens sampled from the batch and calculate mean averages of M_r and T_0. Interestingly, this approach also allows one to calculate standard deviations of M_r and T_0. It is obvious that standard deviations σ_{Mr} and σ_{To} can serve as a measure of the inhomogeneity of the nanotubes in the batch (See appendix for experimental data and discussion).

2.5.2 Combustion

Sometimes a strange, and unexpected, effect is observed in the TGA results (**Figure 2**). The weight trace suddenly goes *backwards* along the abscissa and then continues forward as usual. This behavior becomes easily explainable if the weight trace and the temperature are plotted versus *time*. In this graph, it is evident that the event is accompanied by a sudden loss of a significant fraction of the sample mass, as well as a large spike in the temperature difference (DTA) plot. At the same time, temperature goes up by 10-20 ^{o}C, and then comes down and continues along a linear ramp. We have estimated that the temperature increase rate reaches up to 50 ^{o}C/min during such events and is fairly independent of the nominal furnace heating rare. These are unambiguous signs of combustion (i.e., the sample starts burning and releases a considerable amount of heat very quickly, causing a sharp increase in temperature followed by heat dissipation and a subsequent temperature drop). This behavior is more often observed on as-produced unpurified nanotubes that are "fluffy" and have more metal catalyst. It is noticed that combustion decreases M_r and increases its standard deviation (see Appendix). This probably happens due to ejection of smoke particulates from the sample pan during rapid burning (i.e., there is some poorly controlled weight loss beyond oxidation of carbon). Therefore it's better to avoid conditions that cause combustion.
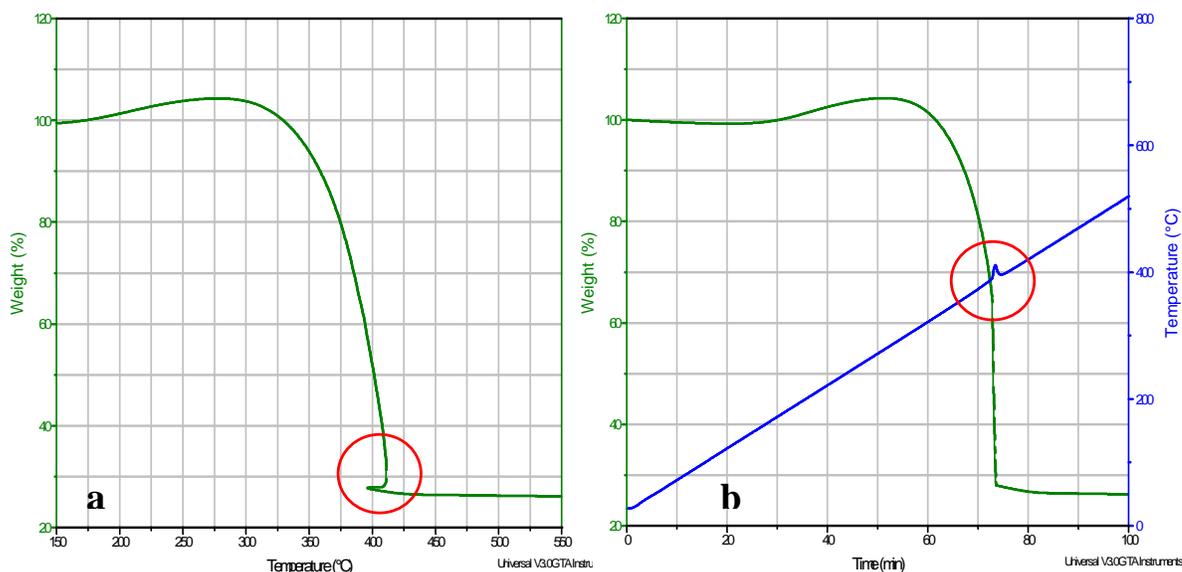
Figure 2: Evidence of nanotube combustion in TGA. (a) Trace going "backward". (b) Temperature spike caused by combustion. Note different abscissa units – temperature on (a) and time on (b).

2.5.3 Heating Rate

Typical heating rates employed in TGA measurements of carbon nanotube specimens are in the 10-20 ^{o}C/min range. It has been noted that heating rate has a pronounced effect on the measured values of M_r and T_0 and their standard deviations (see Appendix). The effect on T_0 has been attributed in the literature to the limited rate of heat conduction into the sample. The effect on M_r is mostly related to combustion that higher ramp rates are more likely to produce. It is found that in as-produced unpurified ("fluffy") samples, combustion is likely to occur at or above 5 ^{o}C/min. The conclusion is that heating rate must be constant in *all* measurements to avoid inconsistency in T_0 measurement, and at or below 5 ^{o}C/min to avoid combustion. Selecting a heating rate of 5 ^{o}C/min is a reasonable compromise, considering that lowering the rate more causes unacceptably long experiments.

2.5.4 Sample Weight

When working with as-produced "fluffy" nanotubes, it is difficult to place more than 2-4 mg of material into a typical 200 μl sample pan. Considering zero stability of modern TGA instruments, this quantity of material is still acceptable, but should be an absolute minimum. Samples of appoximately 10 mg are recommended.

2.6 Suggested Protocol

Based on the discussion above and results of the study reported in the Appendix, the following protocol for TGA measurements is proposed. If this protocol is followed for each sample, it will produce results that can be cross-compared.

1. Heating rate 5 ^{o}C/min. in air. Maximum temperature sufficient to stabilize sample weight (typically 800 ^{o}C).
2. Sample size at least 2 - 4 mg, more if possible.
3. Three separate TGA runs on each sample.
4. Ash content measured independently on microbalance.

Mean values of T_0 and M_{res} are representative of the sample oxidation temperature and ash content. Standard deviations of T_0 and M_{res} are representative of the sample inhomogeneity.

2.7 Appendix

2.7.1 Protocol Development

All TGA experiments were performed using a TA Instruments SDT 2790 TGA with air as a purge gas at a flow rate of 100 sccm. All samples were from the same batch of as-produced ("fluffy") HiPco single-wall carbon nanotubes. The inhomogeneity of the material, the heating rate, combustion, and their combined effect on the results of the TGA experiments were studied. In addition, we investigated the stability of the instrument zero and it's implications in determining precise ash content.

2.7.2 Material Inhomogeneity

Each nanotube specimen was analyzed via TGA three times at each of following heating rates: 1, 2.5, 5, 10, 30 and 100 ^{o}C/min. TGA traces for these experiments are shown on Figures 3 through 8. One can observe that for any given set of experimental parameters, the shape of the TGA curve, as well as the oxidation temperature, T_o, and ash content, M_{res}, vary in each run. Variations in T_o can exceed 10 - 20 ^{o}C, and variations in M_{res} can exceed 5% of the initial sample weight (i.e., these variations are quite significant and cannot be dismissed as an instrument error). These variations are likely due to the inhomogeneity of the starting material. Therefore, ash content and oxidation temperature of the nanotube batch as a whole are best described as a mean of results from at least three runs. As each run takes considerable time (~3 hrs at 5 ^{o}C/min heating rate)

and consumes 2 - 4 mg of the sample, it is impractical to do more than three runs. A sample size of 2-4 mg is sufficient to produce good data, but not too large as to consume a significant fraction of the nanotube material available. It has also been noticed that nanotube materials of different properties have varying standard deviations of T_o (σ_T) and M_{res} (σ_M).   This result could also be due to the varying degree of inhomogeneity in different samples. For example, unpurified and purified HiPco nanotubes have σ_T = ~2.7 ^{o}C and σ_T = ~6.5 ^{o}C respectively (5 ^{o}C/min heating rate). Therefore, σ_M and σ_T values can be used to describe inhomogeneity of the sample – the larger the standard deviation, the more inhomogeneous the sample.
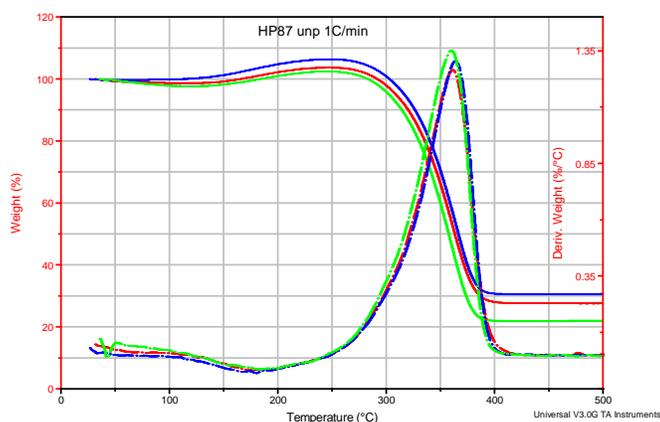
Figure 3: *TGA graphs of unpurified HiPco SWCNT material; three specimens sampled from the same batch; 1 °C/min heating rate in air.*
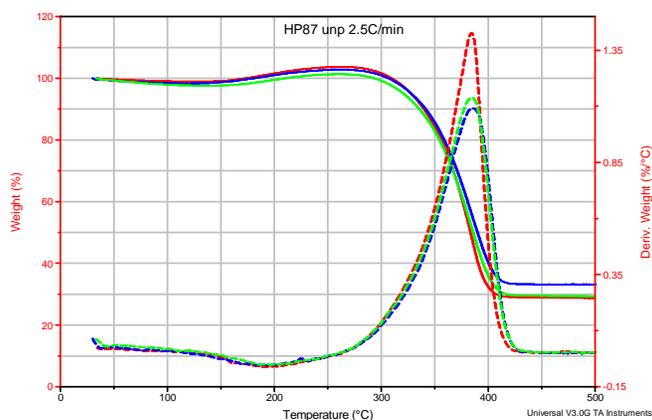
Figure 4: *TGA graphs of unpurified HiPco SWCNT material; three specimens sampled from the same batch; 2.5 °C/min heating rate in air.*
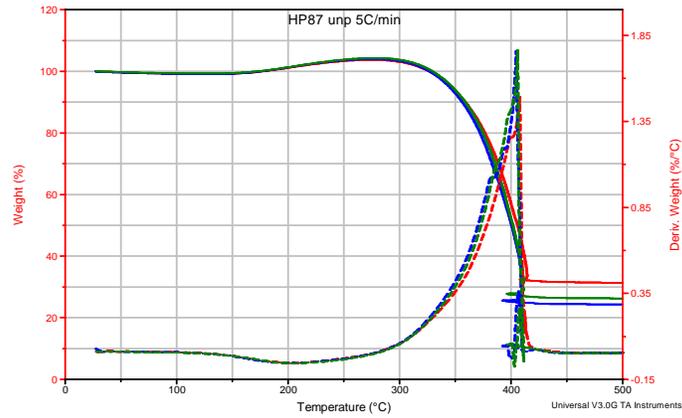
Figure 5: *TGA graphs of unpurified HiPco SWCNT material; three specimens sampled from the same batch; 5 °C/min heating rate in air.*
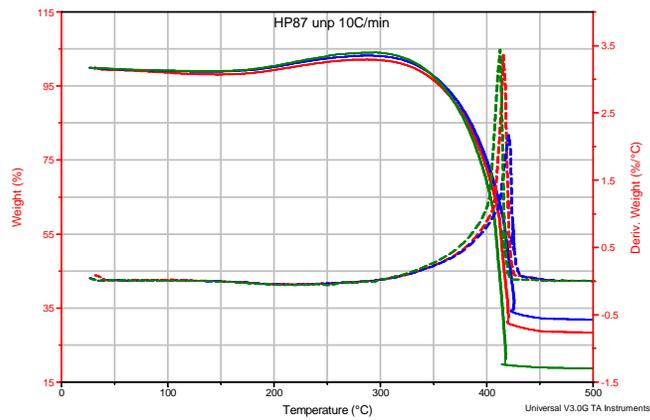
Figure 6: *TGA graphs of unpurified HiPco SWCNT material; three specimens sampled from the same batch; 10 °C/min heating rate in air.*
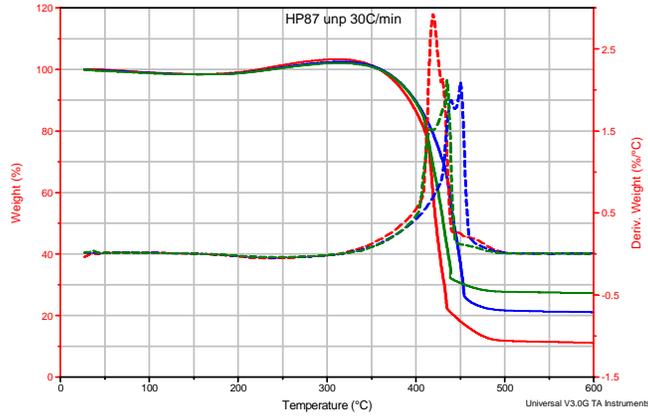
Figure 7: *TGA graphs of unpurified HiPco SWCNT material; three specimens sampled from the same batch; 30 °C/min heating rate in air.*
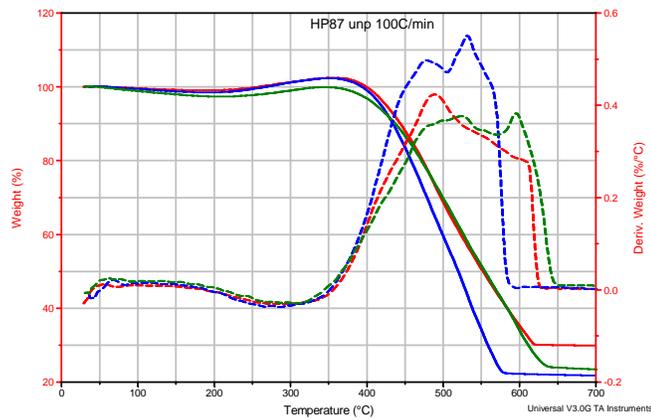
Figure 8: *TGA graphs of unpurified HiPco SWCNT material; three specimens sampled from the same batch; 100 °C/min heating rate in air.*

2.7.3 Heating Rate

Heating rates as high as 100 $^{\circ}$C/min and as low as 1 $^{\circ}$C/min are reported in the literature. As mentioned above, we have done experiments with the following heating rates: 1, 2.5, 5, 10, 30 and 100 $^{\circ}$C/min. **Figure 9** shows that the mean value of T_o increases gradually from 360 to 430 $^{\circ}$C as the heating rate increases from 1 $^{\circ}$C/min to 30 $^{\circ}$C/min. It is difficult to reliably determine T_o (and its standard deviation) for the experiment with a 100 $^{\circ}$C/min heating rate (**Figure 8**) due to the very broad transition with several peaks that are not reproducible (this will be discussed later). The origin of such a significant change in T_o (70 $^{\circ}$C) is usually attributed to the limited rate of heat conduction into the sample. It is important to emphasize that T_o depends on the heating rate, and, therefore, its values produced at different heating rates cannot be directly compared to each other. The inset in **Figure 9** shows that the standard deviation of T_o also increases significantly as the heating rate increases, varying from 1 to 13.5 $^{\circ}$C.
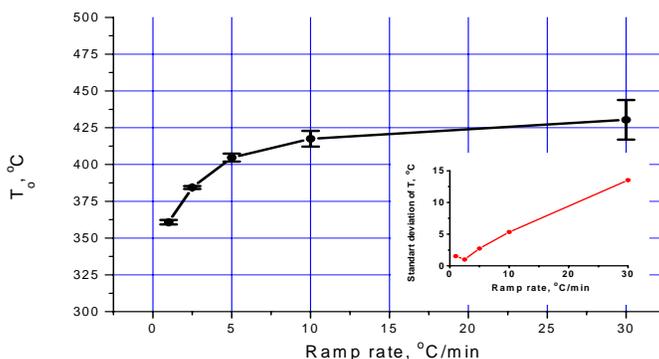
Figure 9: Heating rate dependence of oxidation temperature, T_o, and its standard deviation σ_{To} (inset).

The value of M_{res} and its standard deviation are also dependent on the heating rate. Figure 10 shows that M_{res} for 1, 2.5 and 5 $^{\circ}$C/min heating rates are well within one standard deviation (which is nearly constant), while above 5 $^{\circ}$C/min M_{res} becomes significantly smaller and its standard deviation sharply increases. This observation can be explained by spontaneous combustion of the nanotubes above 5 $^{\circ}$C/min heating rate (i.e., the heat released in the exothermic reaction is enough to sustain rapid burning of the sample). It is impossible to confirm this by direct observation of the sample in the TGA furnace, but the observed behavior of T_o and M_{res} also points in this direction. Combustion, unlike slow oxidation, is an uncontrollable process, strongly dependent on the morphology and size of a particular specimen. Combustion releases particulate

matter (smoke) from the sample in a relatively random fashion, therefore reducing residual mass, which is indeed observed above 5 ^{o}C/min as discussed above (**Figure 10**). A large increase in the standard deviation of M_r is also consistent with this explanation, as the additional mass loss due to smoke release in a particular run can vary significantly with the size and morphology of the specimen. In the absence of combustion, T_o must depend only on the properties of the nanotube specimen. On the other hand, when heating rate is fast enough to produce combustion, the peak in the dM/dt is always reached at the point where combustion begins; therefore, its position depends also on the morphology of the specimen. This will certainly produce larger standard deviations of the T_o, which is consistent with our observations (**Figure 9** inset).
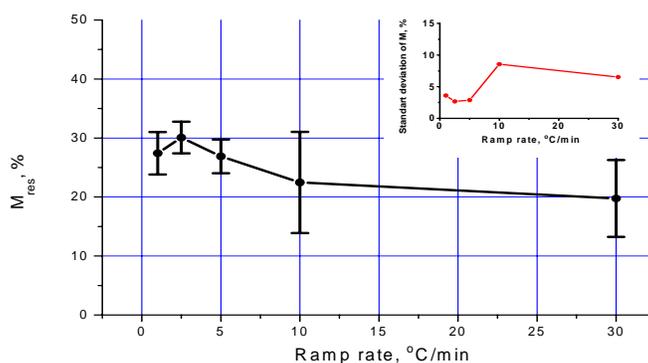
Figure 10: Heating rate dependence of the residual mass, M_{res}, and its standard deviation, σ_{Mres} (inset).

TGA traces obtained at 100 ^{o}C/min heating rate (**Figure 8**) do not exhibit signs of combustion. Instead, mass loss occurs rather gradually in the 400 – 600 ^{o}C temperature range. Derivative weight loss curves do not have well-defined peaks and appear rather irreproducible, making it impossible to define T_o. As noted above, combustion increases with the specimen heating rate up to approximately 50 ^{o}C/min. So, in this case, the rate of the temperature increase in the TGA furnace is actually higher than the maximum heating rate of the specimen that can be achieved even with the help of combustion. This means that there has to be a significant time lag between furnace and specimen temperatures, and that mass loss rate depends mostly on the morphology of the particular sample. This explains the gradual mass loss and poor reproducibility of the derivative weight curves.

TGA results obtained with higher heating rates (allowing combustion) become increasingly less reliable, with standard deviations of T_o and M_{res} rapidly increasing (resulting in a systematic decrease in the M_{res} values). Therefore, it is important to collect TGA data with heating rates that do not allow combustion. For the particular HiPco specimen used in this study, only heating rates of 1 and 2.5 ^{o}C/min preclude combustion. However, we have noticed that purified samples that have much less active catalyst can be run at higher heating rates without combustion.

Selection of the heating rate is also of practical importance. Usually a sample has to be heated to at least 800 ^{o}C, which requires 13.3 hours at a rate of 1 ^{o}C/min, compared to 8 min at 100 ^{o}C/min. Heating fast saves time, so the majority of researchers have used 10 - 20 ^{o}C/min rates. Based on the discussion above, we have selected 5 ^{o}C/min as a compromise, as each run takes less than 3 hours and we avoid combustion for most types of samples.

2.7.4 Sample Compaction

There is a huge difference in the morphology of "as-is" nanotube material and material that has been processed into buckypaper (usually after purification, but sometimes unpurified material is processed into buckypaper by dispersing in a solvent, filtering, and drying). The apparent density of unprocessed, "as-is" "fluffy" material can be 1 - 2 orders of magnitude smaller than that of processed material. It is difficult to place more than 2 - 4 mg of unprocessed material into the sample pan. As a result, some researchers have employed mechanical compaction as a means to increase apparent density and specimen size.

We have compared TGA results of "as-is" material with material compacted in a standard KBr die by applying 2, 5 and 10 tons pressure in a hydraulic press. The values of M_{res} were essentially unaffected, while compacting at progressively higher pressure leads to a 10-20 °C decrease in the T_o values. However, changes in T_o do not follow a uniform trend. T_o decreases from 417 ^{o}C to 395 ^{o}C as compacting pressure goes from 0 to 5 tons and then increases to 403 ^{o}C as compacting pressure increases to 10 tons. Compacting pressure does not affect the standard deviations of M_{res} and T_o. The reasons for this behavior are not clear. We have noticed that combustion still occurs at a heating rate of 5 ^{o}C/min, which is probably related to the presence of a considerable amount of active Fe catalyst particles.

We conclude that it is better to avoid compaction, as results are difficult to predict. Compaction may be necessary for some especially "fluffy" materials, but then results should be considered with full understanding that T_o may have been affected. In these cases, smaller compaction pressure is preferable. Generally, it is advisable not to compact the material by any means, which places the 2-4 mg limit on the sample size for unprocessed material. It may be preferable to use the same sample size for processed materials, as samples of dramatically different mass may behave differently. For example, a much larger sample may heat up slower due to its higher thermal capacity.