

## Thermogravimetric Analysis

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## A Study of Aged Carbon Nanotubes by Thermogravimetric Analysis

### Introduction

Increased use of carbon nanotubes in consumer and industrial products have scientists asking about the implications of CNTs in our environment. Many end product applications include polymer composites, drug delivery systems, coatings and films, military applications, electronics, cosmetics, healthcare, among others.

CNTs are desirable for many applications because of their high surface area to weight ratio. They are lightweight and highly elastic compared to carbon fibers, and deliver higher surface area for increased chemical interaction in its specific application.

Thermogravimetry a simple analytical technique that is frequently used to characterize carbon nanotubes.<sup>1</sup> The Pyris™ 1 TGA delivers accurate results quickly because of its low mass furnace. The Pyris 1 TGA low mass furnace has accurate temperature control and fast cooling for higher sample throughput.

There are various carbon-nano-material classifications, such as single wall carbon nanotubes (SWCNT), or multi-wall carbon nanotubes (MWCNT). A SWCNT is a single tube of some length with its tubular wall having a hexagonal hollow geometry, similar in shape to a fullerene. A MWCNT is one or more tubes within a tube. Fullerenes, also known as Bucky Balls, are hollow spheres. Graphene is a flat sheet of carbon, one atom thick that has the same hexagonal structural geometry as CNTs. CNTs are made from graphene by wrapping the graphene into cylindrical shapes. Specifications of CNTs may describe their diameter and length, as well as the orientation of the lattice wall in regards to the CNT's centerline. There are three types of lattice orientations, armchair, zigzag, and chiral. The difference between these CNT types is the bias or angle that they are wrapped.<sup>2,4</sup>

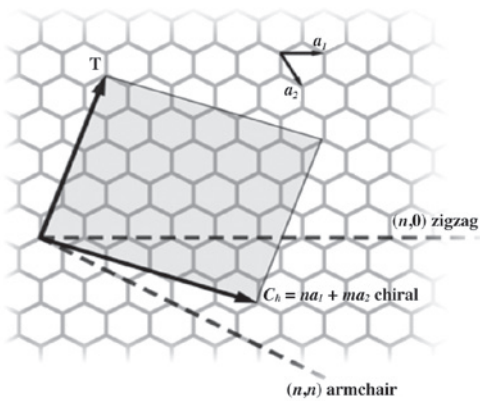


Figure 1. Types of carbon nanotubes, armchair(n,n), zigzag (n,0) and chiral (C<sub>h</sub>). The (n,m) nanotube naming scheme can be thought of as a vector (C<sub>h</sub>) in an infinite graphene sheet that describes how to “roll up” the graphene sheet to make the nanotube. T denotes the tube axis, and a<sub>1</sub> and a<sub>2</sub> are the unit vectors of graphene in real space. This image is the courtesy of Wikipedia.<sup>4</sup>

### Materials Used

Commercially available high purity MWCNT samples were obtained. Analysis of acid washed samples using ICP showed less than 1% of trace elements.

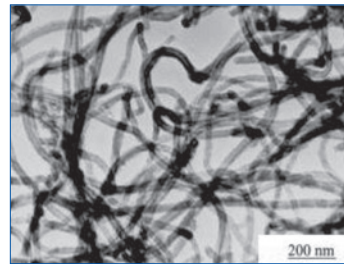
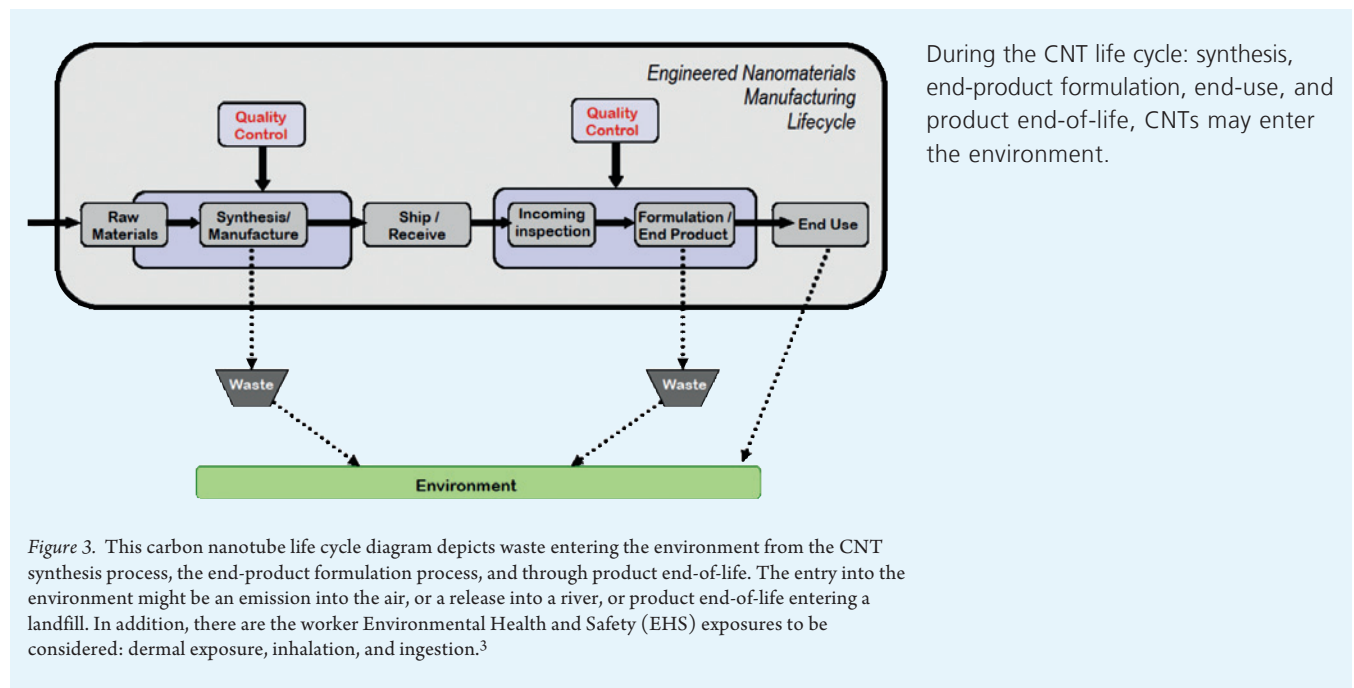


Figure 2. Above, the Transmission Electron Microscope (TEM) image of CNTs indicates that the CNTs have a ~ 20 nm outside diameter and their lengths are much larger than 200 nm.

Table 1 is the manufacturer’s product description before the samples were subjected to UV aging. The far right column explains one of the foremost features of NMs, that is their high surface area in relationship to weight. One gram of Type B CNTs have a surface area that is larger than 200 square meters (>200 m<sup>2</sup>/g). The manufacturer’s CNT outside diameters are verified by the TEM image in Figure 2.

Type	Purity	Outside Diameter	Length	Specific Surface Area
Type A	>95%	8-15 nm	~50µm	>233 m <sup>2</sup> /g
Type B	>95%	10-20 nm	10-30 µm	>200 m <sup>2</sup> /g
Type C	>95%	> 50 nm	10-20 µm	>40 m <sup>2</sup> /g



During the CNT life cycle: synthesis, end-product formulation, end-use, and product end-of-life, CNTs may enter the environment.

Figure 3. This carbon nanotube life cycle diagram depicts waste entering the environment from the CNT synthesis process, the end-product formulation process, and through product end-of-life. The entry into the environment might be an emission into the air, or a release into a river, or product end-of-life entering a landfill. In addition, there are the worker Environmental Health and Safety (EHS) exposures to be considered: dermal exposure, inhalation, and ingestion.<sup>3</sup>



Figure 4. The Pyris 1 TGA.

**Definition:** Thermogravimetric Analysis (TGA) also called Thermogravimetry is a technique in which the mass of a material is monitored as that material is subjected to a controlled temperature program in a controlled atmosphere.

### Method

A general method follows:

Instrument:	Pyris 1 TGA
Sample Size:	> 1 mg, usually 3 mg to 50 mg
Sample Pan:	Ceramic
Temperature Range:	30 °C to 800 °C
Scanning rate:	10 °C/minute or faster
Sample Purge Gas and Rate:	Air at 20 mL/min
Balance Gas and Rate:	Nitrogen at a rate at least 10 mL/min higher than the sample purge rate

### Characterization of nanotubes with TGA

Thermogravimetric Analysis was the first analytical technique chosen to compare the effects of the UV exposure times on the CNTs. TGA is very simple, yet a very accurate analytical technique that delivers results quickly. Studying the oxidation of fullerene C<sub>60</sub> using TGA has been reported.<sup>5,7</sup> The high sensitivity of the TGA, which is in the order of 0.1 micro-gram/min, permitted weight loss determinations at a given

heating rate, within a short time without consuming too much material. The oxidation rates of carbon nanotubes measured in air at atmospheric pressure within the TGA are unique for each CNT sample of different wall thicknesses. Figure 5 shows the decomposition temperatures (i.e. oxidation) for samples run at the same heating rate, varies up to ±40 °C depending on the characteristics of the carbon tubes.

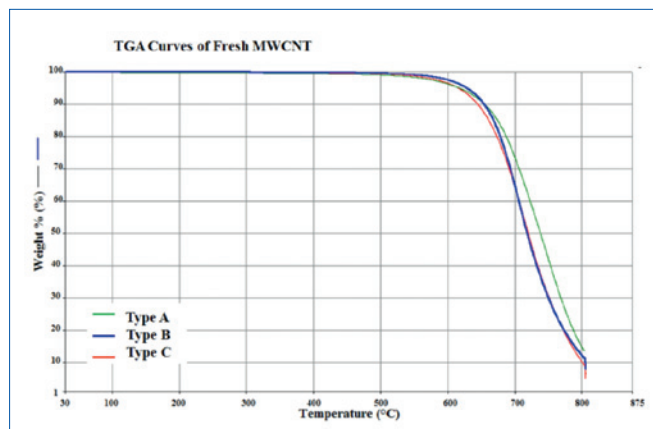


Figure 5. Thermogravimetric analysis of CNTs showing weight loss. Sample weight was about 10 mg, oxygen flow was 20 mL/min. Samples A, B, C, had varying wall thicknesses. See Table 1 for specifications.

### Measuring Aging of Carbon nanotubes

In a laboratory environment, three high purity MWCNT samples that had no specific wrap were analyzed. They were all nearly the same weight and came from the same manufacturing lot. They were subjected to the same UV light source. The intent of the UV light is to simulate sunlight in a controlled manner. Three “A” samples in Figure 5 were exposed to UV for:

- An exposure of 9.0 hours
- An exposure of 5.5 hours
- An exposure of 4.0 hours

### Results

This experiment results in the CNT amorphous carbon decomposing before the structural carbon. All carbon should decompose in the oxidative environment before reaching 900 °C.

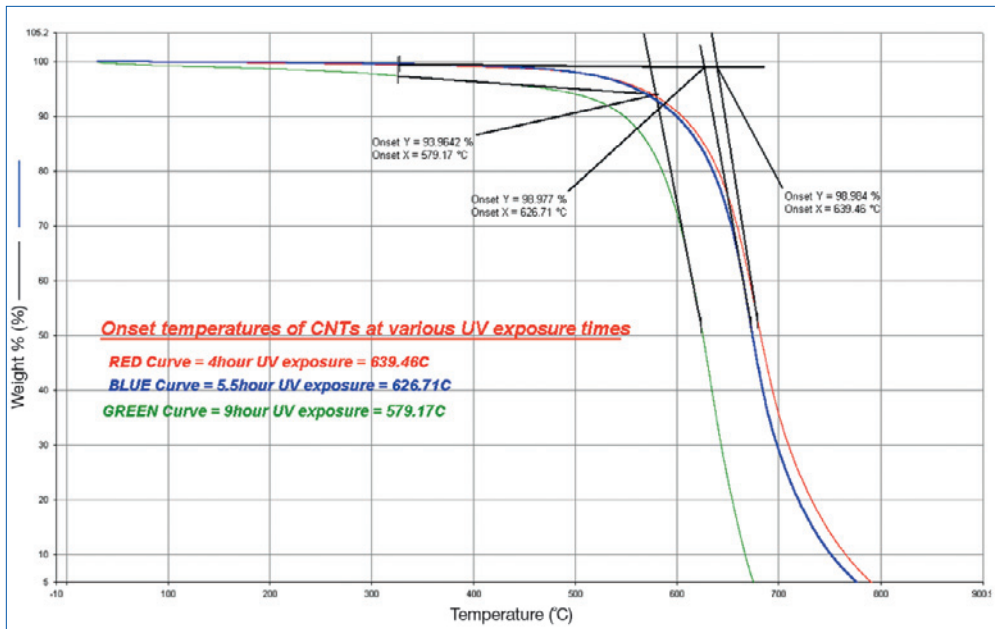


Figure 6. X Axis = Temperature: When observing Thermogravimetric weight loss curves in regards to temperature, the weight loss curves above indicate that CNTs exposed to UV light for 9 hours began decomposition at a lower temperature than the other two samples of shorter exposures.

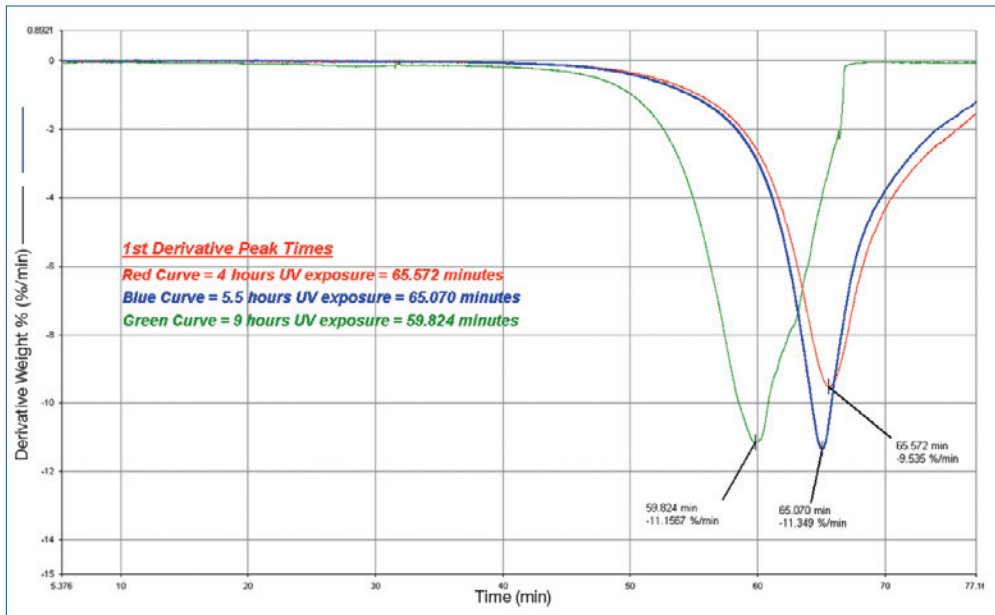


Figure 7. X Axis = Time: To gain a better understanding of the results, the same data file is displayed on a Time X-axis. The 1st derivative curve of each weight loss curve is displayed. The 1st derivative is a widely used tool to compliment the TGA weight loss curve, and like the weight loss curve, the 1st derivative curve is very reproducible. Upon examination of the 1st derivative curves above, the CNT sample with the longest UV exposure decomposes more than 5 minutes before the other two samples of shorter exposure times.

## Summary

Based on the Pyris 1 TGA data collected, UV light has an effect on CNTs. As this study suggests, the longer the CNTs are subjected to UV light, the sooner CNTs decompose when heated to elevated temperatures.

## Further investigation

Because this is early in an entire series of CNT analytical experiments, there are more TGA tests to conduct. It is suggested that a series of isothermal tests be conducted next. They should involve longer UV exposures and similar exposures to this experiment. Based on the scanning data provided, it is suggested that isothermal tests be conducted at 500 °C, 550 °C, 600 °C, and 650 °C. These future isothermal tests would help define the test protocol needed to examine CNTs found in water, soils, or air.

## Conclusion

Thermogravimetry by the Pyris 1 TGA is a simple analytical technique that is frequently used to characterize carbon nanotubes. The Pyris 1 TGA delivers accurate results quickly because of its low mass furnace. The Pyris 1 TGA low mass furnace has accurate temperature control and fast cooling for higher sample throughput.

## References

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## Additional Reading

PerkinElmer, *Nanotechnology and Engineered Nanomaterials – A Primer*, [www.perkinelmer.com/nano](http://www.perkinelmer.com/nano)

PerkinElmer, Nanomaterials Reference Library  
[www.perkinelmer.com/nano](http://www.perkinelmer.com/nano)

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