

Characterizing Environmental Transformation of Multi-walled Carbon Nanotubes and Carbon Nano-Fiber Composites using Thermal Analysis and Related Hyphenated Techniques

E. Sahle-Demessie¹, Amy Zhao¹,

Andrew W. Salamon², Bruce Cassel², Nicholas A Gagliardi³

¹U.S. EPA, Office of Research and Development, NRMRL, 26 W. Martin Luther King Drive

²PerkinElmer Inc. 710 Bridgeport Ave., Shelton, CT 06484

³University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0161

Thermogravimetric analysis (TGA) coupled with gas chromatography and mass spectroscopy (TGA/GCMS), for the evolved gas analysis, has given insight to the stability and kinetics of structural changes and determining adsorbed organics to nanomaterials and nanocomposites. TGA is also an effective technique to confirm dimensions and homogeneity of MWCNT including the presence of trace metal catalyst or other contaminants, and structural defects. The use of TGA/GC-MS brings insight to the affects of UV exposure on MWCNT and CNT-composites. Fast scanning differential scanning calorimetry (Hyper®DSC) was used to accurately determine the heat capacity and investigate the relationship of the rigid-amorphous fraction (RAF) in semicrystalline polymers of nanocomposite systems. These results were compared with other characterization techniques, electron microscopy (SEM and TEM) and X-ray diffraction. With the increase in the commercialization of engineered nanomaterials and the future of nanotechnology rests upon innovative approaches to characterize and manufacture useful complex nanomaterial systems, and assess their use phase and end-of-life environmental transformation. Unlike the mature analytical market for bulk and molecular matter, the current advance from discovery to application in nanotechnology is constrained due to the lack of quick, rapid, reliable and low cost analytical techniques.

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, amongst others. CNTs are desirable for many applications because of their high surface area to weight ratio. They are lightweight, 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 [1]. Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibres known, and have remarkable electronic properties and many other unique characteristics. The bonding in carbon nanotubes is sp^2 , with each atom joined to three neighbors, as in graphite. The tubes can therefore be considered as rolled-up graphene sheets and there are three distinct ways in which a graphene sheet can be rolled into a tube. The first two of these, known as "armchair" and "zig-zag" have a high degree of symmetry. The terms "armchair" and "zig-zag" refer to the arrangement of hexagons around the circumference. The third class of tube, which in practice is the most common, is known as chiral, meaning that it can exist in two mirror-related forms [2, 4]. CNT filled composites have been shown to improve mechanical, thermal, and electrical properties of polymers and are quite effective compared to traditional carbon black microparticles.

The toxicity issues surrounding carbon nanotubes (CNTs) are highly relevant for two reasons: Firstly, as more and more products containing CNTs come to market, there is a chance that free CNTs get released during their life cycles, most likely during production or disposal, and find their way through the environment into the body. During the CNT life cycle: synthesis, end-product formulation, end-use, and product end-of-life, CNTs may enter the environment (Figure 1). In this research the environmental durability of CNT and CNT-modified carbon-fiber-reinforced polymers (CFRPs) was investigated using UV aging and thermal analysis. The study would help to better understand the potential risk of CNT and CNT-based composites in the environment.



Figure 1: Schematic diagram depicts nanomaterial waste entering the environment from Synthesis process, the End-Product Formulation process, through product end-of-life. The Environment might be an air emission, a release into groundwater or a river, or landfill [3,5].

Materials Used for this study

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

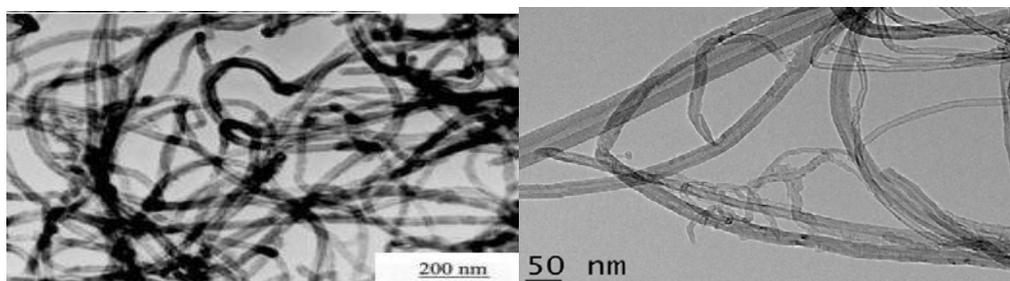


Figure 2: The Transmission Electron Microscope (TEM) images of CNTs indicates that the CNTs have a ~ 20nm outside diameter and their lengths are much larger than 200nm.

Table 1 Manufacturer’s product description before the samples were subjected to UV aging. The manufacturer’s CNT outside diameters are verified by the TEM image in **Figure 2**.

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

Characterization of nanotubes with TGA

Thermogravimetric analysis (TGA) was the first analytical technique chosen to compare the effects of the UV exposure times on the CNTs. TGA is a simple, yet a very accurate analytical technique and it has been used to study the oxidation of fullerene C₆₀ [6-8]. The high sensitivity of the TGA, which is in the order of 0.1 microgram/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 atmospheric pressure oxygen within the TGA is unique for outer and inner diameters of CNT. The temperature for maximum weight loss (i.e. oxidation) for the same heating rate, varies by up to ± 40 °C depending on the characteristics

of the carbon tubes (Figure 3). 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. Sample A had 9.0, 5.5 and 4 hours of UV exposure. These results in the CNT amorphous carbon decomposing before the structural carbon. All carbon should decompose in the oxidative environment before reaching 900°C.

The stability, kinetics and structure of CNT based composites change, however, as to different polymer matrix woven with different amounts of carbon nano-fiber. Also, impact of UV exposure to NP need to be investigated to understand on the potential health and environment risk. The characterization of NP is an essential step in environmental research (Figure 4). Multi-stage de-polymerization correspond to initiated H-H linkages with breakage of chian ends and random scission.

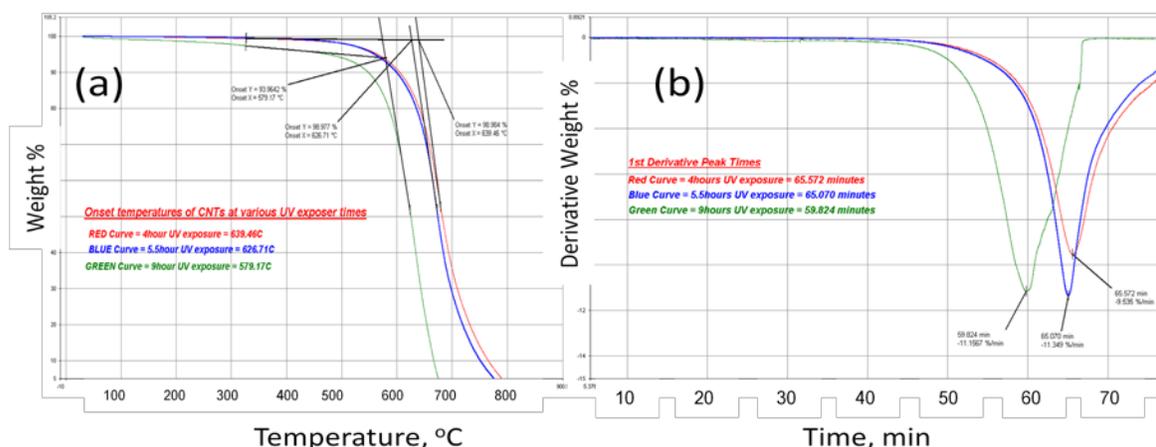


Figure 3: (A) Thermogravimetric weight loss curves versus furnace temperature. CNTs exposed to UV light for 9 hours began decomposition earlier than the other two samples. (B) The 1st derivative curve of each weight loss curve is displayed the differences of peak temperatures are plainly visible. Sample weight was about 10 mg, oxygen flow was 20 mL/min.

Using DSC to study CNT-composites

One rapid way to quantify the effect of a particular filler formulation is to measure its effect on the change in specific heat (C_p) that occurs at the glass transition (T_g). C_p of an amorphous nanocomposite can be usefully partitioned between three entities: (1) unaffected amorphous polymer whose properties are the same as that in the pure amorphous polymer, called the mobile amorphous fraction; (2) the C_p of the filler itself, and (3) the C_p of the polymer, which is immobilized by its attachment to the nanoparticle, the rigid amorphous fraction (RAF). The properties of the composite can be related to the extent of these fractions. The chemical bonding—weak or strong—of the RAF to the nanomaterial filler may be an indicator of the performance of the nanocomposite, and it may be an indicator of how readily it will decompose in the environment. A second T_g —devitrification of the RAF—would indicate a relatively weak bond of the RAF to the nanomaterial filler. Differential scanning calorimetry (DSC) studies showed that evidence that at higher temperatures kinetic energy might free up the rigidly held polymer and reveal a second, but higher and weaker, glass transition attributed to devitrification of the RAF phase. This was the reason for using the HyperDSC technique to achieve access to the high-temperature region and obtain specific heat data, while kinetically delaying the onset of decomposition. Evidence of this devitrification effect has been shown for in the formulation of PMMA and SiO₂. We are providing a rapid method of assessing other formulations for this effect. We observed some evidence of increased C_p at higher temperatures, including analyzing the unfilled plastics—to make any definitive statement about devitrification (Figure 5). One interpretation of this data is that the multiple T_g s are due to devitrification of RAF. Not all portions of this sample showed this effect. The sample for analysis was visibly inhomogeneous. Note: at normal DSC scan rates, or when using a modulated

technique, decomposition would show additional thermal effects above 200 °C, which would mask evidence of devitrification

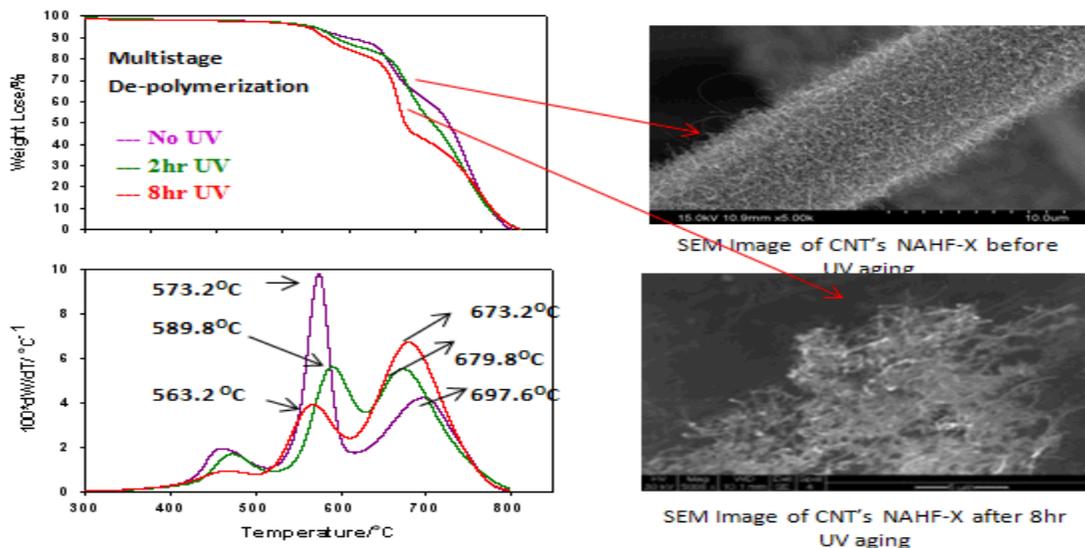


Figure 4. Effects of UV light exposure on thermal stability of nanoadaptive Hybrid fabric

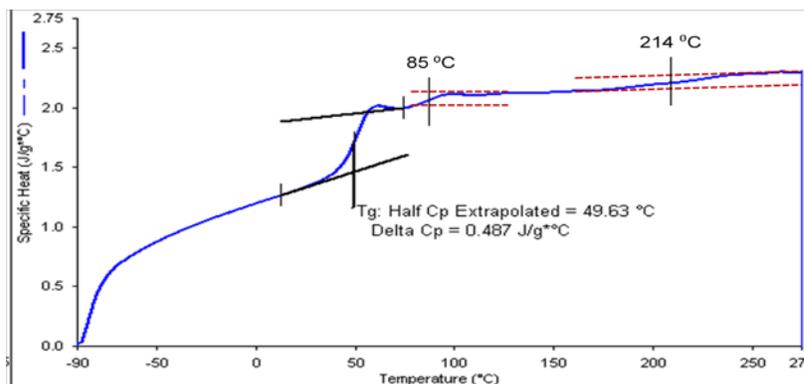


Figure 5. Specific Heat Capacity of uncured epoxy nanocomposite using the 400 °C/minute heat-cool method, showing possible second Tgs..

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