TECHNICAL NOTE

Thermal Analysis

Characterization of Single-wall Carbon Nanotube Production Lots Using the Pyris 1 Thermogravimetric Analyzer (TGA)

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Introduction

Single-wall carbon nanotubes (SWCNTs) have been shown to impart unique mechanical, thermal, and electrical properties when used in a polymer matrix.[1] Their highly conductive nature and large surface areas are utilized to prepare conductive polymer blends and films, improved lithium ion batteries, and super capacitors. Unique optical properties allow for their use as electrodes in display, solarcells, and emerging solid state lighting technologies. The semi-conducting nature of some SWCNT species allow their adaptation to logic devices, non-volatile memory elements, sensors, and security tags.[2] The various methods of fabricating SWCNT materials produce a mixture of carbon allotropes and other production products. Thermogravimetric Analysis (TGA) has been identified as a useful tool to characterize these mixtures via analysis of the weight loss of the sample as it is heated at 5 °C/min in air.[3] This Technical Note relays the experience of running one such SWCNT production lot according the the ISO/TS protocol 11308:2011-(E)[1] using the Pyris™ 1 TGA. This protocol was followed, although not all the steps sited are discussed in this brief note.

The Analyzer

Both the sample and balance purge inputs were connected to a tank of dry, high purity bottled air resulting in a purge rate of around 80 cc/min, which was considered optimum with respect to the criteria proffered in the protocol. The hangdown wire that supports the sample pan in the furnace was selected as nichrome, which offers superior gravimetric performance under the conditions of the test. The TGA was temperature calibrated within two degrees using small pieces of pure alumel, nickel, perkalloy, and iron, whose Curie points are detected at defined temperatures in the presence of a magnetic field as the samples are heated at 5 °C/min in the air atmosphere.

Figure 1. Pyris 1 TGA

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Sample Preparation

The sample analyzed was 'As Prepared' single wall nanotubes from Carbon Solutions Inc. It was a high surface area, fluffy black material composed of various size and shape 'particles'. A slight draft was sufficient to set the particals airborn. The first challenge was to obtain a sufficient quantity of sample—specified as a minimum of 3 mg—in a TGA sample pan. While both the ceramic and platinum autosampler compatible pans were found satisfactory and gave similar results, the platinum pans were found to be easier to load the sample and compress it modestly without getting any material on the outside of the pan. Prior to loading the SWCNT material the pan was tared both in the TGA and in a PerkinElmer AD6 Microbalance. Sample material loading was facilitated with the use of a small funnel (Figure 2) fabricated by cutting the tip and much of the barrel off of a plastic syringe. The outside diameter of the tip was matched to the inside diameter of the pan. A stainless steel rod was used to press the sample through the funnel tip and lightly compact it. The platinum bale of the platinum pan was temporarily bent to the side while loading the sample material (an operation not possible with the ceramic capsules). In the absence of an autosampler, the loaded pan was placed by hand on the hangdown wire of the TGA, the furnace (at 20 °C) raised, the system equilibrated, and the sample weight entered. Moisture loss at the microgram level was evident as the sample was equilibrated in the dry purge.

Figure 2. Funnel, tamper, empty pan, and run sample.

The Temperature Program and Baseline

The heating ramp was started at lab temperature and ran to an upper temperature of 900 °C. Because there was a measurable rate of weight loss at this temperature when running a SWCNT sample an isotherm was applied at 900 °C to allow the samples, which vary somewhat in mass and compaction, to achieve a more reproducible equilibrium weight loss. A representative sample and baseline run can be seen in Figure 3 with time as the X-axis. As can be seen the dwell time at 900 °C is followed by a rapid cooldown to room temperature with the furnace still in position around the sample. This allows the weight of the sample after analysis to be ascertained under the same conditions as it was originally weighed. Four empty pan baselines were run in addition to the four samples in order to obtain an average baseline correction and measure of uncertainty.

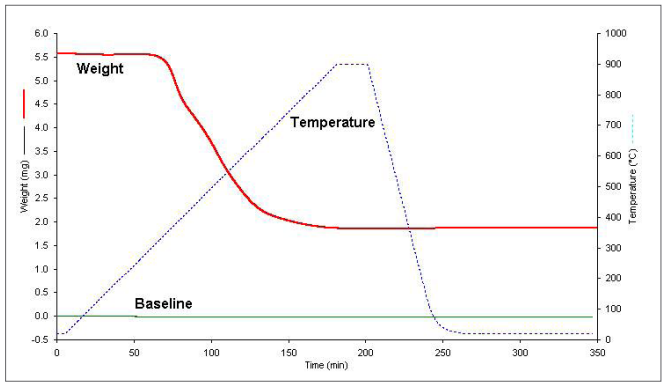

Figure 3. Sample run showing T-Program.

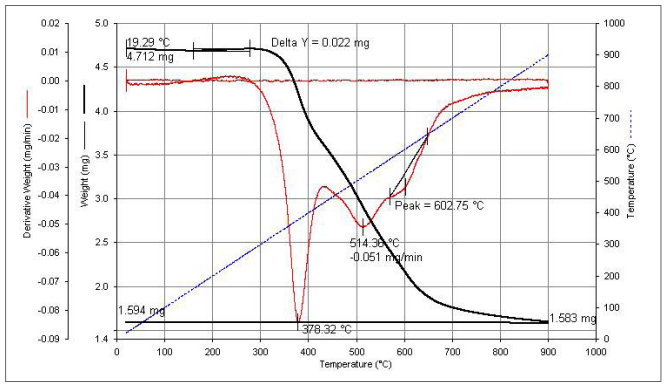

Figure 4. SWCNT calculations are shown above.

Calculations

The weight of the sample is determined roughly one minute after loading. The weight of the air-oxidized remainder is measured after 10 minutes at 900 °C, and the weight is again measured after cooling to the starting temperature. Similar measurements are made on the empty pan baselines, except that at the end of the minute at the starting temperature the weight is zeroed. Per the protocol, any weight loss above 120 °C is also measured, since this is considered to be a side reaction, for example, oxidation of catalyst, which can be corrected for. All measurable baseline effects were used to correct the sample data using averages from four baseline runs. The data is reported with and without the specified corrections, although the magnitude of the corrections (approximately 0.1%) was on the order of the error in the measurement.

Besides determining the percent total weight loss from all types of carbon, the protocol calls for determining the thermal stability of the primary constituent, that is, the temperature of the derivative weight loss curve's primary peak and the total number of peaks in the derivative curve.

Results and Discussion

The table below shows the results of the analysis of the four replicate sample runs that were greater than the cut-off weight of 3 mg. Detailed data appears in the Appendix. Plots of the data appear in Figure 4. The reproducibility of the test is consistent with that of other weight loss-on-ignition thermogravimetric analysis tests. The test reveals that this sample is roughly 33.3% residue and 66.7% carbon of at least two types.

The peaks in the derivative data suggests that there are kinetic differences between the oxidation reactions of SWCNT and another carbon species. A peak resolution algorithm, together with data from oxidation of purified components may be able to allow an estimate of SWCNT yield. The shoulder at roughly 600C has been attributed to chemical changes in the catalyst residue.[4]

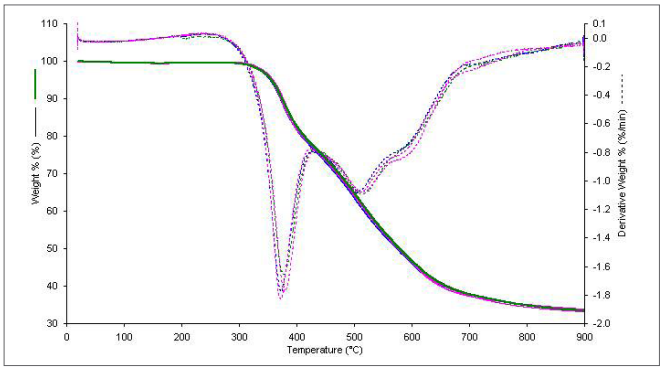

Figure 5. Four Samples of SWCNT.

Table 1. Results

Sample Name	Average	Ave Dev	Std Dev
% Wt at 900 °C without corrections	33.38	0.21	0.27
% Wt at 900 °C with corrections	33.13	0.22	0.29
% Wt after cooldown	33.59	0.20	0.25
% Wt after cooldown with corrections	33.34	0.20	0.26

References

1. "Nanotechnologies-Characterization of single-walled nanotubes using thermogravimetric analysis" ISO Reference # ISO/TS 11308:2011 (E) first edition 2011-11-156. Tans, S.J.; Devoret, H.; Thess, A.; Smalley, R.E.; Geerligs, L.J.; Dekker, C. Nature, 1997, 386, 474. Tans, S.J.; Devoret, H; Thess, A.' Smalley, R.E.; Geerigs, L.J.; Dekker, C. Nature 1997, 386,474.
2. Meo, M.; Rossi, M. Composite Science and Technology, 2006, 66,1597.
3. ISO Reference # ISO/TS 11308:2011(E) first edition 2011-11-156.
4. Arepalli, S.; Nikolaev, P.; Gorelik, O.; Hadjiev, V.; Holmes, W.; Files, B.; Yowell, L.; Carbone, 2004, 42, 1783.

Appendix

Nanotube Samples	Samples				
Measurement	S1 (excluded)	S2	S3	S4	S5
Initial weight (TGA) (mg)	2.584	5.574	5.473	6.909	4.715
Wt gain above 150 (mg)	0.016	0.007	0.020	0.027	0.022
Wt at 900 (mg)	0.891	1.857	1.839	2.281	1.583
Wt Loss at 900 without corrections (mg)	1.693	3.717	3.634	4.628	3.132
Wt at 900 with corrections (mg)*	0.880	1.855	1.824	2.259	1.566
Wt after cooldown (mg)	0.881	1.868	1.848	2.298	1.594
Wt after cooldown with corrections (mg)*	0.870	1.866	1.833	2.276	1.577
%Wt at 900 without corrections	34.481	33.315	33.601	33.015	33.574
%Wt at 900 with corrections	34.048	33.276	33.324	32.694	33.209
%Wt after cooldown	34.094	33.513	33.766	33.261	33.807
%Wt after cooldown with corrections	33.661	33.473	33.488	32.940	33.442
First peak in derivative (°C)	376.5	377.3	373.0	371.8	378.3
Second peak in derivative (°C)	508.6	515.2	502.4	509.3	514.4
Third peak (shoulder) in derivative (°C)	602.4	610.9	609.1	590.4	602.8

*Correction for catalyst weight gain and baseline. See Figure 4 and Baseline Data.

Baselines								
	B1	B2	B3	B4	B5	Average	AveDev	StdDev
Initial weight (TGA) (mg)	0	0	0	0	0			
Wt gain above 150 (°C) (mg)	0.003	0.004	0.004	0.004	0.01	0.005	0.002	0.0028
Wt at 900 (°C) (mg)	-0.001	-0.003	-0.011	-0.004	0.018	-2E-04	0.0073	0.0108
Wt after cooldown (mg)	-0.007	-0.011	-0.015	-0.018	-0.009	-0.012	0.0036	0.0045

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