DETECTION AND QUANTIFICATION OF CARBON NANOTUBES THROUGH THERMAL RESPONSE TO ELECTROMAGNETIC RADIATION

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

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When exposed to an electromagnetic field, the heat generated by CNTs is proportional to the power of the field and the concentration of CNTs exposed. Additionally, the field's frequency, the sample geometry, heat transfer effects and functionalization of the CNTs affect the heating rate of the sample. In order to minimize these effects, we have developed a novel calorimeter system. This system consists of an insulating calorimeter vessel filled with a heat sink fluid. The sample is then placed in a thermally conductive crucible which is submerged in the fluid. The system can be closed to prevent heat loss, with a thermocouple is placed inside. The entire system is then exposed to a non-contact, RF field of constant frequency and constant power. The heat generated by the CNTs in the sample is captured in the fluid and recorded. The recorded temperature rise can then be compared against a calibration curve in order to quantify the concentration of CNTs.

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CHAPTER I

INTRODUCTION

Carbon Nanotubes: Properties and Prevalence

Carbon Nanotubes have become increasingly common as nano-fillers and receptors in manufacturing, research and even the medical field. They have several exceptional properties that make them very useful. Their high strength and aspect ratios make them great for creating high strength coatings and composites. Their electrical properties also make them perfect for creating conductive films or acting as signal receptors.

The high conductivity of CNTs leads to a unique CNT- EM interaction. If CNTs are exposed to electromagnetic radiation while arranged in a network, they will heat. This thermal reaction is highly dependent on the network properties, the radiation frequency, and the concentration of CNTs. This distinct property has been the basis of CNT detection systems in the past and has proven highly accurate [1].

In the past, microwaves were used to determine conductivity and CNT concentrations of doped samples [2]. However, CNTs have also been shown to react to radio waves, which have a much lower frequency [3]. Radio waves (RF) are significantly safer to use than microwaves, and they provide an alternative basis for CNT detection.

Calorimetry: Basic Theory

Calorimetry is a well-established scientific technique. It is a method for accurately and indirectly measuring the change in temperature of a sample. There are several types of calorimetry, but they all operate on the basic concepts of heat transfer [4]. The basic design, shared by most calorimeters, is of a sample placed in a heat sink all in an insulated container.

The temperature of the heat sink is then monitored and related to the temperature rise in the sample.

One of the most common types of calorimetry is solution or reaction calorimetry. In this type, two vessels are nestled within each other. The outer vessel contains a heat sink – usually water – and a thermocouple. This outer vessel is insulated to prevent heat loss to the environment. The inner vessel houses the reaction of interest. At the start of the experiment, all components of the reaction are placed into this vessel. As the reaction proceeds, heat flows into (or out of) the heat sink. This change is monitored, then the first law of thermodynamics is used to determine the energy used or generated by the reaction.

The methods developed herein are very similar to reaction calorimetry. The specific design challenge of this method is the fact that one of the "reaction" components is generated outside the system. In this case, the RF applicator must remain outside the calorimeter system. This means that the system components must be both thermally insulating and RF transparent. The system is also restricted in size and mass because the RF field must reach the sample at sufficient strength.

CHAPTER II

METHODS

Materials

Multi-walled carbon nanotubes (MWCNT) were purchased from Cheap Tubes. MWCNT had a purity greater than 95%, lengths of 10-20 μm and diameter of 30-50 nm. Talcum Powder was purchased from CVS Pharmacy (15% Zinc Oxide). Low viscosity silicone oil was purchased Sigma Aldrich (5 cSt). High density Styrofoam was purchased from Hobby Lobby. All of these materials were used without further purification.

Equipment

A variable power signal generator was purchased from Rigol Technologies (model number DSG 815). This generator creates signals of specified frequency (9 kHz – 1.5 GHz) and power. A power amplifier was purchased from Prana (model number GN 500). This amplifier increases the power of a low frequency signal (100 kHz – 200 MHz) up to 500 W. A parallel plate capacitor, shown in Figure 1, was designed and built for this experiment. The temperature of the samples was measured by a thermal camera from FLIR (S/N 55002441). The temperature was monitored with the ResearchIR software and the temperature was logged to a precision of 0.01°C.

Figure 1. Parallel plate capacitor. Copper disks (diameter 4 in) mounted on a plastic rack.

Sample Preparation

Carbon nanotubes were dispersed in ethanol and sonicated for 15 minutes, until a visually uniform dispersion was obtained. The dispersion was made with 0.05 grams of MWCNT and 50 mL of ethanol, resulting in a concentration of 1 mg/mL. Talcum powder was taken as a representative inert matrix. Samples of varying concentrations were obtained by mixing 0.25 g of talc with a specified volume of MWCNT dispersion as shown in Table 1. The dispersions were allowed to evaporate in the fume hood overnight, then heated in the vacuum oven at 60°C for two hours to drive off any residual ethanol.

Table 1. CNT dispersion volumes.

Sample conc. (wt%)	1	2	3	4	5
CNT mass (g)	0.0025	0.005	0.0075	0.0100	0.0125
Dispersion Vol. (mL)	2.5	5.0	7.5	10.0	12.5

Note: Volumes calculated based on a solution concentration of 1 mg/mL and total inert mass of 0.25 g.

Experimental Setup

A calorimeter prototype was carved from Styrofoam. The recess of the calorimeter was filled with low viscosity silicone oil, which acted as the heat sink. The CNT-talc sample was placed in a boron nitride crucible. The crucible was placed in the recess of the calorimeter so that the crucible was submerged in the fluid above the height of the sample. A Styrofoam cap was placed over the CNT sample without covering the calorimeter fluid, as show in Figure 2A. The entire calorimeter was placed between the parallel plates of the capacitor, spaced at 2 inches. The FLIR Camera was positioned over the sample and angled as in Figure 2B, so that it was looking directly down on the sample. The signal generator was set to 107 MHz, and the system was set to produce 100 W of power. The samples were irradiated for two minutes each. Temperature vs time data was collected via the ResearchIR software.

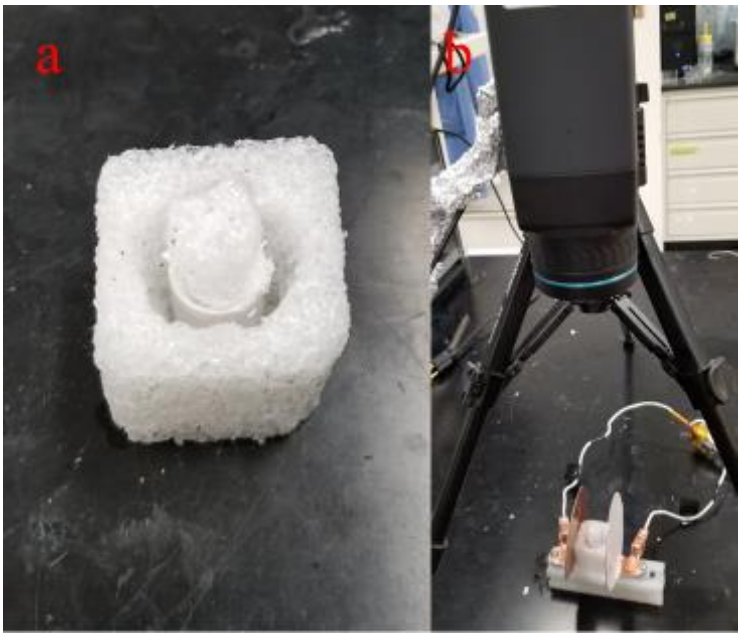

Figure 2. Calorimeter experiment design. The (a) open top calorimeter allows the (b) FLIR camera to view the fluid from directly above.

CHAPTER III

RESULTS

Uniformity Results

The samples were first analyzed for uniform heating of the calorimeter fluid. As the samples were heated, thermal videos of the system were collected. Figure 3 shows a representative image of the expressed heating. The circular area of the sample appears cold because the Styrofoam cap blocks the FLIR camera's view. The heating of the calorimeter fluid, however, is clearly shown. The total temperature gradient across the entire fluid was less than 2 degrees in every case. This indicates that heat transfer through the fluid was sufficiently high to maintain a fairly uniform heating profile.

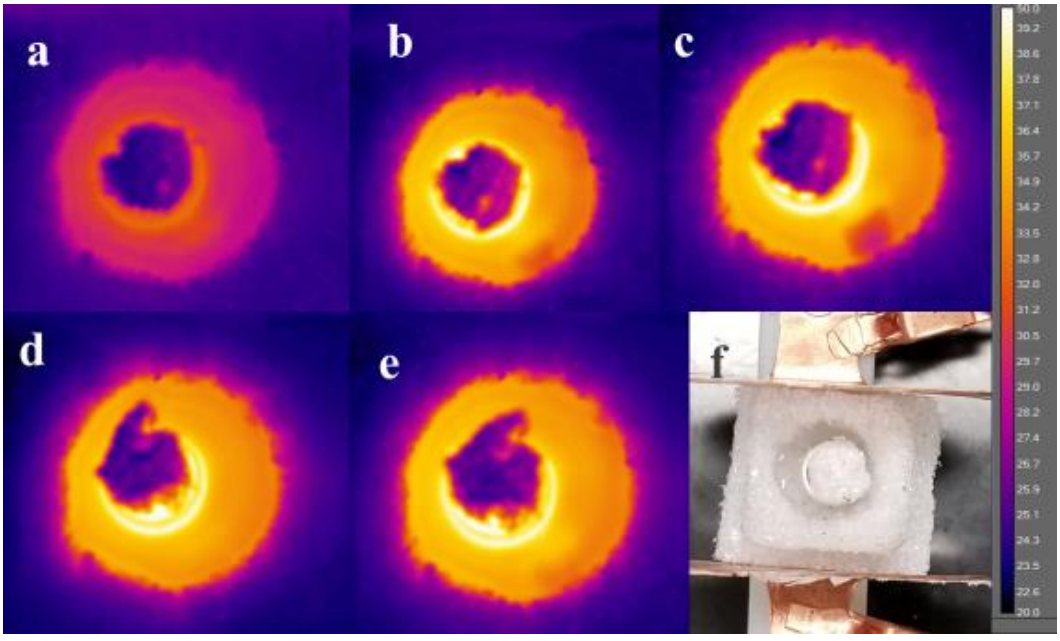

Figure 3. Heating profile of calorimeter fluid. The heating profile of the (a) 1 wt%, (b) 2 wt%, (c) 3 wt%, (d) 4wt%, and (e) 5 wt% samples after 100 s of radiation at 100 W and 107 MHz.The physical view of the FLIR camera is shown in (f).

In a fully enclosed calorimeter, the temperature would need to be monitored by a thermocouple, which could be inserted into the fluid without allowing excessive heat loss

through an open cap. A uniform heating profile is essential for this single point measuring technique to be sufficiently reliable. Based on the heating profile of the fluid, the temperature could be monitored from any single point and the measured temperature would be an accurate representation of the fluid temperature as a whole.

Total Heating Results

Thermal videos of the system were analyzed for total temperature change in the calorimeter fluid. The ResearchIR software was used to extract the maximum temperature of the fluid versus time. The extracted data was then plotted using MATLAB. The resulting data can be seen in Figure 4. Five seconds after data logging began, the RF radiation was initiated. The samples were heated for 120 seconds, then allowed to cool (shown as a decrease in temperature in Figure 4).

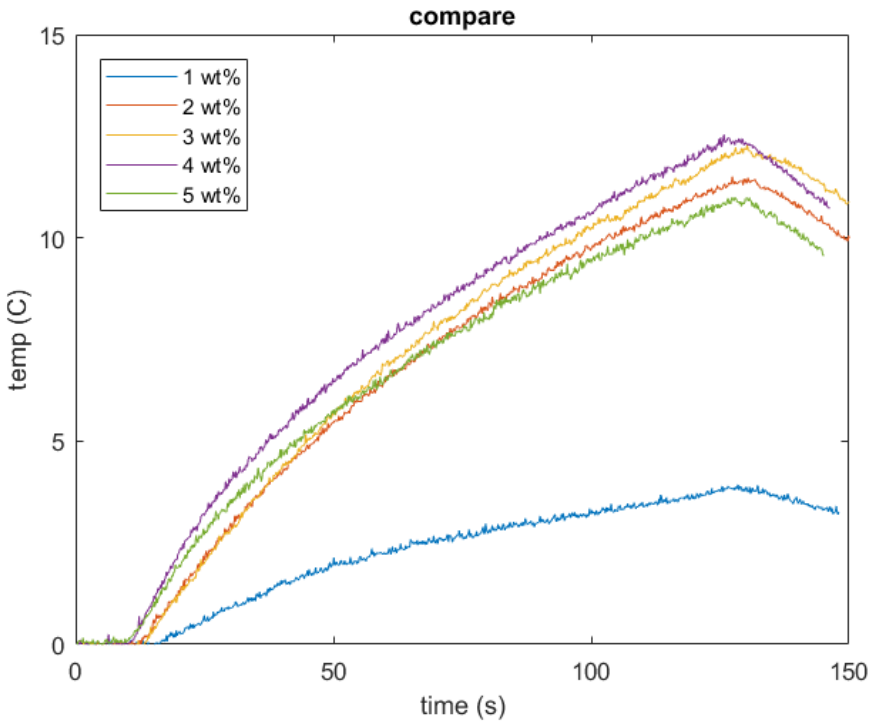

Figure 4. Relative heating curves of 1-5 wt% samples. The temperature on the y-axis represents the change in temperature over its initial value.

The samples generally followed the expected trend, with two notable exceptions. First, the 1 wt% sample heated dramatically less than anticipated. While the other samples heated more than 10°C, the 1 wt% heated by less than 5°C. This dramatically low heating is likely the result of a poorly percolated network. At this concentration and in this system, the CNTs may not form a fully percolated network, which would decrease the resistive heating of the sample.

It should also be noted that the 5 wt% sample does not conform to the predicted relationship between CNT loading and heating response. This sample, predicted to heat the most, shows the second to least heating. The most probable cause of this discrepancy is reflected power. It has been established that a highly conductive sample will reflect applied electromagnetic radiation. Reflected radiation is not absorbed and therefore cannot contribute to heating. The amount of reflected power is known to increase dramatically with the conductivity of the sample. The 5 wt% sample likely reflected significantly more power than the other samples. This would naturally lead to lower temperature changes because significantly less power is being absorbed.

CHAPTER IV

CONCLUSION

Process Analysis

The results of these experiments suggest that a fully closed calorimeter is a viable system for CNT detection. The uniformity of the calorimeter fluid means that a thermocouple can be used to monitor the heat generation accurately. This means that a fully closed calorimeter is possible, which would allow for complete capture of the heat generated by the tubes. If complete heat capture is achieved, then the lower detection limit of the system is theoretically extremely small because the radiation can be applied for as long as necessary to obtain a relevant rise in temperature. Additionally, the CNT loaded samples generally follow the expected trend: increased weight percent correlates to increased thermal reaction.

In order for a full calorimeter to be practically created and operated, certain key issues must still be addressed. Primarily, the sub-par heating of the 5 wt% sample must be accounted for. If this issue truly is the result of reflected power, then it should be possible to tune the RF parameters to adjust for this. Lowering the applied power or adjusting the frequency of the source. This adjustment would be similar to those made by an automatic impedance matching system. Such systems adjust the application frequency to cancel out the conductive and resistive components of a mismatched network. This causes maximum power to be absorbed in the sample.

A practical model of a calorimeter would, ideally, be designed to maximize the temperature rise of the fluid. It is for this reason that silicone oil was chosen as the fluid (silicone oil has a fairly low heat capacity). This can also be accomplished by minimizing the interference

between the sample and the RF source. Interference can be minimized by decreasing the size of the calorimeter and minimizing the Styrofoam and oil necessary in the system. Adjusting the frequency and impedance matching may also help with this.

Overall, the calorimeter system is highly promising. It requires further testing and development, but it has the potential to become a standard for CNT content analysis. When working properly, this system should be able to definitely find the maximum possible CNT concentration is a system. Though it is not yet complete, this system is worth further development.

Process Applications

A full calorimeter system, capable of reliably detecting low concentrations of CNTs, has a variety of potential applications across the field of nano-material science. The predominate application is likely as a quality control test. This system could potentially be used in a lab or production facility to verify that CNT loaded parts or processes are not releasing nanotubes into the environment. Once fully developed, this system could be used to perform a standardized test which allows the technician to certify a maximum CNT content of any given sample.

This system holds additional promise because of its potential for adapted design. With further testing and development, this system could potentially become hand-held or portable, allowing for field testing of an environment for CNT contamination. It could also be adjusted to analyze compact solid or liquid samples. Currently, the system is being designed to work on powdered samples, but when it is complete, the same principles can be applied to alternative sample forms. Because the system is based on RF instead of microwaves, this system may even

be able to analyze aqueous samples. Altogether, this system has the potential to become one of the most versatile and definitive measurements of carbon nanotube loading.

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