EXPERIMENTAL STUDY OF GRAPHENE AND CARBON NANOTUBES THERMAL SENSING PROPERTIES

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ABSTRACT

Today there are several new and interesting Nano-particle materials on the market providing good electrical conductivity. Examples are carbon Nano-tubes and different versions of graphene derivatives, often provided as powder. In particular, the materials available were Multi-Walled Carbon Nanotubes in Epoxy matrix and Reduced Graphene Oxide (rGOH). An initial literature survey underlined the lack of measurements and information about the conductivity of these materials during heating up or curing. This work is part of a larger project aiming at producing "sensing structural composite material", i.e. a composite material with integrated Nanoparticles, as eg. Carbon-nano-tubes or graphene, working as sensors reporting the status of the material during heating up, curing and/or tensioning. The principal results concerns the evaluation of the specific conductivity during heating for both materials (rGOH and MWCNT in Epoxy Matrix) with the realization of an experimental model for the gradient of the specific conductivity with temperature. The linearity underlines the possibility of using the properties of these materials to create sensors, not only for strain (with the advantage of high Gauge Factors), but also for temperature.

1 INTRODUCTION: CARBON NANOTUBES AND GRAPHENE

The principal aim of this experimental work is to study thermal sensible properties of Graphene and Multi Walled Carbon Nanotubes (MWCNT). In particular, the materials available for experimental investigations are Carbon Nanotubes in Epoxy matrix and Reduced Graphene Oxide (rGOH).

Carbon nanotubes (CNTs) are tubes made of carbon with diameters typically measured in nanometers. Carbon nanotubes often refers to single-wall carbon nanotubes (SWCNTs) with diameters in the range of a nanometer. They were discovered independently by Iijima and Ichihashi [1] and Bethune et al. [2] in carbon arc chambers similar to those used to produce fullerenes. Carbon nanotubes also often refer to multi-wall carbon nanotubes (MWCNTs, also sometimes used to refer to double- and triple-wall carbon nanotubes) consisting of nested single-wall carbon nanotubes. Carbon nanotubes can exhibit remarkable electrical conductivity. They also have exceptional tensile strength and thermal conductivity, because of their nanostructure. These properties are expected to be valuable in many areas of technology, such as electronics, optics, composite materials (replacing or complementing carbon fibers), nanotechnology, and other applications of materials science.

A more detailed view has been considered on the effect of CNT inside Epoxy matrix. The mechanical and electrical properties of the composite with different weight percentages of nanotubes have been investigated in [3]. Conductivity measurements on the composite samples showed that the insulator-to-conductor transition took place for nanotube concentration between 0.5% and 1 wt.%. The electrical and thermal conductivities of epoxy composites containing $0.005 \setminus 0.5$ wt% of single-walled (SWNTs) or multi-walled (MWNTs) carbon nanotubes have been also studied in [4]. The MWNT composites had an electrical percolation threshold of 0.005 wt%, whereas the thermal conductivity of the same samples increased very modestly as a function of the filler content.

Graphene is an allotrope of carbon in the form of a single layer of atoms in a two-dimensional hexagonal lattice in which one atom forms each vertex. Graphene has a special set of properties which set it apart from other allotropes of carbon. In proportion to its thickness, it is about 100 times stronger than the strongest steel. It conducts heat and electricity very efficiently and is nearly transparent. In its traditional form, graphene is one atomic layer thick and usually exists as a film of sorts; however, the proliferation of graphene research and testing has led to the creation of various graphene forms, each used for unique purposes. These forms include graphene films produced through chemical vapor deposition (CVD), graphene oxide (GO), reduced graphene oxide (rGO) and graphene nanoplates (GNPS). The material studied in this thesis project was Reduced Graphene Oxide. There are numerous ways to produce rGO such as annealing, hydrazine vapor treatment, and microwave reduction.

Studies conducted on thin graphene layers underline the possibility of temperature sensing applications. In [5], a temperaturedependent study of thermal (10300 K) and electrical (103000 K) transport in annealed RGO films indicates the potential application of RGO films for sensing temperatures across an extremely wide range. Also applications with a highperformances flexible temperature sensor composed of polyethyleneimine and rGO have been realised [6]. The prepared sensor exhibits high sensitivity (1.30% $°C^{-1}$), linearity (R2 = 0.999), accuracy (0.1 °C), and durability (60 d) for temperature sensing between 25 and 45 °C.

2 EXPERIMENTAL

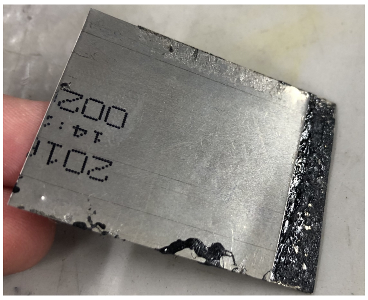
2.1 Set-Up

Principally the evaluation of the specific conductivity of the different materials has been realized by a Bio-Logic Potentiostat and two different ovens. Temperature measurements in the ovens have been made by a thermocouple and the different geometric data have been measured using a caliber. To collect data from different sources a LabView Script has been realized. Finally Matlab has been used to post process results.

2.2 MWCNTs in Epoxy Matrix

As concerns the CNTs forest impregnated by a epoxy film (from Hexcel) on Steel Sheets, the mean value of conductivity for cured samples is about 0.24 (S/m). Moreover the variance of the values obtained from different samples (with different number of layers and different geometry) is

6.7×10^{-4}. It was also interesting to collect data on the level of current during heating up in order to study the sensing properties of the Carbon Nanotubes.



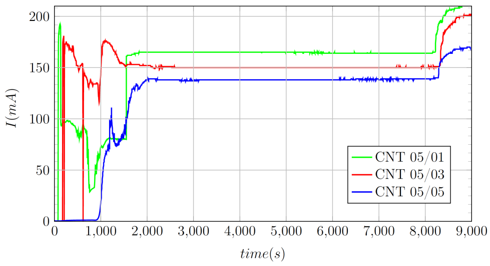


Figure 1. Sample and Measurements during curing

Considering the geometry of the sample a value of $d\sigma/dT$ $(S/m)/°$C has been get. The mean value of $d\sigma/dT$ is 3.45E-4 $(S/m)/°$C. The value of conductivity during the cure has been also measured. On average the value of conductivity has been increased by the treatment (considering the value 0.24 S/m), but the values are not stable. After that, the support of the nanotubes has been replaced, using a carbon fibre prepreg. The principal problem with this kind of acquisition is linked with the mechanical characteristics of the prepreg before curing. Moreover the curing process has squeezed the matrix making not easy the following measurements. The principal problem is linked with the clamping and with the fact that the samples do not offer a continuum field for the propagation of the current. To understand (at least) if there is a dependence from the temperature of the value of the conductivity, the samples have been tested during heating up and cooling down cycle: there is a dependence from the temperature of the value of the current (we can see it considering the abrupt decreasing of current after the abrupt cooling down).

2.3 Graphene (rGOH)

As for the MWCNT we studied the conductivity of a Reduced Hydrogenated Graphene Oxide (a coated Kapton film from Danubia NanoTech [7]) in different conditions starting from a Single Layer configuration. Each layer is 0.5cm*4cm. First of all, a single layer of rGOH has been analysed. Clearly, to define a conductivity is necessary to define the resistivity of the material. In this case is not simple because we should have the area of the cross section of the film. Graphene films exhibits a stable behaviour. The value of the current seems to depend weakly from the sample and clearly the difference is due to different geometric characteristics and imperfections. The law tesion/current is linear. At this point, we put the graphene layer inside a prepreg sandwich made up of 4 layers. We have noticed a weak growth of the current for a fixed level of voltage $(1V)$ from the previous test. This phenomenon could be explained considering that the prepreg has a better value of conductivity, so putting the film inside it we increase the global conductivity of the sample. At this point the samples have been cured under vacuum. In order to avoid the oxidation of the film, we waited the Tamb before removing the samples from the vacuum pump. After that we have tested the samples with the potentiostat at *Tamb*. The value of conductivity seems to be unchanged. The next step has been to measure the level of current for a fixed voltage during heating up. In Figure 2.3, the Temperature is measured in the oven, while the sensor measures inside the material. The delayed signal is therefore due to heating up. Moreover, to avoid the oxidation of the samples, they have been placed under vacuum. This has made the measurements quite unstable and complicated: first of all the action of the vacuum make worse the grip of the cable, then, since the film is very fragile, the action of the pup has destroyed most of the samples. For the survived ones we have realized a linear model where the samples exhibit a linear behaviour increasing temperature. Using that linear model we obtain a value of $dI/dT = 0.0001173$ with a Root Mean Squared Error: 0.000346. (according to the F-test we can apply the linear model; F-statistic vs. constant model: 739, p-value = 1.08e-34). Further tests should be done to have a more numerous selection of values of the dI/dT, but the principal future goal is to find a way to test the samples under vacuum without destroying the most of them!

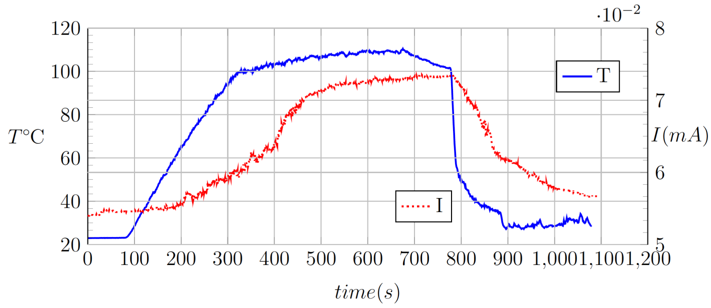


Figure 2. Sample and Measurements during Heating

3 CONCLUSION

Talking about the MWCNTs, the most of the results have been obtained for the case study of Metal Sheets with MWCNTs inside epoxy matrix. In this case there were enough data to realize and experimental linear model for the gradient of the specific conductivity with temperature. As concerns rGOH, also this time we could estimate a value for the $d\sigma/dT$, but probably the most interesting results is that to perform this kind of experiment a complete different set-up is needed in order to measure in a more easily way the current through the material. A solution could be the use of an hot press. Another important result is that to avoid the oxidation of the graphene film during heating and curing, the measurement of the conductivity must be realized in a vacuum package. On the whole, we can say that the linearity of the law $d\sigma/dT$ underlines the possibility of using the properties of these materials to create sensors, not only for strain (with the advantage of high Gauge Factors), but also for temperature.

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