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CNT composites for aerospace applications

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Carbon nanotubes were synthesized by thermal arc plasma process after optimization of the synthesis parameters. These samples were then analysed by scanning and transmission electron microscopes (SEM and TEM), in order to establish the morphology of the nanostructures. Atomic force microscopy (AFM) and electron diffraction studies were also carried out before using the sample for the composite material preparation. Composites of epoxy resin with curing agent as well as a mixture of graphite and carbon nanotubes were prepared with varying proportions of the mixture. The electrical resistivity of the material was studied under varying pressure and voltage conditions. Preliminary results of these studies present interesting features which are reported here.

Keywords: Carbon nanotubes; Composites; Aerospace

1. Introduction

The study of nanotubes has advanced tremendously in a relatively short time since its initial discovery in 1991 by Iijima [1]. The properties of these nanostructures are so unique and enhanced that it is finding applications in various spheres of life – span from bio-medical, to optical, to outer space [2–15].

Essentially two families of carbon nanotubes exist: SWNT or (single wall nanotubes), that are constituted by only one rectilinear tubular unity and the other MWNT (multi wall nanotubes), that are constituted by a series of coaxial SWNT. Though generally

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both types have high aspect ratio, high tensile strength, low mass density, etc., the actual values could vary depending on whether it is SWNT or MWNT. Of the two types, SWNT is better suited for mechanical applications.

Owing to their exceptional morphological, electrical, thermal and mechanical characteristics, carbon nanotubes yield a material particularly promising as reinforcement in the composite materials with metallic matrixes, ceramics and polymers. The key factor in preparing a good composite rests on good dispersion of the nanotubes, the control of the bonding between nanotubes and matrix and the density of the composite material [2]. Besides the type of nanotubes (SWNT, MWNT) the synthesis modes (arc discharge, laser, CVD) are important variables since they determine the perfection of the structure and the reactivity of the surface.

2. Experiment

Carbon nanotubes were synthesized in a DC arc plasma system in helium atmosphere at a pressure of 600 torr. The arc was struck between two electrodes consisting of a high purity graphite rod and a block of graphite. The discharge is typically carried out at a voltage of 24 V and a current in the range of 100–120 A. Some of the evaporated carbon condenses on the tip of the cathode, forming a slag-like hard deposit. The deposit, essentially on the cathode, consists of bundles of carbon nanotubes mixed with a small quantity of amorphous carbon.

The as-synthesized samples were characterized by means of SEM, TEM and AFM. Figures 1 and 2 show SEM and TEM images respectively of the CNTs synthesized. SEM image was recorded using ISI ABT – DS 130 S microscope and TEM by JEOL JEM 2010 microscope.

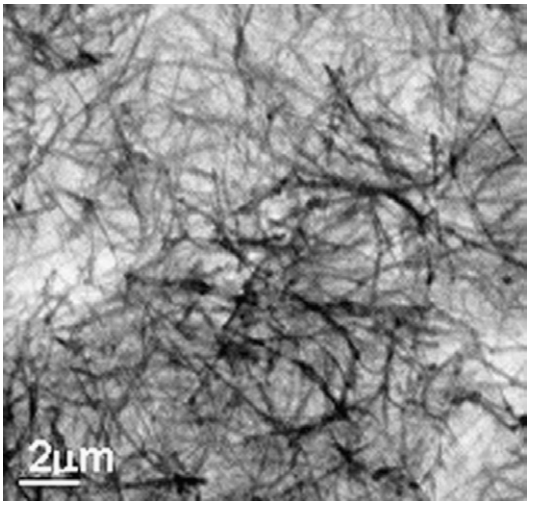

Figure 1. SEM image of as-synthesized CNTs.

2.1. *Nanotube composites*

Due to the unique properties of carbon nanotubes they are being widely studied as a constituent of composite material. CNT based composite materials are increasingly being considered for mechanical, electrical and space applications. Even studies on biosensor composites based on functionalized nanotubes and nanoparticles are reported [12–15]. They are also being studied for their suitability and application in aerospace and aeronautical fields. A prospective application in aerospace that is being widely studied, including our work reported here, is the improvement of electrical properties of composites made from carbon nanotubes and epoxy resin [16–18]. To start with it was decided to mix the epoxy resin with graphite. The purpose was to make a light, thin and mechanically strong composite material to cover electric circuits against external electromagnetic interference, this is very important for air- and space-craft. The epoxy resin that was used is a commercial Shell product Epon 828. Two types of curing agent were used along with the resin; mainly A1 curing agent and PAP8 agent. Also some of the resin + curing agent samples were mixed with 20 wt% of graphite and these were used for the analysis of the electrical resistivity studies. We stress that the first curing agent possesses polar groups in its chemical composition, whereas the second agent contains benzene groups. As a consequence, the mechanical properties of composites where the PAP8 agent has been used turn out to be improved [16]. However, the stability of the mechanical properties, under varying pressure conditions, as well as the corresponding resistivity behavior, has not been investigated yet. In the present work we partially fill the gap concerning the electrical transport properties.

The composite was made by manually mixing the micron sized (particle size ~20 microns) graphite powder in the resin + curing agent. Care was taken to avoid air bubbles in the mixture. The experiments were performed in two stages; initially two types

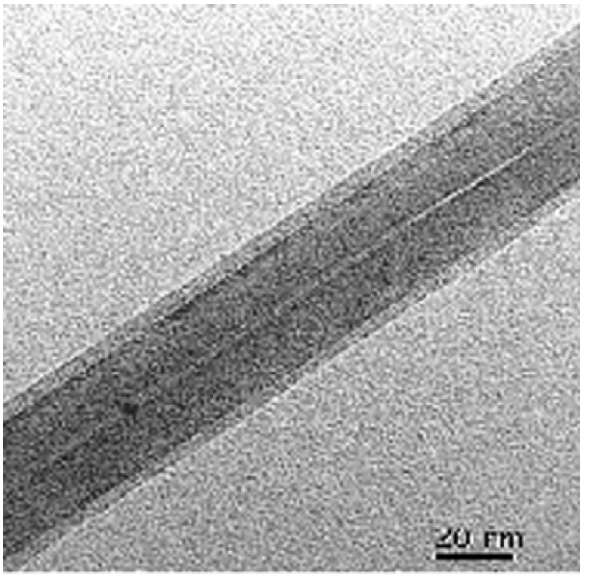

Figure 2. TEM image of CNT.

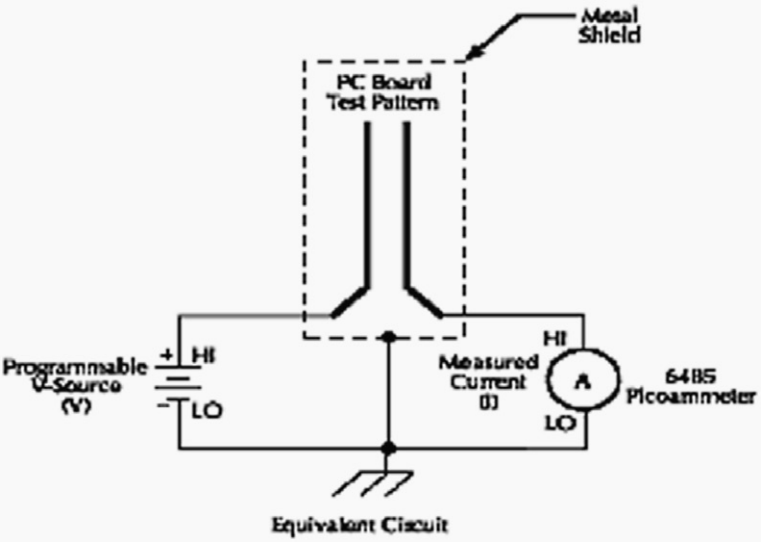

Figure 3. Schematic of circuit used for electrical measurements (taken from Keithley 6485 Picoammeter manual).

of resin with curing agents were used to find the one most suitable for the earlier defined applications. In the second stage this resin was mixed along with the CNT to study the change/enhancement of the electrical property. In order to comply with the standard specification of the U.S. military authorities, we tested the electrical properties of the composite materials, making use of "Y" shaped electrical circuits (as shown in figure 3) having two parallel lines as the tail of the "Y" with a 1 mm gap between them and a length of about 2.5 cms. The circuits were made on a PC base with silver print and the two arms of the "Y" were connected to the picoammeter and a high voltage supply. The composite mixtures were spread, like thin films, on the circuit and electrical resistance tests were carried out using Keithley 6485 Picoammeter with short circuit protection.

The current through the sample was recorded for three different applied DC voltages, namely 200 V, 500 V and 1000 V.

The resistance and the resistivity were then calculated. In the first step the experiment was repeated under three different pressures – atmospheric, 10^{-2} mbar and 10^{-6} mbar. The low pressure measurements indirectly gave the effect of moisture on the resistivity values of the samples. The plots in figures 4–7 show the resistivity vs. applied voltages for various samples under varying voltage and pressure conditions. In the second step, for studying resistivity versus concentration, the data was taken under atmospheric pressure conditions only.

3. Results and discussion

3.1. *Studies with resin and graphite*

Analysing the data it is observed that the resistivity of samples with the curing agent A1 is found to be a few times lower than the samples with curing agent PAP8. It is

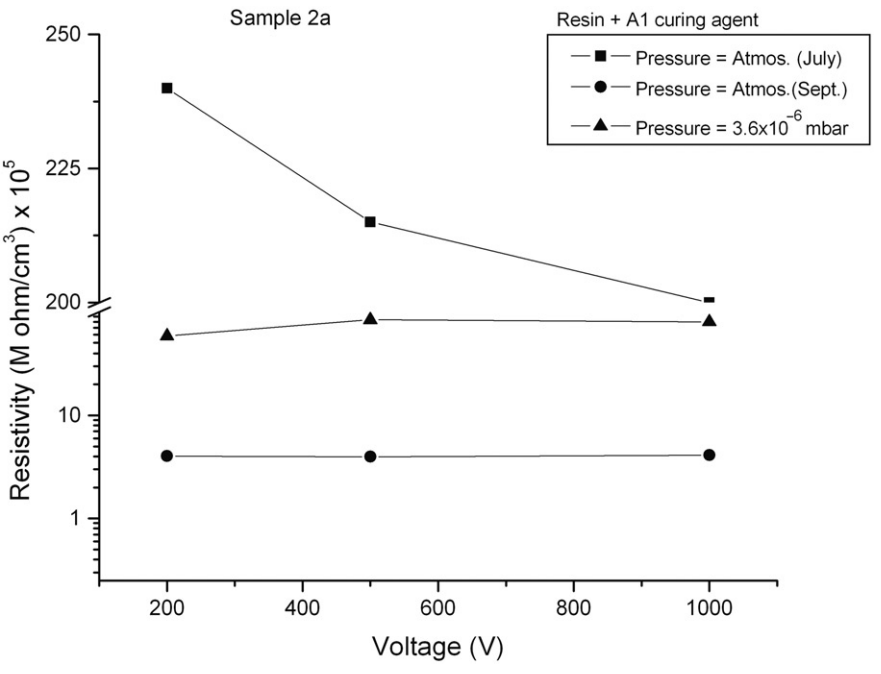

Figure 4. Plot of resistivity vs. voltage for the sample. Resin + A1 with no graphite added.

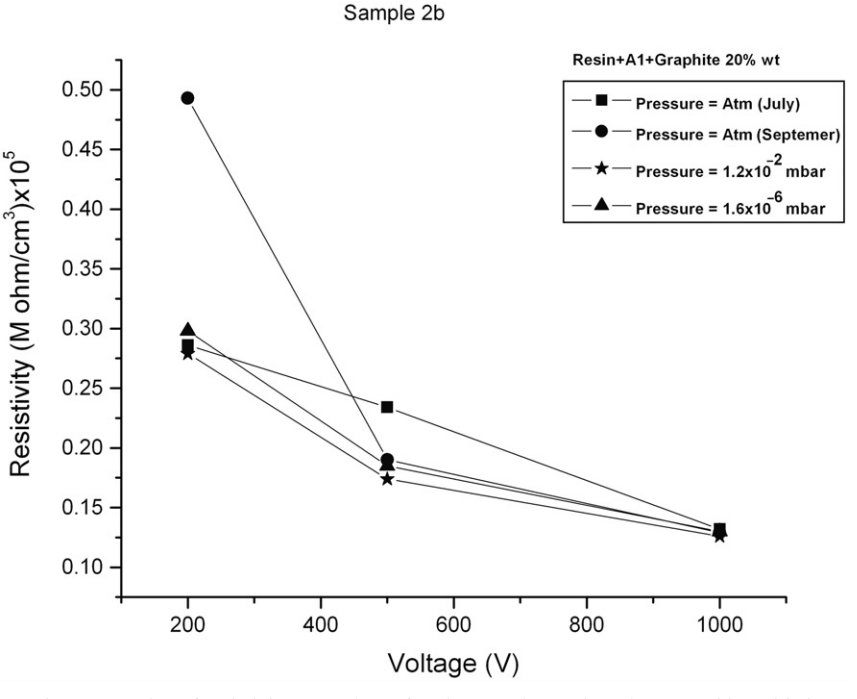

Figure 5. Plot of resistivity vs. voltage for the sample. Resin + A1 + graphite added.

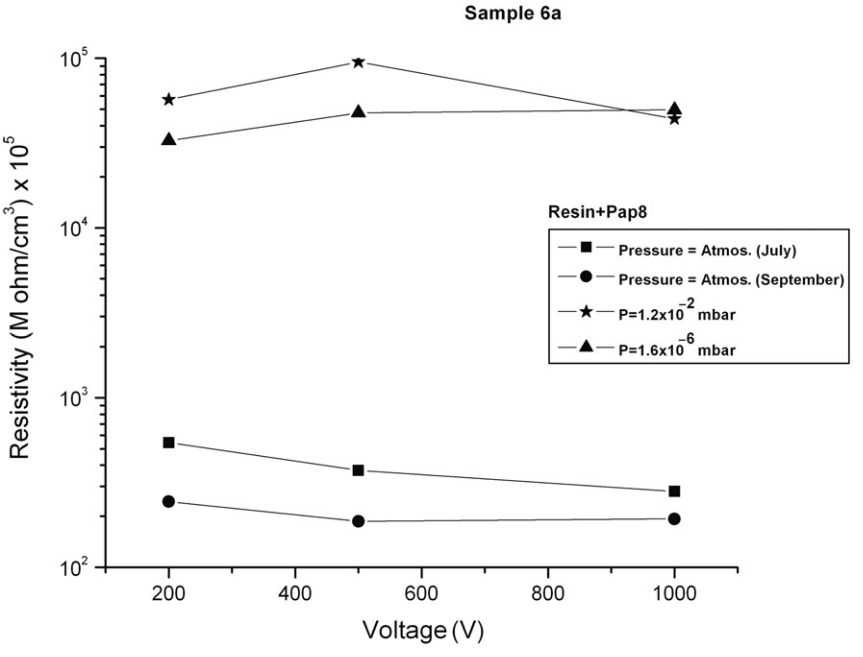

Figure 6. Plot of resistivity vs. voltage for the sample. Resin + PAP8.

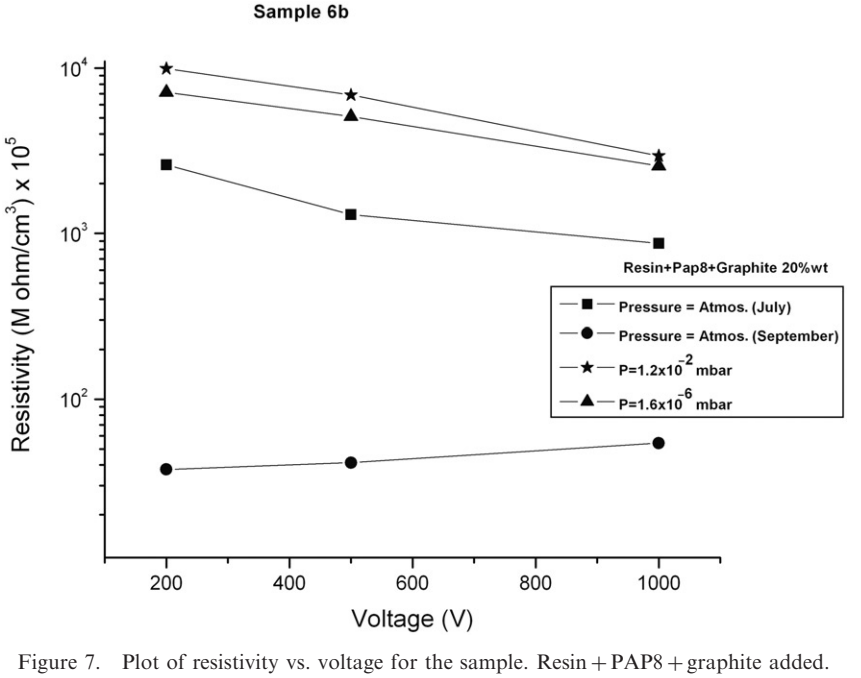

Figure 7. Plot of resistivity vs. voltage for the sample. Resin + PAP8 + graphite added.

important to note that the absolute change in resistivity is less over a wide voltage range of 200 volts to 1000 volts for the sample with A1 curing agent (as seen from figures 4 and 5), whereas for the sample with PAP8 curing agent the resistivity changes marginally more with increasing voltage. Note that the resistivity data were collected with the same samples at two different times of the year (i.e., July 2005 and September 2005) in order to have a rough estimate of the influence of climatic and environmental conditions on the performance. It appears, from a preliminary analysis of the data (figures 6 and 7), that the resistivity values of composites employing PAP8 agent shows a large difference between atmospheric and low pressure conditions and its behavior was not affected by the addition of graphite. In the case of composites with A1 curing agent the behavior is quite different (figures 4 and 5), i.e., the stability of the material increases as graphitic additions are included. This seems to favor the use of A1 curing agent from the point of view of the optimization of its use in aerospace applications.

3.1.1. Variation of resistivity with pressure/humidity. It is expected that when the ambient pressure is decreased while doing the resistivity measurements the humidity is also decreased resulting in higher resistivity values. The resistivity values for all the samples show some variation when done in atmosphere as compared to when done in low pressure. However, this variation gets reduced when graphite is added to the resin. From the plots shown previously we observe that, for the first sample (i.e. sample with curing agent A1 – figures 4 and 5), under different pressure conditions, the resistance changes very little. Instead in the second sample, the resistance undergoes remarkable variations under different pressure and humidity conditions, as seen in (figures 6 and 7). This feature might constitute a drawback for the use of the corresponding curing agent PAP8 for composite devices working under standard aerospace conditions, where the values of the pressure can undergo substantial variations.

3.1.2. Variation of resistivity with graphite addition. It is observed that the resistivity change is very large – near to three orders of magnitude when 20% graphite is added to the resin + A1 curing agent, whereas for the PAP8 curing agent the increase in resistivity due to addition of graphite is comparatively only marginal, of about three to five times. The above results, when considered in totality, give a broad spectrum wherein we find that the resin + A1 curing agent + graphite seems to be an ideal candidate for applications in various pressure ranges as well as voltage ranges. The Resin + A1 + graphite has the lowest changes in the resistivity values for voltages from 200 V to 1000 V and also for a pressure difference of atmospheric to 10^{-6} mbar.

3.2. *Studies of resin with CNTs*

3.2.1. Composite preparation. The composite with CNT is prepared in this way: to start with the CNTs are weighed and the required wt% of the CNT is mixed in isopropylic acid and ultrasonicated for 30 mins. Then this solution is mixed with a known quantity (weight) of resin and heated in an oven for 2 hrs at 80°C. The alcohol evaporates off and the resin with CNT is again sonicated for 15 mins. Immediately after

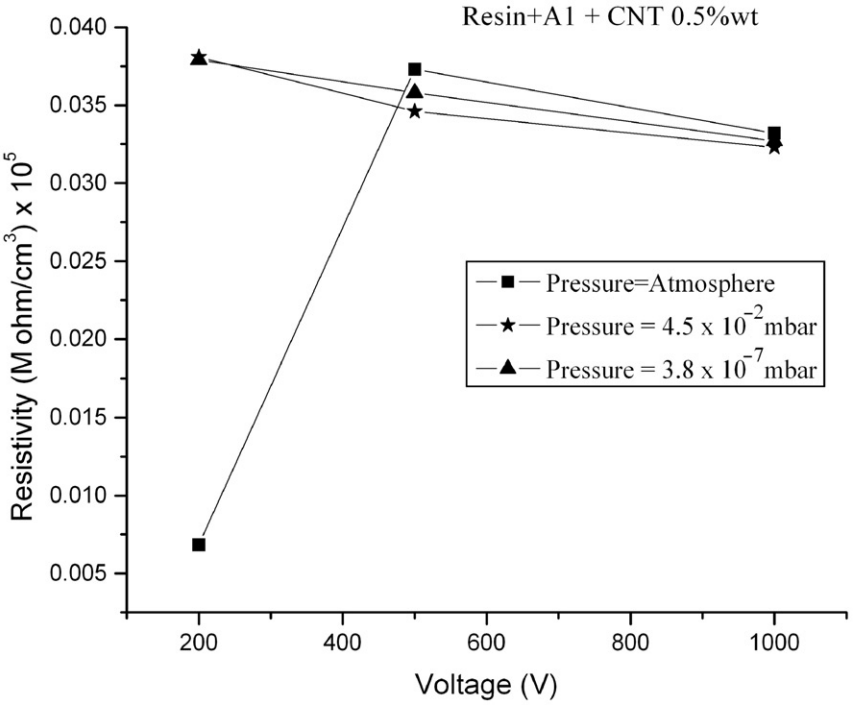

Figure 8. Plot of resistivity vs. voltage for composites of Resin A1 with CNT's.

this the hardener A1 is mixed and the mixture is applied on the surface of the electrical circuit and allowed to set.

The first step. Resistivity measurements were performed for composites with A1 resin in combination with carbon nanotubes (shown in figures 1 and 2). Composites were made replacing graphite with CNTs. The quantity of CNTs added was 0.5 wt% of the resin mixture. Figure 8 shows the plot of resistivity vs. voltage for this sample. As can be observed the resistivity value changes drastically with the addition of a small quantity of CNTs. The Resin A1 with no graphite or CNT has a resistivity in the range of few tens of M ohms $(\times 10^5)/\text{cm}^3$ whereas when 0.5 wt% of CNT is added the resistivity reduces by a factor of 10^3 to values ranging from 0.01 to 0.04 MΩ $(\times 10^5)/\text{cm}^3$. Also when these values are compared with the composite of resin A1 with graphite (refer to figure 5), we observe that the resistivity 20 wt% of graphite is ten times higher than the addition of a small fraction of CNT.

The second step. Composites of resin A1 mixed with both graphite as well as CNTs were studied separately with two compositions of 0.1 and 0.5 weight%. Figures 9–12 show the plot of these studies done under atmospheric conditions.

Resistivity measurements were performed for composites with A1 resin in combination with graphite and carbon nanotubes. Comparing figures 9 and 10 it can be seen that the resistivity decreases for the CNT composite (a few hundred mega ohm

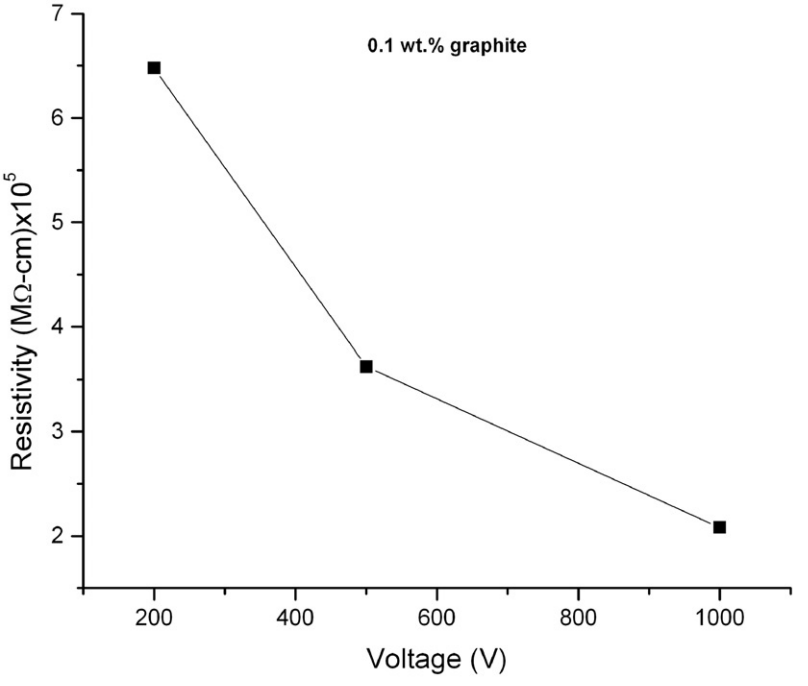

Figure 9. Plot of resistivity vs. voltage for 0.1 wt% of graphite.

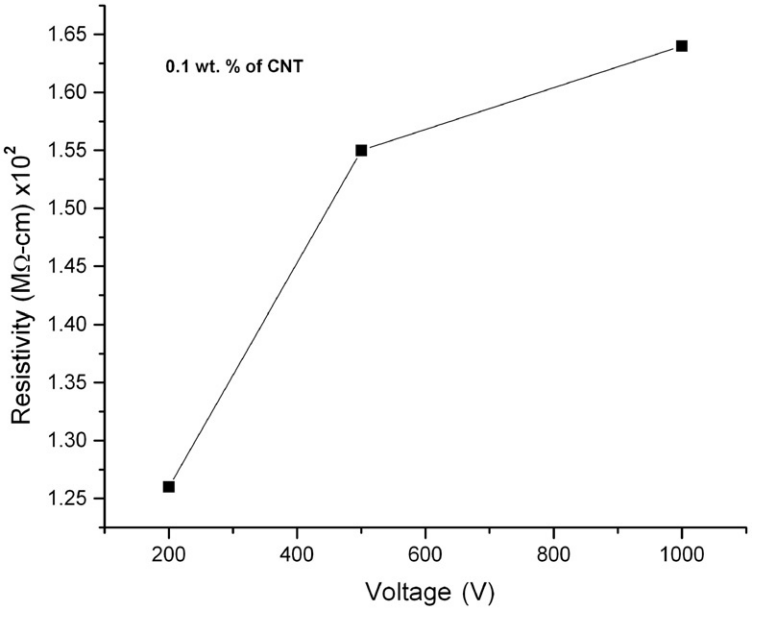

Figure 10. Plot of resistivity vs. voltage for 0.1 wt% of CNT's.

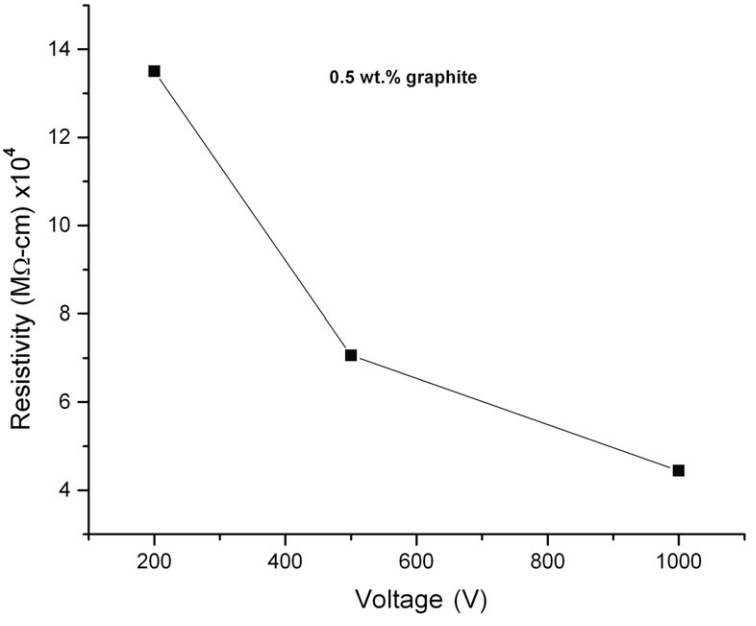

Figure 11. Plot of resistivity vs. voltage for 0.5 wt% of graphite.

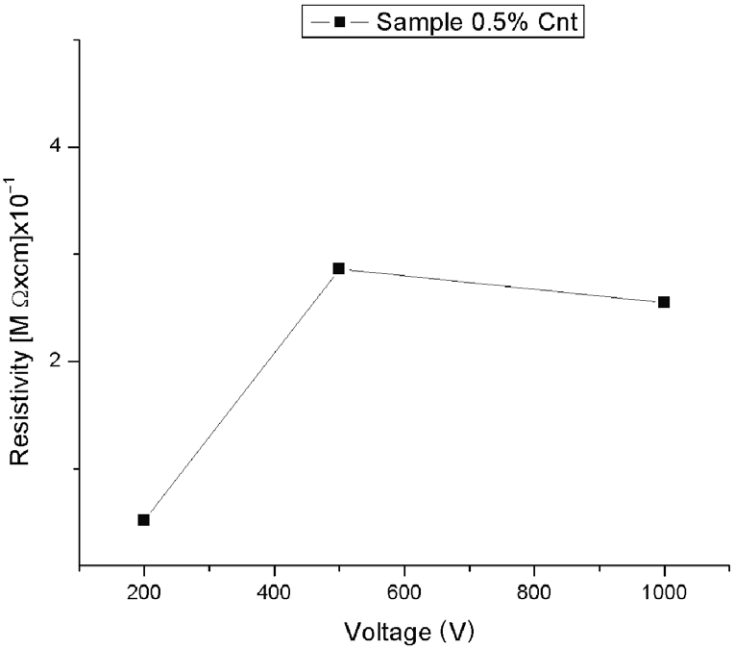

Figure 12. Plot of resistivity vs. voltage for 0.5 wt% of CNT's.

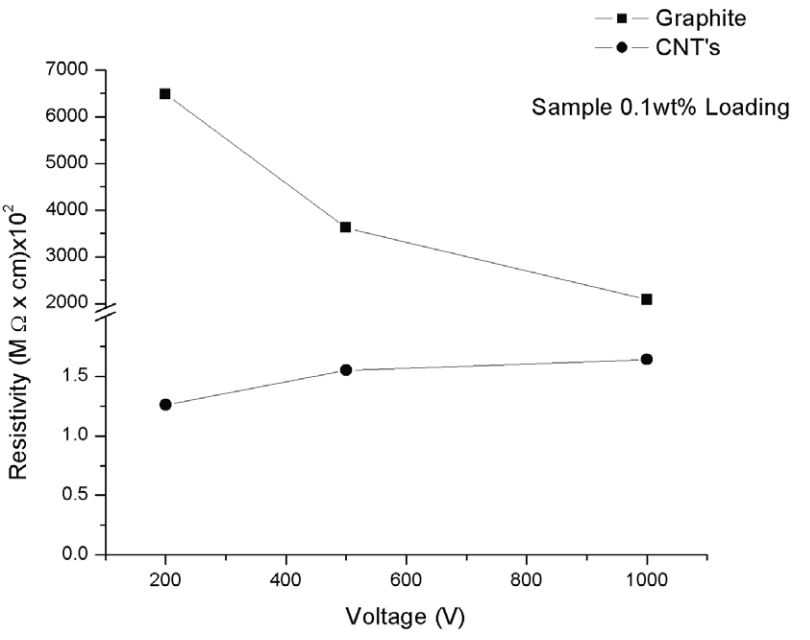

Figure 13. Comparison between graphite and 0.1 wt% of CNTs.

centimeters) by three orders of magnitude as compared to graphite composite (few hundred thousands mega ohm centimeters).

Comparing figures 11 and 12, which show plots for 0.5 wt%, it can be seen that the difference in the resistivity between the addition of CNTs and graphite amounts to six orders of magnitude (CNT $-$ a few $\times 10^5$ and graphite $-$ a few $\times 10^{11}$). As it can be seen, an increase of wt% from 0.1 to 0.5 of graphite only decreases the resistivity by a few times, whereas, in the case of CNTs, an increase of 0.1 to 0.5 wt% decreases the resistivity by three orders of magnitude. The resistivity value changes drastically with the addition of a small quantity of CNTs.

As can be seen in the plot of figure 13, the resistivity decreases drastically from thousands of mega ohms to hundred mega ohms with even a small (0.1 wt%) addition of CNT. Further increase (0.25 wt%) in CNT concentration results in the resistivity value of 9.19 MΩ (a decrease of two orders of magnitude). An increase of CNTs to 0.5 wt% results in the decrease of resistivity to 0.05 MΩ, i.e., again a change by two orders of magnitude. The concentration of 0.25 wt% was considered only for the CNT sample but not for graphite.

The plots in figures 13 and 14 clearly show a negative slope for graphite and a positive one for CNT based composite. That is, the filler inside the composite based on graphite particles, owing to their 0-D structure, is surrounded by resin. Hence, the electrical conductivity is hampered by the surrounding resin or, in other words, the resistivity of the graphite based composite is due to the resin, which is an insulating material, and thus exhibits a negative slope. In contrast, for the CNT based composite, the 1-D type structure enhances the chance of having a nanotube, nanotube contact, and thus it overcomes the high resistivity of the resin. This effectively results in the

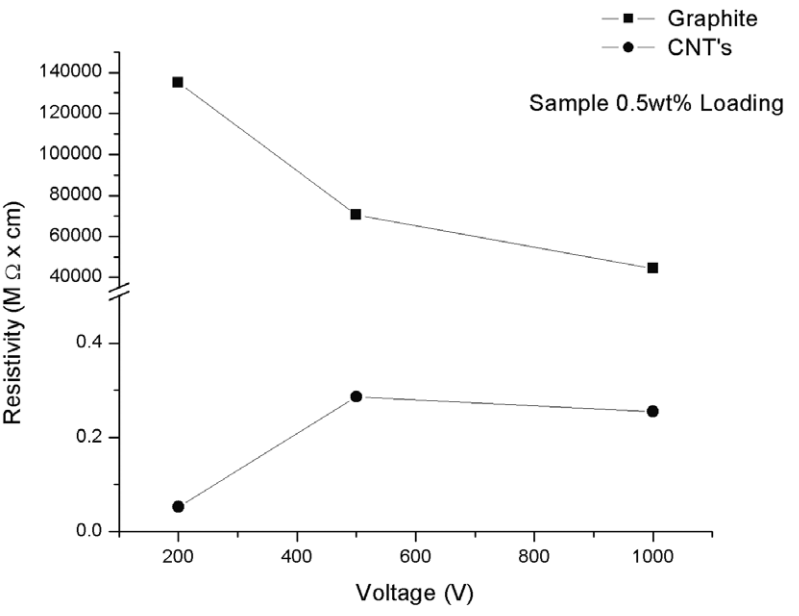

Figure 14. Comparison between graphite and 0.5 wt% of CNTs.

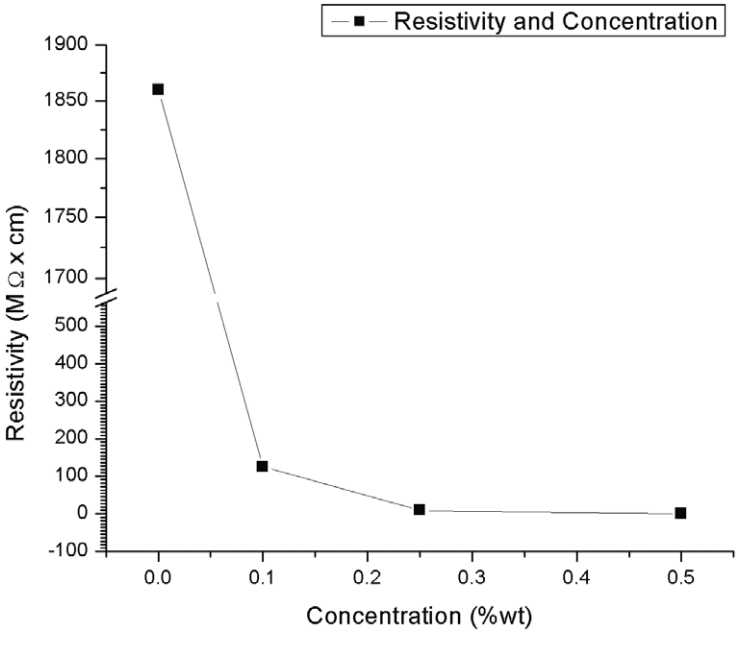

Figure 15. Plot of resistivity for composites with various CNT concentrations.

metallic like behavior of the composite – in which the resistivity increases with increasing voltage. Figure 15 shows a comprehensive plot of resistivity for various concentrations of CNT based composite. It is seen clearly the sharp fall in resistivity (from few thousand MΩ to few hundred MΩ) for even a small change in the concentration of 0.1 wt%.

4. Conclusions and outlook

We carried out a systematic study of the electrical properties of polymeric composite materials based on CNTs. The composite is obtained using the A1 curing agent, selected for the stability of the corresponding composite over a wide range of pressure values, in comparison with a different curing agent (namely PAP8). Benchmarking the resistivity properties of composites based on CNTs with those containing micron-sized graphite particles as a constituent, shows the advantages of using CNTs. The change in the resistivity values for CNT-based composites turns out to be significant, even for small changes in the added CNT percentage. These results might be important for determining the most suitable "recipe" for the realization of composite materials for high-fidelity circuits in aerospace applications, or even in devices exposed to disturbances predominantly electromagnetic in their nature. In the future it is planned to study CNT based composites with PAP8. Also, we plan to study the composite behavior in controlled humidity environments and for different temperatures.

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