

LNF-08/ 04 (P)
February 6, 2008

PROPERTIES OF NANOCOMPOSITES BASED ON RESIN AND CARBON NANOTUBES

S Bellucci¹⁺, F Micciulla^{1,2}, N Pugno³

¹ INFN-Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044 Frascati, Italy

² University of Rome "La Sapienza", Department of Aerospace and Astronautics Engineering,
Via Eudossiana 18, 00184 Roma, Italy

³ Politecnico di Torino, Dept. of Structural Engineering, Corso Duca degli Abruzzi 24, 10129
Torino, Italy

Abstract

A systematic study of the electrical properties of polymeric composite materials based on carbon nanotubes (CNTs), carried out at INFN-Laboratori Nazionali di Frascati is reviewed. The purpose was to make a light, thin and mechanically strong composite material to cover electric circuits against external electromagnetic interference. The epoxy resin that was used as a polymeric matrix is a commercial Shell product Epon 828. Two types of curing agent were used along with the resin, namely the A1 curing agent and PAP8 agent. 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 carbon nanotubes. The change in the resistivity values for carbon nanotubes based composites turns out to be significant, even for small changes in the added carbon nanotubes 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. It is planned also to present in future reports a study of carbon nanotubes based composites with PAP8. Also, we plan to show the composite behavior in controlled humidity environments and for different temperatures. Finally preliminary results on the mechanical characterization of the nanocomposites will be presented elsewhere.

*Published on
Reserch Signpost, The Nanomechanics in Italy*

⁺ Presenting author, [mailto: bellucci@lnf.infn.it](mailto:bellucci@lnf.infn.it)

1. INTRODUCTION

Since the discovery of carbon nanotubes (CNT's) in 1991 by Iijima [1] and the awareness of their novel mechanical thermal and electrical properties, an extensive research in the field of CNT/nanocomposites started. In fact, the introduction of carbon nanotubes as a structural element in nanocomposites should improve the material properties and, therefore, a large variety of applications are imaginable in different fields: in electronics such as devices in nanoelectronics, field emitters; in materials such as reinforcing materials; in bio-medicine; in aerospace [2-12]. The key factor in preparing a good composite rests on good dispersion of the nanotubes, the control of the bonding between nanotubes and matrix, the density of the composite material [2]. Many companies have started to sell ended products that contain CNT's, by now. The progress in bulk synthesis and purification [17-18] make carbon nanotubes available in larger quantities at falling prices. The progress in developing nanocomposites with carbon nanotubes gives them the function of reinforcing structural element [19] and yields new electrical and thermal conductivity material.

The polymer-based composites are popular in electronic appliance housings due to their light weight, low cost, high

strength and easy processing. The major part of these is in use to insulate electrical circuits against the atmospheric agents, only. Many polymeric materials are transparent to electromagnetic (EM) radiation and provide no shielding against electromagnetic interference (EMI). In electronic and communication applications, the EMI pickups by electronic components raise serious problems, such as noise enhancement and malfunction of electronic instruments.

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 both the 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. Besides, the type of nanotubes (SWNT, MWNT) the synthesis mode (arc discharge, laser, CVD) etc 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. 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 24V and a current in the range of 100 – 120 A. Some amount of the evaporated carbon condenses on the tip of the cathode, forming a slag-like hard deposit. The deposit essentially in the cathode consists of bundles of carbon nanotubes mixed with small quantity of amorphous carbon.

The as-synthesised samples were characterized by means of SEM, TEM and AFM. Figures 1 and 2 show SEM images.

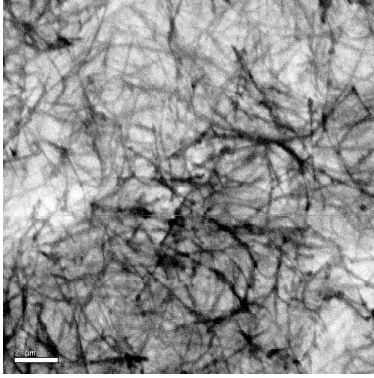


Fig.1 : SEM images of CNT with arc discharge.

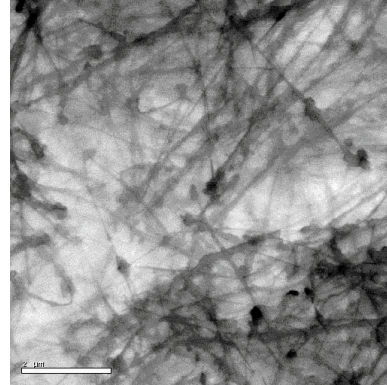


Fig. 2: SEM image of CNT which shows straight and long nanotubes.

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 [9-12]. They are also being studied for the suitability and applications in aerospace and aeronautical fields. A prospective application in aerospace that is widely studied, including our work reported here, is the improvement of electrical properties of composites made from carbon nanotubes and epoxy resin [13-15]. 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 crafts. 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 behaviour, has not been investigated yet. In the present work, we fill up this gap, in the part 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 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 Fig. 3) having two parallel lines as the tail of the “Y” with 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, 500 and 1000 V.

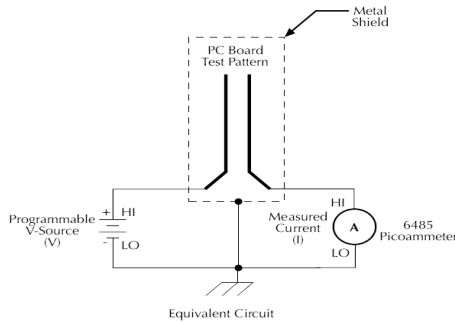


Fig. 3: Schematic of circuit used for electrical measurements (taken from Keithley 6485 Picoammeter manual).

The resistance and the resistivity were then calculated. In the first step the experiment was repeated under three different pressures – atmospheric, 10^{-2} and 10^{-6} mbar. The low pressure measurements gave indirectly the effect of moisture on the resistivity values of the samples. The plots in Figures 4, 5, 6 and 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 condition only.

3. RESULTS AND DISCUSSION

A. Studies with resin and graphite

Analysing the data it is observed that the resistivity of samples with curing agent A1 is found to be a few times lower than the samples with curing agent PAP8. It is important to note that the absolute change in resistivity is less over a wide voltage range of 200 to 1000 volts for the sample with A1 curing agent (as seen from Figures 4 & 5), whereas for the sample with PAP8 curing agent the resistivity changes marginally more with increasing voltage. Notice 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 their performance. It appears, from a preliminary analysis of the data (Figs. 6 & 7), that the resistivity values of composites employing PAP8 agent shows a large difference between atmospheric and low pressure conditions and its behaviour wasn't affected by the addition of graphite. In the case of composites with A1 curing agent the behaviour is quite different (Figs. 4 & 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.

It is observed that the resistivity change is very large – near about 3 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 3

to 5 times. These above results when considered in totality gives 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 to 1000 V and also for a pressure difference of atmospheric to 10^{-6} mbar.

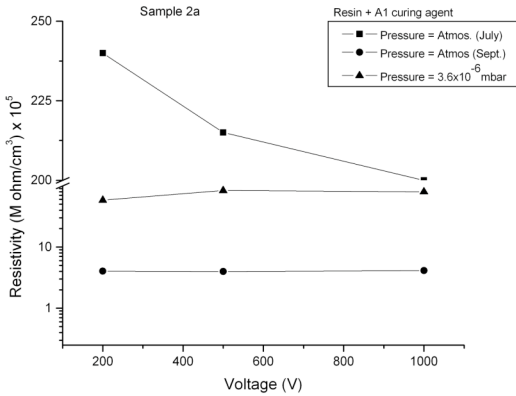


Fig. 4: Plot of resistivity vs. voltage for the sample Resin + A1+graphite added.

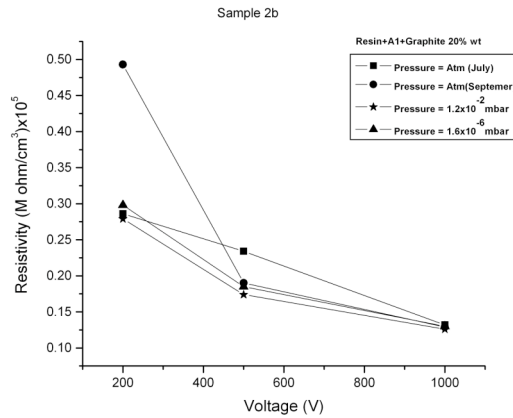


Fig. 5: Plot of resistivity vs. voltage for the sample Resin+A1 with no graphite added

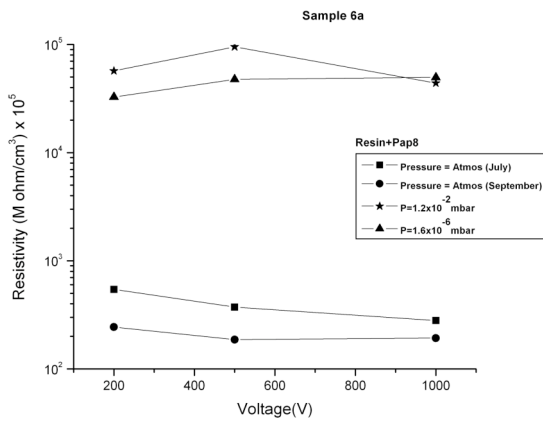


Fig. 6: Plot of resistivity vs. voltage for the sample Resin + PAP8

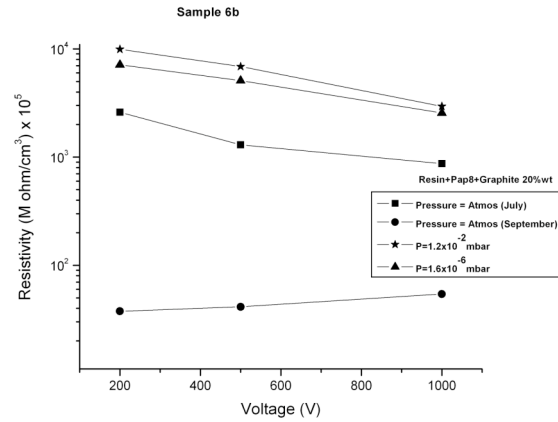


Fig. 7: Plot of resistivity vs. voltage for the sample Resin + PAP8 + graphite added.

3.1 Variation of resistivity with pressure/humidity

It is expected that when the ambient pressure is decreased while doing the resistivity measurements the humidity also gets 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 above 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.

3.2 Variation of resistivity with graphite addition

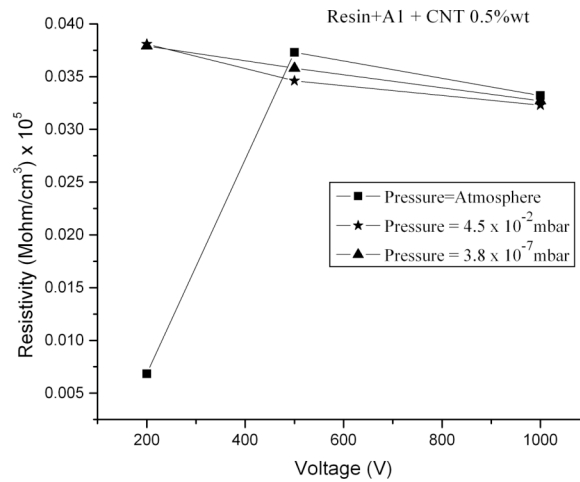


Fig. 8 : Plot of resistivity vs voltage for composites of Resin A1 with CNT's

B. Studies of Resin with CNTs

Composite preparation

The composite with CNT is prepared in this way: to start with, the CNTs are weighed and required wt% of the CNT is mixed in Isopropyl alcohol and ultrasonicated for 30 mins. Then this solution is mixed with 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 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 Fig. 1 & 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 values 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 ($\times 10^5$) /cm³ whereas when 0.5 wt% of CNT is added the resistivity reduces by a factor of 10³ to values ranging from 0.01 to 0.04 Mohms ($\times 10^5$)/cm³. Also when these values are compared with the composite of resin A1 with graphite (refer Fig. 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 shows 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 (few hundreds mega ohm cm) by 3 orders of magnitude as compared to graphite composite (few hundred thousands mega ohm cm).

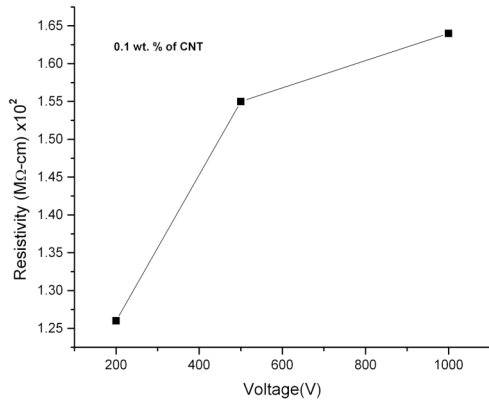


Fig. 9 : Plot of resistivity vs voltage . for 0.1wt% of Graphite.

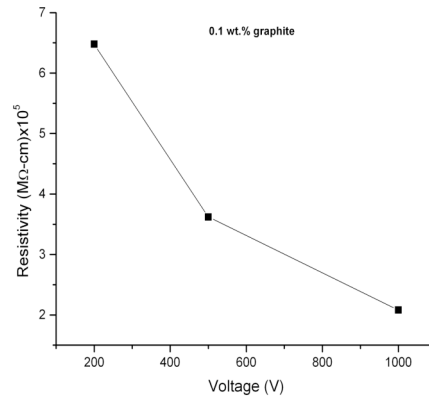


Fig. 10 :Plot of resistivity vs voltage for 0.1wt % of CNT's

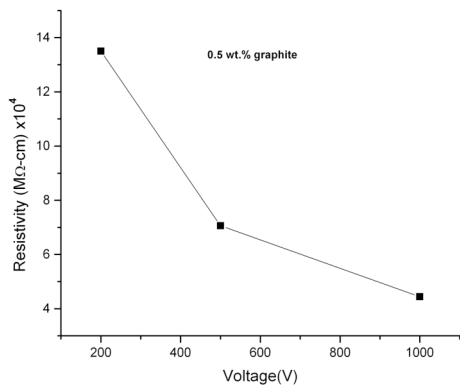


Fig. 11 : Plot of resistivity vs voltage for 0.5wt % of graphite.

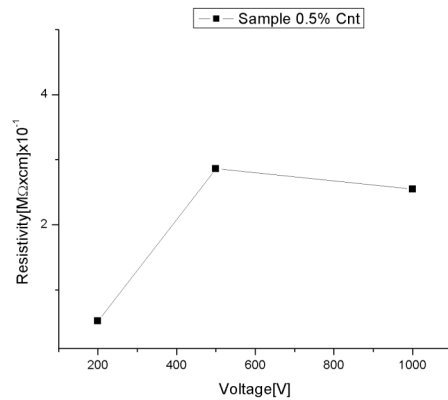


Fig. 12 : Plot of resistivity vs voltage for 0.5wt% of CNT's.

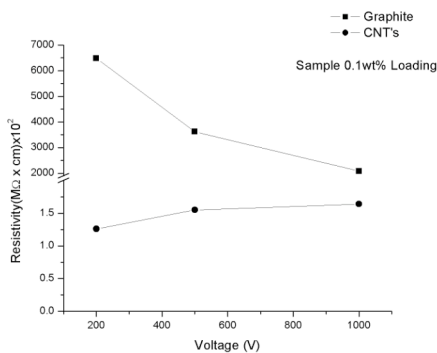


Fig.13: Comparison between graphite and 0.1 wt% of CNTs.

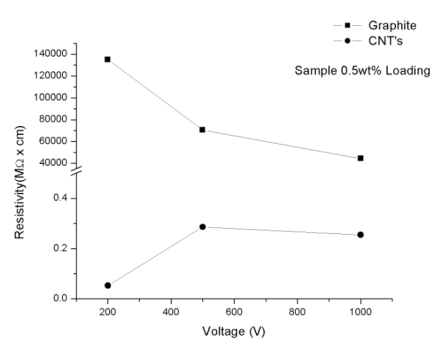


Fig.14: Comparison between graphite and 0.5wt% of CNTs.

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 6 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 3 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 M Ω (a decrease of 2 orders of magnitude). An increase of CNTs to 0.5 wt % results in the decrease of resistivity to 0.05 M Ω , i.e. again a change of two orders of magnitude. The concentration of 0.25%wt was considered only for CNT sample but not for graphite.

The plots in the Figures 13 and 14 clearly show the negative slope for graphite and a positive one for CNT based composite. That is graphite particles' based composite due to its 0-D structure is surrounded by resin and its electrical conductivity is hampered by the surrounding resin; or in other words the graphite based composite's resistivity is due to the resin which is an insulating material and so exhibits a negative slope. Whereas for CNT based composite, the 1-D type structure enhances the nanotube – nanotube contact and thus overcomes the high resistivity of the resin. This effectively results in the metallic like behaviour of the composite – in which the resistivity increases with increase in voltage.

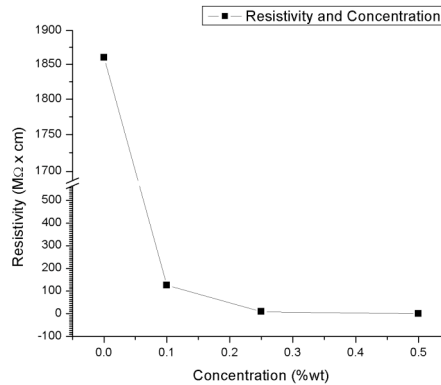


Fig 15: Plot of resistivity for composites with various CNT concentrations .

4. CONCLUSIONS AND OUTLOOK

We carried out a systematic study of the electrical properties of polymeric composite materials based on CNTs [20]. 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 behaviour in controlled humidity environments and for different temperatures.

REFERENCES

- 1] Iijima S., *Nature* (London) **354**, 56 (1991).
- 2] Ahn C H et al. 2004 Springer Handbook of Nanotechnology, Bharat Bhushan Editor.
- 3] S. Bellucci, *Phys. Stat. Sol. (c)* **2**, 34 (2005).
- 4] S. Bellucci, *Nucl. Instr. Meth. B* **234**, 57 (2005).
- 5] S. Bellucci, *Atti XVII Congresso AIV*, Ed. Compositori (2005), p. 61, ISBN 88-7794-495-1.
- 6] S. Bellucci, C. Balasubramanian, F. Mancina, M. Marchetti, M. Regi, F. Tombolini, *3rd International Conference on Experimental Mechanics*, Proc. of SPIE Vol. 5852 (2005), p. 121, ISSN 0277-786X, ISBN 0-8194-5852-X.
- 7] S. Bellucci, *CANEUS 2004-Conference on Micro-Nano-Technologies*, Nov. 2004, Monterey, CA, USA, AIAA paper 2004-6752.
- 8] S. Bellucci, C. Balasubramanian, G. Giannini, F. Mancina, M. Marchetti, M. Regi, F. Tombolini, *CANEUS 2004-Conference on Micro-Nano-Technologies*, Nov. 2004, Monterey, CA, USA, AIAA paper 2004-6709.
- 9] Bottini M., Bruckner S., Nika K., Bottini N., Bellucci S., Magrini A., Bergamaschi A., Mustelin T., *Toxicology Letters*, **160**, 121 (2006).
- 10] M. Bottini, L. Tautz, H. Huynh, E. Monosov, N. Bottini, M. I. Dawson, S. Bellucci, T. Mustelin, *Chem. Commun.* **6**, 758 (2005).
- 11] M. Bottini, C. Balasubramanian, M. I. Dawson, A. Bergamaschi, S. Bellucci, T. Mustelin, *J. Phys. Chem. B*, **110**, 831 (2006).
- 12] M. Bottini, A. Magrini, A. Di Venere, S. Bellucci, M. I. Dawson, N. Rosato, A. Bergamaschi, T. Mustelin, *Journal of Nanoscience and Nanotechnology*, **6**, 1381 (2006).
- 13] Lau K-T and Hui D 2002 “The revolutionary creation of new advanced materials - carbon nanotube composites”, *Composites: Part B* 263-277.
- 14] M.J. Biercuk et al., *Appl. Phys. Lett.*, **80**, 2767 (2002).
- 15] S. Narasimhadevara et al., “Processing of carbon nanotube epoxy composites”, Masters Thesis, University of Cincinnati.
- 16] G. Rinaldi, “Materiali per l'ingegneria”, Ed. Siderea, Roma.
- 17] P.Nicolaev,M.J. Bronikowski,R.K. Bradley ,F.Rohmund,D.T. Colbert,K.A. Smith,R.E. Smalley, *Chem.Phys.Lett.*,313 (1999)91.
- 18] I.W Chiang,B.E.Brisson,R.E. Smalley, J.L. Margrave, R.H. Hauge, *J. Phys. Chem. B*105 (2001) 1157
- 19] Florian H. Gojny, Jacek Nastalczyk, Zbigniew Roslniec,Karl Schulte, *Chem.Phys.Lett.* 370 (2003) 820-824
- 20] S. Bellucci, C. Balasubramanian, F. Micciulla, G. Rinaldi, CNT Composites for Aerospace Applications, *J. Exp. Nanoscience*, vol. 1-2 **DOI:** 10.1080/17458080701376348 First Published on: 03 July 2007