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Screening Electromagnetic Interference Effect using Nanocomposites

S. Bellucci,[*1] *C. Balasubramanian,*[1,2] *G. De Bellis,*[1,3] *F. Micciulla,*[1,4] *G. Rinaldi*[3]

Summary: We carried out a systematic study of the electrical properties of carbon nanotube-based polymeric composite materials. Our purpose was the production and characterization of a light, thin and mechanically strong new composite material able to cover electric circuits against external electromagnetic interference. As polymeric matrix we used a commercial Shell product Epon 828 epoxy resin. Two types of curing agent were used along with the resin, namely A1 and PAP8 agent: the composite was obtained using the A1 curing agent, selected for the stability of the corresponding material over a wide range of pressure values. Setting the resistivity properties of carbon nanotube-based composites against those containing micro-sized graphite particles as constituent we showed the advantages of using carbon nanotubes. The change in the resistivity values for carbon nanotubes-based composites turned out to be significant, even for small changes in the added carbon nanotubes percentage. We also plan to show the composite's behavior in controlled humidity environments and for different temperatures. These results might be important for determining the most suitable "recipe" for the realization of composite materials useful to high-fidelity circuits applications, or even in devices exposed to predominantly electromagnetic noise.

Keywords: carbon nanotubes; electromagnetic interference; nanocomposites; resistivity

Introduction

Polymer-based composites are popular in electronic applications due to their light weight, low cost, high strength and easy processing. The major part of these is used to insulate electrical circuits against atmospheric agents uniquely. Many polymeric materials are transparent to electromagnetic radiation and provide no shielding against electromagnetic interference (EMI). In electronic and communication applications, the EMI pickups by electronic components give rise to serious problems, such as noise enhancement and malfunction of electronic instruments.[1] In order to avoid such drawbacks, the developing of materials with both typical composite and EMI shielding properties is thus required.

Since their discovery in 1991 by Iijima[2] carbon nanotubes (CNTs) attracted attention of researchers worldwide for their novel mechanical, thermal and electrical properties; an extensive research in CNT/nanocomposites field thus soon started. Essentially two families of CNTs exist: single-walled nanotubes (SWNTs), made up by only one rectilinear tubular unity (a "graphite sheet" rolled into a cylinder) and multi-walled nanotubes (MWNTs), that are constituted by a series of coaxial SWNTs. Though generally both types have high aspect ratio, high tensile strength, low mass density, etc. the actual values can be different, depending on whether it is SWNT

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[1] INFN-Laboratori Nazionali di Frascati, Via E. Fermi 40, 00044 Frascati, Italy
E-mail: bellucci@lnf.infn.it

[2] Department of Environmental, Occupational and Social Medicine, University of Rome Tor Vergata, Via Montpellier 1, I-00133 Rome, Italy

[3] Department of Chemical Engineering and Materials, University of Rome "La Sapienza", Via Eudossiana 18, 00184 Roma, Italy

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

or MWNT. Besides the type of nanotube, the synthesis mode (arc discharge, laser, CVD) is an important variable since it affects the perfection of the structure and the surface reactivity. Early theoretical works and recent experiments have confirmed that introducing CNTs as structural element in composites should improve material properties, therefore promising a large variety of applications in different fields: nanoelectronic devices, reinforcing materials, bio-medicine, aerospace and so forth.[3–13] A prospective application in aerospace that is widely studied, including our work reported here, is the improvement of electrical properties of composites made of CNTs and epoxy resin.[14–16] The key factors in preparing a good composite rest on good filler dispersion, control of nanotubes-matrix bonding, and density of the composite material; the main problem is in creating a good interface between nanotubes and the polymer matrix and attaining good load transfer from the matrix to the nanotubes during loading.

Many companies have started to sell products that contain CNTs, by now. The progress in bulk synthesis and purification[17–18] make CNTs available in larger quantities at lower prices; recent advances in developing nanocomposites with CNTs gives them the function of reinforcing structural elements[18] and yields new electrical and thermal conductivity materials.

Experimental Part

CNTs were synthesized by means of a DC arc plasma system in helium atmosphere at a pressure of 600 torr. The arc is sparked between two electrodes consisting of a high purity graphite rod and a graphite block. The discharge is typically carried out at voltage of 24V and current in the range of 100 ÷ 120 A. Some amount of the evaporated carbon condenses on the cathode tip thus producing a slag-like hard deposit. The latter essentially consists of bundles of CNTs mixed with small quantity of amorphous carbon. The as-synthesised samples were characterized by means of SEM, TEM and AFM analysis (see Figure 1,2).

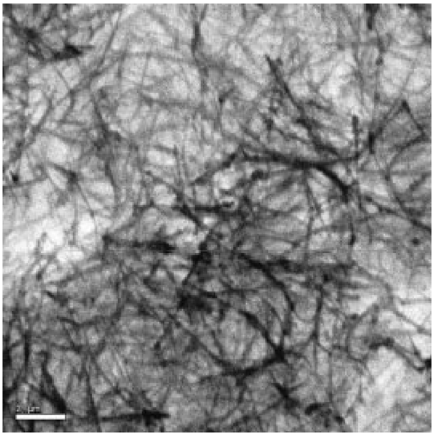

Figure 1.
SEM image of CNTs synthesized by arc discharge.

The epoxy resin used for making CNT-based composite material is a commercial Shell product Epon 828. In order to have a whole picture, analysis of the electrical properties of samples with analogous amount of graphite as filler were performed: the results have showed the advantages of using CNTs.

Two types of curing agent were used along with the resin: Polyaminoalkylolic curing agent (namely A1) and Polyaminophenolic curing agent (namely PAP8). The first one was obtained by reacting Tetraethylenepentamine with formaldehyde; the

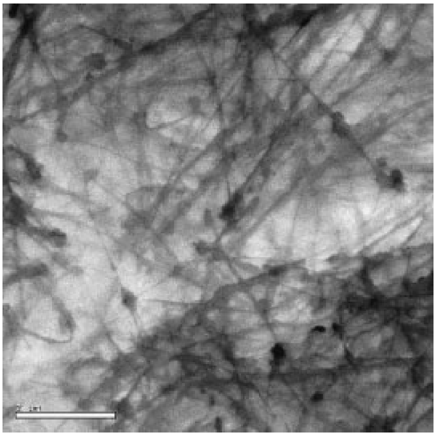

Figure 2.
SEM image of straight and long CNTs bundles.

molecular ratio (1:1) between the reagents determines on the Aminogroups of the Polyamine[6]; the second one was similarly obtained by reaction between TEPA, formaldehyde and phenol, in molecular ratio (1:1:0.8); the CH_2O was gradually added to a solution of phenol in TEPA; after thermal treatment, the CH_2O creates the condensation and the insertion of phenylic group onto the amino groups of the TEPA.[7]

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 with PAP8 agent turn out to be improved.[18] However, the stability of the mechanical properties under varying pressure conditions, as well as the corresponding resistivity behaviour, had not been yet investigated. In present work, we fill up the gap relating to the electrical transport properties.

The experiments were performed in two stages. Initially two types of resin with curing agents were used to find the one most suitable for earlier defined applications. In the second stage the selected resin was mixed along with CNTs to study the change/enhancement of the electrical properties.

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 depicted in Figure 3, having two parallel lines as the tail of the "Y", with 1 mm gap between them and a length of about 2.5 cm. Circuits were made on a PC base with silver print, and the two arms of the "Y" were connected to the picoammeter and to high voltage supply. The composite mixtures were spread on the circuit like thin films, and electrical resistance tests were carried out using Keithley 6485 Picoammeter with short circuit protection.

Current through the sample was recorded for three different applied DC voltages (200, 500 and 1000 V), resistance and resistivity were then calculated. In the first step the experiment was repeated under three different pressures, atmospheric, 10^{-2} and 10^{-6} mbar. Low pressure measurements gave indirectly the moisture's effects on the resistivity of the samples. The plots in Figure 4–7 show resistivity versus applied voltages of several samples under varying voltage and pressure conditions. In the second step data was only taken under atmospheric pressure condition, with the aim of studying the behavior of resistivity versus filler concentration.

Results and Discussion

Resin & graphite

The composite was made by manually mixing the micro-sized (~20 μm) graphite

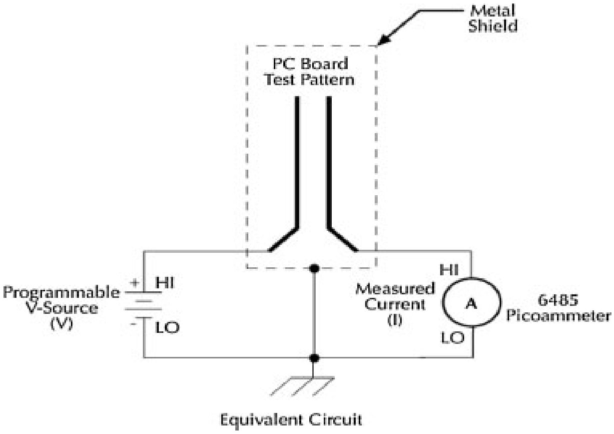

Figure 3.
Schematic of circuit used for electrical measurements.

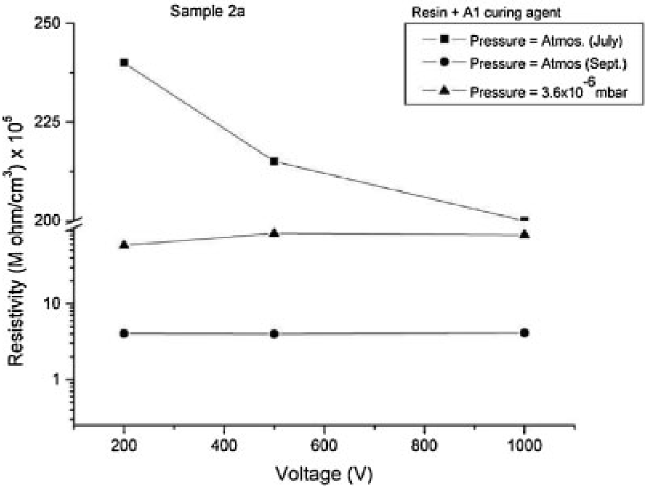

Figure 4.
Plot of resistivity vs voltage for resin/A1 sample with no graphite added.

powder in the resin and curing agent. Care was taken to avoid air bubbles in the mixture. Data below reported show that samples with A1 curing agent have resistivity a few times lower than ones with curing agent PAP8. It's worth to note that the absolute change in resistivity is less over a wide voltage range from 200 to 1000 volts for the sample with A1 curing agent (Figure 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 (July 2005 and September 2005), in order to have a rough estimate of the influence of climatic and environmental conditions on their properties. From preliminary analysis it appears that resistivity values of composites employing PAP8

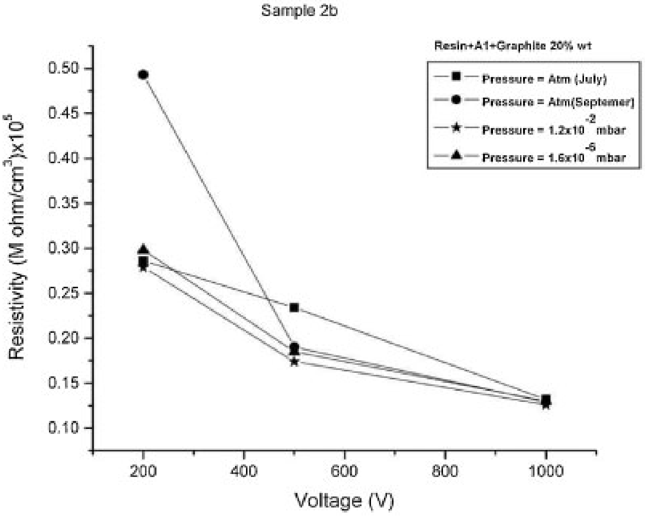

Figure 5.
Plot of resistivity vs. voltage for resin/A1 sample with graphite added.

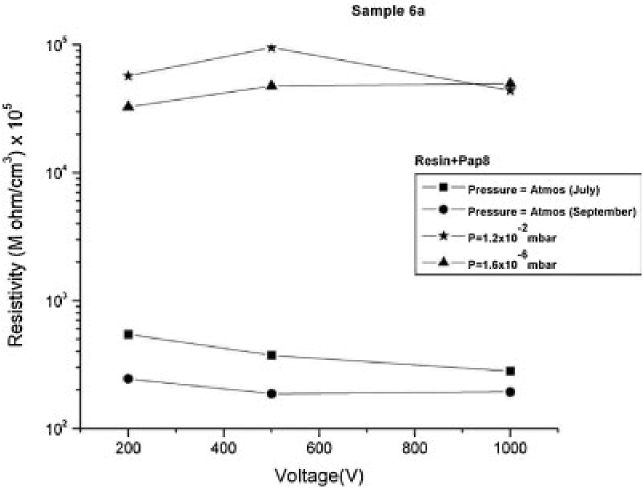

Figure 6.
Plot of resistivity vs. voltage for resin/PAP8 sample with no graphite added.

agent shows a large difference between atmospheric and low pressure conditions and its behavior wasn't affected by the addition of graphite (Figure 6,7). Composites with A1 curing agent have quite different behavior (Figure 4,5), i.e. the stability of the material increases as graphitic additions are included. This surely suggests the use of A1 curing agent for aerospace applications.

Variation of Resistivity with Pressure/Humidity
It is expected that when the ambient pressure is decreased the humidity also gets decreased, thus resulting in higher resistivity measured values. Every samples showed some variation when resistivity measurements were taken at low pressure compared to values obtained at atmospheric pressure. However, this variation gets reduced when graphite is added to the

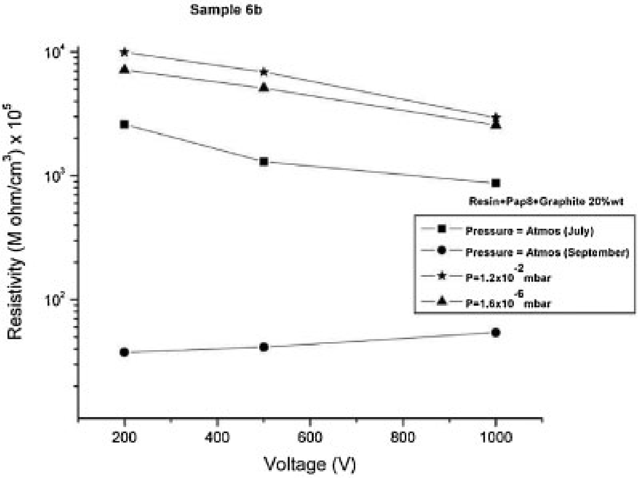

Figure 7.
Plot of resistivity vs voltage for resin/PAP8 sample with graphite added.

resin. From the above reported plots, it can be noted that for the first sample (A1 curing agent – Figure 4,5) there are few changes in resistance under different pressure conditions; instead in the second sample (PAP8 curing agent – Figure 6,7) the resistance undergoes remarkable variations under different pressure and humidity conditions. This feature might constitute a drawback to the use of PAP8 curing agent for composite devices working under standard aerospace conditions, where the pressure values can undergo substantial variations.

Variation of Resistivity with Graphite Addiction

It was observed that the resistivity change is very large, by about 3 orders of magnitude, when 20% graphite is added to resin/A1 samples, whereas for resin/PAP8 samples the increase in resistivity due graphite addiction is comparatively marginal, of about 3 to 5 times. Such results give a broad spectrum wherein we find that the resin/A1/graphite material seems to be an ideal candidate for applications in various pressure ranges as well as voltage ranges: this material has the lowest changes in the resistivity values for variations of both voltages from 200 to 1000 V and pressure from atmospheric to 10^{-6} mbar.

Resin & CNTs

Carbon nanotube-based composite is prepared by the following procedure. CNTs are weighed and required wt% of the CNT is mixed in isopropylic alcohol and ultrasonicated for 30 mins. Such a solution is then mixed with a known quantity of resin (1 gr used) and heated in 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 added (26wt%), and the mixture is applied on the surface of the electrical circuit and allowed to set.

Resistivity measurements had been performed for composites with resin/A1 in combination with graphite (Figure 5); nanocomposites were made replacing graphite with CNTs. The quantity of CNTs added was 0.5wt% of the resin mixture. Figure 8 shows the plot of resistivity vs voltage for this sample. As can be observed the resistivity values change drastically by addictions of small quantities of CNTs. The resistivity of resin/A1 samples with no graphite or CNTs (Figure 4) lies in the range of few tens of MΩ/cm^3($\times 10^5$) whereas it decreases by a factor of 10^3 to values ranging from 0.01 to 0.04 MΩ/cm^3($\times 10^5$) when 0.5 wt% of CNT is added. Also

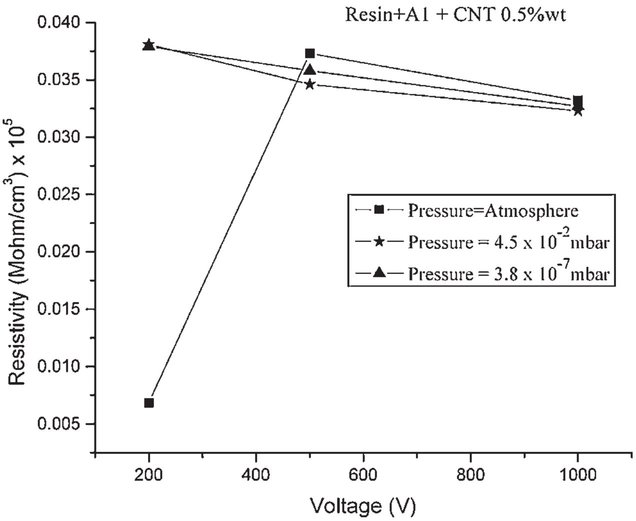

Figure 8.
Plot of resistivity vs voltage for composites of resin/A1 with CNT's.

comparing these values with those of resin/A1/graphite samples (Figure 5) one can observe that the resistivity of 20wt% graphite material is ten times higher.

Composites of resin/A1 mixed with both graphite as well as CNTs with two compositions (0.1 and 0.5 wt %) were separately studied: measurements carried out under atmospheric conditions proved that the resistivity decreases for CNT composite (10^2 MΩ×cm) by 3 orders of magnitude as compared to graphite composite (10^5 MΩ×cm).

Figure 9,10 show a very marked difference in the resistivity behavior between the addition of CNTs and graphite, up to 6 orders of magnitude. 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 the same wt% results in a resistivity lowering of 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 9, the resistivity decreases drastically from thousands to hundred MΩ×cm with even a small (0.1 wt%) addition of CNTs. Further increase (0.25 wt%) in CNTs concentration results in the resistivity value of 9.19 MΩ ×cm (a decrease of 2 orders of magnitude). An increase of CNTs to 0.5 wt% yields a decrease in resistivity values, down to 0.05 MΩ×cm, i.e. again a 2 orders of magnitude variation (Figure 11). The concentration of 0.25 wt% was considered only for CNTs but not for graphite samples.

Plots in Figure 9–11 also clearly show a negative slope for graphite and a positive one for CNT-based composite. That is explained by the following consideration: due to its 0-D structure graphite particles are enclosed in the matrix, so the material 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, thus exhibiting a negative slope. The other way round, for CNT-based composite, 1-D type structure enhances the tube-tube contact, thus overcoming the high resistivity of the resin: this effectively results in a metallic-like behavior of the composite, in which the resistivity increases at higher voltage.

Conclusions and Outlook

In this work we characterized polymeric CNTs-based composite materials, from the point of view of their electrical properties.

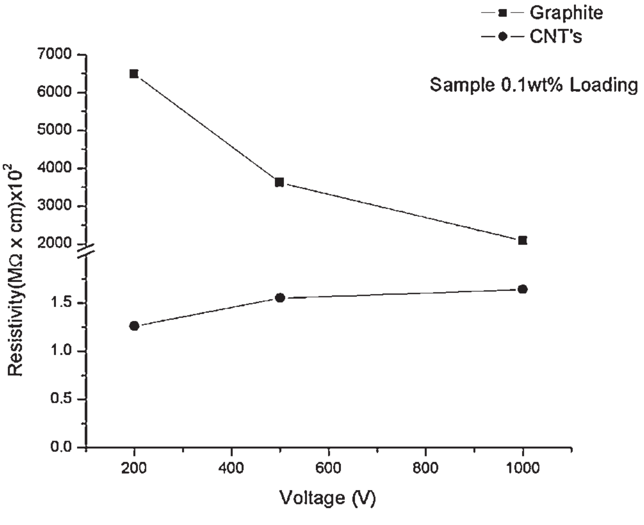

Figure 9.
Comparison between graphite/CNTs 0.1 wt% composites.

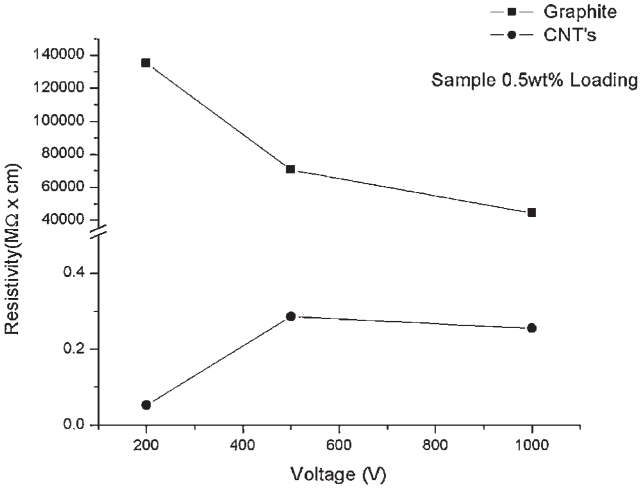

Figure 10.
Comparison between graphite/CNTs 0.5 wt% composites.

We realized the composite by making use of the A1 curing agent, selected for the stability of the corresponding material 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 micro-sized graphite particles as 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 CNTs 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

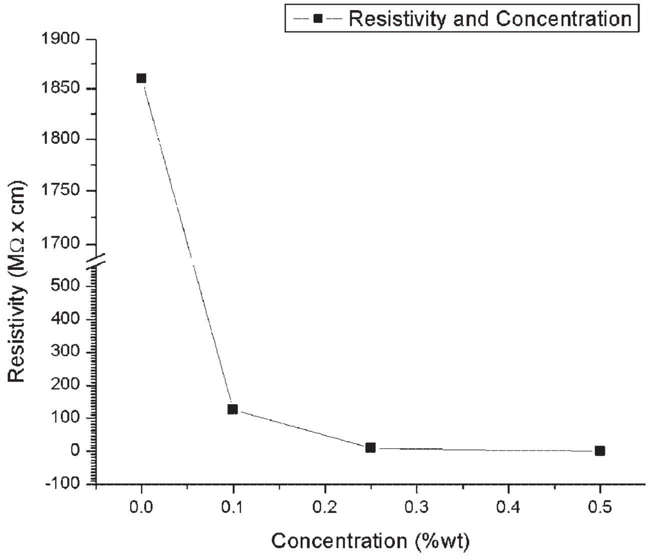

Figure 11.
Plot of resistivity for composites at various CNTs concentrations.

predominantly electromagnetic noise. In the future it is planned to study CNT-based composites with PAP8 curing agent. Also we plan to study the composite's behavior in controlled humidity environments and for different temperatures.

[1] W. S. Jou, H. Z. Cheng, C. F. Hsu, *J. Alloys and Compounds* **2006**, *35*, 462.
[2] S. Iijima, *Nature* (London) **1991**, *354*, 56.
[3] C. H. Ahn, et al., *Springer Handbook of Nanotechnology* (**2004**, Bharat Bhushan Editor).
[4] S. Bellucci, *Phys. Stat. Sol. (c)* **2005**, *2*, 34.
[5] S. Bellucci, *Nucl. Instr. Meth. B* **2005**, *234*, 57.
[6] G. Rinaldi, D. Rossi, *Polymer International* **1993**, *31*, 227–233.
[7] G. Rinaldi, D. Rossi, *Polymer International* **1993**, *31*, 339–345.
[8] M. Bottini, S. Bruckner, K. Nika, N. Bottini, S. Bellucci, A. Magrini, A. Bergamaschi, T. Mustelin, *Toxicology Letters*, **2006**, *160*, 121.
[9] M. Bottini, L. Tautz, H. Huynh, E. Monosov, N. Bottini, M. I. Dawson, S. Bellucci, T. Mustelin, *Chem. Commun.* **2005**, *6*, 758.
[10] M. Bottini, C. Balasubramanian, M. I. Dawson, A. Bergamaschi, S. Bellucci, T. Mustelin, *J. Phys. Chem. B* **2006**, *110*, 831.
[11] M. Bottini, A. Magrini, A. Di Venere, S. Bellucci, M. I. Dawson, N. Rosato, A. Bergamaschi, T. Mustelin, *Journal of Nanoscience and Nanotechnology*, **2006**, *6*, 1381.
[12] K. T. Lau, D. Hui, *"The revolutionary creation of new advanced materials - carbon nanotube composites"*, Composites: Part B **2002**, 263–277.
[13] M. J. Biercuk, et al., *Appl. Phys. Lett.* **2002**, *80*, 2767.
[14] S. Narasimhadevara, et al., *"Processing of carbon nanotube epoxy composites"*, Master Thesis, University of Cincinnati.
[15] P. Nicolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith, R. E. Smalley, *Chem. Phys. Lett.*, **1999**, *313*, 91.
[16] I. W. Chiang, B. E. Brison, R. E. Smalley, J. L. Margrave, R. H. Hauge, *J. Phys. Chem.* **2001**, *B105*, 1157.
[17] F. H. Gojny, J. Nastalczyk, Z. Roslniec, K. Schulte, *Chem. Phys. Lett.* **2003**, *370*, 820–824.
[18] G. Rinaldi, "*Materiali per l'ingegneria*", Eds., Siderea, Roma.