Chapter 10
Electrical Properties and Electromagnetic Shielding Effectiveness of Carbon Based Epoxy Nanocomposites

S. Bellucci, F. Micciulla, I. Sacco, L. Coderoni, and G. Rinaldi

Abstract Designing and engineering of new kind of electromagnetic interference (EMI) shielding for electronic systems and devices is a pressing need due to the wide range of using of several electronic devices. Electromagnetic (EM) shields have to guarantee high performances and right operation of electronic systems and to prevent the electronic pollution. Electronic systems are getting faster, smaller high frequency of clock and high energy in small dimension, so they generate, as effect, thermal drawback, and mechanical, as well. They are used in several electronic equipments and it is easy to find them in common life: communications, computations, automations, biomedical, military, space and other purposes. Nanocomposites based on Carbon Nanotubes (CNTs) give powerful and multifunctional materials with very high performances: mechanical, thermal, electrical properties. It is possible to achieve lighter and cheaper EM shields than the actual ones. Examples of new materials that can come from nanotubes are many: high conductors that are multifunctional (electrical and structural), highly anisotropic insulators and high-strength, porous ceramics and others.

Keywords Carbon nanotubes • Nanocomposites • Shielding material • Toxicology

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10.1 Introduction

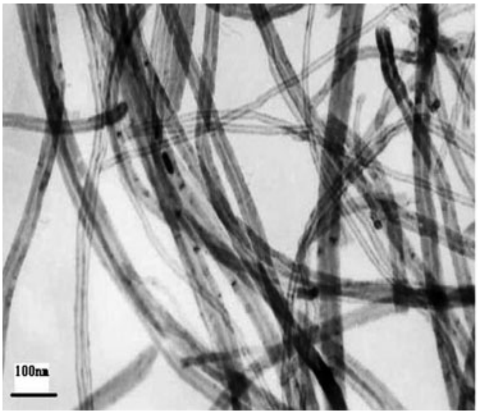
The studies of nanotubes have advanced very fast in a relatively short time since its initial discovery in 1991 by Iijima [1]. Carbon nanotubes are an allotropic structure of Carbon. In the solid phase it can exist in three allotropic forms: graphite, diamond and buckminsterfullerene. Essentially two families of carbon nanotubes exist: firstly, SWNT or (single wall nanotubes), that are constituted by only one rectilinear tubular unity and, secondly, MWNT (multi wall nanotubes), that are constituted by a series of coaxial SWNT. Though generally 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 nanotubes, the control of the bonding between nanotubes and matrix and the density of the composite material [2].

Here we want to study a nanostructured polymeric coating with multifunctional behavior as electromagnetic shielding. The nanocomposites, obtained by modification of polymeric resins with nanometer size filler, nowadays represent a new class of materials to which the scientific community and the industrial world are dedicating particular attention. In brief, the fascinating characteristics of these nanostructured materials stem from the possibility to suitably combine customary polymer materials with nanometer size fillers, thus, creating new materials with outstanding properties [3].

The materials produced are nanostructured composites, using a polymeric matrix (in this case it is a thermosetting resin, precisely an epoxy resin EPIKOTE 828) loaded with conductive nanofillers, such as carbon nanotubes (CNTs) and an amorphous carbon structure as Carbon Black that is a typical used material for electromagnetic shielding. Different types of nanotubes have been employed, both commercial SWNTs and MWNTs, as well as nanotubes produced at the National Institute of Nuclear Physics-National Frascati National Laboratories (INFN-LNF), where each type of nanofillers is present at different concentrations, i.e. 0.1–0.25% and 0.5% wt (percentage valued on the resin weight). The nanocomposites characteristics obtained in this way have been compared with those of the same resin loaded with the carbon black – the filler generally used for conductive coatings for shielding. Therefore, 12 mixtures (resin + filler) have been produced; in fact, three different concentrations of filler and four types of charges have been used.

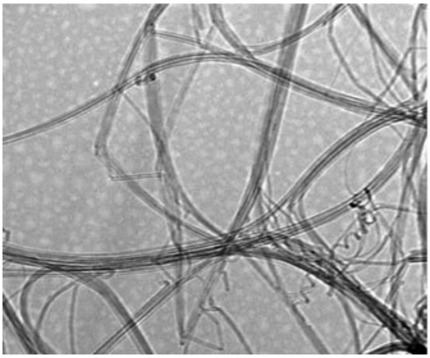
10.2 Materials

The matrix used in this work is a modified epoxy resin DGEBA, namely a commercial product of Hexion group, called Epikote 828 (viscosity 100 $\div$ 150 Pa s at 25°C and specific gravity 1.16 g/cm^3). The resin is liquid at medium-low viscosity at room



Apparent density	*2,1 g/cm* ^{3}
Length	*0,5÷200 μm*
Diameter Type 2	*20÷40 nm*
Method of synthesis	*CVD*
Purity	*>95wt%*
Surface area (BET)	*40÷600 m* ^{2} */g*

Fig. 10.1 TEM micrography of multiwalled nanotubes



Apparent density	*0,3g/cm*^{3} *a 25°C*
Length	*10÷50μm*
Diameter	*1÷2nm*
Method of synthesis	*CVD*
Composition	*Purity>95wt% with SWNTs>90wt%*
Surface area (BET)	*400 m*^{2} */g*

Fig. 10.2 TEM micrography of singlewalled

temperature and it is hardened by the curing reaction with polyamines. The curing agent, called A1 (specific gravity 1.02 g/cm^3 and viscosity 0.21 Pa*s a 25°C) is obtained from a common TEPA (tetraethylenepentamine) put in reaction with formaldehyde (CH_2O) [4]. In earlier papers, our group investigated the influence of two important parameters affecting the electrical performance of nanocomposites, i.e. climatic conditions (both environmental pressure and humidity), as well as the comparison of two different curing agents [5, 6], showing that the results in terms of electrical conductivity of the nanostructured composites are more stable and reproducible when the A1 hardener is selected.

As a filler, in this study, CNTs that have been employed are:

- Commercial Mwnt produced by Heji, the characteristics of which we report below, along with a TEM micrograph (Fig. 10.1):
- SWNT produced by Heji with the characteristics given in the table and the morphology shown in the TEM micrograph below (Fig. 10.2):
- CNTs produced by INFN at Frascati, are shown in Fig. 10.3. They have been obtained by the method of arc discharge, based on the electric arc primer in the

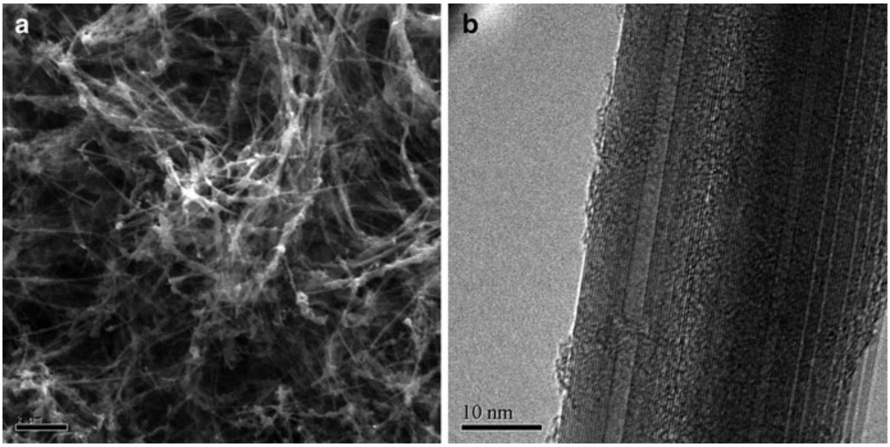


Fig. 10.3 (**a**) Detail at 5000× with multiwalled nanotubes produced at Frascati, that forming a tangled network; (**b**) bundle of multi-wall nanotube produced at Frascati with external diameter of about 15 nm and internal one of about 5 nm

presence of an inert gas (helium gas was used). The equipment used for the synthesis by arc discharge was described earlier [7, 8]. Such a kind of Cnt, owing to its chemical purity and low defectivity.

- Carbon black is a particulate form of industrial carbon which has a microstructure "nearly-graphitic", but unlike the graphite, the layers' orientation is random [9, 10]. Carbon black used here is Printex 90 (mean particle diameter 14 nm, BET Surface Area 300 m^2/g, volatile matter at 950°C(%) ~1), generously provided to our group by Evonik Degussa GmbH.

10.3 Experiment

The mixture of resin containing nanotubes (after solvent's evaporation) was mixed with the curing agent; then it was poured into brass mould in which the mixture would be dripped. When the resin was hard it was possible to obtain a bar (size 10 mm × 10 mm × 80 mm); after that the bar was divided into "cubes" (size 10 mm × 10 mm × 10 mm) on which the electrical measurements were carried out. We measured the current intensity, in order to obtain the value of the resistance and, consequently, that of the resistivity (or conductivity).

The electrical measurements have been realized using a Keithley 6485 picoamperometer. We used the "two-probe method" according to the specifics ASTM D257 and ASTM D4496-04. Using a power card in DC, we performed tests on each "cube" at different voltages: 50, 100, 200, 300, 500, 750, and 1,000 V. The current intensity was measured at four time intervals: 2, 10, 60, and 120 s. Each type of mixture (i.e. the mixture containing carbon black, the one with Mwnt,

Table 10.1 Resistivity values concerning the voltage of 1,000 V at the time of 120s

Resistivity values ρ				
Matrix (Epon + A1)				
Resistivity ρ			1,294E+05 MΩ × cm	
Matrix + carbon black	0.1%	0.25%	0.5%	wt
Resistivity ρ	4,45E+04	2,85E+04	1,86E+04	MΩ × cm
Matrix + CNTs	0.1%	0.25%	0.5%	wt
Resistivity ρ	1,26E+04	7,28E+03	5,47E+03	MΩ × cm
Matrix + Mwnt	0.1%	0.25%	0.5%	wt
Resistivity ρ	2,18E+04	1,35E+04	4,76E+03	MΩ × cm
Matrix + Swnt	0.1%	0.25%	0.5%	wt
Resistivity ρ	1,69E+04	1,27E+04	12,80E+00	MΩ × cm

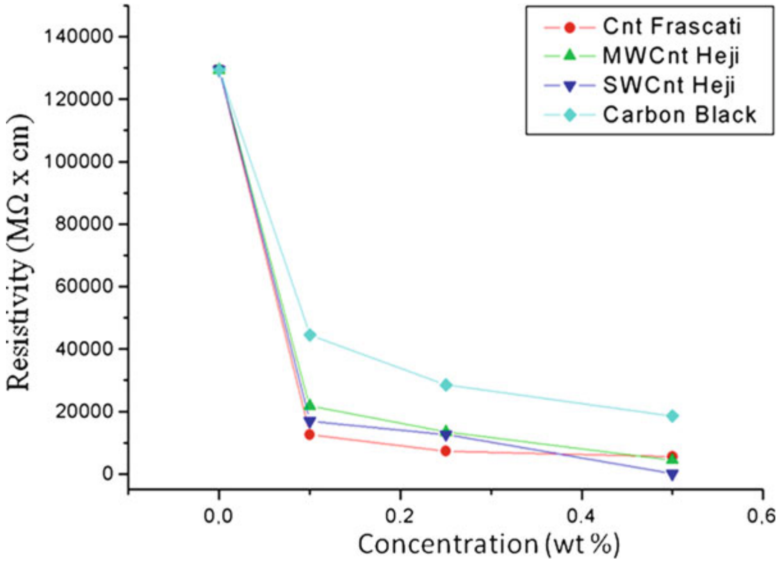


Fig. 10.4 Plot of resistivity vs. concentration for different fillers

Swnt and with INFN-Cnts) was loaded at different concentrations of fillers, such as 0.1%, 0.25% and 0.5% wt (estimated percentage on the weight of the resin). From each mixture we obtained 12 "cubes", and each one was tested. The obtained values are shown in the following Table 10.1.

It shows that all types of Carbon nanotubes (both commercial ones and those produced at INFN) have higher conductivity than carbon black, which is generally used as a filler in conductive coatings for shielding. At equal percentage, the INFN CNTs based composites have lower resistivity than the ones based on Commercial ones. That is also true for SWNT until 0.25% wt of CNTs loaded, going below resistivity of SWNT goes down strongly relate to the other types of CNTs. Figure 10.4 illustrates the concentration versus Voltage. It is possible to see how the SWNT shows the best performance at 0.50%wt. Until that value, their behavior is close to value of INFN- CNTs. Increasing the amount of nanotubes, the mechanism of percolation is activated, in which an interconnected network is formed (so we are beyond the percolation threshold), in order to create a preferential way for the current passage inside the loaded matrix [11].

Interestingly, one can find in literature the evidence for a similarly strong dependence of the resistivity on several parameters, including the presence of metallic impurities and defects. At much higher concentrations than we have considered, i.e. for percolation threshold above 12%, and using a polystyrene matrix, rather than epoxy resins, an increased composite conductivity corresponding to a higher defect density in the carbon nanofiller is observed [12, 13].

Notice that recently we have also carried out a comparative study in various microwave frequency ranges, i.e. in X-band (8–12 GHz), Ka-band (26–37 GHz) and W-band (78–118 GHz), of the electromagnetic shielding effectiveness provided by different forms of nanocarbon dispersed (Commercial CNTs and Carbon Black) in epoxy resin in low concentration (0.5 wt%) [13].

There, we have found that shielding effectiveness of the investigated composites in microwaves is determined mostly by the conductivity of nanocarbon inclusions. Consequently, utilizing well purified defect-free or chemically modified CNTs we can improve drastically the shielding effectiveness of such a composite, without changing the volume fraction of nanocarbon inclusions. The analysis indicates that polymer composites with SWNT could be used as an effective and lightweight EMI shielding material.

The unusual mechanical properties of CNTs render them an ideal class of reinforcement for composite materials. The research along this direction has been growing with both encouraging and discouraging results [14–22]. In order to estimate the mechanical behavior of nanocomposites loaded with CNTs, both the stress and the Young modulus have been measured following the ASTM D638 standard. Different types of CNTs have been used, including commercial ones (both SWCNTs and MWCNTs from both Heji and Aldrich company), as well as CNTs made by ourselves at LNF – INFN. Figure 10.5 shows the percentage variations of the stress (σ) and the Young modulus (E) in loaded nanocomposites, compared to unloaded ones.

The measurements have been obtained averaging over 4–5 samples for each experimental point [23]. The best results have been achieved loading the composite with CNTs – LNF ($\sigma = 34.77\%$; E = 22,45%) and the worst ones have been obtained using MWCNT from Heji ($\sigma = -4{,}64\%$; E = 1,40%). A different method of synthesis has been used to make CNTs (Commercial CNTs made by CVD; CNTs LNF – INFN made by arc discharge) and it determines a different morphology of the nanostructures (many defects). The CNTs made by arc discharge present low defects and their structure is very close to the ideal structure of CNTs. Mechanical properties are largely influenced by the dispersion uniformity rather than by chemical functionalization. In fact, the poor dispersion creates agglomerates inside the matrix and it reduces the mechanical behavior of the composite. The results show the existence of Rheological threshold regions for a uniform dispersion, changing upon the type and chemical reactivity of CNTs. The

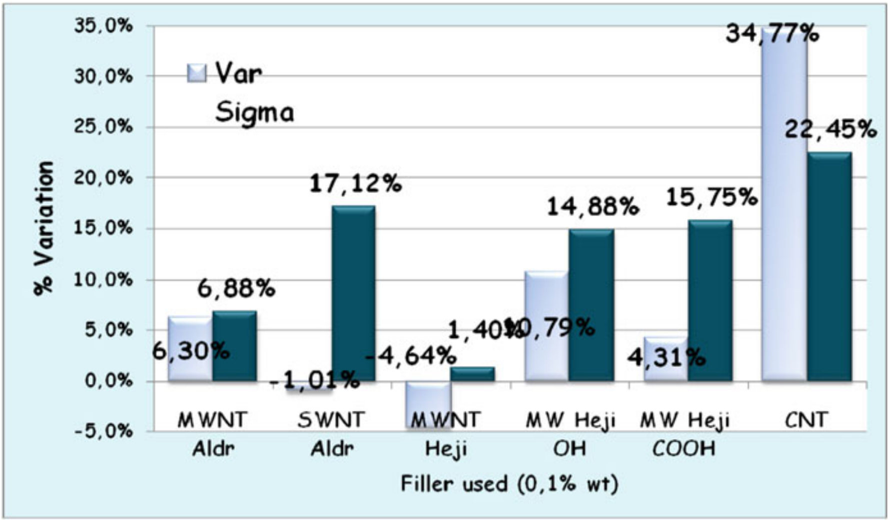


Fig. 10.5 σ and E% variations with respect to the resin

dispersion depends on this threshold, on the mixing method, as well as on the type of CNTs (e.g. functionalized and nonfunctionalized).

It is remarkable that there is such a strong influence of the synthesis method used: thanks to the better dispersion and lower concentration of topological defects, CNTs synthesized by the arc discharge method show remarkable improvements of both elastic modulus and σ, as compared with the unfilled resin.

Notice that in our present investigation the CNT based composite materials have been prepared at a relatively low ratio. The question is to carry out the same kind of investigation on higher ratios, in order to determine the percolation limit for those one-dimensional composites.

We relate to the studies on EM shielding and mechanical properties with the aim to contribute to the important toxicological screening strategy necessary to identify the potential toxic effect of CNTs. Thus, we aim to prevent risk exposure and to develop safe biomedical applications. The results of our comparative study of toxicological effects and physico-chemical properties of CNTs reveal that shape, size, chemical contaminants and concentration are all parameters that influence CNT biological effects [24, 25]. Interactions between different types of CNTs and T lymphocytic cells Jurkat have been studied first. CNTs have been shown to induce apoptosis on T lymphocytic cells Jurkat. SWNTs, the most effective, have been the smallest nanomaterials tested. This result supports the finding that SWNTs are more toxic than MWNTs [26]. Moreover, it points out the importance of surface area and small dimensions in cellular toxicity. As expected, CB has proved to be the least effective. Thus, it is the material structure in CNTs that strongly induces alteration in cell behavior. However, we have to keep in mind that SWCNTs and MWNTs contain metal contaminants. Catalytic metals like iron, molybdenum and cobalt may be toxic at high concentration [27, 28], and may increase the real toxic effect of CNT. The comparison of the effects of the sample of CNTs with (MWNTs and SWNTs) or without (ADP-CNT and CB) catalytic metals has helped us to evaluate the toxic effects of these new materials versus the contaminants. It is important to underline how the cytotoxicity of carbon nanotubes increases significantly when carbonyl (CdO), carboxyl (COOH), and/or hydroxyl (OH) groups are present on their surface [29]. Carbon nanotubes can induce cell death, either after contact with cell membranes, or after their internalization Thus, the main message from this study is that CNT, independently of the type of preparation and presence of contaminants, deeply affect cell behavior.

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