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Analysis of Microwave Absorbing Properties of Epoxy MWCNT Composites

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Abstract—In the ongoing search for new materials for microwave absorption applications, Carbon Nanotubes deserve a special consideration due to their outstanding properties. In this paper, microwave absorbing properties of epoxy resin based composites containing commercial Multi Walled Carbon Nanotubes used as fillers have been analyzed. The complex permittivity of the composites was measured in a wide frequency band (3–18 GHz). The absorbing properties of a single-layer absorber backed by a metallic plate considering several concentration of CNTs was simulated taking into account the measured permittivity.

1. INTRODUCTION

There is an increasing demand for lightweight and Radar Absorbing Material (RAM) in both commercial and military applications. Carbon Nano Tubes (CNTs) and graphene have already been investigated for microwave absorption applications [1–5] due to their great thermal stability, reluctance toward chemical agents and excellent mechanical and electrical properties. CNTs are much more attractive for the preparation of RAMs with respect to graphene and graphene oxide [6] since they have a lower cost of production and are less troublesome to disperse in host polymers. Even at low filler contents, they can improve mechanical and electrical performances of the host polymer [7].

Moreover, CNTs have aspect ratios (i.e., length vs diameter ratio) that can exceed 1000. These special properties make CNTs excellent candidates for high strength and electrically conductive polymer nano-composite applications.

Hence, the analysis of electromagnetic properties of composites based on different polymers matrix and CNTs is a very popular topic in material sciences. Recently, CNTs with epoxy resin have also been addressed (see for example [8–13]).

In this paper, the properties of a commercial epoxy resin filled with different concentrations of Multi Walled Carbon Nano Tubes (MWCNTs) were analysed. Starting from the samples realization, the complex permittivity was measured in a wide frequency range (3–18 GHz) with a commercial sensor. The microwave absorbing properties of a one-layer absorber backed by a metallic plate were then investigated by means of numerical simulations considering a plane wave incidence on the dielectric stratification and a transmission line approach [14].

In Section 2, the sample preparation, morphological analysis and complex permittivity determination are addressed. In Section 3, the simulation results of the reflection coefficient of one-layer absorber for normal and oblique incidence are discussed.

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2. CNT COMPOSITES CHARACTERISTICS

The samples were prepared using a commercial epoxy resin: Epilox, T 19-36/700. It is a modified, low viscosity epoxy resin with a reduced crystallization tendency. It was chosen because it is thermoset and can withstand high temperatures. Commercial MWCNTs were used (Nanothinx, diameter 6–10 nm, length > 10 μm, purity > 90%) and samples with different MWCNT concentrations (0.5, 1, 3, 5wt.%) were prepared. Weight percentages greater than 7 wt.% were not considered because in that case it is very difficult to realize homogeneous samples and it is not cost effective.

2.1. Morphological Analysis

MWCNTs used in this work were analysed by Raman spectroscopy [15]. The Raman spectra were obtained using a Renishaw micro-Raman system with the 514 nm green laser and a Charged-Coupled Device (CCD) as a detector. The microscope used a 50X objective lens to focus the laser beam on each sample surface, and the size of the focused laser spot on the sample was 2 μm. All measurements of the MWCNTs powder were performed at room temperature (see Fig. 1). In the Raman spectrum of MWCNTs two wavenumber ranges are most relevant; the first feature, located in the range of 1000–1700 cm^{-1}, is related to the G and D bands of carbon. They are the peaks used to estimate defects (D) and graphitization grade (G). The second spectrum range (2200–3500 cm^{-1}) is the second-order Raman spectrum. In these features we can identify the overtone of the D vibration mode, G' or 2D band, and the second order of the D and G peak. Field Emission Scanning Electron Microscopy (FESEM Zeiss Supra-40) images of cryo fractured samples are shown in Fig. 2. They show the outer CNT structures

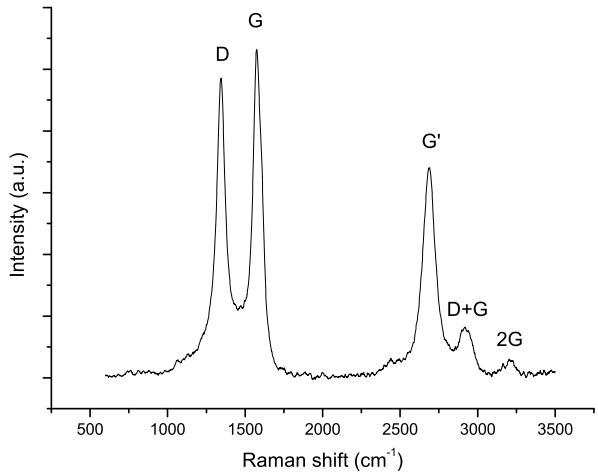
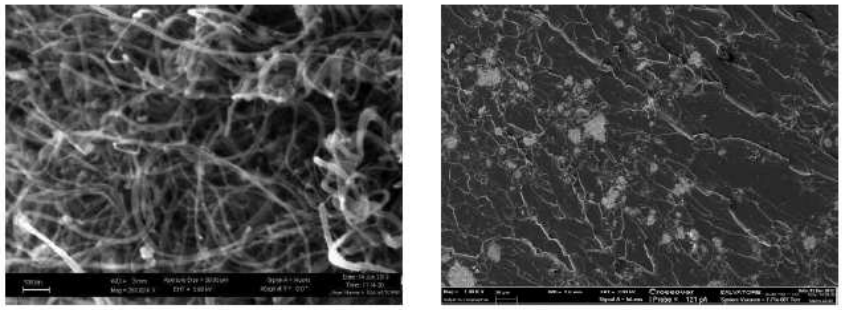


Figure 1. Raman spectrum of MWCNTs.



(a) (b)

Figure 2. (a) FESEM analysis on bundle of MWCNTs as it is. (b) Nanocomposite at 3% of MWCNTs.

and the dispersion degree of the filler inside the polymeric matrix. CNTs, because of Van der Waals forces, are usually bundled (see Fig. 2(a)). Most bundles unbind when a strong shear force is applied.

2.2. Sample Preparation

The MWCNTs were dispersed in Epilox in different concentrations using the following procedure [16]:

- MWCNTs and Epilox T 19-36/700 quantities were weighted with a digital balance and preliminary mixed together.
- The mixture was dispersed using an UltraTurrax mixer for 10 minutes in order to create a well dispersed solution.
- A curing agent (Epilox Hardner H 10-31: liquid, colourless, modified cycloaliphatic polyamine apoxide adduct) was added to the mixture in 6 : 10 ratio with respect to epilox and was stirred mechanically for 10 minutes.
- The nanocomposite was sonicated for 30 minutes in order to help the unbind of MWCNT bundles.
- The mixture was slowly poured into cylindrical molds with a diameter of 20 mm.
- The nanocomposite was degassed in a vacuum chamber for 20 minutes.
- The final product was dried in an oven for 3 hours at 70° C.

An example of pure epilox and epilox with MWCNT samples is shown in Fig. 3(b). The samples shape and thickness was defined in order to measure their dielectric properties as explained in Section 2.3.

(a) (b)

Figure 3. (a) Measurement setup. Agilent sensor (85070D) and Network Analyzer (E8361A). (b) Samples compared with a one euro coin.

2.3. Complex Permittivity Measurements

The complex permittivity of pure Epoxy resin filled with MWCNTs was measured in the frequency range 3–18 GHz using a commercial capacitive sensor (Agilent 85070D) and a Network Analyzer (E8361A, see Fig. 3(a)). A standard calibration short/air/water was performed before each measurement. This measurement system was chosen because it allows a wide-band characterization and can be used on samples of small dimensions. Free-space measurements, for example, require at least 150×150 mm samples, whereas the waveguide method needs an accurately manufactured sample to be inserted in the waveguide and many waveguides of different dimensions are necessary to cover a wide frequency range [17]. In our study, in order to satisfy the requirements of the measurement setup, cylinders of 20 mm in diameter and around 15 mm in thickness were used. Agilent 85070D dielectric probe kit is particularly suited for measurements on liquids with a typical accuracy on the dielectric constant of $\pm 5\%$ and of ± 0.05 on $\tan\delta$. It can be used also on solids, as written in the manual of the instruments, provided that samples have a smooth, flat surface with gap-free contact at the probe face. Several measurements were done on reference solids with known characteristics (plexiglass, crystal, gold) in order to check the feasibility of the measurements on solid samples.

Various samples for each type were made to check the repeatability of our fabrication procedure. Particular attention was paid to the realization of a smooth and flat surface in order to ensure a good contact with the probe.

On each sample, the measurement was done several times with different sensor positions in order to check the homogeneity of the sample. In Fig. 4 results for composites having different MWCNT concentrations (0.5, 1, 3, 5 wt%) are shown and compared with pure Epilox resin. As expected, both the real and imaginary part of the permittivity increase with the increase of the MWCNT concentrations [18].

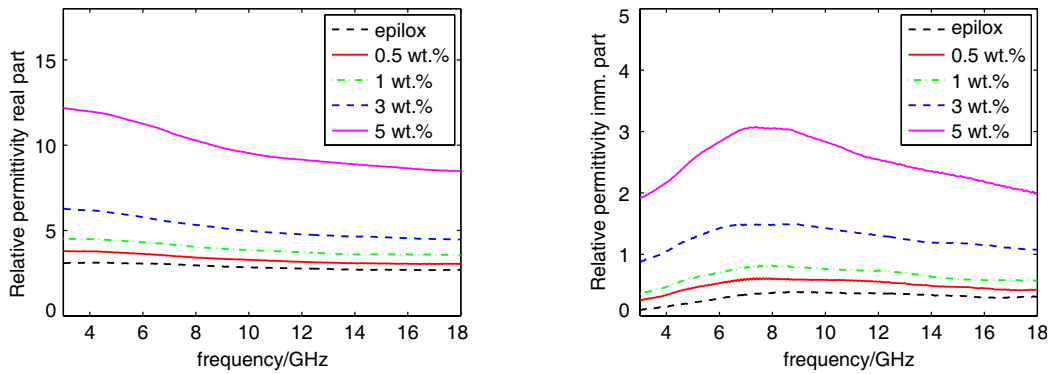


Figure 4. Complex permittivity of the pure Epoxy resin and with different MWCNT concentrations.

3. NUMERICAL RESULTS

Starting from the knowledge of the permittivity, the absorbing properties of polymers with different contents of MWCNTs were analysed considering one-layer of given thickness (d), backed by a metallic plate (see Fig. 5). Considering an incident plane wave with parallel (TM) and perpendicular (TE) polarization, the one-layer absorber can be modelled as a transmission line of given modal impedance (see Fig. 6):

$$Z_{1,2}^{TE} = \frac{\omega\mu}{k_{z1,z2}} \tag{1}$$

$$Z_{1,2}^{TM} = \frac{k_{z1,z2}}{\omega\epsilon} \tag{2}$$

where $\omega = 2\pi f$, μ is the magnetic permeability and the longitudinal (k_z) propagation constant of the plane wave in medium 1 and 2 are defined as:

$$\begin{aligned} k_{z1} &= k_1 \cos\theta \\ k_{z2} &= \sqrt{k_2^2 - k_{x1}^2} = k_0\sqrt{\epsilon_{r2} - \sin^2\theta_i} \end{aligned} \tag{3}$$

being $k_{x1} = k_{x2} = k_1 \sin\theta$. For dielectric absorbers the permeability is unity.

Modelling the transmission line of length d with the 2-port transmission matrix A defined as:

$$\begin{aligned} a_1 &= A_{11}b_2 + A_{12}a_2 \\ b_1 &= A_{21}b_2 + A_{22}a_2 \end{aligned} \tag{4}$$

where a_1, a_2, b_1, b_2 are incident (a_i) and reflected (b_i) power waves at port 1 and 2, the reflection coefficient at the input port can be written as:

$$\Gamma_i = \frac{A_{21} - A_{22}}{A_{11} - A_{21}} \tag{5}$$

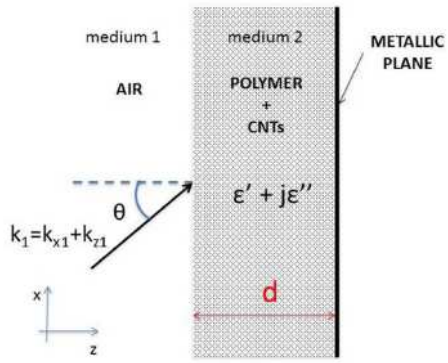


Figure 5. One-layer absorber backed by a metallic plate.

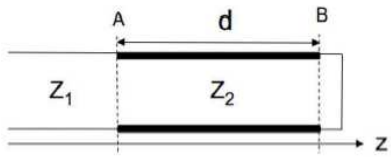


Figure 6. The transmission line model of the one-layer absorber.

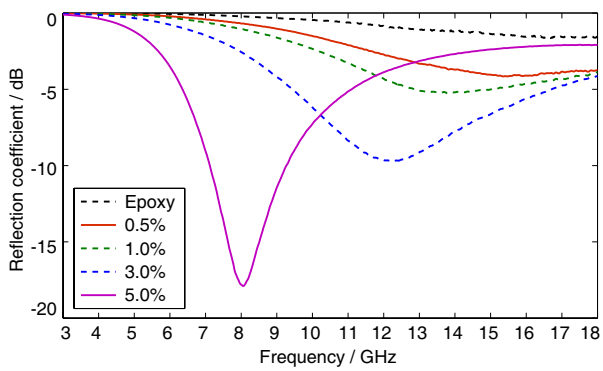


Figure 7. Reflection coefficient, thickness $d = 3\,\text{mm}$, normal incidence for different MWCNT concentrations.

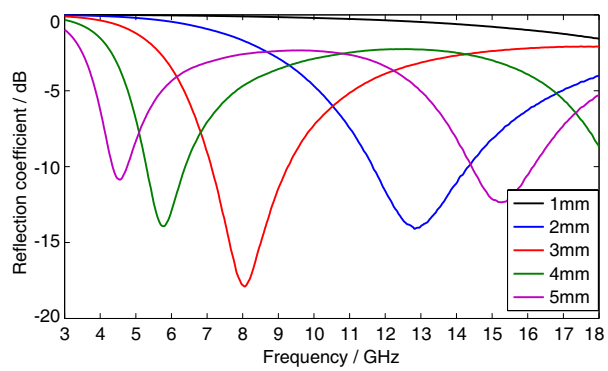
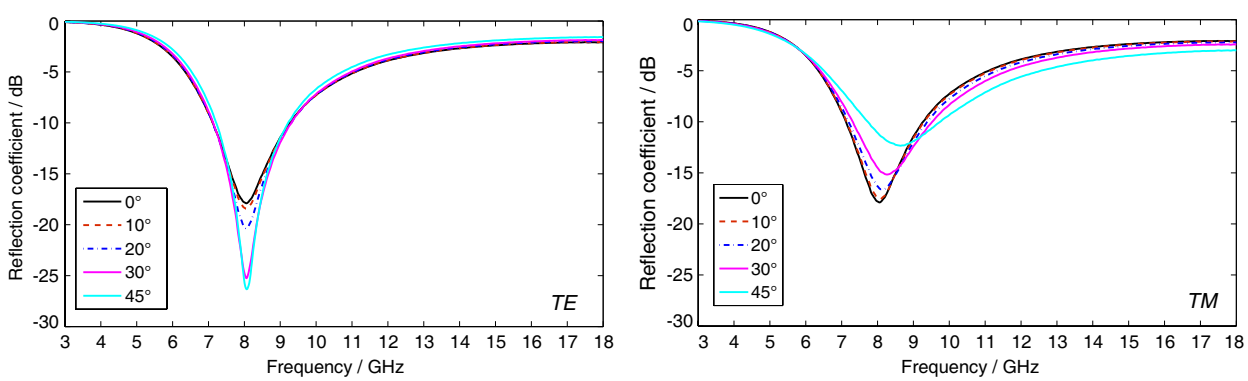


Figure 8. Reflection coefficient, normal incidence, MWCNT 5 wt.% for different thicknesses.



(a) (b)

Figure 9. Reflection coefficient ((a) TE polarization, (b) TM polarization) at different angle of incidence for the case 5 wt.% (thickness $d = 3\,\text{mm}$).

where the matrix terms can be evaluated as a function of the modal impedances of medium 1 (free-space) and medium 2 (layer of composite).

The reflection coefficient obtained for a normal incidence of one-layer of thickness $d = 3\,\text{mm}$ for different CNT concentrations is shown in Fig. 7 considering the values of complex permittivity measured for each case. As expected, the increase of the relative permittivity values with the concentration produces a minimum in the reflection coefficient. For a 5% concentration a peak of $-18\,\text{dB}$ at $8\,\text{GHz}$ is obtained. The position of the minimum can be tuned by varying the thickness of the layer as shown in Fig. 8. Fig. 9 presents a 5% concentration with different angles of incidence for both TE and TM polarization showing that the reflection coefficient remain less than $-10\,\text{dB}$.

4. CONCLUSION

In this paper, a type of MWCNTs as filler in Epoxy resin for application as microwave absorber was analysed. Samples with different concentrations (0.5, 1, 3, 5 wt.%) of the same type of MWCNTs were made. Their complex permittivity was measured with an Agilent capacitive sensor in a wide frequency band (3–18 GHz). To analyse the microwave absorbing properties, a one-layer structure backed by a metallic plate with a plane wave incidence was modelled with a transmission line approach. The reflection coefficient, for normal and oblique incidence, was calculated by considering in the model the measured permittivity values.

Our study clearly show that the values of complex permittivity increase by increasing the filler concentration.

The reflection coefficient evaluated for a one-layer geometry can reach $-18\,\text{dB}$ for 5 wt.% MWCNTs concentration. This result confirm the possibility of multi-walled nanocomposites to be a candidate as microwave absorber.

Next steps will be oriented to increase performance of our nanocomposite using other types of MWCNTs and to analyse and tune an n-layer structure.

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REFERENCES

1. Neo, C. P. and K. Vardan, "Optimization of carbon fiber composites," *IEEE Trans. on Electromagnetic Compatibility*, Vol. 46, No. 1, 102–106, 2004.
2. Said, A., L. Bednarz, R. Daussin, C. Bailly, and X. Lu, "Carbon nanotube composites for broadband microwave absorbing materials," *IEEE Trans. Microwave Theory and Techn.*, Vol. 54, No. 6, 2745–2754, 2006.
3. De Rosa I. M., F. Sarasini, M. S. Sarto, and A. Tamburrano, "EMC impact of advanced carbon fiber/carbon nanotube reinforce composites for next-generation aerospace applications," *IEEE Trans. on Electromagnetic Compatibility*, Vol. 50, No. 3, 556–563, 2008.
4. Koledintseva, M. Y., J. Drewniak, and R. Dubroff, "Modeling of shielding composite materials and structure for microwave frequency," *Progress In Electromagnetics Research B*, Vol. 15, 197–215, 2009.
5. Kumar Das, C. and C. V. Sudhakar, "CNT based and graphene based polymer nanocomposites for radar absorbing applications," *Journal of Materials Science and Engineering B2*, Vol. 6, 368–375, 2012.
6. Singh, V. K., A. Shukla, M. K. Patra, L. Saini, R. K. Jani, S. R. Vadera, and N. Kumar, "Microwave absorbing properties of a thermally reduced graphene oxide/nitrile butadiene rubber composite," *Carbon*, Vol. 50, 2202–2208, 2012.

7. Bhagwan, F. J., M. Sawant, M. Kulkarni, and P. K. Brahmankar, "Dispersion and performance properties of carbon nanotubes (CNTs) based polymer composites: A review," *Journal of Encapsulation and Adsorption Sciences*, Vol. 2, 69–78, 2012.
8. Micheli, D., C. Apollo, R. Pastore, and M. Marchetti, "X-band microwave characterization of carbon-based nanocomposite material, absorption capability comparison and RAS desing simulation," *Composites Science and Technology*, Vol. 70, 400–409, 2010.
9. Dombovari, A., N. Halonen, A. Sapi, et al., "Moderate anisotropy in the electrical conductivity of bulk MWCNT/epoxy composites," *Carbon*, Vol. 48, 1918–1925, 2010.
10. Micheli, D., R. Pastore, C. Apollo, M. Marchetti, G. Gradoni, V. M. Primiani, and F. Moglie, "Broadband electromagnetic absorbers using carbon nanostructure-based composites," *IEEE Trans. Microwave Theory and Techn.*, Vol. 59, No. 10, 2633–2646, 2011.
11. Chang, J., G. Liang, S. Cai, and Y. Li, "The production of carbon nanotube/epoxy composites with a very high dielectric constant and low dielectric loss by microwave curing," *Carbon*, Vol. 50, 689–698, 2012.
12. Micheli, D., C. Apollo, R. Pastore, D. Barbera, R. B. Morles, M. Marchetti, G. Gradoni, V. M. Primiani, and F. Moglie, "Optimization of multilayer shields made of composite nanostructured materials, " *IEEE Trans. on Electromagnetic Compatibility*, Vol. 54, No. 1, 60–68, 2012.
13. Micheli, D., R. Pastore, G. Gradoni, V. M. Primiani, F. Moglie, and M. Marchetti, "Reduction of satellite electromagnetic scattering by carbon nanostructures multilayers," *Acta Astronautica*, Vol. 88, 61–73, 2013.
14. Savi, P., D. Trinchero, R. Tascone, and R. Orta, "A new approach to the design of dual-mode rectangular waveguide filters with distributed coupling," *IEEE Trans. on Microwave Theory and Techniques*, Vol. 45, No. 2, 221–228, 1997.
15. Dresselhaus, M. S., G. Dresselhaus, R. Saitoc, and A. Joriod, "Raman spectroscopy of carbon nanotubes," *Physics Reports*, Vol. 409, 47–99, 2005.
16. Chiolero, A., M. Castellino, P. Jagdale, M. Giorcelli, S. Bianco, and A. Tagliaferro, "Electrical properties of CNT-based polymeric matrix nanocomposites," *Carbon Nanotubes — Polymer Nanocomposites, Yellampalli Siva INTECH Open Access Publisher*, 215–230, Rijeka, Croatia, 2011.
17. Kumar, A., S. Sharma, and G. Singh, "Measurement of dielectric constant and loss factor of the dielectric material at microwave frequency," *Progress In Electromagnetics Research B*, Vol. 69, 47–54, 2007.
18. Giorcelli, M., P. Savi, A. Delogu, M. Miscuglio, M. H. Yahya, and A. Tagliaferro, "Microwave absorption properties in epoxy resin multi walled carbon nanotubes composites," *International Conference on Electromagnetic in Advanced Applications (ICEAA13)*, Torino, Italy, Sept. 9–13, 2013.