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Graphene and MWCNT thick films: preparation and RF electrical properties study

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Abstract

Carbon materials are well known for being a versatile class of materials able to transmit an electrical signal when used as fillers in composites. Among numerous carbon fillers, carbon nanotubes and graphene have been extensively investigated for the last thirty years. This paper compares graphene and carbon nanotube electrical (i.e. resistive and reactive) properties in the microwaves range up to 3GHz. The transmission and reflection parameters of both the microstrip transmission lines and patch antennas loaded with 33wt.% of graphene and multiwalled carbon nanotubes (MWCNTs) were analysed. Interestingly, for an identical composite matrix composition, different scattering parameters stemmed from the different morphology of the films, the diverse interactions between the graphene nanoplatelets, the MWCNTs and the polymeric binders in conjunction with the intrinsic electrical characteristics of the two carbon materials.

Keywords: graphene, nanotubes, thick films, screen printing, carbon films

1. Introduction

The incorporation of micro- and nano-phase carbon particles in polymers has been a commonly employed technology to improve material performance since the early 1990s. The filler type and its concentration in polymer composites allows the material properties to be tuned [1-2]. Among carbon

fillers, carbon nanotubes (CNTs) and graphene have been the most commonly adopted in the last decade [see e.g. 3,4].

As far as concerns CNTs, some recent examples of their application according to their electrical, mechanical, and thermal properties and their influence on the composite characteristics are reported in [5-8]. CNTs, with their tubular structure, could be considered as seamless cylinders formed by rolled-up graphene sheets with carbon atoms covalently bonded with each other through sp^2 hybridization. Depending on the number of layers of the graphene sheets, they are further categorized into single-walled, double-walled and multi-walled CNTs. Evaluating defectiveness and graphitization grade is an important way to classify the quality of CNTs.

Graphene, and in particular graphene nanoplatelets and their derivatives (i.e. reduced graphene oxide), is another interesting carbon material that has been studied in composites and compared to CNTs [9]. Graphene is the thinnest and lightest sp^2 carbon nanomaterial, consisting of a one-atom-thick planar sheet of sp^2 -bonded carbon atoms in a honeycomb crystal lattice and possesses extraordinary properties: excellent thermal and electrical conductivity, large surface area, fast heterogeneous electron transfer rates and high mechanical strength. Monolayer graphene can be synthesized for particular applications, but in composites, where the quantities of materials are relevant, it is not possible to use monolayer graphene. In this case, graphene nanoplatelets are more appropriate. Also in this case, as for CNTs, defectiveness and graphitization grade could be used to classify the graphene quality and, as a consequence, its performance in composites.

Among the different investigations concerning carbon based composites, a “niche” field is represented by thick films [10]. Their possible applications span from gas sensors and RFID [11,12], to actuators and conductive electrodes [13-14], and microwave sensors [15]. Screen printing constitutes the most employed additive manufacturing technique for the deposition of thick films [16].

In this work, we report a comparison between MWCNT and Graphene nanoplatelet screen-printed films. The two carbon materials and their films were morphologically and structurally investigated by Field Emission Scanning Electron Microscopy (FESEM) and Raman (level of defectiveness and graphitization). The scattering parameters (S_{11} and S_{12}) of the microstrip lines and of the inset-feed patch antennas properly loaded with a thick film were measured and the characteristics of the different films compared. The measured data were compared to the full-wave simulations of CST Microwave Studio.

2. Materials and methods

A. Carbon filler and composite

The MWCNTs were produced using combustion chemical vapour deposition by Nanothinx (Greece) and commercially labelled as NTX-1. Their nominal characteristics are: external diameters 15-35 nm, internal diameters 3.5-12 nm, length $\geq 10 \mu\text{m}$, surface area 200-250 m²/g and bulk density 0.16 g/cm³.

The Graphene nanoplatelets, produced by NanoInnova (Spain), and commercially labelled C97. The manufacturer declared a surface area of $\sim 45 \text{ m}^2/\text{g}$ and a carbon content over 98.9 wt.% (EDS).

α -terpineol (Sigma-Aldrich, b.p. 220°C), of Butvar 98 polyvinyl-butyril (PVB, molecular weight 40.000–70.000 g/mol. determined by size exclusion chromatography, Sigma-Aldrich), polyvinylpyrrolidone (PVP, average molecular weight 360.000 g/mol., Sigma-Aldrich), and linoleic acid ($\geq 99\%$, Sigma-Aldrich) were employed for the formulation of the organic vehicle of the screen printing paste.

B. Films preparation

α -terpineol-based screen printing pastes comprising a thermoplastic binder with two components (i.e. polar and non-polar) additives, and two different carbon fillers were prepared. 33 wt.% of MWCNT, and Graphene Nanoplatelet particles were employed as conductive fillers in the final paste

formulation. The organic vehicle was composed of 6.0 wt.% of Butvar (PVB), 1.7 wt.% of polyvinylpyrrolidone (PVB) and 3.1 wt.% of linoleic acid. PVB (non-polar polymer) and PVP (polar polymer) constituted the binder part of the vehicle. Furthermore, PVB was also used as a thickener in order to improve the paste viscosity and enhance the thixotropic effect during printing. Because of the absence of any cross-linking agent (i.e. transition metal salts) the thermal curing of the linoleic acid was hindered. Thereby, the linoleic acid was just used as a wetting agent and dispersant additive to functionalize the carbon filler surface and prevent its agglomeration. All the paste components were pre-solubilized in anhydrous ethanol before being mixed and sonicated for 16 h by using a titanium ultrasonic horn. The ethanol was removed by evaporation under reduced pressure at 40°C. The pastes, containing the three different carbon fillers, were printed across a 3x3 mm² gap between a copper-etched microstrip onto an FR-4 substrate by means of a 230 mesh/inch polyester screen (see Fig. 1). Film thicknesses of 30-40 µm were attained by repeating the printing procedure three times. A drying step between layer deposition was carried out at 125 °C. The final thermal curing aimed at evaporating the solvent (i.e. α -terpineol) was performed in a muffle at 160 °C for 3 hours.



Fig. 1: Examples of carbon film obtained using screen printing technique.

C. FESEM

In order to analyze the structure of the carbon particles and composite films, FESEM analysis was performed with a ZEISS SUPRATM 40 Field Emission Scanning Electron Microscope.

D. Raman Characterization

Raman spectroscopy on MWCNTs and graphene nanoplatelets was performed using a Renshaw Ramascope MicroRaman, equipped with an Argon green laser (excitation at 514.5 nm at 50 mW). Measurements were taken at different points for each carbon sample, with a 50-x objective.

E. Microwave film characterization and modeling

In order to compare the behaviour of the films with MWCNTs and graphene, the films were printed across the gap of a microstrip line and the scattering parameters of the lines were measured with a Network Analyzer (Agilent E8361A). These lines were also modelled using a full-wave software (CST Microwave Studio) and the simulated results compared with the measurements.

3. Results and discussion

A. FESEM characterization

FESEM characterizations were performed on carbon materials and films. Some significant FESEM images for carbon materials are reported in Fig. 2 while in Fig. 3 are reported FESEM images of printed films.

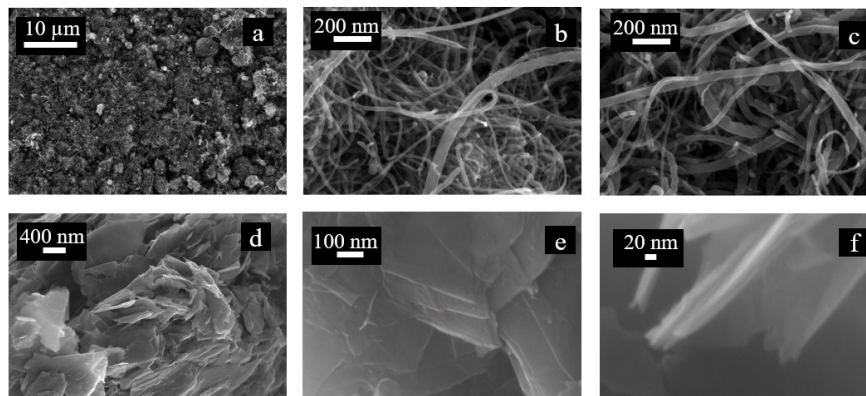


Fig. 2: FESEM images of: a), b), c) MWCNTs; d), e), f) Graphene nanoplatelets

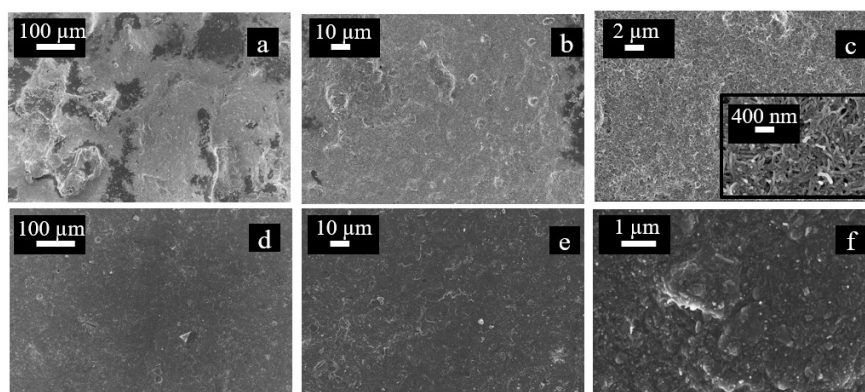


Fig. 3: FESEM images of screen printed films produced using as filler: a), b),c) MWCNTs; d), e), f) Graphene nanoplatelets.

MWCNTs appeared very entangled (see Fig. 2a). Bundles of few microns in diameter are visible. When the magnification increases (Fig. 2b and 2c,) it is possible to appreciate the isolated MWCNTs with nominal tubes diameters in the range 15-35 nm, as claimed by the producer.

Graphene is organized in nanoplatelets as reported in Fig. 2d where platelets of few nanometers in thickness are formed by graphene layer. Increasing magnification, it is possible to observe the flakes structures as showed in Fig. 2e. At the very high magnification (800 KX, Fig. 2f) transparent structure could be observed.

Figures 3a-c show the MWCNTs uniformly distributed into the polymer matrix. MWCNT diameters increased due to the coating layer comprising the PVP and PVB binders as showed in the inset of Fig. 3c. Fig. 3d-f show the morphological structure of film containing graphene nanoplatelets. In Fig. 3f a disordered structure of graphene nanoplatelets could be observed. This is due to the PVP binder exerting a specific action during the dispersion of Graphene nanoplatelets into the screen-printing paste vehicle. Indeed, PVP high molecular mass together with its polar functional groups (the pyrrolidone ring) contributed to delaminate and deform (i.e. bending) the graphene layers resulting into a disordered structure composed of random arranged flakes. (Fig. 3f).

B. Raman characterization

Raman analyses were performed on graphene nanoplatelets and MWCNTs. Their spectra are shown in Fig. 4. In Raman signal on carbon materials there are two main peaks: D and G peak [17]. The D peak (breathing mode, A_{1g}-band) is positioned in the 1300-1400 cm⁻¹ range and it is related to the edge disorder in carbon structure. The G peak (Tangential Mode, E_{2g}-band) is positioned in the 1550-1615 cm⁻¹ range and corresponds to the stretching mode of sp² bonds in the graphite plane. A second order peaks could be observed in the range 2500-3500 cm⁻¹. These peaks represent the graphitization of the carbon material. In particular, the peak called 2D in this region is important in graphitic material [18]. Its asymmetric shape is index of multilayer structure [19]. Graphitization of carbon material could be also appreciated observing the peak width, that became important for the evaluation of graphitic material. More the peak sharpness increase more the material is graphitized. The ratio between the intensity of D and G peak (I_D/I_G) is used to evaluate the ratio between disordered and graphitized structures in the carbon material tested.

In our case we evaluated the I_D/I_G ratio by fitting the D and G peak with appropriated curves and calculating its area. This area takes into account peak intensity and its shape, with particular emphasis on its width. The fitting procedure performed on all the Raman spectra made it possible to calculate the I_D/I_G ratio and fill Table 1. Graphene nanoplatelets Raman spectra showed very sharp G peak and asymmetric 2D peak (shoulder on the left) that is index of multilayer structures as expected. Graphene nanoplatelets reported the lowest I_D/I_G ratio. Graphitization grade influence the carbon material electrical properties [19].

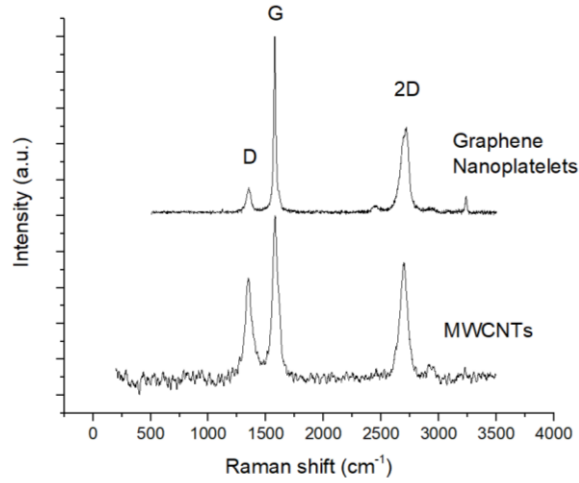


Fig.4: Raman spectra for MWCNTs and Graphene Nanoplatelets

| Carbon material | I_D/I_G |
|------------------------|-----------|
| MWCNTs | 0.78 |
| Graphene nanoplatelets | 0.21 |

Table 1: I_D/I_G ratios for MWCNTs and Graphene nanoplatelets.

C. Microwave film characterization

In order to understand the differences in the radiofrequency range between the MWCNT and graphene films, we considered a microstrip line (width 3mm) printed on a FR-4 substrate (nominal dielectric constant 4.3, loss tangent 0.02, thickness 1.56 mm) with a centered gap (see Fig. 5). A film of graphene or MWCNT of dimensions 3x3mm was screen printed across the gap. The scattering parameters of the lines were measured after a standard 2-port calibration with a network analyzer.

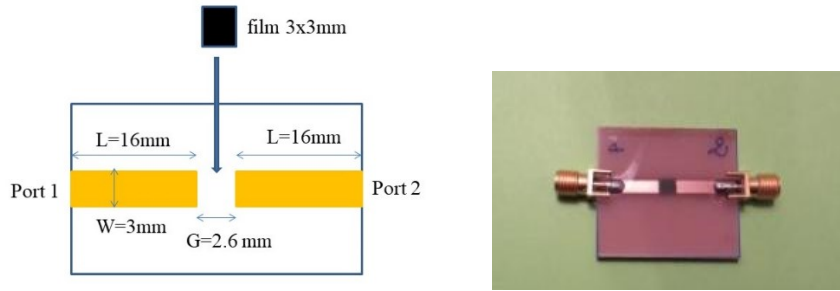


Fig. 5 Sketch of the microstrip line with a centered gap (left panel). Realization of the line on a FR-4 substrate (right panel).

Fig. 6 displays the transmission coefficients (i.e. scattering parameter S_{21}) of the graphene and MWCNTs-loaded microstrip lines. Both samples were compared to the “reference” (i.e. no gap) copper microstrip line. Needless to say, the transmission coefficient of the two carbon materials is severely lower than the etched copper line one [20], [21]. Not surprisingly etched copper conductive traces are largely conductive compared to screen printed fillers. Indeed, the sheet resistance of conductive elements (i.e. MWCNTs or Graphene) within a thick film is mainly determined by their level of interconnection [22]. Therefore, the relatively low curing temperature (160°C) used for the removal of the paste’s solvent is not sufficient to accomplish the sintering of the filler. Furthermore, bulk resistivity of MWCNTs (i.e. $1.6 \times 10^{-5} \Omega\text{m}$ for ballistic limit for a single CNT [20]) is three order of magnitude higher than the corresponding copper value. On the other hand, graphene’s resistivity is comparable to the one of silver. However, such a behavior is ascribable to a single graphene layer [23]. Graphene thick films inevitably tend to resemble graphite resulting in lower electronic conductivity. In addition, the morphological characteristics of the composite materials must be taken into account in order to compare the electrical properties of the graphene and MWCNT films (see Fig. 6). In fact, the large aspect ratio of the MWCNTs [24] improves the level of electrical interconnectivity between nanostructures compared to the graphene nanoplatelets. In the same figure the solid lines represent the simulated results obtained with CST Microwave Studio. In the case of graphene, the measured data were fitted considering a film about 60 S/m, whereas in the case of MWCNTs the specific conductivity turned out to be 180 S/m.

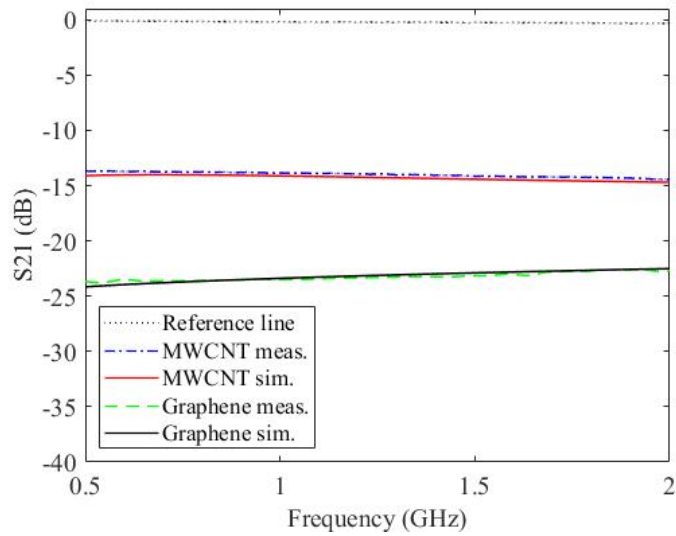


Fig. 6. Transmission coefficient of microstrip lines loaded with MWCNT and graphene thick films (33wt.%).

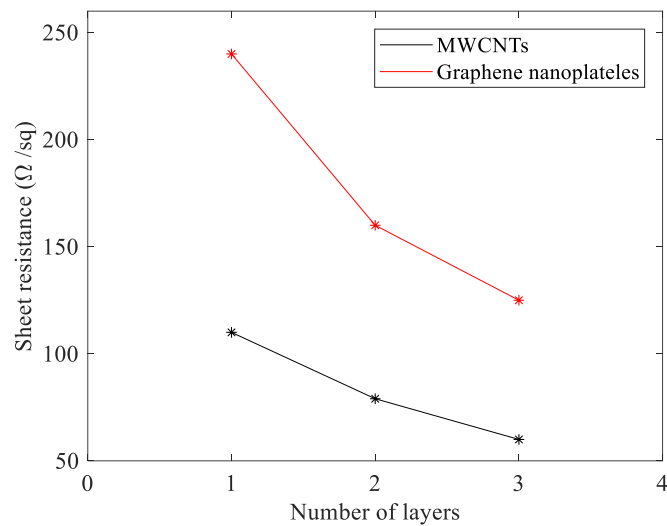


Fig. 7. Sheet resistance (four-probe measurements) for different screen-printed layers of graphene and MWCNTs composites cured at 160°C for 3 h.

Besides, FESEM micrographs (Fig. 1 and 2) show a discontinuous arrangement of the nanoplatelets and perhaps a damage of the graphene structure (see Fig. 2f). Thereby, the electron diffusion through the nanoplatelets may result hindered by the electrical resistance associated to the interface between the graphene planes. Moreover, while the MWCNTs are coated by the polymeric matrix, the two binders (specially the PVP because of its higher molecular weight) interpose between the graphene planes causing the distortion of the structure and therefore a lower electronic conductivity. Fig. 7 reports the sheet resistance data (measured in DC) graphene and MWNCT films. Obviously, the sheet

resistances of both composites decrease as the number of printed layers (thickness) increases. Nevertheless, the graphene film shows as much as twice the sheet of the MWCNT one. This outcome agrees with the behavior of the two films in the microwaves range. In fact, the simulated results (solid lines, Fig. 6) obtained by modeling the film as a sheet resistance are $R=1100$ Ohm/sq in the case of graphene and $R=400$ Ohm/sq in the case of the MWCNTs.

D. An example of application: inset-feed patch antennas

An inset-fed microstrip patch antenna is designed to operate at 4.36 GHz (patch 15×12 mm², feed line width of 3 mm for 50Ω impedance, see Fig. 8). The feed inset and spacing (6 mm and 1 mm respectively) are chosen to provide the best impedance match between the feed line and the patch. The original design was modified by adding a stub of length of 15 mm including a centered gap of 3 mm, as proposed in [25]. The antenna was fabricated on FR4 substrate (nominal dielectric constant of 4.3 and loss tangent of 0.02). A film of graphene or MWCNT, both 33wt.% of size 3×3 mm² of three layers in thickness was deposited across the gap.

The reflection coefficients of both antennas (loaded with MWCNTs and graphene nanoplatelets) were measured by using a network analyzer and contrasted with an etched antenna comprising only the copper patch and the 6 mm stub (see Fig. 8). This latter device was considered the reference (resonant frequency 4.12GHz). The antenna loaded with graphene film shows a resonant frequency of 4.5GHz, while a wide band resonating around 4.05 GHz characterizes the MWCNT antenna. Therefore, the data seem to suggest an inductive frequency shift (toward higher frequencies) caused by the graphene and a capacitive (to the lower frequencies) brought about by the MWCNTs with respect to the reference antenna. This behaviour was also verified by means of a full-wave simulations with CST Microwave Studio, 2018 (see Fig. 8 dashed lines). The inset-feed microstrip antenna, the stubs and the ground plane were modeled as copper with conductivity 5.8×10^7 S/m. The FR4 substrate was modeled by using a function describing the frequency dependence of the real part of permittivity and $\tan(\delta)$. Although the Drude model may be used to simulate the microwave behavior of graphene'

flakes [26], it could not be applied to the present case because of the composite nature of the film. Indeed, the Drude model does not take into account the dielectric relaxation possibly associated to the polar binder. Therefore, the composite thick films scattering parameters were modeled through their surface impedance $Z=R+jX$ (Ohm/sq). In the case of MWCNTs film fitting between the measurements and the simulations was obtained considering $R=100$ and $X=-550$, whereas in the case of graphene the values were $R=1000$ and $X=+4000$. The Graphene high R compared to MWCNTs reflects the characteristics already shown in Fig. 6 and 7. Nonetheless, R values attained by microwaves simulation do not exactly correspond DC sheet resistance of the films because of the skin effect. Furthermore, the simulated X values (positive for the graphene and negative for the MWCNTs) agree with the inductive (i.e. MWCNTs) and Capacitive (i.e. Graphene) resonant frequency shifts reported in Fig. 8.

However, such a different behavior cannot be explained neither in terms of kinetic inductance nor in terms of chemical capacitance. Indeed, the graphene kinetic inductance stemming from the motions of plasmons does not contribute to any impedance change unless the operative frequency of the antenna lies in the THz range [27, 28]. On the other hand, any contribution to the impedance due to the chemical capacitance (associated to the electronic density of states) of both carbon materials is not to be expected because of the high operative frequency [29].

Nevertheless, it is well known that dielectric properties of polymer-carbon materials composites strongly depend on the electrical (i.e. conductivity), chemical (i.e. functional groups), geometrical (i.e. aspect ratio, specific surface area, and consequently percolation threshold), and morphological (i.e. dispersion into the matrix) properties of the filler [24], [30].

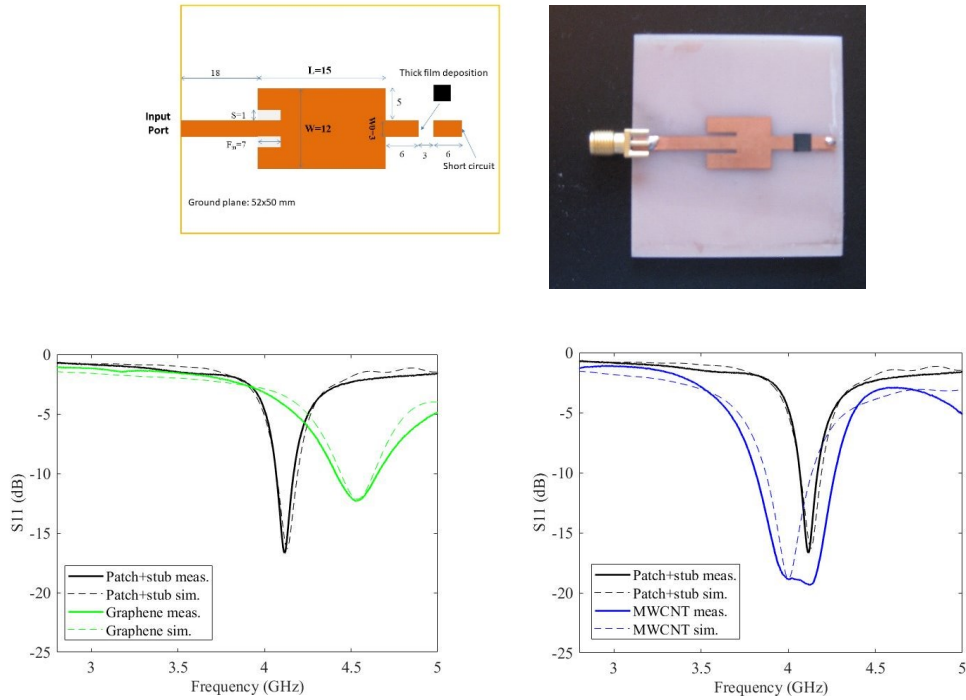


Fig. 8 Reflection coefficient of inset-feed patch antenna loaded with films compared with the patch + stub configuration. Left panel graphene, right panel MWCNTs.

Hence, the different electronic density (i.e. band structure) of graphene nanoplatelets and MWCNTs can affect the antenna resonant frequency. Indeed, the rolling of a graphene sheet at a particular angle (i.e. chirality) results in a large variety of single walled carbon nanotubes characterized by a distribution of electronic structures (i.e. metallic and semiconductor) [31-33]. Although MWCNTs are statistically metallic, their concentric structure comprised of interspaced folded graphene sheets inevitably generates an electronic density of state quite different compared to randomly distributed graphene flakes. Needless to say, such a difference affects the extension of the interaction between the carbon materials and the binder(s) at the graphene platelets (or MWCNTs)/polymer interface. In other words, since the two nanostructures possess two distinct electronic distribution, the effect of the van der Waals (intermolecular) forces (e.g. dipole-dipole, dipole-induced dipole, London dispersion forces, hydrogen bonds) [34], [35] regulating the filler-binder interaction may lead to different dielectric behaviors for the two cases [30]. These aspects can be particularly relevant for polar

binders dielectrically relaxing in the microwave region like the PVP and PVP + PVB mixtures [35]. In addition, the interfacial electrical properties (i.e. surface impedance) of the two carbon are affected by the chemisorption, through the carboxylic-mediated covalent bond, of the linoleic acid used as dispersant in the paste formulation [36]. MWCNTs and Graphene platelets band structures may differently impact on the -COO surface adsorption and therefore on the surface charge of the composite. For instance, it has been already reported [37], [38] that wrinkling of graphene nanoplatelets (see Fig. 3) and their surface treatment (i.e. with linoleic acid) can lower the dielectric permittivity of graphene. Furthermore, a high enough wt.% (over the percolation threshold) of graphene nanoplatelets distributed inside the polymeric medium can function as nanoscale electrostatic capacitors [39]-[43]. Therefore, the dielectric permittivity lowering (with respect to the gap dielectric, that is the FR-4, and the MWCNTs) can produce a reduction of the antenna capacitance, reflecting into an impedance increase and, in turn causing the resonant frequency to shift to higher frequency. On the other hand, the large surface area of the MWCNTs may the dielectric permittivity relatively high by providing multiple sites for interfacial polarization slightly shift to lower frequencies the resonant frequency [30].

4. Conclusions

Two different films, containing different carbon materials at 33wt.% (MWCNTs and Graphene nanoplatelets) have been produced by screen printing technique. PVB and PVP were used as the binder to print tracks on FR4 substrates. The carbon materials were investigated from a morphological point of view and their graphitization grade was evaluated by Raman spectroscopy. The morphological and electrical characterization of the carbon-based films were performed.

A detailed investigation of the composite morphology of the films by using FESEM revealed different arrangements of the two fillers across the film. Specifically, MWCNTs appeared to be uniformly covered with the binders without any relevant curling, while the graphene nanoplatelets, most likely because of the interaction of the more polar and heavier of the binders (PVP), were disorganized, partially disrupted and wrinkled. These characteristics also affected the electrical conductivity and radiofrequency scattering parameters. In particular, the improved electrical interconnectivity throughout the film of the MWCNTs, stemming from their high aspect ratio, led to low sheet resistances ($R_{sh} \approx 60 \text{ } \Omega/\text{sq}$ in DC). On the contrary, the disarrayed graphene and curled nanoplatelets caused a lower level of electrical percolation across the composite slowing down the electron diffusion ($R_{sh} \approx 120 \text{ } \Omega/\text{sq}$ in DC). Consequently, the microwave transmission coefficient (S_{21}) of the MWCNT thick films inserted into a microstrip transmission line was higher (around 10 dB) than that of their graphene counterpart. Moreover, the dielectric properties of the films turned out to be affected both by the different morphology of the two composites and by the various interactions at the polymer carbon filler interface. Indeed, the different electronic density of the two nanomaterials may impact on both the Van der Waals dipole forces (i.e. permanent and induced) and the chemical effect (i.e. chemisorption of linoleic acid) dictating the interaction between the filler, binder, and dispersant. These effects can account for the resonant frequency “inductive” shift (to higher frequencies) of the graphene-loaded antennas when compared to the MWCNT-loaded or merely copper etched antennas. Indeed, as previously reported, the surface functionalization of graphene nanoplatelets (and steric interaction with polymers) causes a dielectric permittivity decrease, which is due to a surface impedance increase, and ultimately a shift in the resonant frequency of the return loss of the antenna. On the other hand, the high specific surface area of the MWCNTs produced an extended interfacial polarization, avoiding a significant resonant frequency shift.

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Competing interests

The authors declares that there is no conflict of interest regarding the publication of this paper.

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