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Full Length Article

A study of the electromagnetic shielding mechanisms in the GHz frequency range of graphene based composite layers

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ABSTRACT

We report on the mechanisms of the electromagnetic interference shielding effect of graphene based paint like composite layers. In particular, we studied the absorption and reflection of electromagnetic radiation in the 4–20 GHz frequency of various dispersions employing different amounts of graphene nanoplatelets, polyaniline, and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), special attention given on the relative contribution of each process in the shielding effect. Moreover, the influence of the composition, the thickness and the conductivity of the composite layers on the electromagnetic shielding was also examined.

1. Introduction

The rapid development and use of modern fast electronics, operating mainly in the GHz frequency range, have resulted in harmful effects on highly sensitive electronic equipment as well as on life. As a result, a lot of efforts have been focused on the development of effective electromagnetic shielding materials. These materials should exhibit effective shielding performance as well as other appropriate physical properties, especially in applications regarding aircraft, aerospace, automobiles, and fast-growing next-generation portable flexible electronics and wearable devices [1].

Polymer nanocomposites have received much attention for electromagnetic shielding applications, [2–7] because of their light weight, resistance to corrosion, flexibility, good processibility and low cost, as compared to conventional metal-based materials. Many carbon-based nanomaterials including carbon filaments, carbon nanofibers, carbon nanotubes (CNTs), and more recently graphene, have been used as conductive fillers to fabricate composite materials for electromagnetic shielding, because of their excellent characteristics [5–16], the respective shielding depending on both absorption and reflection of the incoming electromagnetic radiation. The performance of such polymer composites strongly depends on the distribution of the individual carbon-based fillers within the polymer matrix, which affects the electron percolation between the separated particles and subsequently the electrical conductivity of the composites. As a result, high content and good dispersion of the carbon-based nanomaterials are usually required in order to get a composite exhibiting effective electromagnetic shielding. On the other hand, a high content of conductive carbon-based fillers may lead in a degradation of the mechanical properties and poor processibility of the composites, due to severe agglomeration and poor filler-matrix bonding, as well as worse conductivity, due to bad surface morphology. Therefore, further studies are required regarding the optimization of the properties and the electromagnetic shielding performance of composites based on carbon nanomaterials.

Recently, homogeneous and uniform paint-like nanocomposite layers, consisting of graphene nanoplatelets, PANI:HCl and PEDOT:PSS, were developed in our laboratory using simple/low cost preparation techniques and were found to exhibit quite effective shielding ability in the GHz frequency range [17]. In this work, we investigate the optimization of the electromagnetic shielding performance of such paint-like layers, we study the physical mech-

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anisms leading in the observed electromagnetic shielding and we determine the relation between the electromagnetic shielding and the thickness and the conductivity of the nanocomposite layers.

2. Experimental

The electromagnetic shielding layers were deposited on 16 cm by 16 cm foam board by brushing paint-like dispersions in deionized water, prepared by ultrasonication, as described in details in our previous work [17]. The main nanomaterial employed was graphene nanoplatelets, provided by EMFUTUR Technologies Ltd. Spain, 5 μm wide, with an average 5 nm thickness, a bulk density of 0.03–0.1 g/cc, a carbon content of >99.5 wt%, an oxygen content of <1% and a residual acid content of <0.5 wt%. PEDOT/PSS solution (Clevios^{TM} PH 1000) was employed as both a binder and a conductive medium, while, for the improvement of the electromagnetic shielding performance, Polyaniline:HCl (PANI:HCl) was added, prepared by polymerizing aniline hydrochloride in 1 M HCl using ammonium peroxydisulfate as an initiator in an ice bath according to IUPAC standard procedure [18]. All compositions were slowly stirred for 2 h in order to remove the trapped air bubbles and to ensure reasonable macroscopic homogeneity. The as prepared mixtures were spread on the foam board substrates using a brush follow by natural drying. The deposition procedure was repeated for several times until a material of the required thickness was prepared. Samples were visually inspected and characterized by scanning electron microscopy, using a JEOL JSM 6362LV electron microscope.

The EMI characterization of the samples was performed at 4–20 GHz, which is typical for wireless communications, such as satellite communications transmissions, Wi-Fi devices, cordless telephones, and weather radar systems, using a Hewlett-Packard 8722 ES vector network analyzer and two sets of microwave standard-gain horn antennas (Advanced Technical Materials Inc., ATM) covering the frequency range mentioned above. The setup used was similar to that used by other groups [11]. In particular, horn antennas were placed at a distance of 40 cm, every sample was placed in the middle of each set of horn antennas, and the scattering parameters (S-parameters; S_{11}, S_{12}, S_{22}, S_{21}) of each sample were recorded. Prior to every measurement, an absorbing chamber was created using typical multi-layer carbon-based polyurethane foam, broadband microwave absorbers (ECCOSORB AN-77, Emerson & Cuming Microwave Products, Inc., Randolph, MA) over all surfaces except the top, in order to eliminate the interaction with the surrounding environment.

3. Results and discussion

During the trial to optimize the paint-like dispersion, it was found out that a composition ratio exists, which can provide the best rheological behavior of the dispersion, leading in homogeneous and uniform nanocomposite layers. PANI being an HCl "doped" compound, releases some acid when in contact with water, this depending on the amount of water and PANI. Regarding the graphene platelets, these were obtained by the producer employing chemical exfoliation, therefore they still had some polar groups left. However, the dispersability of graphene is influenced by the ionic strength of the solution, therefore, more acid means less dispersability. In addition to that, the acidity of graphene promotes the release of more acid from PANI, the same appearing because of PEDOT, which is blended with PSS, a polyacid compound. Finally, PANI disperses better in acidic suspensions whereas graphene does not. As shown, there exist optimum suspension compositions at about 1/1 (graphene/PANI), above or below that, the paint-like composition is lumpy and does not spread nicely with the brush. Therefore, equal amounts of graphene and PANI result in suspensions that behave the best from the paint point of view. On the other hand, as discussed in our previous work, increased graphene content results in a better shielding effect. Therefore, optimum paint contents should be chosen so that homogeneous and uniform nanocomposite layers exist exhibiting effective electromagnetic shielding.

Various dispersion were prepared employing different amounts of graphene platelets, PANI and PEDOT/PSS, so that both compositions with optimum shielding performance can be obtained and a correlation between basic characteristic of the layers and effective shielding can be obtained. Dispersions with a graphene platelets content of 0.17 g/ml up to 0.75 g/ml were produced, the respective deposited composite layers having a thickness in the range 0.2–3 mm and a conductivity of 0.04–0.33 S.

For all deposited layers, the electromagnetic wave absorption and reflection were investigated in the 4–20 GHz frequency range. Absorption and reflection are the major electromagnetic attenuation mechanisms of the electromagnetic interference shielding effect (SE). In order to better understand the effect of the shielding mechanisms, the contribution of both absorption and reflection mechanisms to the total SE (SE_T) should be quantified [19]. The utilized electromagnetic interference shielding effect characterization setup described in the experimental part, directly measures the transmitted (T) and reflected power (R), while the absorbed power (A) can be calculated using the power balance equation:

$$A = 1 - T - R \tag{1}$$

The reflected (R) and the transmitted power (T) are given by:

$$R = |S_{11}|^2 = |S_{22}|^2 \tag{2}$$

$$T = |S_{12}|^2 = |S_{21}|^2 \tag{3}$$

where $|S_{11}|^2$ represents the reflected power from Port 1 to itself, and $|S_{12}|^2$ represents the power transferred from Port 2 to Port 1. (In general, S_{NM} represents the power transferred from Port M to Port N in a multi-port network).

The electromagnetic interference shielding effect by reflection and absorption can be calculated using the following equations based on the S-parameters:

$$SE_R = 10\log_{10}\left(\frac{1}{1-|S_{11}|^2}\right) \tag{4}$$

$$SE_A = 10\log_{10}\left(\frac{1-|S_{11}|^2}{|S_{12}|^2}\right) \tag{5}$$

The electromagnetic interference SE is a measure of the material ability to attenuate the EM waves' intensity and is expressed in decibels (dB). The higher the SE value the better the attenuation.

Taking into account the equations above, the overall electromagnetic interference SE is calculated as follows:

$$SE_T = SE_R + SE_A = 10\log_{10}\left(\frac{1}{|S_{12}|^2}\right) = 10\log_{10}\left(\frac{1}{|S_{21}|^2}\right) \tag{6}$$

Using the above formalism and the obtained results, the absorption, reflection and transmission of the electromagnetic radiation were determined for all samples. Fig. 1a and b presents the respective results for two of the samples, those having a graphene/PANI ratio of: (a) 2.5 and (b) 1.5, the rest of them exhibiting more or less similar behavior. As can be seen, the reflection seems approximately constant as a function of the frequency, for the spectral region under investigation, while the absorption increases constantly with frequency, this latter trend dominating the total electromagnetic interference shielding effect SE (SE_T). Regarding the relative contribution of absorption and reflection in the

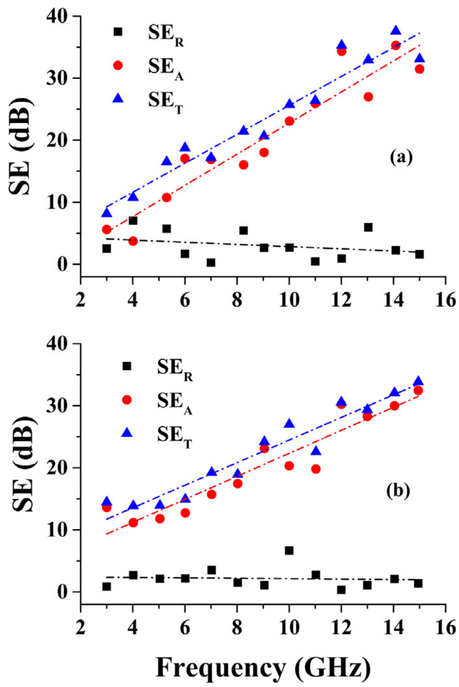

Fig 1. Total, absorption and reflection GHz electromagnetic interference effect in graphene platelets, PANI and PEDOT/PSS layers, with a graphene/PANI ratio of: (a) 2,5 and (b) 1,5.

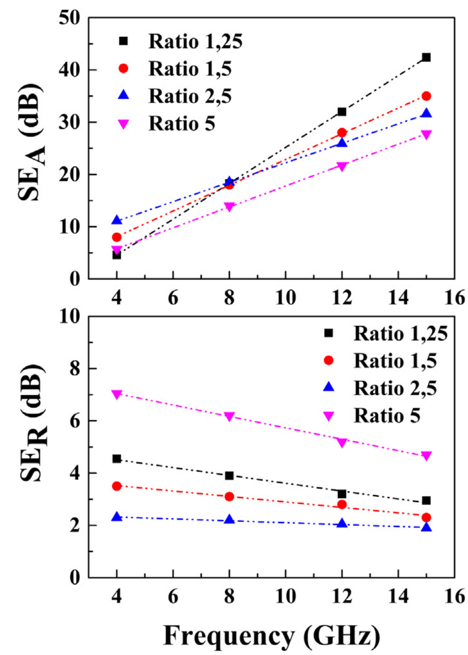

Fig. 2. Frequency dependence in the GHz range of the absorption and reflection electromagnetic interference effect in graphene platelets, PANI and PEDOT/PSS layers, for various graphene/PANI ratios.

effectiveness of the layers under investigation, this is approximately similar only around 3 GHz, while for higher frequencies, the shielding effectiveness is dominated by absorption. Therefore, the electromagnetic shielding in the 4–20 GHz frequency range of the samples studied comes mainly from absorption of the incoming radiation and increases with increasing frequency. Regarding the shielding effectiveness of the graphene platelets, PANI and PEDOT/PSS layers, this is quite large for frequencies above 10 GHz, similar or superior of commercial products. Finally, comparing graphs (a) and (b), a general first conclusion is for graphene/PANI ratios near 1, reflection becomes weaker while absorption stronger, as compared with larger graphene/PANI ratios.

As a next step, the influence of the composition of the dispersions on the reflection and the absorption of the electromagnetic radiation was examined, focusing on the graphene/PANI ratio. Fig. 2 presents the frequency dependence of absorption and reflection of GHz electromagnetic radiation in graphene platelets, PANI and PEDOT/PSS paint like layers, for various graphene/PANI ratios. Absorption increases with frequency for all composition examined, the rate of increase being larger for layers with a graphene/PANI ratio near 1, approaching values above 40 dBs at 15 GHz. In contrast, reflection reduces with increasing frequency, the rate of decrease being more than one order of magnitude smaller than that of the increase in the absorption case. Moreover, for the lower graphene/PANI ratios, the reflection is more effective as the ratio approaches 1, except the case of the large ratio of 5, where reflection is larger.

Then, the research was focused on the better understanding of the influence of the layer composition on the shielding efficiency as well as how conductivity and thickness are affecting its effectiveness. As already reported in our previous work [10], the shielding is based on the graphene nanoplatelets and supported by PANI:HCl, while PEDOT:PSS plays mainly the role of the binder. However, it was found out that as the graphene nanoplatelets content was increasing, not only the resulting suspension was lumpy and was not spreading nicely with the brush, but also the final layers were inhomogeneous, non-uniform and chapped, easily detached from the substrate, a behavior affecting electrical, mechanical and shielding properties. As an example, graphene/PANI ratios near 1 and a graphene content of around 5 g at 20 ml volume of PEDOT:PSS were found to maximize the conductivity. Moreover, the composition used was found to slightly affect the final possible thickness. In that respect, no mono-parametric function could efficiently describe the behavior recorded for layer of various compositions.

Table 1
Results of the fitting of the obtained electromagnetic shielding result using a two-variable model.

Coefficient	Value	95% confidence bounds
k	3.585	(−39.81, 46,98)
n	0.385	(−1.822, 2.592)
m	1.697	(−6.347, 9.741)
C	−27.77	(−33.25,−22.28)

In particular, both conductivity and thickness were found to affect the shielding effectiveness, together with surface morphology and uniformity. In general, their increasing was found to result in an increase of SET, but not in a monotonic way. In a trial to correlate the electromagnetic interference shielding effect in various samples having different composition with their conductivity and thickness, a two-variable model was developed, frequency used as an independent variable. Taking into account the characteristics recorded for each sample and using MATLAB, a function was created, that could sufficiently predict the shielding effect of a sample:

$$SE_T = k * L^n * S^m + C$$

where L is the thickness, S the conductivity and k, C constants. The results of fitting are presented in Fig. 3, where we can see that indeed the shielding efficiency depends on both conductivity and thickness, the first dependence being more pronounced. Moreover, the determined values for the constants k and C as well as the exponents n and m are shown in Table 1. In any case, the obtained results although clearly proved the electromagnetic shielding effectiveness of paint like layers based on graphene nanoplatelets, PANI:HCl

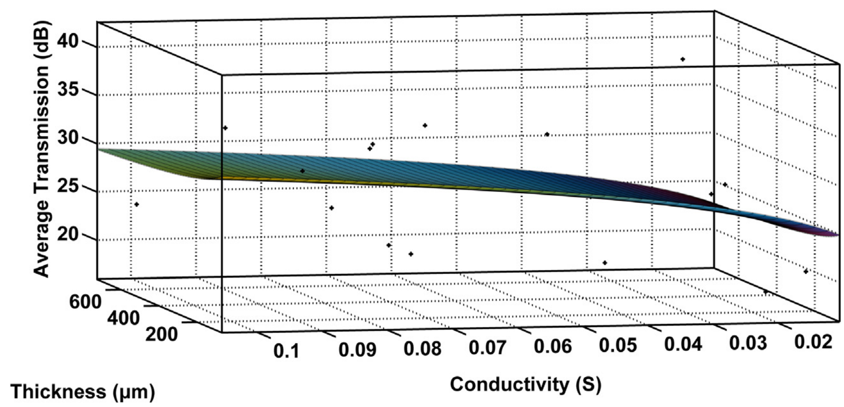

Fig. 3. Dependence of the average total GHz electromagnetic interference effect in graphene platelets, PANI and PEDOT/PSS layers on their conductivity and thickness.

and PEDOT:PSS, they also indicated the need for further optimization of the layer composition and the better understanding of the mechanisms leading in the observed functionality.

4. Conclusions

Results were presented related to the mechanisms of the electromagnetic interference shielding effect of paint-like nanocomposite layers consisting of graphene nanoplatelets, PANI:HCl and PEDOT:PSS in various concentrations. As was shown, an optimum paint content should be chosen so that homogeneous and uniform nanocomposite layers could be developed, exhibiting effective electromagnetic shielding. The electromagnetic shielding in the 4–20 GHz frequency comes mainly from absorption of the incoming radiation, which increases with increasing frequency, the respective reflection being almost constant and weak. Best mechanical, electrical and electromagnetic shielding properties were observed for a graphene/PANI ratio near 1. Finally, a two-variable model developed indicated that the shielding efficiency depends on both conductivity and thickness, the role of conductivity being more pronounced.

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