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Nanostructured composite layers for electromagnetic shielding in the GHz frequency range

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ABSTRACT

We report on preliminary results regarding the applicability of nanostructured composite layers for electromagnetic shielding in the frequency range of 4–20 GHz. Various combinations of materials were employed including poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), polyaniline, graphene nanoplatelets, carbon nanotubes, Cu nanoparticles and Poly(vinyl alcohol). As shown, paint-like nanocomposite layers consisting of graphene nanoplatelets, polyaniline PEDOT:PSS and Poly(vinyl alcohol) can offer quite effective electromagnetic shielding, similar or even better than that of commercial products, the response strongly depending on their thickness and resistivity.

1. Introduction

In recent years, various high frequency electronic devices have been developed and used in mobile communication, radio navigation, television and various other signal processing and transmission systems. All these systems result in an increasing of the electromagnetic radiation background, which, being different from the natural one, can introduce a complex influence on biological systems as well as in the operation of electronic devices. This is known as electromagnetic interference, an effect that can cause malfunction of sensitive medical devices and robotic systems or even become harmful to life [1].

In order to address the electromagnetic interference problems, it is necessary to develop materials that can absorb or reflect the electromagnetic radiation of a particular range of frequencies, these materials offering electromagnetic shielding. The shielding materials normally must possess good electrical conductivity and dielectric constant, properties found in metals [2]. As a result, metals such as aluminium, copper and steel have been employed for electromagnetic shielding, in forms like sheet metal, metal screen and metal foam. The construction of a shield is very important for its effectiveness since any holes in the shield or mesh must be significantly smaller than the wavelength of the radiation that should be kept out, or the shield will not effectively block the incoming radiation. In that respect, there are several limitations in the applicability of metals in shielding applications since they are heavy, not easily handled/applied and they suffer from corrosion. As a result, the scientific community is trying hard the last few years to develop new shielding materials, trials that has been significantly supported by the advances in materials science and nanotechnology.

Conducting nanostructured layers and composites have gained popularity for electromagnetic shielding applications, especially in the GHz frequency range, because they present several advantages over conventional metals, such as light weight, corrosion resistance, flexibility, etc. As an example, polymer composites containing carbon-based fillers (e.g., graphite, carbon black, carbon fibers, and carbon nanofibers [3–7]) have been investigated for use as shielding materials in the high frequency range, owing to their unique combination of electrical conduction, polymeric flexibility, and light weight. More recently, graphene and polyaniline have also been tested as shielding materials [8–12], however, the so far results did not allow yet their use in commercial applications and further research is required regarding layer composition, growth methods and understanding of the underlying mechanisms.

In this work we present experimental results related to the electromagnetic shielding properties of paint-like nanocomposite layers based on graphene nanoplatelets. As found out, these nanocomposite s exhibit quite effective shielding in the GHz spectral

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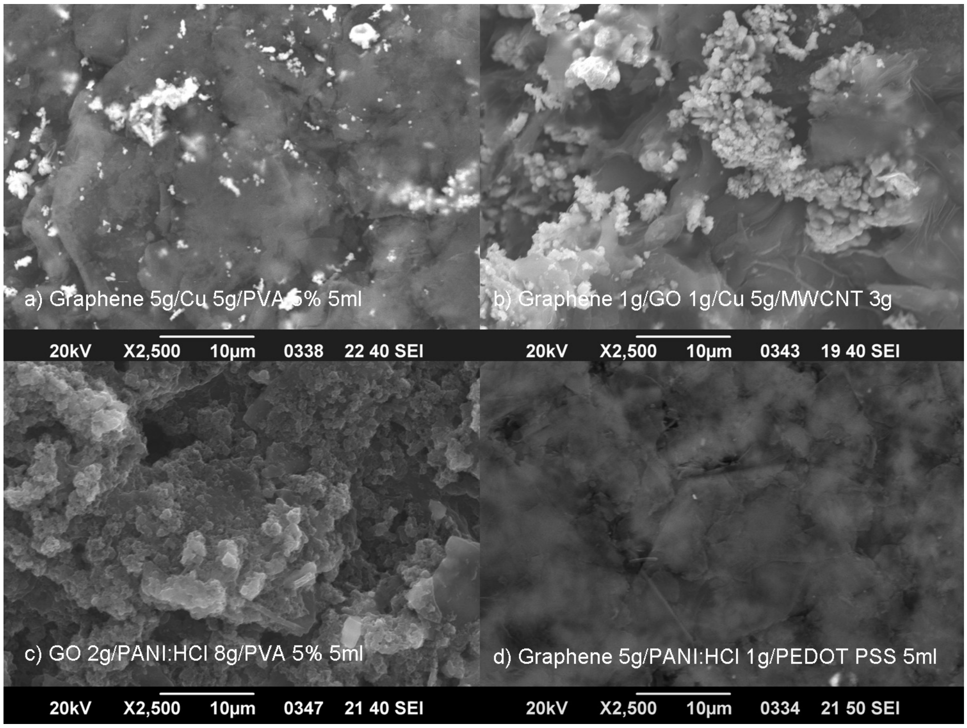

Fig. 1. SEM images of various nanocomposite layer compositions.

range, comparable to that of commercial products, while their effectiveness is depending on the resistivity and the thickness of the layers.

2. Experimental

The electromagnetic shielding layers under investigation were applied on 30 cm × 30 cm foam board by brushing paint-like dispersions in deionized water, prepared by ultrasonication. 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/cm^3, a carbon content of >99.5 wt%, an oxygen content of <1% and a residual acid content of <0.5 wt%. Other nanomaterials used in the initial trial were:

(a) Cu nanoparticles, obtained by the reduction of copper salts with hydrazine in the presence of polyvinylpyrrolidone. The Cu nanoparticles were solution mixed with the other materials used to prepare the shielding layer.
(b) Commercial conductive multi wall carbon nanotubes (MWCNT) (carbon purity min 95%, number of walls 3–15, outer diameter 5–20 nm, inner diameter 2–6 nm, length 1–10 μm, apparent density 0.15–0.35 g/cm^3, loose agglomerate size 0.1–3 m) provided by EMFUTUR Technologies Ltd. Spain.
(c) Homemade graphene oxide sheets (GO), 1–1.2 μm in size, 5 nm thick, with an average number of 16 layers, prepared according to a modified Hummers' method [14]. The obtained material was quite clean, with small traces only of potassium besides oxygen and sulfur.

In addition poly(vinyl alcohol) (PVA) was used in some cases as a binder (Mowiol® 18-88 from Sigma Aldrich), while, PEDOT/PSS solution (Clevios™ PH 1000) was employed as both a binder and a conductive medium. Finally, for the improvement of the electromagnetic shielding performance, Polyaniline:HCl (PANI:HCl) was added in some of the dispersions, prepared by polymerizing aniline hydrochloride in 1 M HCl using ammonium peroxydisulfate as a initiator in an ice bath according to IUPAC standard procedure [13]. 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. Finally, layers of similar thickness made from commercial electromagnetic shielding were prepared and used as standards in order to evaluate both the performance of the experimental setup for the transmission measurements and the effectiveness of nanocomposite layers under investigation. Samples were visually inspected and characterized by scanning electron microscopy. SEM characterization was performed using a JEOL JSM 6362LV electron microscope. Regarding the transmission measurements, these were performed in air, using a Hewlett-Packard 8722 ES vector network analyzer and four sets of microwave standard-gain horn antennas covering the range 3–24 GHz. Prior to every measurement, an absorbing chamber was created using typical microwave absorbers (ECCOSORB AN-77, Emerson & Cuming Microwave Products, Inc., Randolph, MA) over all surfaces except the top, and each sample was placed in the middle of each set of horn antennas.

3. Results and discussion

Initially, several layers of various nanocomposites based on different combinations of materials were prepared and tested, so that the one exhibiting optimum electromagnetic shielding can be chosen and studied further. Four types of material combinations were examined:

(a) graphene nanoplatelets with Cu nanoparticles and PVA,
(b) graphene nanoplatelets with MWCNT, GO and Cu nanoparticles,
(c) GO with PANI:HCl and PVA,
(d) graphene nanoplatelets with PEDOT:PSS and PANI:HCl.

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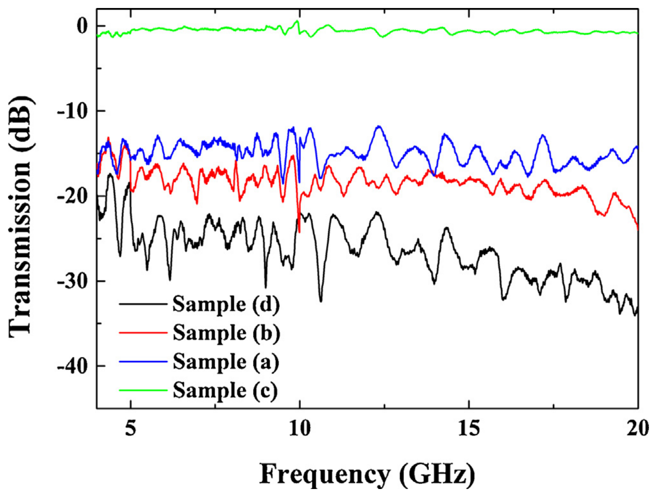

Fig. 2. Transmission of nanocomposite layers with different composition as a function of frequency. Sample (a): graphene nanoplatelets with Cu nanoparticles and PVA. Sample (b): graphene nanoplatelets with MWCNT, GO and Cu nanoparticles. Sample (c): GO with PANI:HCl and PVA. Sample (d): graphene nanoplatelets with PEDOT:PSS and PANI:HCl.

Visual inspection, including inspection with an optical microscope, of the samples after drying indicated that all of them were macroscopic homogeneous, uniform and crack free. Microscopic characterization by SEM revealed that the each of the composite has a different structure and surface morphology. Fig. 1 shows SEM images of the four composite formulations, where one can see that the first two are quite inhomogeneous in terms of conductive/non-conductive regions, a fact based on the strong contrast. The formulations based on GO have a rough surface and granular appearance while the graphene nanoplatelets based formulations, including PANI:HCl and PEDOT:PSS, show the best homogeneity and conductivity, permitting the clear observation of the embedded graphene platelets. Therefore, the graphene nanoplatelets based formulations seem to form nanocomposites with better homogeneity and uniformity that the GO based ones.

An example of electromagnetic shielding performance in the spectral region 4–20 GHz of layers with a thickness of about 7×10^{-4} m, consisting of the four material combinations described earlier is depicted in Fig. 2. As can be seen, the sample consisting of graphene nanoplatelets, PEDOT:PSS and PANI:HCl is more promising, allowing a reduction of the incident radiation by 20–30 dB, depending on the frequency used. This attenuation is quite large, compared with that induced by a layer of the commercial product of a similar thickness. As a conclusion, the shielding effect of layers consisting of graphene nanoplatelets, PEDOT/PSS and PANI:HCl were further studied so that both the basic characteristics leading to a maximum shielding performance can be determined as well as their influence on its electromagnetic shielding can be found.

Several nanocomposite layers were then deposited, having different relative concentrations of graphene nanoplatelets, PANI:HCl and PEDOT:PSS (Table 1 indicates the concentration of the samples used), having various thicknesses in the range 100–500 μm. The electromagnetic shielding performance of these nanocomposite layers was found not depending on the amount of PEDOT:PSS used. This can be clearly seen in Fig. 3a, which presents the average transmission in the frequency ranges 5–10, 10–15 and 15–20 GHz, respectively, for layers deposited from solutions consisting of different volumes of PEDOT:PSS, the respective amount of graphene nanoplatelets and PANI:HCl kept the same. In contrast, the amount of graphene nanoplatelets and PANI:HCl used for the preparation of the dispersion was found to strongly influence the electromagnetic shielding, the effect of former being more important. This can be seen in Fig. 3b, which presents the average transmission in the frequency ranges 5–10, 10–15 and 15–20 GHz, respectively, for layers deposited from dispersions with a different ratio of the amount of graphene nanoplatelets and PANI:HCl, while the respective volume of PEDOT:PSS was kept the same. Therefore, the electromagnetic shielding performance is based mainly on the graphene nanoplatelets. Following these results, PANI:HCl seems to support the shielding performance, while PEDOT:PSS, although improves the conductivity, plays mainly the role of the binder above a threshold concentration (20 mL for 7 g suspended solids). Finally, an interesting observation concerns the decrease of the transmission of the sample as the frequency increases, approaching a constant value above 10 GHz.

Table 1
Composition of the samples studied.

Samples	Graphene (g)	PANI (g)	PEDOT (mL)
A	5	2	20
B	5	2	30
C	5	2	40
D	4	3	40
E	3	4	40
F	2	5	40
J	5	2	30
K	2.5	1	15
L	1	2.5	15
G	3.75	1.5	22.5
H	2.5	1	15
I	1.25	0.5	7.5

Regarding the influence of the basic characteristics of the nanocomposite layers on the electromagnetic shielding performance, both resistivity and thickness were observed to significantly affect the functionality of the layers, as shown in Fig. 4a and b. In the first case, the average transmission in the frequency ranges 5–10, 10–15 and 15–20 GHz, respectively, is shown for samples of different thickness but of the same resistivity, while, in the second case, the presented average transmission corresponds to samples of the same thickness but of different resistivity. As can be clearly seen in Fig. 3a, an increase of the thickness by a factor of 4, results in an increase of the attenuation by almost two orders of magnitude. Concerning the influence of resistivity on the average transmission, a reduction of the attenuation by more than two orders of magnitude is obtained when the resistivity is doubled. Finally, it

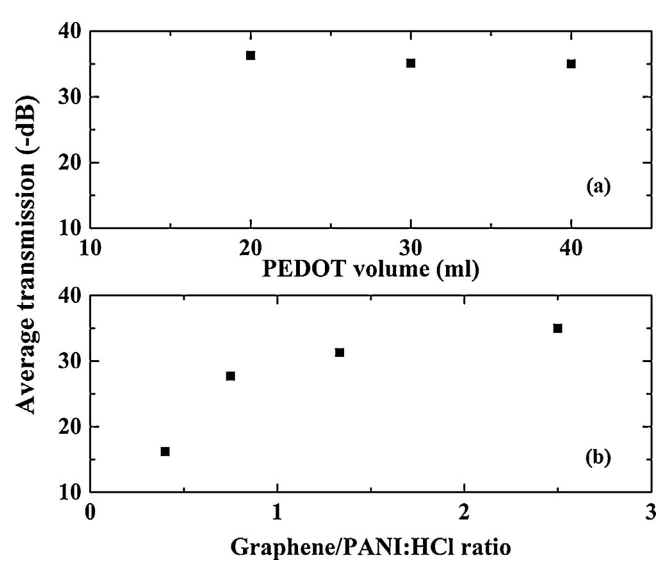

Fig. 3. Variation of the average transmission of the nanocomposites as a function of: (a) the amount of PEDOT:PSS used and (b) the ratio of the amount of graphene nanoplatelets and PANI:HCl employed, for the frequency range 5–10 GHz.

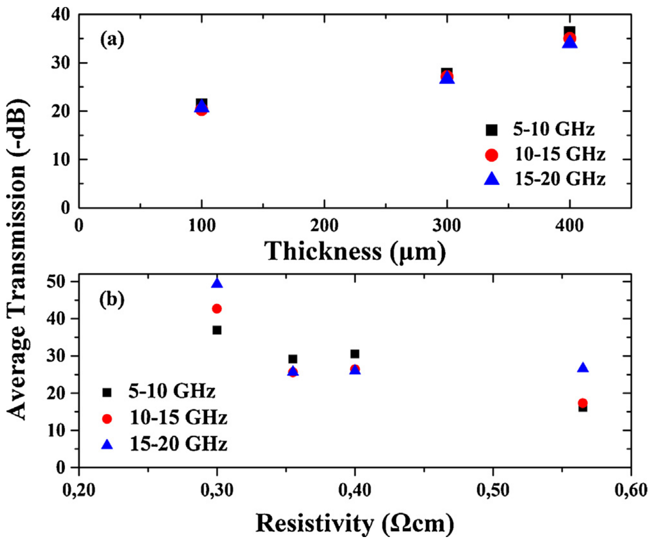

Fig. 4. Influence of: (a) the nanocomposite thickness and (b) its resistivity on its average transmission for the frequency range 5–20 GHz.

is worth mentioning that in the cases of large thickness and low resistivity, the electromagnetic shielding of our samples was found to be more effective by at least an order of magnitude with respect to the commercial product used as a standard.

These are preliminary results and further research is going on in order to clarify the origin of the electromagnetic shielding observed in the graphene nanoplatelets, PANI:HCl and PEDOT:PSS nanocomposite layers. Emphasis is given on the investigation of the relative contribution of absorption and reflection in the observed attenuation as well as the understanding of the underlying mechanisms and how the basic characteristics of the layers affect their functionality.

4. Conclusions

Results were presented related to the electromagnetic shielding performance of paint-like nanocomposite layers consisting of graphene nanoplatelets, PANI:HCl and PEDOT:PSS. As was shown, this formulation results in homogeneous and uniform layers inducing quite effective attenuation of electromagnetic radiation in the frequency range 4–20 GHz, with a response even better than that of commercial products, at least for layers with large thickness and low resistivity. The shielding performance was found to be based mostly on the graphene nanoplatelets and supported by PANI:HCl. In contrast, PEDOT:PSS played mainly the role of the binder, at least above a threshold concentration (20 mL for 7 g suspended solids). Finally, both resistivity and thickness were observed to significantly affect the functionality of the layers.

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