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Zinc oxide-graphene based composite layers for electromagnetic interference 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 interference shielding in the frequency range of 10–20 GHz. The layers, based on commercially available graphene nanoplatelets and ZnO nanopowder grown using a hydrothermal procedure, were found to induce quite effective attenuation of electromagnetic radiation in the frequency range 10–20 GHz of around −30 dBs, this depending on the ZnO nanopowder/graphene nanoplatelets ratio and the frequency employed.

1. Introduction

Recently, there have been an increased number of applications of electromagnetic waves in the Ku-band (12.4–18 GHz) for radar, military aircraft and satellite communication [1]. As a result, much attention has been devoted to develop material acting as electromagnetic interference (EMI) shields, EMI being a well-known problem in the operation of electronic devices [2]. These shielding materials are able to disable an electromagnetic wave to penetrate into a certain space through an absorption and/or reflection process. Conventionally, conductive metallic panes and meshes are used for isolating spaces or devices from radiation [3]. However, they have many disadvantages such as heaviness, lack of flexibility and high costs of processing. In addition, some metals have an intrinsic cut-off frequency, normally below or not far from the low-GHz range, which restricts their use for GHz-shielding applications.

The present needs are thus to find broad-band shields, able to neutralize electromagnetic radiation up to the GHz frequency range, a requirement arising from the fast development of electronics, operating at enhanced data transfer speeds that require higher frequencies [4]. Furthermore, the miniaturization of such components demands high performance and lightweight manufacturing materials. Nanocomposite polymeric materials offer several advantages over traditional metals and ceramics used for EMI shielding since they can be easily shaped into a wide variety of morphologies and are substantially lighter. Since polymers are electromagnetically transparent, the incorporation of suitable conductive nanoparticles is required for effective EMI shielding, while, the tailoring of their properties offers the possibility of tuning both the effectiveness and the frequency range of applications. Regarding the type of nanoparticles that can be used, three main alternatives exist, metals, metal oxide and carbonaceous. Reports have shown that the respective electromagnetic interference shielding is influenced by the enhancement of the electrical conductivity after their addition [5]. The incorporation of metal particles or nanowires from Ag [6,7] or Cu [7,8] have been reported, which however suffer from corrosion, and in addition, it is difficult to obtain their good dispersion and efficient incorporation into polymers. Carbonaceous particles in contrast, have gained

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increasing attention since they are chemically resistant, lightweight and more compatible with polymers. Graphite, carbon black, carbon fibers, carbon nanofibers and graphene have already been investigated for use as shielding materials in the high frequency range [9–13]. Finally, composites containing metal oxide nanostructures [14–18] are also potential candidates for effective EMI shielding, a prospect supported by the possibility of having metal oxide nanostructures of various morphologies with excellent properties using simple, low cost and environmental friendly chemical growth techniques to control their characteristics through the deposition parameters [19,20].

Graphene based materials, engineered via simple, low cost preparation techniques were recently studied in our laboratory, showing highly effective electromagnetic interference shielding in the GHz frequency range [12]. However, these graphene based formulations are extremely black, which is not the most desired color for presentable applications. On the other hand, as already mentioned in the literature, pure and doped ZnO is a good candidate for these applications, which has also the advantage of white color. In this work, we present preliminary results regarding ZnO nanopowder/graphene nanoplatelets based composite layers suitable for electromagnetic interference shielding in the 10–20 GHz frequency range, a composite material that never tested before for such an application. For this purpose, commercially available graphene platelets were employed, while, ZnO nanopowder was developed using a simple, low cost and environmental friendly hydrothermal procedure [21–24].

2. Experimental

The electromagnetic interference shielding layers, with thickness of around 900 nm, were deposited on 16 cm by 16 cm foam board by brushing paint-like dispersions in deionized water. Commercially available graphene nanoplatelets were used, provided by EMFUTUR Technologies Ltd. Spain, with 5 μm width, 5 nm thickness and a bulk density of 0.03 to 0.1 g/cm^3. The carbon content of the graphene nanoplatelets was >99.5 wt%, the oxygen content < 0.1%, while, a residual acid content of <0.5 wt% existed. The synthesis of ZnO nanopowder was performed using zinc acetate ($Zn(CH_3COO)_2$) as zinc precursor through the hydrothermal procedure. In the initial stage of the preparation, two approaches were employed so that the effect of oxygen source was studied, using H_2O (50 ml) in the first case and a ratio of 2-propanol:H_2O (50 ml:0.2 ml) in the second one, with the addition of 0.4 g $Zn(CH_3COO)_2$ in both cases. The solution was placed in Pyrex glass bottles with autoclavable screw caps and heated at 95 °C for a set period varied between 24 and 72 h. After the end of each induction period, the excess of solution was removed from the bottle and the as-grown powder was dried in a laboratory oven for 24 h at 95 °C. The characteristics of the ZnO powder were investigated using X-ray diffraction (XRD) in a Siemens D5000 Diffractometer with Cu K_α ($\lambda = 1.54056$ Å) for 2-theta = 30.00–70.00°, step size 0.05° and step time 5 min/°. Moreover, their morphology and content were examined using scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS), with a JEOL JSM 6362LV electron microscope and an INCA X-act dry cooling detector (Oxford) attached to the SEM, the respective operating parameters being: HV mode, operating voltage 20 kV, magnification 20,000, collection time corresponding to minimum 500,000 counts, in order to have a good accuracy.

During the preparation of the paint like dispersions, 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 air 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 SEM and EDS.

Finally, the transmission measurements of the prepared samples 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 10–20 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

Since a large quantity of ZnO nanopowder with suitable characteristics was required, the initial trials were focused on the optimization of the growth. Two approaches were chosen (based on a sufficient amount of powder prepared) and employed: (a) a solution of 50 ml H_2O and 0.4 g $Zn(CH_3COO)_2$ for synthesis period of 72 h and (b) a solution of 50 ml 2-propanol and 0.2 ml H_2O, keeping the amount of zinc precursor and growth period constant. The structural and morphological properties of the as grown ZnO nanopowder were then studied in XRD and SEM. As found out, the second approach was more promising since it resulted in homogeneous and uniform spherical grains with a diameter 100–200 nm, as shown in Fig. 1. Moreover, the respective nanopowder had better crystallinity, as one can observe in Fig. 2, which presents XRD patterns of the as-prepared powder at 95 °C using a solution based on a ratio of 2-propanol:H_2O. The diffraction peaks are consistent with the wurtzite ZnO hexagonal P6(3)mc structure (according to JCPDS card file No. 36-1451), the pattern indicating all the characteristic peaks of ZnO, while the determined lattice parameters values of $\alpha = 3.2504$ Å and $c = 5.2055$ Å indicate a very high crystalline quality of the chemically grown ZnO. Similar XRD patterns were also found for all nanopowder samples checked. In contrast, in the case of the pure water solution, the XRD pattern of the as grown nanopowder was consistent with ε-$Zn(OH)_2$ [19]. Therefore, it seems that the presence of 2-propanol compared with solely H_2O favored the precipitation of ZnO powder, a behavior similar to that observed in the presence of NaOH [20]. Following these results, a solution made from 50 ml 2-propanol and 0.2 ml H_2O with 0.4 g $Zn(CH_3COO)_2$ for 72 h at 95 °C was repeated for ten times for the growth of 5 g ZnO nanopowder, which was further used for the preparation of the composites.

Regarding the preparation of the composite layers to be tested as electromagnetic shields, the initial idea was to generate an inorganic cement using as binder $ZnCl_2$. However, this approach was unsuccessful, since, although the final layers had good mechanical properties, they were absorbing water from the atmosphere, a behavior causing a rapid degradation of both the samples and their functionality. Therefore, only one layer employing $ZnCl_2$ was finally tested, while the rest of the samples were prepared without any binder, since they presented better stability in the environment and quite effective electromagnetic

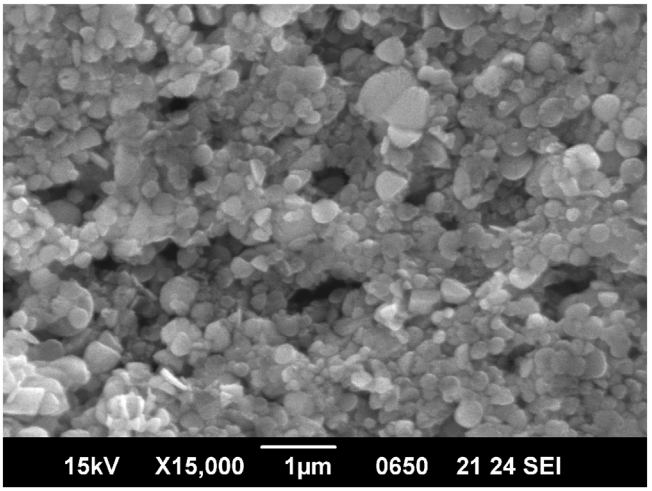

Fig. 1. SEM image of ZnO nanopowder grown using zinc acetate with 2-propanol:H_2O.