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Expanded graphite–nanoferrite–fly ash composites for shielding of electromagnetic pollution

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ABSTRACT

Expanded graphite (EG) was incorporated into fly ash matrix along with nanoferrite γ-Fe_2O_3 particles so that the resultant conductive fly ash composite can be used for electromagnetic shielding in microwave range. Conductivity of composites lies in the range 0.34–32.86 S/cm. TEM images show that fly ash particle (0.87 μm) is covered by sheets of EG containing the magnetic nanoparticles. Complex parameters have been calculated from experimental scattering parameters (S_{11} and S_{21}) using theoretical calculations given in Nicholson–Ross and Weir algorithms. The microwave absorption properties of the composites have been studied in the 8.2–12.4 GHz (X-band) frequency range which shows a shielding effectiveness up-to 90 dB, which strongly depends on dielectric loss and weight fraction of fly ash and γ-Fe_2O_3 in EG matrix.

1. Introduction

A shield acts in two ways against electromagnetic radiation, either by total refection or complete absorption of radiation. If electromagnetic (EM) waves indenting on the surface of a conducting shield then its attenuation occurs exponentially. The depth at which the EM field decreases to $1/e$ of the incident value is called the skin depth (δ), and for highly conductive materials, such as metal, it is given by the following equation [1,2]:

$$\delta = \sqrt{2/\sigma\omega\mu_o} \quad (1)$$

where σ (S cm^{-1}) is the electrical conductivity, ω is the angular frequency and μ_0 is the magnetic permeability. It is observed that at a given frequency, the high conductivity, magnetic permeability, thickness and dielectric constant of the materials are important for better electromagnetic interference (EMI) shielding [3]. Therefore, metals are good reflectors and commonly used for EMI shielding. On the other hand absorption based shield can be made using carbon-based materials [4,5], such as carbon black [6], graphite [1], graphene oxide (GO) [2], carbon fibers [7,8], and conducting polymers [9,10], along with some magnetic and dielectric filler. Graphene is a promising EMI shielding candidate due to their lightweight, high conductivity, and high mechanical properties. In the case of graphene/epoxy composites exhibited shielding effectiveness (SE) ~ 21 dB in the X band at a 15 wt% loading [11]. In the graphene–iron oxide composite, high aspect ratio of iron oxide has advantage in EMI shielding compared to pure graphene. Earlier studies have been done on the development of composites having both conducting and ferromagnetic properties by the incorporation of ferrite particles such as Fe_3O_4, manganese–zinc ferrite particles. The shielding in the frequency range of 8.2–12.4 GHz (X band) is more important for radar and radio communications applications [12].

The EMI SE of a composite material depends mainly on the filler's intrinsic conductivity [13], dielectric constant, and wt% ratio. Beside high electrical conductivity, it is very high surface area of graphene [14] which makes it a unique candidate to having moderate EMI shielding [15] in polymer composites with light weight. The primary mechanism due to reflection loss SE_R is the result of interaction between conducting particles in the conducting material (free electron or vacancy) and electromagnetic field [16] and it has relationship with the value of σ_r/μ_r. The absorption loss is quantified through μ_r, σ_r [17]. Due to sp^2 bonded carbon atoms partially reduced graphene oxide (RGO) [18] having high electrical properties. However, graphene lacks in magnetic properties and hence participated less in absorption of EM waves. In order to overcome this limitation we have incorporated different wt% ratios of iron oxide (γ-Fe_2O_3) [19–22] in EG matrix which absorbs more electromagnetic interference because of its magnetic permeability. It is not only environmental friendly but also has abundant natural supply, thus rendering the material inexpensive.

Here, we report, the waste material of coal power plant – fly ash which can be used as dielectric filler in EG matrix containing magnetic nanoparticles [20,21] to customize the properties of fly ash for EMI SE applications. The obtained results of composite are focused on the conductivity, shielding measurements and surface

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morphology and nanostructural/microstructural analysis of EG/γ-Fe_2O_3/fly ash three phase systems. Octadecylamine (ODA) has been used as a capping agent in composites. The vibrating sample magnetometer (VSM) study of composites with different amounts of EG, γ-Fe_2O_3 and fly ash have been carried out to find their magnetic induction and hence its effect on EMI shielding absorption. The composites having thickness 2.5 ± 0.1 mm have shown high value of shielding effectiveness ranging from 45 to 90 dB (∼99.99%) in the microwave range (X-band).

2. Experimental section

2.1. Materials

Natural graphite (Loba Chemie, India) has been used to synthesize expanded graphite (EG) and RGO. Methanol and iron acetylacetonate has been procured from Merck, India. Double distilled water (specific resistivity of 10^6 Ω-cm) used for have been preparing aqueous solutions and for filtration purpose. ODA has been procured from Across Organics, USA. Fly ash is used after removing unburned carbon and other oxides and named as treated fly ash.

2.2. Synthesis of expanded graphite

Graphite intercalated compound (GIC) is obtained by mixing natural graphite with mixture of acids consisting of concentrated H_2SO_4 and HNO_3 by stirring at room temperature and keeping for 24 h to form the GIC which is then rapidly expanded at temperatures between 800 and 900 °C to form EG [23,24]. The EG is dispersed in methanol for ultra-sonication and centrifuged at 15,000 rpm to obtain a stable suspension. But, it is observed that EG is not transformed in single or double layer graphene sheet because of insufficient oxidation of natural graphite while doing acid treatment or inadequate pressure that builds-up during thermal and chemical exfoliation.

2.3. Synthesis of graphene oxide

Modified Hummer's process [25,26] is used to synthesize graphene oxide (GO). The graphite powder (5 g) and $NaNO_3$ (5 g) is mixed into concentrated H_2SO_4 (230 ml). $KMnO_4$ (40 g) is added gradually with stirring and cooling, so that the temperature of the mixture is not allowed to reach beyond 20 °C. The mixture is then stirred at 35 °C for 2 h, and deionized water (200 ml) is added. The reaction is stirred for 1 h by the addition of a large amount of deionized water (300 ml) and 30% H_2O_2 solution (30 ml), causing violent effervescence and an increase in temperature to 100 °C, after which the color of the suspension changes to bright yellow. The suspension is washed with 1:10 HCl solution (100 ml) in order to remove metal ions. The paste collected is dried at 60 °C. The resultant powder is dispersed in distilled water followed by stirring and ultrasonication for 3 h.

2.4. Synthesis of reduced graphene oxide

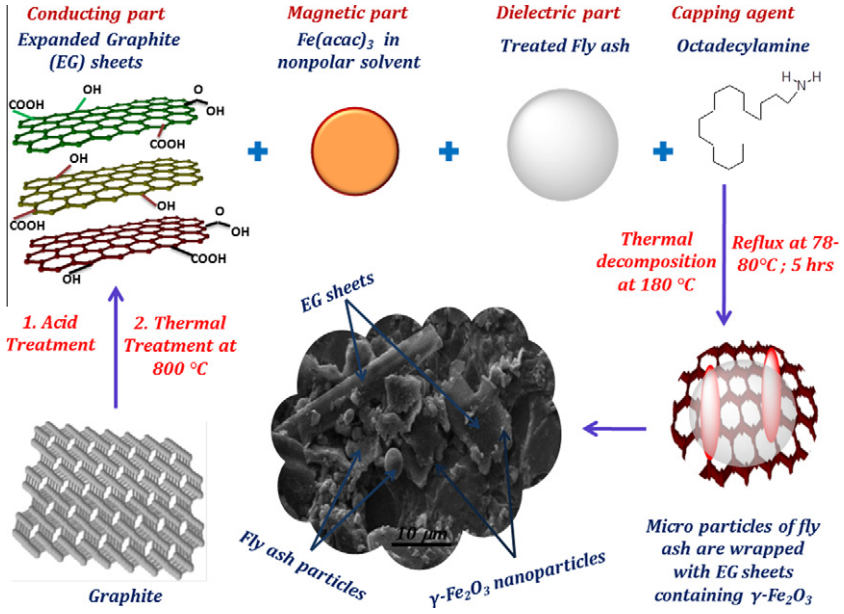
1gm of GO was dispersed in 1000 ml distilled water followed by stirring and ultrasonication for 3 h, 10 ml of hydrazine hydrate is added with continuous stirring for 24 h. Make the temperature of the solution to 95 °C. The suspension is washed thoroughly with distilled water. The paste collected after filtration is reduced graphene oxide which is heated at 60 °C in vacuum.

2.5. In situ synthesis of γ-Fe_2O_3 nanoparticles in fly ash, EG and the RGO matrix

The EG, iron acetylacetonate, fly ash and ODA were mixed in methanol and refluxed for 5 h at 80 °C. The subsequent mixture is further heated to 230 °C and checked simultaneously with external magnet until the magnetic property appear in the sample. The composites of EG, γ-Fe_2O_3 and fly ash have been formed with varying ratios of EG, γ-Fe_2O_3 and fly ash and are abbreviated as EGFFA111 where EG, $Fe(acac)_3$ and fly ash are taken in 1:1:1 wt. ratio, EGFFA112 where EG, $Fe(acac)_3$ and fly ash are taken in 1:1:2 wt. ratio, EGFFA121 for 1:2:1 ratio, EGFFA211 where EG, $Fe(acac)_3$ and fly ash are taken in 2:1:1 ratio respectively. RGOFFA111 consists RGO, $Fe(acac)_3$ and fly ash in 1:1:1 ratio.

2.6. Materials characterization

The surface morphology of EG, fly ash and EG/γ-Fe_2O_3/fly ash composites have been examined using scanning electron microscope (SEM, Zeiss EVO MA-10) at an acceleration voltage 10.0 kV and transmission electron microscope (TECNAI G^2T30, u-TWIN). The element mapping distribution of the samples were analyzed by energy dispersive X-ray spectroscopy which is associated with SEM. The magnetic measurements of the ferrite as well as conducting composites were carried out using the vibrating sample magnetometer (VSM), Model 7304, Lakeshore Cryotronics Inc. USA. The dc electrical conductivity of EG composites has been measured by a standard four-probe technique on pressed rectangular pallets of dimension 13.0 × 7.0 × 1.00 ± 0.1 mm^3 at room temperature in order to eliminate contact resistance effects, using Keithley programmable current source (model 6221) and nanovoltmeter (model 2182A). Electromagnetic shielding and dielectric measurements [27–29] have been carried out using Agilent E8362B Vector Network Analyzer in the 8.2–12.4 GHz (X-band) microwave range. The composite has compacted in a piston cylinder assembly at 60 MPa for 5 min into a 2.0 ± 0.2 mm thick rectangle pellet with a dimension to fit the waveguide dimensions. For detailed explanation on the testing fixture setup and specimen mounting see supporting material document. The electromagnetic attributes i.e. complex permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) and permeability) ($\mu^* = \mu' - i\mu''$) of EG/γ-$Fe_2O_3$/fly ash composite, have been calculated from experimental scattering parameters (S_{11} and S_{21}) using



Scheme 1. Schematic representation of preparation of different composites of EG/γ-Fe_2O_3/fly ash with varying ratios of EG, γ-Fe_2O_3 and fly ash using ODA as a capping agent in the organic medium.