Synthesis and characterization of nickel coated exfoliated graphite for microwave absorber applications

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Abstract

Microwave absorbing material of nickel coated exfoliated graphite (Ni-EG) was prepared by electroless deposition in alkaline coating bath. The coating time, which is an important factor to achieve good coverage of Ni particles over exfoliated graphite (EG), was properly controlled during the process. Morphology and phases of Ni-EG were investigated by means of SEM and XRD, respectively. Electromagnetic (EM) properties of Ni-EG/epoxy composites were recorded using VNA over the frequency range of 2-18 GHz. Ni-EG/epoxy composites exhibit significant microwave absorption properties for coating time 10, 20, 30 and 40 minutes. Specially, reflection loss value reached -23.7 dB at 10.9 GHz with 6.0 GHz (8.1-14.1 GHz) and 2.0 GHz (10.1-12.1 GHz) of -10 and -20 dB absorption bandwidths, respectively for 40 minutes of deposition time. Therefore, the proposed material has a great potential for stealth applications.

Keywords: Electroless, nickel coated exfoliated graphite, composite, microwave absorption, coating time.

Introduction

With the advancement of GHz communication amenities, military, civil and radar technologies; electromagnetic interference (EMI) have emerged as a serious threat for human health. Therefore, the demands for microwave absorbing material have aroused to solve the EMI problems **[1]**. Commercially, a microwave absorbing material should show thin thickness, broad absorption bandwidth and strong absorption concurrently. Well documented microwave absorbing materials such as ferrite, ceramics and Carbaneous materials have not full filled the above mentioned requirements **[2]**. Hence, a new type of material needs to be design that should exhibit exceptional microwave absorbing properties.

Carbon material i.e. exfoliated graphite (EG) is a potential microwave absorbing material because of its interesting multifunctional characteristics such as very low density, unique mechanical, thermal and electrical properties **[3]**. However, uncoated EG as a single filler cannot full fill the requirement of high microwave absorption performances **[4]**. It is expected that magnetic material coated EG would exhibit excellent microwave absorbing performance due to increase in the charge transfer between magnetic material and EG. Thereby, the composite composed of magnetic material-EG hybrid structure would give the combined effect of dielectric and magnetic properties **[5]**. Furthermore, magnetic material coating of EG has been found to promote homogeneous dispersion of EG in polymer matrix. The homogeneous dispersion may be helpful for Ni-EG based composites to fully utilize the microwave absorption properties. Therefore, the improved properties of magnetic material coated EG finds applications in EMI shielding, microwave absorbers and stealth technology.

Electroless Nickel (Ni) coating has been regarded as suitable method to change the physical and chemical properties of materials **[6-7]**. The aforementioned coating technique can be used to tailor permeability and permittivity of the material. In this proposed work, an attempt has been made to coat EG with Ni by electroless deposition and investigated their microwave absorption properties. Furthermore, it has been shown that microwave absorption performance can be tuned by simply varying the time for which EG has been dipped in the coating bath.

Experimental

Preparation of exfoliated graphite

Natural flake graphite (NFG) (purity, 99.61 wt%; average flake size, 500 μm; received from Sigma Aldrich), potassium permanganate (assay, 99.0%: obtained from Qualigens) sulfuric acid (assay, 98.0% by Fisher Scientific) and nitric acid (assay, 70.0%, purchased from Fisher Scientific) was used for fabrication of EG.

The exfoliated graphite (EG) was synthesized by means of thermal treatment **[8]**. NFG, intercalating and oxidizing agent; HNO_3/H_2SO_4 (2:1 by weight) kept in a percolation disc and mixed homogeneously by glass rod at room temperature. The prepared graphite intercalated compound (GIC) was then added with HnO_3 and $KMnO_4$ in porcelain dish for 2-4 minutes and finally taken in a beaker and exposed to furnace at 800˚C to form EG powder.

Electroless nickel deposition

For the Ni coating, Nickel sulphate ($NiSO_4•6H_2O$, 98.2%), ammonium chloride (NH_4Cl, 99%), tri-sodium citrate ($Na_3C_6H5O_7•2H_2O$, 99–100%), sodium hypophosphite ($Na_2H_2PO_2•H_2O$, 99%) and ammonia solution (25%) were used to prepare an alkaline coating bath (obtained from M/S Loba Chemie and Qualigens fine chemicals).

Electroless dip coating method was adopted for Ni deposition on EG **[9]**. **Table 1** represents the bath composition and functions of the ingredients. In the present work, as synthesized EG was dipped in prepared bath solution for 10, 20, 30 and 40 minutes. A constant temperature of 85˚C was maintained during deposition process to attain Ni particles on EG. Throughout the coating process pH value was adjusted to be ~8.5.

Table 1. Bath composition and functions of the ingredients.

Chemical	Quantity (g/1000 ml)	Function
Nickel sulphate	30	Ni ion source
Ammonium chloride	40	Chelating agent
Sodium tri-citrate	20	Bath stabilizer
Sodium hypophosphite	25	Reducing agent
aqueous ammonia	As required	Maintains pH(8.5)

Preparation of composites

Composite samples were prepared using epoxy (PG100, provided from M/S Resinova Chemie, India) as the matrix material and PHY161 (supplied by M/S Resinova Chemie, India)) as binder in the weight ratio of 10:1. Initially, Ni-EG (15 wt %) was uniformly dispersed in ethanol solution at room temperature. EG dispersed solution was mixed with epoxy resin and stirred for one hour in order to achieve homogeneous dispersion of Ni-EG in epoxy media. Curing agent was introduced in the mixture and mechanically mixed. The mixture was slowly poured into cylindrical mold (inner diameter 3.0 mm, outer diameter 7.0 mm) to form the composite structure. Finally, composite samples were dried in oven at 70°C for 4 hours to achieve complete polymerization.

The Ni coated EG (Ni-EG) was characterized by X-ray diffraction (XRD, Panalytical XPert for ultra-fast X-ray diffraction using Cu kα radiation), The uncoated EG and Ni coated EG with different deposition times were analyzed by scanning electron microscopy (SEM, EVO MA 15, Zeiss) to study the morphology and phases. The electromagnetic properties of the Ni-EG/epoxy composites were investigated by Agilent vector network analyzer (VNA) E8364B in frequency range of 2-18 GHz.

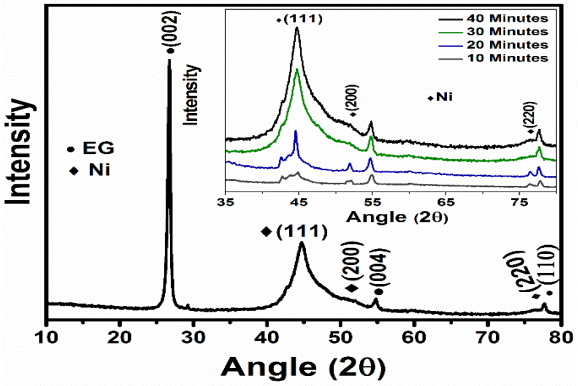

Fig. 1. XRD pattern of Nickel (Ni) coated exfoliated graphite powder for coating time 40 minutes. The inset represents the variation in Ni (111), Ni (200) and Ni (220) peaks with coating time 10, 20, 30 and 40 minutes.

Results and discussion

X-ray diffraction (XRD) pattern for Ni coated EG have shown in **Fig. 1**. A peak around 2θ of 26.5°, 54.8° and 77.4° corresponds to the graphitic carbon (002), (004) and (110) plane (JCPDS 41-1487). Other peaks observed at 2θ = 45°, 52° and 76.4° correspond to the nickel (111), (200) and (220) planes, respectively (JCPDS 87-0712) **[9]**. The intensity of Ni (111) is found to be increased with increase of coating time that is attributed to the prolong exposure of EG in coating bath that enabled dense coating of Ni over EG. Therefore, this confirmed the occurrence of Ni particles on EG. This will further be confirmed by SEM analysis.

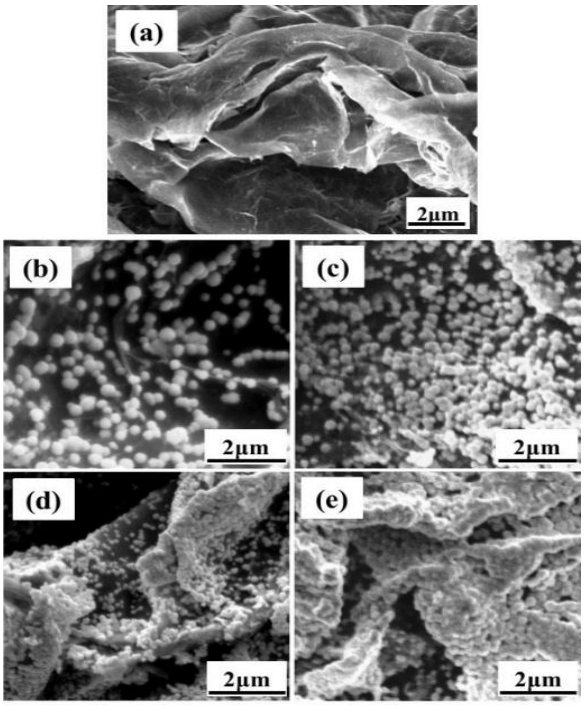

Fig. 2. SEM images of EG (a), electroless Ni coated EG for coating time 10 minutes (b), 20 minutes (c), 30 minutes (d), and 40 minutes (e).

Fig. 2(a-e) show the scanning electron microscope (SEM) images of EG and Ni coated EG. From **Fig. 2(a)** it can be seen that EG contains large numbers of galleries

and pores that will facilitate Ni particles to go deep into EG; provides well adhered special structure i.e. Ni coated EG. It is worth to notice that presence of small number of Ni particles on EG is observed in **Fig. 2(b&c)** for coating time 10 and 20 minutes, respectively. Whereas, very dense coating of Ni particles on EG was observed with coating time 30 and 40 minutes, respectively as shown in **Fig. 2(d-e)**. Therefore, electroless Ni coating process turned out to be simple and effective way to design Ni-EG hybrid structure in order to obtain superior microwave absorption properties.

Measurements by vector network analyzer (VNA) in frequency range 2–18 GHz for Ni-EG/epoxy composites show simultaneous increase in real (μ′) and imaginary permeability (μ″) and decrease in real (ε′) and imaginary permittivity (ε″) with increase in coating time **[10]** as shown in **Fig. 3(a-d)**. This is due to increase and decrease in weight share of Ni and EG, respectively for same weight of Ni-EG in epoxy. This shows that with increase in coating time the effect of dielectric losses diminishes, while influence of magnetic losses increases on the electromagnetic properties of composites. Further, real and imaginary permeability increases with increasing coating time. Thus, the loss mechanism for Ni-EG/epoxy composite comprises dielectric loss and magnetic loss simultaneously.

Microwave absorption performances of Ni-EG/epoxy composites were calculated using complex permeability, permittivity, frequency and thickness based on transmission-line theory **[11]**. **Fig. 3** represents the calculated RL of Ni-EG/epoxy composites with 15 wt% loadings at various coating times (tc) in the frequency range of 2–18 GHz with 3.0 mm of composite thicknesses. The minimum reflection loss increases with the increases of Ni coating time. It is worth to note that sample with 40 minutes of coating time exhibits strong microwave absorption performance than samples with coating time 10, 20 and 30 minutes; which signifies that high density of Ni particles on EG gives rise to additional magnetic loss other than dielectric loss that enhanced the resulting effective absorption performances.

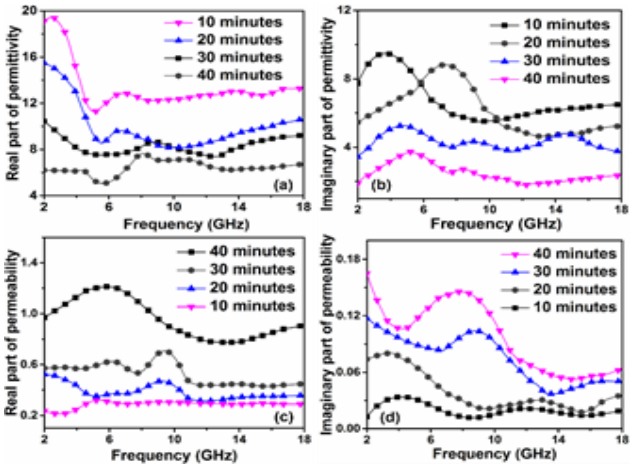

Fig. 3. Frequency dependence of (a) real, (b) imaginary part of permittivity, (c) real and (d) imaginary part of permeability for Ni-EG/epoxy composites with 10, 20, 30 and 40 minutes of coatings.

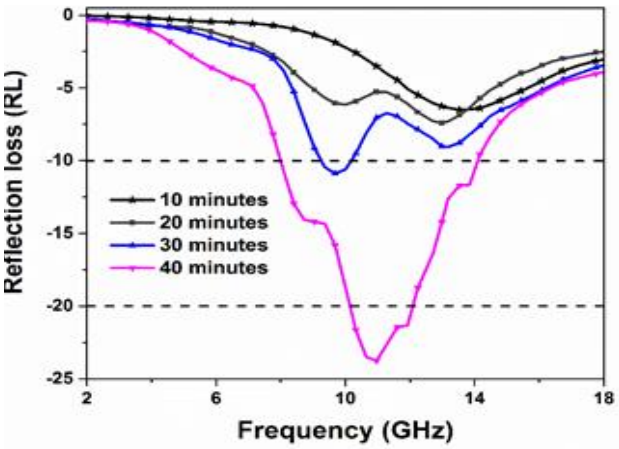

Fig. 4. Reflection loss curves of Ni-EG/epoxy composites with 10, 20, 30 and 40 minutes of coating at the thickness of 3.0 mm.

From **Fig. 4**, for Ni-EG (tc, 40 minutes), the minimum reflection loss is -23.7 dB at 10.9 GHz with 6.0 GHz (8.1-14.1 GHz) -10 dB bandwidth (more than 90% absorption) and 2.0 GHz (10.1-12.1 GHz) -20 dB bandwidth (more than 99% absorption). Composite samples with Ni-EG (tc, 10 minutes), Ni-EG (tc, 20 minutes) and Ni-EG (tc, 30 minutes) fillers show good microwave absorption in high frequency range of 8.0-14.5 GHz but only Ni-EG (tc, 30 minutes)/epoxy composite managed to reach the -10 dB absorption bandwidth mark that begins from 9.2-10.3 GHz and RL reached -10.9 dB at 9.7 GHz.

It is obvious from the reflection loss results that only Ni-EG/epoxy composite with 40 minutes of deposition time was able to touch the -20 dB absorption. This is attributed to very dense coating of Ni over EG. From the above discussion we can also conclude that for a given loading and thickness, the absorption properties can alter by simply changing coating time. Aforementioned properties of Ni coated EG/epoxy composite exemplified it as a promising microwave absorbing candidate for practical applications.

Conclusion

Ni coated EG was obtained by electroless coating method for coating time of 10 to 40 minutes in a step of 10 minutes. X-ray diffraction (XRD) and Scanning electron microscope (SEM) probes were used to determine the existence of nickel particles over EG surface. They show an increase in Ni particle density with increase in coating time. Composites were synthesized by using Ni-EG as filler in epoxy to study the effect of coating time on electromagnetic properties of the composites. The microwave absorption properties of Ni- EG/epoxy composites with coating time of 10, 20 and 30 minutes are less compared to Ni-EG/epoxy composite with coating time of 40 minutes. It was observed that RL of Ni-EG (tc, 40 minutes)/epoxy composite for 15% of loading reached -23.7 dB at 10.9 GHz with -10 and -20 dB absorption bandwidths begin from 8.1-14.1 GHz and 10.1-12.1 GHz, respectively. Thus, Ni-EG hybrid structure has turned out to be a great microwave absorbing material for various strategic applications.

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