

Coating of Cobalt Ferrite Nanoparticles on Carbon Fibres by Electrophoretic Deposition Method for Magnetic and Microwave Studies

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ABSTRACT: Sol gel method was employed to synthesize Cobalt ferrite (CoFe_2O_4) nanoparticles and these particles were successfully deposited on micron size carbon fibres (CFs) using electrophoretic deposition (EPD) method to study microwave absorption properties. A well stabilized suspension of cobalt ferrite nanoparticles was prepared in acetone media with a pH value of 2 and iodine acted as a stabilizing agent. Two different parameters such as voltage and time were taken into account, respectively to investigate their effect on uniformity, the amount of deposition and thereafter microwave absorption. Field-Emission Scanning electron microscopy (FE-SEM), Energy-dispersive X-ray (EDX) and X-ray Diffractometer (XRD) were employed to study morphology, crystallographic phase and composition of powder, respectively. To investigate the magnetic and reflection loss (RL) property, Permagraph and vector network analyser (VNA) were used. Particle size distribution and zeta potential was obtained by Dynamic Light Scattering (DLS) device. The results proved that EPD can be applied for microwave absorbing materials. It was then seen that by increasing voltage and time to 25V and 10 min, amount and uniformity of deposited nanoparticles were increased and this led to a RL of -9dB in vicinity of 8 to 12 GHz.

KEYWORDS: Cobalt ferrite nanoparticles, Carbon fibre, EPD, Absorption.

I. INTRODUCTION

EPD method has been vastly used to fabricate controlled coatings and has gained a lot of interest in last few decades. A characteristic feature of this process is that colloidal particles suspended in a liquid medium migrate under the influence of an electric field (electrophoresis) and are deposited onto an electrode. All colloidal particles that can be used to form stable suspensions and that can carry a charge that can be used in EPD. This includes materials like polymers, pigments, dyes, ceramics and metals. H. Salimkhani et al. studied EPD of Nano- Fe_3O_4 on CFs, microwave absorptive properties of their composites and the parameters controlling stability of suspension [1,2]. Y. Hayash et al. investigated nanostructured film composed of the CoFe_2O_4 embedded in the metal Co matrix fabricated by the EPD of Co-ferrite particles and electroplating of metal Co in combination [3]. N. Shellhammer studied splitting of water into hydrogen and oxygen through an oxygen and hydrogen sub-cycle. Therefore, he proposed that EPD can be employed to deposit nanoparticles of CoFe_2O_4 into 3D felt substrates as an electro catalyst to improve the kinetically slow anodic reaction of the oxidation of ammonium sulphite and he also determined the EPD conditions and suspension properties of CoFe_2O_4 [4]. AJ. Krejci investigated that the reason that nanoparticles are suspended in nonpolar solvents, the origin of charges in nonpolar solvents and finally, the effects of introducing an electric field to a NP suspension will be

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explained. The main particles they concentrated on, were CoFe_2O_4 and Fe_3O_4 [5]. S.J. Kelly et al. employed EPD method to investigate magnetization properties of Ni-Zn-Ferrite particles on silicon substrate for high frequency applications [6]. G. Jian et al. employed EPD method for the preparation of CoFe_2O_4 films on $\text{Al}_2\text{O}_3/\text{Pt}$ substrates. They also studied Influences of suspension parameters such as solvents, iodine additive, and charged polymer on the suspension stability [7]. Nowadays, Radar absorbing materials (RAMs) are one of the most interesting fields to explore. RAMs can be categorized as impedance matching or resonant absorbers. They are fabricated from resistive and/or magnetic materials. The conventional microwave absorption materials such as metallic powders of iron, cobalt and nickel are relatively expensive and quite heavy, which restricts their application in fields requiring low price and lightweight [8, 9]. The application scope of RAMs nowadays, is in a large variety of fields such as aerospace and aeronautics, electromagnetic (EM) protection from natural phenomena (lightning) and intentional interfaces [10, 11]. Here in this study we will concentrate on preparing an optimized conditions for EPD of CoFe_2O_4 to control suspension, uniformity of coating and proper composite fabrication. Another goal of this study is to evaluate effect of coating morphology on microwave absorptive properties and also magnetic properties of and elemental analysis of $\text{CoFe}_2\text{O}_4/\text{CFs}$ will be discussed.

II. RELATED WORK

1. Materials

Pure iodine (99.85%), acetone (99%), citric acid (99%) and ammonia (30%) supplied by Alpha Chemika in India, Pure $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sulphuric acid (98%) and nitric acid (65%) supplied by Merck, carbon fibres ($D=0.7\mu\text{m}$) supplied by Chongqing Joywell Trade Co, China Ltd, Epoxy (Viscosity in $25^\circ\text{C}=1.75$ MPa.S and specific weight 1.15 g/cm³) and its hardener (Viscosity in $25^\circ\text{C}=1.1$ MPa.S and specific weight= 1.0 g/cm³) were all purchased and used without further purification.

2. Synthesis of CoFe_2O_4 nanoparticles

The CoFe_2O_4 nanoparticles were prepared by sol-gel auto-combustion method. The stoichiometric amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a certain amount of deionized water. Citric acid was then added to the mixture solution with a constant stirring, and then an ammonia solution was added to adjust the PH value to 7. Subsequently, the solution was slowly evaporated to obtain a gel. The gel was decomposed at 200°C for 2h, and then the obtained powder was heat treated at 996°C for 2h in air.

3. Preparation of suspension

Acetone was used as an inorganic solution. For preparation of each suspension, 75 mL of above mentioned solutions were employed. For each 75 mL solution, 0.3g CoFe_2O_4 powder and 0.03g iodine as a stabilizing agent was added and the pH of all samples were adjusted to be 2 using 0.2 M nitric acid. Subsequently, the prepared suspensions were ultrasonicated for 15 minutes. CFs were treated with 65w% nitric acid for 4 hours, washed with deionized water and dried at 120°C for 24 hours to increase interfacial bonding strength between nanoparticles and CFs. [11].

4. EPD procedure

A cylindrical borosilicate glass beaker was used as the bath. A stainless steel electrode with dimensions of 2.5×10 cm and a bunch of pan based CFs with approximate dimensions of 2.5×10 cm were taken as anode and cathode, respectively. The distance between anode and cathode was adjusted to be 3 cm. A power supply of DC with a maximum voltage of 45V and 5A was employed for EPD process. Various number of deposition processes were conducted to optimize procedure. To determine optimum voltage amount, firstly, time was taken constant and voltage was altered from 5V to 25V by a 5-volts step and each process took 4 minutes. Secondly, voltage was taken constant and five different deposition times from 2 to 10 minutes by a 2-minutes time step was performed in 25V. Each time, the $\text{CoFe}_2\text{O}_4/\text{CFs}$ were carefully extracted from suspensions and immersed in distilled water for several seconds in order to have loose particles segregated and prevent sudden evaporation of acetone at ambient temperature which in turn causes propagation of micro cracks on $\text{CoFe}_2\text{O}_4/\text{CFs}$ coating.

5. Fabrication of composites from $\text{CoFe}_2\text{O}_4/\text{CFs}$

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CoFe₂O₄/CFs were cut carefully to the length of 3mm. 0.2g CoFe₂O₄/CFs was mixed with 0.2g epoxy and the mixture was then vibrated slowly until become homogenous. An aluminium substrate with dimensions of 2×1 was employed and before using, was dipped in a 70%w sulfuric acid at temperature of 80oC for 3 hours to increase the interfacial bonding strength between epoxy and substrate. The epoxy and CoFe₂O₄/CFs mixture was slowly laid on substrate in a way that completely covered the surface in which the thickness of coating was adjusted to be less than 1 mm and finally two drops of hardener was added to composition.

6. Materials characterization

XRD of the CoFe₂O₄ nanoparticles was studied using a Bruker AXF (D8 Advance) with a Cu Ka radiation source ($\lambda=0.154056$ nm) generated at 40 kV and 35 mA under the angle of 10 to 80 degrees. FE-SEM images and EDX analysis were both taken (by MIRA3 FEG-SEM, Tescan, Czech) to investigate morphology of deposition and participating element, respectively. DLS analysis (by Nanotracs Wave, Microtrac, USA) was used to determine the particle size distribution and Zeta potential of the suspension. The microwave absorption properties and RL of CoFe₂O₄/CFs composites measured over the frequency range of 8–12 GHz by VNA (model HP) at room temperature. The magnetic properties of CoFe₂O₄/CFs composites were studied with a VSM (C300) at room temperature.

Table 1
Comparison between Numerical and Experimental data

Sample	a	b	cd	
Time (min)	10	10	4	4
Voltage (V)	25	25	10	10

III. EXPERIMENTAL RESULTS

Table.1 is presenting parameters of different samples with a different coating voltage and different coating time. 4 samples were chosen to be characterized and they were named (a), (b), (c) and (d).

1. Structure and particle size of CoFe₂O₄

Fig.1 shows XRD patterns of CoFe₂O₄ and CoFe₂O₄/CFs. It is easily seen that main peaks of CoFe₂O₄ and CoFe₂O₄/CFs patterns correspond to each other according to JCPDS card No. 22-1086 and this confirms deposition of CoFe₂O₄ nanoparticles on CFs. Six diffraction peaks at $2\theta = 30.085, 37.058, 47.150, 53.446, 56.975$ and 62.587 can be assigned to scattering from the (220), (311), (400), (422), (511) and (440) planes of the CoFe₂O₄ crystal lattice. Sharp peaks indicate that the nanoparticles have crystallized well enough as well as maximum formation of spinel structure has occurred.

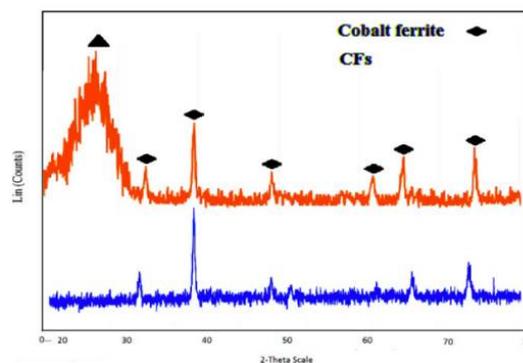


Fig. 1. XRD pattern of CoFe₂O₄ and CoFe₂O₄/CFs

Fig.2 shows DLS analysis of 0.3g of suspended CoFe_2O_4 particles in acetone medium. As it is seen from the figure, size distribution of particles is in range of 30 to 70 nm. But the sharp peak corresponds to 50 nm which is a dominant particle size distribution in suspension. DLS was also employed to determine zeta potential of suspension in which it was recorded to be 28 mV.

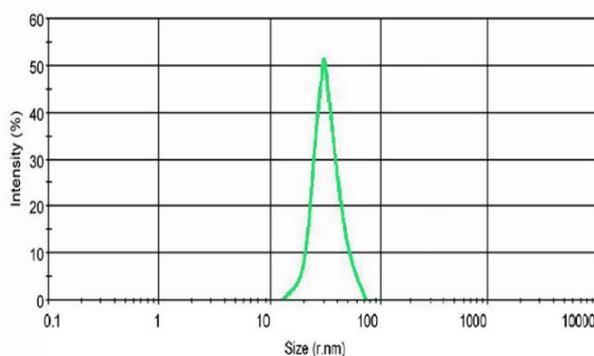


Fig.2. DLS curve of suspended CoFe_2O_4 nanoparticles in acetone solution

3.1 Surface morphology of $\text{CoFe}_2\text{O}_4/\text{CFs}$

As it is observed from (a) and (b) in Fig. 3, CoFe_2O_4 Nanoparticles have uniformly deposited on CFs. Uniformity of coating is apparent from both figures. Thank to iodine for generating such a high zeta potential amount in acetone containing suspension. Fig. (b), is presenting a high density coating of particles with a larger magnification. Both samples have been coated under the voltage of 25 V for 10 minutes. The other parameters influencing coating morphology and amount of deposition are voltage and time. Fig. (c), demonstrates a coating performed under the voltage of 10 V for 4 minutes. As you can see, vacancies are all over the CF. This means; in such a lower voltage, particles are not attended to attack CFs due to a lower generated electric field. The other factor decreasing density is not immersing $\text{CoFe}_2\text{O}_4/\text{CFs}$ right after extracting from suspension. As you can see from Fig. (d), evaporation of acetone has left porosities behind which in turn intrinsically influences density, thereafter microwave absorption property of final product. Nevertheless, the morphology of this sample is weigh better than sample (c). Using EPD method, morphology of coating can be controlled and thereafter microwave absorption is affected.

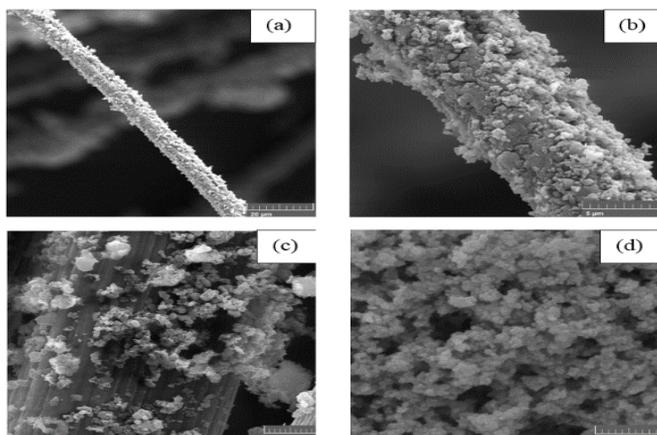


Fig.3. FE-SEM images of (a), (b), (c) and (d) samples of $\text{CoFe}_2\text{O}_4/\text{CFs}$

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Fig.4 presents EDX analysis of sample (a). As it is observed from the figure, only peaks related to Carbon, Oxygen, Iron and Cobalt exist in composition. Therefore, there is not any trace of impurities. Carbon amount seems to be the dominant element in composition. By employing a simple qualitative calculation, ratios of C/Fe and C/Co can easily be obtained so that the effect of different ratios of them on RL of samples can be determined.

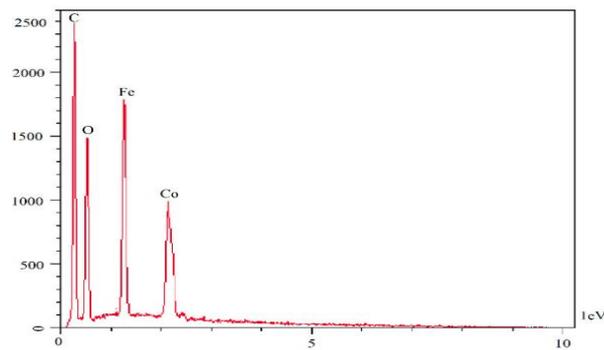


Fig.4. Presents EDX analysis of CFs/Co₂Fe₂O₄

3.2 Magnetic properties

Magnetic properties of as-synthesized CoFe₂O₄ was measured by VSM at room temperature and is shown in Fig. 5. Results revealed a noiseless hysteresis loop proving ferromagnetivity of nanoparticles. As it is observed from the figure, curves indicate a soft magnetic property for the synthesized powder. Coercive force (H_c) and remanence (B_R) were also calculated to be 0.21 KOe and 0.92 KG, respectively.

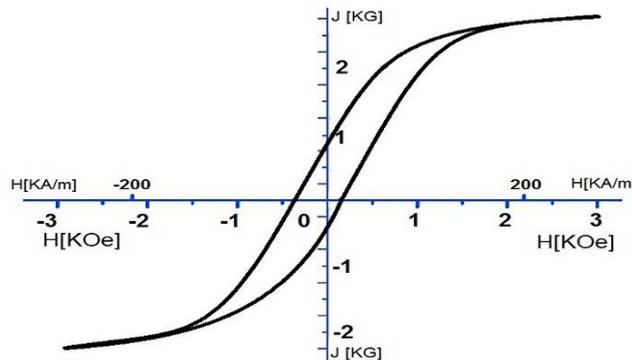


Fig.5. Hysteresis loop of synthesized CoFe₂O₄ nanoparticles

3.3 Characterization of microwave attenuation

The reflection loss (RL) of a microwave absorption layer backed by a perfect conductor was calculated by the following equations:

$$RL = 20 \log \frac{Z_{in} - 1}{Z_{in} + 1} \quad (1)$$

$$Z_{in} = \sqrt{\frac{\mu_r}{\epsilon_r}} \left[\tanh \left(\frac{2\pi f d}{c} \sqrt{\mu_r \epsilon_r} \right) \right] \quad (2)$$

As we know, the design of EM waves absorbing materials with low reflection requires two important conditions. The first is “impedance matching characteristic” in which the intrinsic impedance of material is made equal to the

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impedance of free space. The second is “attenuation characteristic” in which the incident EM waves must enter and get attenuated rapidly through the material layer, thus reducing the emerging wave to an acceptable low magnitude. It can be noticed from relation (1) and (2) that the combinations of six parameters (ϵ' , ϵ'' , μ' , μ'' , f and d) where $Z_0 = \sqrt{\mu_0/\epsilon_0}$ is the impedance of the free space; μ_r and ϵ_r are the relative permeability and permittivity of the absorber; f is the frequency of the electromagnetic wave; d is the thickness of the absorber; c is the velocity of light in free space, determine the microwave absorption of the composites. The minimizing reflection of incident plane wave can occur when Z_{in} is close to the constant Z_0 . Fig. 6 shows variation in the RL against frequency of all samples with different CoFe_2O_4 coating content in frequency range of 8-12 GHz.

As we can see here, the strongest RL of -9 dB at 11.5 GHz occurred in (a); As shown in Fig.6, sample (a) presents a high microwave absorption in the frequency range of 8–12 GHz compared to the other coatings, which indicates that the Z_{in} of (a) should match Z_0 most when the thickness of the composite is 1 mm and at the frequency range of 8–12 GHz. The lower reflection loss of the (b), (c) and (d) can probably be attributed to lower amount of coatings, lower density and vacancies. However, RL results for (b), (c) and (d) are not much distinguishable.

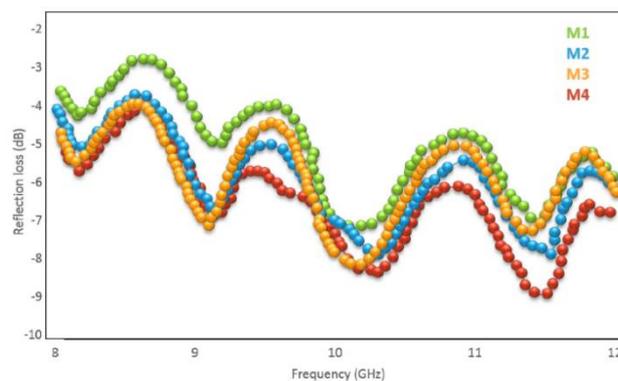


Fig.6. Variation of RL against frequency for samples of (a), (b), (c) and (d)

IV. CONCLUSION

Result from EPD process in this study revealed that this method can be applicable in fabricating microwave attenuating composites. Maximum RL of approximately -9 dB can be achieved by this method only by controlling vital parameters of suspension and morphology of coating. The following results were obtained from each step of this experiment:

1. CFs appeared as a wide peak in XRD analysis.
2. DLS analysis approved the estimated particle size distribution from FE-SEM images.
3. Zeta potential was measured to be 28mV and iodine had great influence on that.
4. FE-SEM analysis showed a crack free, continuous, non-agglomerated and uniform coating.
5. EDX analysis showed no impurities.
6. Coercive force (H_c) and remanence (B_R) were also calculated to be 0.21 KOe and 0.92 KG, respectively
7. The best microwave attenuation was related to (a) sample with a RL of -9 dB at 11.5 GHz.

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