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Study on the Magnetic and Microwave Properties of Electrophoretically Deposited Nano-Fe_3O_4 on Carbon Fiber

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Abstract

Microwave absorbing paints made of magnetite (nano-Fe_3O_4) coated carbon fibers (MCCFs) play an important role in wireless data communication, local area network, satellite television, heating system, vehicles stealthing and so on. In this study production of MCCFs composites using electrophoretic deposition (EPD) technique has been investigated. For this purpose, the Fe_3O_4 nanoparticles with an average size of 50 nm were synthesized by reduction of Fe (III)-tri-ethanolamine in an aqueous alkaline solution and then a uniform and compact Fe_3O_4 thin-film was coated on the surface of nitric acid treated carbon fiber by EPD method. The crystal structure, morphology and particle size distribution of the powders and composites were examined using the X-ray diffraction (XRD), scanning electron microscopy (SEM) and dynamic light scattering (DLS) techniques, respectively. The magnetic properties and the microwave absorption behaviors of the MCCFs were determined in the form of epoxy matrix composites using a J-H hysteresis loop tracer and a vector network analyzer (VNA, at the X-band frequency range), respectively. According to the results, the XRD patterns of composites and nano powders showed that in temperature of 80 0C Fe_3O_4 phases have been formed. Moreover, the strongest reflection loss (RL) of MCCFs was recognized to be −7.8 dB (i.e. absorbing 83%) at 9.3 GHz for a layer containing 50%wt MCCFs with 2 mm in thickness. Electrophoretic deposition was introduced as a suitable method for production of MCCFs due to its low cost, easy productivity and time efficiency.

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Keywords: Electrophoretic deposition; Fe_3O_4 Nano-powder; Carbon fibers coating; Magnetic material.

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1. Introduction

Nowadays the popularity and use of electronic devices for various applications increases, progressively. All of these electronic devices work within a range of frequency of electromagnetic (EM) waves which is produced by a power source, Osouli-Bostanabad et al. (2015), Osouli-Bostanabad and Kianvash (2013). The microwave absorption materials have attracted a lot of attention in recent years, but the conventional microwave absorption materials such as metallic powders of iron, cobalt, nickel and ferrites are relatively expensive and quite heavy, which restricts their use in applications requiring low price and lightweight, Zenga and Xu (2010), Jun et al. (2009), Liua et al. (2011), Meng et al. (2011). Therefore, the demands to develop microwave absorbing materials with "thin and lightweight" characteristics are increased. Recently, carbon based composite materials have been developed for microwave absorption applications. These composites have possessed high mechanical strength and elastic modulus, good carrying capacity and low electrical resistivity (10−2 Ωcm), for which they are increasingly recognized as the practical structures for absorbing applications, Fan et al. (2008), Jun et al. (2009). In this regard, Osouli et al. coated carbon fibers with magnetite thin layer by electro-deposition technique, Osouli-Bostanabad et al. (2015). Fan et al. employed low-temperature wet chemical method for preparation of Fe_3O_4 coated carbon fibers, Fan et al. (2008). As an important magnetic material, Fe_3O_4 has been reported extensively in view of its excellent microwave absorption properties, Osouli-Bostanabad et al. (2015), Osouli-Bostanabad and Kianvash (2013), Meng et al. (2011). As compared with the other advanced deposition methods, the EPD process can be adjusted easily for a special purpose. For instance, only with a small change in deposition bath design the coating can be made on cylindrical, flat or any other shaped substrate. Morphology and thickness of a deposited film can be easily controlled through simple adjustment of the applied voltage and deposition time, Osouli-Bostanabad et al. (2015). Considering these unique properties of carbon fibers (CFs) and Fe_3O_4, we tried to prepare Fe_3O_4 films on CFs, which are expected to exhibit good radar-absorbing properties. In this investigation, magnetite (Fe_3O_4) coated carbon fibers (MCCFs) was successfully fabricated by the cathodic electrophoretic deposition method and the microstructure, magnetic and reflection loss properties of MCCFs composites were then studied, thoroughly.

2. Materials and method

Nano-Fe_3O_4 was synthesized in an alkaline solution of $Fe_2(SO_4)_3$-xH_2O (12357 Sigma-Aldrich) stabilized by tri-ethanolamine (TEA) (2922 13 10 Merck) within the sedimentation medium of NaOH (2815 11 00 Merck). All chemicals were used without further purification. The concentrations in the bath were 0.09 M Fe (III), 0.1 M TEA, and 1 M NaOH. The solution was made by adding Fe^{3+} solution dropwise into a mixture of stirred TEA and NaOH solutions at 60 °C. After a while, the reaction mixture was heated up to 80 °C for 1 hr until black colored particles were recognized. Finally, to preparation of a colloidal solution with a meticulously determined composition before doing the EPD process, the resulting Fe_3O_4 nanoparticles were gathered by a magnet and washed with acetone for a few times, that is necessary for achieving a stable suspension with a good dispersion of nanoparticles and obtaining the good ability to control the surface charge of particles in order to have a successful EPD process.

PAN based CFs of 7–8 μm in diameter and 10 cm in length were used as the substrates to synthesize MCCFs. Before electrophoretic deposition, The CFs chatodes were treated with nitric acid (65 wt.%) for 4 h at room temperature in order to enhance the interfacial adhesion between the films and CFs, Liua et al. (2011), Meng et al. (2011), Fan et al. (2008), and then washed thoroughly and dried for 24 h at 120 °C. Pure iron sheet (99.99%) served as anode.

In general, electrophoretic deposition accomplished in the organic solvents so in this work acetone was used as dispersing media. 0.6 g of iodine was dissolved in a mixed solution containing 200 mL acetone and 10 ml HCl (0.2 $mol.L^{-1}$) solution as electrolyte. The stable suspension was prepared using dispersion of 0.8 g Fe_3O_4 as-synthesized powder with a mechanical stirrer. EPD process was done using a direct current supplier with a constant voltage of 32.6 V. In order to improve the quality of electrophoretically coated magnetite, multi-step coating was performed in such a way that each sample was deposited electrophoretically in three steps (i.e. the deposition was conducted three times), and after each step the agglomerated parts were removed from the surface. The time of the mentioned steps was 15 min, 6 min and 15 min, respectively. After each step, the sample was rinsed with acetone.

The microstructure and morphology of Fe_3O_4 powder and MCCFs composite were characterized using XRD (Siemens D5000 X-Ray diffractometer, Germany-Cu Kα radiation, k =1.5405 A˚), FE-SEM (MIRA3 FEG-SEM, Tescan, Czech), respectively. Dynamic Light Scattering (DLS (Nanotrac Wave, Microtrac, USA)) was used in order to determine the particle size distribution and Zeta potential of the suspension. The magnetic properties of MCCFs composites were studied with a Permagraph (C300) at room temperature. The microwave absorption properties and reflection loss (RL) of MCCFs composites measured over the frequency range of 8–12 GHz by vector network analyzer (VNA model HP) at room temperature. For microwave absorption measurements, the MCCFs composites were cut into short fragments (2–3 mm in length) and mixed with desired amount of epoxy resin with the aid of mechanical agitation. The mixtures poured into a rectangular mold with the dimension of 10 mm× 21 mm×3 mm. The weight fraction of MCCFs was measured to be 50%.

3. Results and discussions

Figure 1 presents the typical XRD patterns for as-synthesized nano-Fe_3O_4 powder (a) and MCCFs (b). All the peaks in Fig. 1a can be categorized as spinel structure of Fe_3O_4 phase with lattice constant a=8.391Å, which is in good agreement with JCPDS, No. 19-0629. No diffracted peaks other than those from Fe_3O_4 suggested higher purity of as-synthesized magnetite phase and also the strong and sharp peaks indicating well crystallization of synthesized magnetite particles. The peaks illustrated in Fig. 1b may be attributed to Fe_3O_4 and graphite phases. The broadened peak around 26° can be allocated to the graphitic structure of CFs. Furthermore, the nine diffraction peaks at 2θ angles of 18.96, 29.24, 36.66, 37.54, 44.84, 53.92, 57.4, 63.34 and 73.93 seems to be the characteristic peaks for spinel structure of Fe_3O_4 phase that can be attributed to scattering from the (111), (220), (311), (222), (400), (422), (511), (440) and (533) planes of the Fe_3O_4 crystal lattice, respectively.

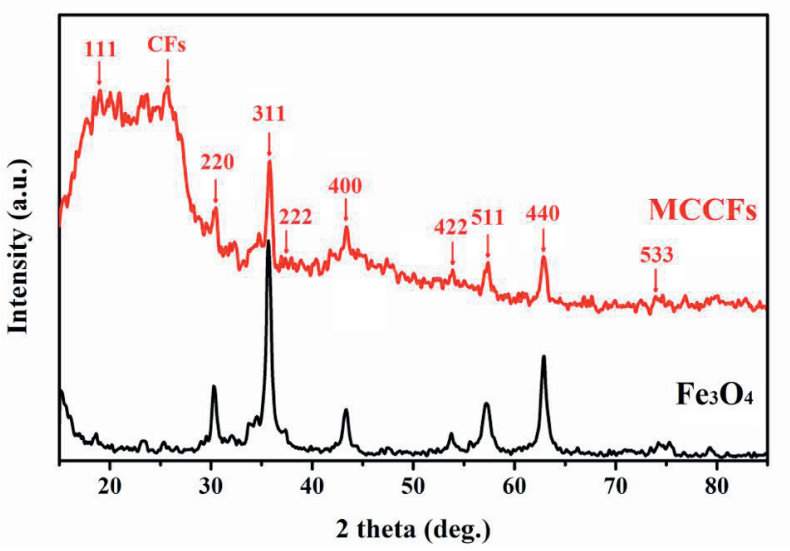

Fig. 1. Typical XRD patterns of as-synthesized nano-Fe_3O_4 powder and MCCFs.

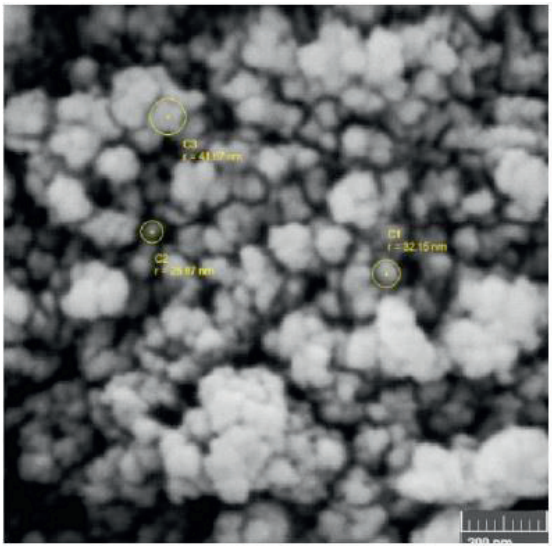

Fig. 2. FE-SEM image of the as-prepared Fe_3O_4 nanoparticles.

Figure 2 shows the FE-SEM micrograph of as-synthesized Fe_3O_4 powder with an average crystalline size much smaller than 50 nm. Some Fe_3O_4 particles with the approximate size of 30 nm have been recognized in FE-SEM image.

From the DLS calculation the zeta potential of suspension was determined to be 6.2 mV. The mobility of the suspend powders depends on the zeta potential of the particles so in this case regard to the result of DLS examination the stabilized nanoparticles in electrolyte would be having a slow mobility, so we need a prolonged EPD process, but the deposition rate for a constant applied voltage decreases with increasing the deposition time and also the tendency toward the formation of the agglomerate increases with increasing the EPD time and deposition of nano-magnetite particles mainly occur in the certain areas on the surface of CFs, which leads to the formation of aggregates instead of homogeneous coating layer. This is while the short time EPD process with this low mobility of suspended particles leads to the formation of very thin and inhomogeneous magnetite coating layer. As previously mentioned, using a multi-step coating method in which the time steps are equal to the 15 min, 6 min and 15 min, respectively, is an effective way to control the thickness of the magnetite coating layer, which by reducing aggregation of these nano-particles (Fe_3O_4 nano-particles) a uniform and homogenous coating can be achieved and consequently, the electromagnetic absorption properties of the products could be improved.

Figure 3 shows the DLS results of Magnetite powder which demonstrate the distribution of particles in the electrolyte. As it is illustrated, the average size of particles is about 50 nm and the particles are distributed in the

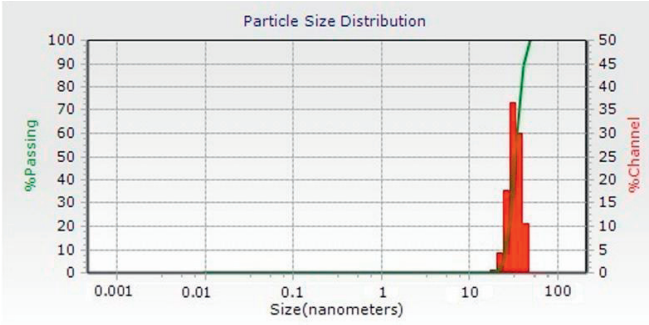

Fig. 3. Particle size distribution of Fe_3O_4 particles as a function of volume of Fe_3O_4 particles.

range of 36.4 to 59.8 nm. There is also the probability of existence of smaller and larger particles which is not reported in Fig. 3 because those ranges are fewer than 10% of quantity. The fine distribution range of particles and the spherical morphology of them that was illustrated according to FE-SEM micrographs (Fig. 2) could help prepare a stable suspension due to Browinian motions of particles and consequently well dispersion and stability of suspended particles yield to uniform deposits. In addition the spherical shape of particles reduces the demagnetization process following by enhancement of coercivity.

Figure 4 illustrates the FE-SEM images of the surface morphology of MCCFs. As it was mentioned earlier, EPD process was done in three steps. This is an advantage of EPD process over the other more convenient advance coating methods. This simple trend makes it possible to separate the agglomerated part of coating and let the surface to be smooth and dense. Another advantage of this simple trend is to make it possible to produce a homogenous and high quality coating while it is dense and smooth enough to be compared with the results of the other coating methods. As can be seen in the specimen deposited for one step (15 min) (Fig. 4a), the fibers are not thoroughly

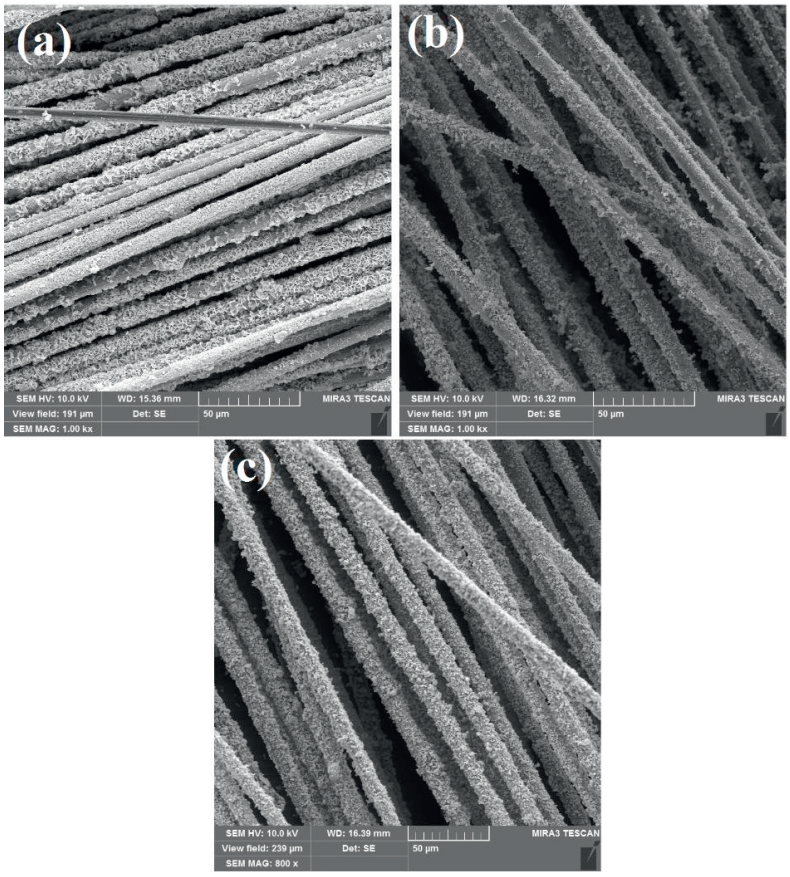

Fig. 4.FE-SEM images of MCCFs coated in (a) one step; (b) two steps; (c) three steps.

coated. By increasing the deposition steps (Fig. 4b) (15 and 6 min), a uniform coating layer is formed on the CFs, but still some discontinuities can be observed. The formation of dense film and uniform distribution of nano-Fe_3O_4 on the carbon fiber surface is observable in Fig. 4c (15, 6 and 15 min).

Figure 5 shows the hysteresis loop of carbon fibers material coated by Fe_3O_4 nanoparticles in three steps. The saturation magnetization (Js), coercivity (Hc) and residual magnetization (Br) of MCCFs is respectively about 6.25 emu.g^{-1}, 76.8 Oe, and 0.88 emu.g^{-1}.

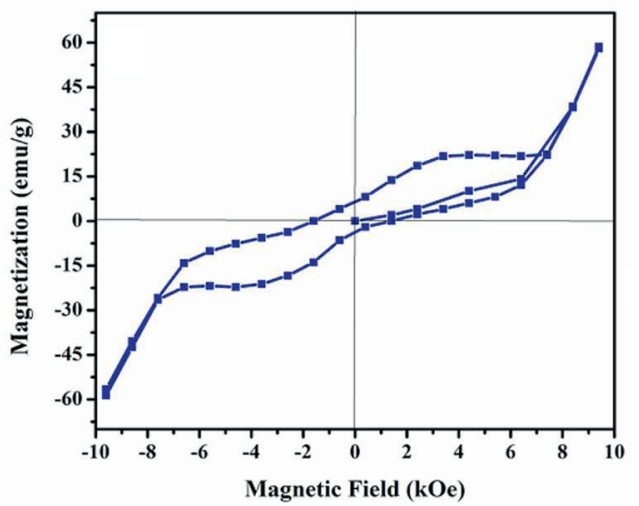

Fig. 5. The magnetic hysteresis loop of MCCFs.

Figure 6 shows the reflection loss (RL) of MCCFs (with a weight fraction of 50%) in the range of 8–12 GHz for a layer with thickness of 2 mm. The strongest RL of −7.8 dB (i.e. absorbing 83%) at 9.3 GHz occurred in the sample deposited for three steps.

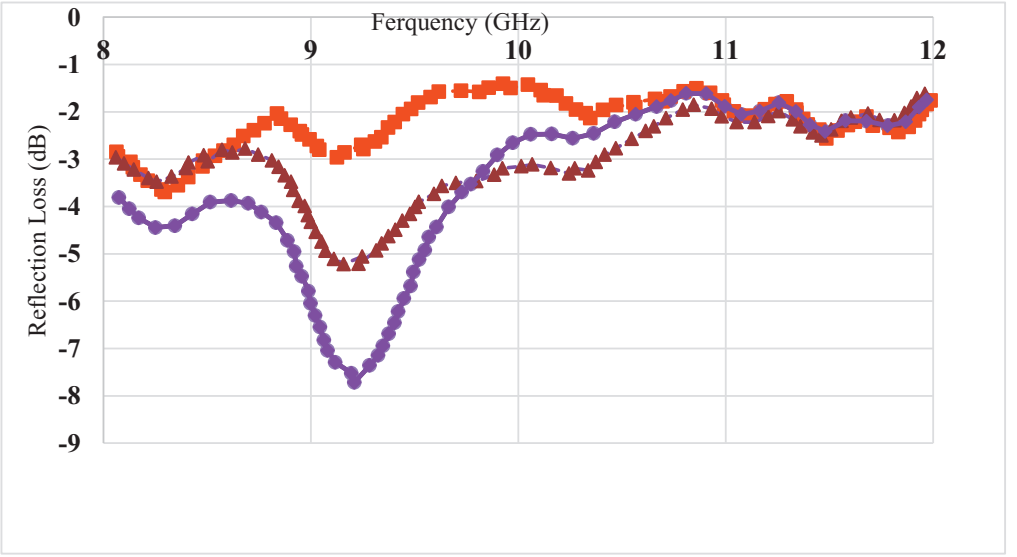

Fig. 6. Reflectivity curves of samples coated in (a) one; (b) two; (c) three steps.

4. Conclusion

Fe_3O_4 nanoparticles were synthesized and successfully coated on the carbon fiber surface using electrophoretic deposition method. The morphology of surface of the MCCFs produced by EPD technique is uniform, dense and smooth enough to be compared with the other coating methods. The strongest RL of MCCFs is about −7.8 dB at 9.3 GHz for a layer with the thickness of 2 mm.

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