Preparation and properties of functional particle Fe$_3$O$_4$-rGO and its modified fiber/epoxy composite for high-performance microwave absorption structure

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Abstract

Microwave absorbing materials have been becoming a countermeasure and security media for radio environment, and also becoming the main military force attached by the world. In this study, experimental data, theoretical researches and FEKO—a 3D structure and electromagnetic field analysis simulation tool, namely, FEldberechnung bei Korpern mit beliebiger Oberflache, are effectively combined. Through systematic studies on electromagnetic parameters and microwave absorbing properties of high-performance absorbing functional particle Fe$_3$O$_4$-rGO (i.e. reduced graphene oxide), single-layer composite Fe$_3$O$_4$-rGO@EP/GF (epoxy/glass fiber) and multi-layer structure composite Fe$_3$O$_4$-rGO@EP/fiber, combined with the simulation calculations of material structures, design on the microwave absorption performances of fiber/resin structural composites is achieved. In particular, under the guidance of FEKO simulations, a multi-layer structure composite with two layers of Fe$_3$O$_4$-rGO@EP/GF with different Fe$_3$O$_4$-rGO added amounts as the absorbing layer and carbon fiber (CF) reinforced EP as the reflecting layer is prepared, which has an effective absorption bandwidth of 8.43–12.40 GHz, almost covering the whole X-band, and $R_{\text{min}}$ (minimum reflection loss) up to $-34.60$ dB at 10.37 GHz. The relevant experimental results are basically consistent with the FEKO simulation results. This study is helpful to improve the developing efficiencies and properties of microwave absorbing structure composites with both excellent mechanical properties and outstanding microwave absorbing performances, especially conducive to industrial productions.

1. Introduction

In today’s world, radar, infrared detection technology and electronic technology are developing rapidly. For the electromagnetic wave (EMW) can be absorbed effectively by absorbing materials to improve the performance of electronic equipment or hide targets in the radar system, a lot of researches have been conducting on effective EMW absorbing materials in the fields of electromagnetic interference and stealth technology. At present, EMW absorbing materials have been becoming a countermeasure and security media for the radio environment, and also becoming the main military force attached by the world.

At present, researches on microwave absorbing fiber/resin composites mainly include two directions, one is a multi-layer structure absorbing material, and the other is a periodic structural absorbing material. Jae-Hun Choi et al [1] on the basis of obtaining ideal SiC/EP single-layer dielectric material, by using CST simulation and ideal dielectric constant guidance obtained a multi-layer alternating structure, thereby further improving absorbing performance of the composite, its effective absorption bandwidth reached 3.4 GHz, and strongest
absorption intensity was $-31.0 \text{ dB}$ at $-9.9 \text{ GHz}$. Se-Won Eun et al. [2] produced the tested material glass/EP-MWCNT and introduced the ‘split sample’ test method, which, used to measure the reflection and absorption to electromagnetic waves, could analyze quantitatively the effects of layering by implementing layering with different thickness and position in the same sample, test results showed that the minimum reflection loss ($RL_{\text{min}}$) of the material prepared was $-52.9 \text{ dB}$, resonance occurring at $10.01 \text{ GHz}$, and the effective absorption bandwidth was $8.3\text{–}12.4 \text{ GHz}$, almost covering the whole X-band. In addition, the effects of fiber lamination angle [3], pulp modification degree [4, 5] and special hollow fiber [6] on the microwave absorbing properties of composites were studied too. Kai-Lun Zhang et al. [7] used self-assembly technology to manufacture broadband periodic structural absorbing material with GO solution and PP fabric, through coupling multiple resonances and edge diffraction, the periodic structure absorbing material prepared had more than $90\%$ absorption in the whole measurement frequency range (2–40 GHz, 75–110 GHz); in addition, it showed high absorption intensity ($RL < -15 \text{ dB}$) over a wide frequency range (62.73 GHz). Wei-Li Song et al. [8] accelerated the design of high-efficiency microwave absorbing dielectric composites by allowing attenuation evaluation diagrams; based on this, combined with CST simulation and periodic structural absorber, a composite which could cover X-band and Ku-band was prepared. Qin FX et al. [9] coupled carbon nanotubes (CNT) and GO with metal wire via electrodeposition, and adjusted the dielectric properties of the prepared supercomposites by controlling the thickness and morphology of CNT and the degree of thermal reduction of GO, so as to obtain good microwave absorption performances. Ping-juan Liu et al. [10] studied the effects of composite modes of lossy particles and fibers on absorption performance, through synthesizing functional particles on fiber, higher dielectric properties and losses could be obtained, combined with the structure, the effective absorption bandwidth was further improved; Micheli D et al. [11] analyzed the possibility of designing a multilayer structure to provide the specific microwave response by adopting a new optimization design method and finally using a swimming intelligent algorithm. In addition, the planar patterns [12] and three-dimensional structures [13], perforated structures [14] and theoretical calculations [15] of repeating units of periodic structural absorber were studied too. Composites with repeating meta-structures possess excellent EMW absorption properties. However, although their repeating unit cells used all are simple, there are still certain requirements for the dielectric parameters of these materials, and their array repeating meta-structures need multiple processing and precision control for the external dimensions, so the industrialization of periodic structure absorbing materials costs high.

Main purpose of this study is, by effective combination of experimental data, theoretical researches and FEKO simulation, to improve the developing efficiencies and properties of multi-layer structure EMW absorbing composites, so that they could possess similar microwave absorbing performances as periodic structure absorbing materials while maintaining outstanding mechanical properties, which are conducive to industrial production. The specific research contents mainly include: (1) Preparation and composition structure, morphology and EMW absorbing properties of functional particle $\text{Fe}_3\text{O}_4$-rGO; (2) Electromagnetic parameters, microwave absorbing property and mechanism of single-layer composite $\text{Fe}_3\text{O}_4$-rGO@EP/GF; (3) Structural design and microwave absorbing performances of multi-layer structural composite $\text{Fe}_3\text{O}_4$-rGO@EP/fiber.

2. Experimental section

2.1. Materials

The commercial graphene oxide suspension (GO) (1 mg ml$^{-1}$) was supplied by Tangshan Jianhua Technology Co., Ltd, China. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was purchased from Tianjin Damao Chemical Reagent Factory, China. Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) was obtained from Tianjin Beichen Founder Reagent Factory, China. Sodium hydroxide (NaOH) was purchased from Tianjin Jinfeng Chemical Co., Ltd, China. All the above reagents were of analytical grade and used directly without further purification.

Epoxy resin E51 (EP, Average epoxy resin value of 0.51) was purchased from Nantong Xingchen Synthetic Material Co., Ltd, China. Polyetheramine (PEA) (Jeffamine D400, $M_n = 400 \text{ g mol}^{-1}$, $\text{PDI} = 1.1$) was bought from Shanghai Jingchun Chemical Reagent Co., Ltd, China. Carbon fiber cloth was purchased from Jiangsu Tianniao High technology Co., Ltd, China. E-glass fiber cloth was supplied by Jiaxing Baotai Composites Co., Ltd, China.

2.2. Synthesis of $\text{Fe}_3\text{O}_4$-rGO absorbing function particles

$\text{Fe}_3\text{O}_4$-rGO was prepared by a co-precipitation method. Weigh 2.04 g of ferric chloride hexahydrate and 1.50 g of ferrous chloride tetrahydrate, add them into 100 ml of GO solution with a concentration of 1 mg ml$^{-1}$, and agitate ultrasonically for 20 min. In a nitrogen atmosphere, drop 0.2 g ml$^{-1}$ of sodium hydroxide solution until pH value of the solution mixed of 10, stir at $90 \text{ ℃}$ for 2 h. Add 50 mg of reducing agent ascorbic acid (L-AA) and
stir at 80 °C for 4 h to fully reduce GO. The target product Fe₃O₄-rGO was obtained after magnetic separation and freeze-drying.

2.3. Preparation of fiber/EP absorbing composite
Preparation of single-layer composite Fe₃O₄-rGO@EP/GF: a certain mass of absorbing functional particles Fe₃O₄-rGO was added into the mixture of epoxy resin and curing agent PEA with mass ratio of 1:0.55 and dispersed uniformly by ultrasonic agitation, and then the Fe₃O₄-rGO@EP resin obtained was brushed manually on glass fiber cloth, the structure-function composite integrated Fe₃O₄-rGO@EP/GF was prepared by a hot pressing process, the specific process included: the prepreg obtained by brush coating was pre-cured at 90 °C for 35 min to reach the gel state, then heated to 135 °C and cured at 5 MPa for 1 h, finally cured at 135 °C and 15 MPa for 2 h, then cooled to obtain the final composite.

Preparation of multi-layer composite Fe₃O₄-rGO@EP/CF: absorbing functional particles Fe₃O₄-rGO with mass fraction of 10 wt% and 12 wt% were added into the mixture of epoxy resin and curing agent PEA with mass ratio of 1:0.55 respectively and dispersed uniformly by ultrasonic stirring, and then these Fe₃O₄-rGO@EP resins were manually brushed, respectively, on glass fiber cloth, then 10 wt% Fe₃O₄-rGO@EP/GF prepreg and 12 wt% Fe₃O₄-rGO@EP/GF prepreg were obtained. CF/EP prepreg was prepared by hand brushing mixture of epoxy resin and curing agent PEA with the mass ratio of 1:0.55 onto carbon fiber cloth. In order to control the filling amount of functional particles in each layer of composite, Fe₃O₄-rGO@EP/GF prepreg prepared was heated to gel state, then CF/EP prepreg, 12 wt% Fe₃O₄-rGO@EP/GF gel prepreg and 10 wt% Fe₃O₄-rGO@EP/GF prepreg were laid, respectively, then the structure-function integrated multi-layer fiber/EP composite was prepared by a hot pressing process, the specific process of which is the same as that of the above-mentioned composite Fe₃O₄-rGO@EP/GF.

In order to ensure the contents of fiber, functional particle and resin in prepared composites Fe₃O₄-rGO@EP/GF and Fe₃O₄-rGO@EP/CF, and the repeatability of the above-mentioned preparation processes, the following procedures should be strictly implemented: (1) Before being manually brushed with resin, the fiber cloth was weighed to obtain its initial mass A. (2) Prepare the mixed solution of resin and particle in strict accordance with the content of functional particle. Of course, in order to fix the wet resin content in the brushed fiber cloth, more mixture was needed, because during the brushing process, a certain amount of mixed solution was left in the container and brushing tool used. After many experiments, the residue was determined to be about 2.3 wt%. (3) During the subsequent hot pressing process, strictly control its temperature and pressure to prevent the infiltration resin extruding from the fiber cloth, and finally obtain the required composite, weigh it and express as B. By comparing A and B, the contents of resin and functional particle could be determined, and only which with the appropriate contents of resin and functional particle could be used for the subsequent experiments.

2.4. Characterizations
Crystallization characteristic of Fe₃O₄-rGO was determined by an x-ray diffraction (XRD, HAOUYUAN DX-2700B) using CuKα radiation (λ = 1.5406 Å). The magnetic property of material was determined with a vibrating sample magnetometer (VSM, Lake Shore7410, America Micro Sense) at room temperature. The surface compositions and elemental distributions of materials were examined by an x-ray photoelectron spectroscopy (XPS, EscaLab 250Xi). A Fourier transform infrared spectrometer (Nicolet ISS0) was used to record the chemical structure and bonding property of sample in a wavenumber range from 400 to 4000 cm⁻¹. Morphologies and surface characteristics of Fe₃O₄-rGO and rGO were investigated by a Field emission scanning electron microscopy (SEM, Hitachi SU8010) at accelerating voltages of 15 kV. A transmission electron microscope (TEM, JEOL-2100F) was used to observe the micro-morphology of sample at an accelerating voltage of 20 kV.

2.5. EMW absorbing property test
The permittivity and permeability of all materials were obtained with a vector network analyzer (Agilent N5244A, Keysight, USA). For EMW absorbing functional particles, they were mixed with paraffin at a mass ratio of 3:7, melted and pressed into a cylindrical ring with an inner diameter of 3.04 mm, an outer diameter of 7.00 mm and a thickness of 2.50 mm, and then their electromagnetic parameters were measured in the frequency range of 2–18 GHz. For the EP/fiber composites, they were cut into a 22.70 × 10.00 × 2.50 mm rectangular parallelepiped and their electromagnetic parameters were obtained by the waveguide method in the frequency range of 8.2–12.4 GHz. The permittivity and permeability of more than 10 samples were tested for each composite, and their average values were the electromagnetic parameters of the composite in this frequency range. Figure 1(a) is the schematic diagram of the reflectance test principle of the arch method and figure 1(b) is the microwave darkroom environment diagram.
3. Results and discussion

3.1. Composition and absorbing performance of functional particle Fe3O4-rGO

Figure 2(a) is the XRD spectrum of absorbing functional particle Fe3O4-rGO prepared, and all of its peaks correspond to the Fe3O4 standard card (JCPDS 88-0315). Peaks at $2\theta = 18.1, 30.1, 35.4, 43.1, 53.4, 57.0, 62.6$ and $74.0^\circ$ can be attributed to the $(111), (220), (311), (400), (422), (511), (440)$ and $(533)$ planes of the cubic lattice structure of Fe3O4. There is no weak broad peak in the range of $20^\circ$–$30^\circ$, indicating that Fe3O4 loaded on rGO sheets can prevent their re-stacking effectively. An XPS test was performed, and the results are shown in Figure 2(b) and (c). The main constituent elements of Fe3O4-rGO are C, O, and Fe, as shown in figure 2(c), its XPS spectrum has two characteristic peaks 711.18 and 724.88 eV from Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ respectively [23], and no $\gamma$-Fe$_2$O$_3$ peak is observed, indicating that there is no $\gamma$-Fe$_2$O$_3$ in the material system [21–25], thereby further confirming that the oxide loaded on the surface of rGO is magnetite Fe3O4 [24–29].

Figure 2(d) is the FTIR spectra of Fe3O4, rGO and Fe3O4-rGO. Pure Fe3O4 shows its unique lattice absorption peak at 592 cm$^{-1}$. Peaks of $\gamma$-C–O stretching vibration, $\gamma$-C–OH deformation vibration, $-\text{COO}^-$ stretching vibration and C–C bond of carbon skeleton in rGO appear at $1066, 1286, 1560$ and $1618$ cm$^{-1}$ [30, 31], indicating that rGO is reduced by ascorbic acid, but not completely. Compared with the other two materials, the lattice peaks of Fe3O4 also appear in the infrared spectrum of Fe3O4-rGO, indicating that Fe3O4 is synthesized on the surfaces of rGO sheets. In addition, the peaks of $-\text{COO}^-$ stretching vibration and $-\text{C}–\text{OH}$ deformation vibration almost disappear, the peak of $-\text{COO}^-$ stretching vibration decreases slightly, and the peak of C–C bond of carbon skeleton almost remains unchanged, indicating that most of the Fe-O bonds are formed by Fe3O4 and $-\text{C}–\text{OH}$ on the surface of GO and a few by $-\text{COOH}$, which can further increase the reduction degree of GO and facilitate the dispersion of rGO.

Figure 2(e) is the XRD spectrum of absorbing functional particle Fe3O4-rGO prepared, and all of its peaks correspond to the Fe3O4 standard card (JCPDS 88-0315). Peaks at $2\theta = 18.1, 30.1, 35.4, 43.1, 53.4, 57.0, 62.6$ and $74.0^\circ$ can be attributed to the $(111), (220), (311), (400), (422), (511), (440)$ and $(533)$ planes of the cubic lattice structure of Fe3O4. There is no weak broad peak in the range of $20^\circ$–$30^\circ$, indicating that Fe3O4 loaded on rGO sheets can prevent their re-stacking effectively. An XPS test was performed, and the results are shown in Figure 2(b) and (c). The main constituent elements of Fe3O4-rGO are C, O, and Fe, as shown in figure 2(c), its XPS spectrum has two characteristic peaks 711.18 and 724.88 eV from Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ respectively [23], and no $\gamma$-Fe$_2$O$_3$ peak is observed, indicating that there is no $\gamma$-Fe$_2$O$_3$ in the material system [21–25], thereby further confirming that the oxide loaded on the surface of rGO is magnetite Fe3O4 [24–29].

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Figure 1. Diagrams of the reflectance test principle of the arch method (a) and the microwave darkroom environment (b).
is SEM images of Fe3O4-rGO and GO, the one with relatively great magnification, after being reduced by ascorbic acid. It can be seen that GO has certain folds, which are conducive to the composite modification by particles [32]. In addition, Fe3O4 is formed on the surface of rGO sheets, almost completely covering them. Combined with XRD results, it can be known that Fe3O4 is generated between rGO sheets too, which can improve the dispersion uniformity of rGO and Fe3O4 [33]. Figure 2(f) is a TEM image of Fe3O4-rGO, showing that Fe3O4 nanoparticles with the particle size of 10–25 nm are relatively evenly distributed on the surface of rGO. Figure 2(g) shows the magnetic characteristics of the material. Fe3O4-rGO possesses superparamagnetism, Hc = 45.3 Oe, Ms = 52.7 emu g⁻¹, indicating that this functional particle is soft magnetic material, which will contribute to the energy conversion, transmission and attenuation of EMW [17, 34]. Figure 2(h) shows the EMW absorption performances of Fe3O4-rGO/paraffin composites with different thicknesses calculated by the transmission line theory based on the electromagnetic parameters measured by the coaxial method of VNA. It
can be seen that when the test thickness is 2.5 mm, the material has effective absorption (RL less than 10 dB) from 10.92 to 17.18 GHz, most covering X-band and Ku-band; when the test thickness is 3 mm, $RL_{\text{min}}$ of this material is $-35.95$ dB at 10.64 GHz. All these show that the absorbing particles prepared possess good absorption performance, and can be used as effective functional particles for preparing structural absorbing composites.

3.2. Absorbing property and mechanism of single layer Fe$_3$O$_4$-rGO@EP/GF

According to the transmission line theory, microwave absorption characteristics are highly dependent on the complex permittivity and complex permeability of materials. The electromagnetic parameters of functional particle Fe$_3$O$_4$-rGO are quite different from those of resin and fiber, while the electromagnetic parameters of resin/fiber composites can be improved to a certain extent by increasing its filling amounts [35, 36], thereby obtaining better EMW absorbing abilities. The dielectric properties of GF/EP composites filled with different functional particle Fe$_3$O$_4$-rGO loadings were tested by VNA to guide the design and preparation of final composite, and figure 3 is the electromagnetic parameters of GF/EP composites filled with Fe$_3$O$_4$-rGO from 2 to 12 wt%. It can be seen from figures 3(a) and (b) that when the filling amounts of Fe$_3$O$_4$-rGO increase from 2 wt% to 12 wt%, values of the real part of dielectric constant ($\varepsilon'$) of Fe$_3$O$_4$-rGO@EP/GF composites in X-band fluctuate between 4.17–4.43, 4.39–4.76, 4.40–4.79, 4.67–4.97, 5.17–5.68 and 5.26–5.69 respectively, while values of their imaginary part $\varepsilon''$ change between 0.16–0.43, 0.18–0.4, 0.16–0.42, 0.17–0.54, 0.61–1.23 and 0.75–1.38 respectively. As expected, with the increase of the amounts of Fe$_3$O$_4$-rGO added, $\varepsilon''$ values of composites increase.
from 4.2 to 5.5, while $\varepsilon''$ values from about 0.2 to 1.2 on average. It can also be seen from figures 3(c) and (d) that when the filling amounts of Fe$_3$O$_4$-rGO increase from 2 wt% to 12 wt%, values of the real part of permeability ($\mu'$) of Fe$_3$O$_4$-rGO@EP/GF composites in X-band fluctuate between 0.97–0.99, 0.97–1.02, 0.95–1.05, 0.98–1.07, 0.96–1.12 and 0.96–1.19 respectively, while values of their imaginary part ($\mu''$) change between 0.01–0.05, 0–0.04, 0–0.04, 0–0.07, 0.02–0.24 and 0.01–0.22 respectively. At low addition, that is, less than 8 wt%, there are little changes in values of $\mu'$ and $\mu''$ of composites, but when additional amounts of functional particles Fe$_3$O$_4$-rGO are higher than 8 wt%, values of $\mu'$ and $\mu''$ of composites will be greatly improved. As is known to all, the real parts ($\varepsilon'$ and $\mu'$) of electromagnetic parameters represent their storage capacities to electromagnetic energy, while the imaginary parts ($\varepsilon''$ and $\mu''$) show their loss capacities to electromagnetic energy [37]. Therefore, the addition of absorbing functional particles improves the electromagnetic balance in composite EP/GF and increases their loss ability to EMW, which can also be confirmed from figures 3(e) and (f). The functional particles in this study are composed of Fe$_3$O$_4$ and rGO. For component rGO, on the one hand, they help to construct the conductive networks in composites, on the other hand, the defects and oxygen-containing functional groups on their surfaces tend to accumulate electrons and cause electron polarization, thus giving materials a high degree of polarization, which will lead to stronger polarization relaxation. At the same time, its polar oxygen-containing functional groups can also generate stretching vibration and bending vibration in the electromagnetic field, which should also be one of the reasons for the sudden changes of dielectric loss tangent $\tan \delta_e$ in some frequency band, and these can improve the effective absorption to EMW and the ability to dissipate electromagnetics. In addition, polar oxygen-containing functional groups can lead to additional charge rearrangement and orbital hybridization, making the electric dipole polarized, which is very important for improving the dielectric constant and microwave absorption performances. The contribution of dipole polarization to dielectric loss is usually explained by Cole-Cole semi-circles, each of which represents a Debye relaxation process. The relationship between $\varepsilon'$ and $\varepsilon''$ can be expressed as follows.

$$
\left( \varepsilon' - \frac{\varepsilon_s + \varepsilon_m}{2} \right)^2 + \left( \varepsilon'' - \frac{\varepsilon_s - \varepsilon_m}{2} \right)^2 = \left( \varepsilon_m \right)^2
$$

(1)

Where: $\varepsilon_s$ and $\varepsilon_m$ are the static permittivity and relative permittivity at the high frequency limit.

Figure 4 shows the $\varepsilon' - \varepsilon''$ curves for 2 wt% Fe$_3$O$_4$-rGO@EP/GF and 12 wt% Fe$_3$O$_4$-rGO@EP/GF. It can be seen that both composites have two distinct Cole-Cole semi-circles, corresponding to two Debye relaxation processes, which should be attributed to the polarization relaxation of rGO or Fe$_3$O$_4$, respectively. As is known to all, the relaxation process is usually caused by the delay of molecular polarization relative to the changing electric field in a medium. With the increase of additional amounts of functional particle Fe$_3$O$_4$-rGO, the polarized groups and defects in rGO and the interface between Fe$_3$O$_4$ and rGO all increase, leading to a large number of interface polarization and strong dipole polarization, therefore, the Cole-Cole semi-circles of 12 wt% Fe$_3$O$_4$-rGO@EP/GF composite is stronger [38].

Functional particle Fe$_3$O$_4$-rGO exhibits superparamagnetism, so with the increase of its contents in composites and the boundary conditions of material compositions (hysteresis effect and magnetic induction intensity of the magnetic domain wall), values of $\mu'$ and $\mu''$ will increase. In particular, as can be seen from figures 3(c) and (d), when the contents of the functional particles greater than 8 wt%, values of $\mu'$ and $\mu''$ of composites will increase significantly. Magnetic losses are caused by eddy current effects, natural and exchange resonances. Figure 3(f) shows multiple resonances in 9–12 GHz. Eddy current loss comes from changes in magnetic flux density in an alternating electromagnetic field. If the magnetic loss of material is only caused by

![Figure 4. $\varepsilon' - \varepsilon''$ curves of (a) 2 wt% Fe$_3$O$_4$-rGO@EP/GF and (b) 12 wt% Fe$_3$O$_4$-rGO@EP/GF.](image)
eddy current loss \( (C_0 = \mu''(\mu')^{-1}f^{-1} = 2\pi\mu_0\sigma d^2) \) [39], its value should be kept constant, independent of frequency change [38, 40]. From figure 5, it can be seen that the \( C_0 \) of 12 wt% \( \text{Fe}_3\text{O}_4\)-rGO@EP/GF in 8.2–9 GHz is a constant. Therefore, its magnetic loss in the relevant frequency band should mainly be eddy current loss. In other frequency bands, the loss values keep changing, inferring that natural resonance and exchange resonance exist in the material system [6, 16]. In addition, it can be seen from figure 5 that when the addition amounts of functional particles more than 8 wt%, the contribution of natural resonance and exchange resonance in magnetic loss increases.

According to the transmission line theory, the dielectric constant and permeability measured by the coaxial method are used to calculate the EMW reflection loss value of composite EP/GF according to formulas (2) and (3).

\[
\begin{align*}
R_L (dB) &= 20 \log \left| \frac{Z_{in} - 1}{Z_{in} + 1} \right| \\
Z_{in} &= \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh \left( j \frac{2\pi fd}{c} \sqrt{\mu_r\varepsilon_r} \right)
\end{align*}
\]

Where: \( Z_{in} \) is the normalized input impedance of the metal-supported microwave absorption layer, \( \varepsilon_r \) and \( \mu_r \) are the complex permittivity and permeability of composite, \( c \) is the velocity of EMW in the free space, \( f \) is the frequency of EMW and \( d \) is the thickness of the absorbing material.

Figure 6 shows the relationship between frequency and RL of 10 wt% \( \text{Fe}_3\text{O}_4\)-rGO@EP/GF and 12 wt% \( \text{Fe}_3\text{O}_4\)-rGO@EP/GF with different thicknesses calculated. It can be seen that the two composites all have certain absorption ability in X-band. When the thickness of composite 10 wt% \( \text{Fe}_3\text{O}_4\)-rGO@EP/GF is 3 mm, its RL \(_{min}\) is only \(-15.46\) dB at 12.07 GHz, and effective absorption bandwidth is 2.56 (9.84–12.40) GHz. When the
thickness of composite 12 wt% Fe$_3$O$_4$-rGO@EP/GF is 3 mm, its $R_{\text{Lmin}}$ is only $-17.79$ dB at 11.85 GHz, and effective absorption bandwidth is 1.83 (9.98–10.61, 11.16–12.36) GHz. All of these show that the single-layer composite Fe$_3$O$_4$-rGO@EP/GF possesses poor absorbing performance and needs further improvement.

### 3.3. Microwave absorbing properties of multi-layer fiber/EP composite

Compared with the single-layer composites, the double-layer composites are more conducive to the flexible design of the overall dielectric properties of the system, and the requirements to the dielectric parameters of each layer in it are not as high as those in single-layer composites, so it is easier to achieve high performances under the low process requirements. Therefore, a two-layer structure absorbing composite composed of an absorbing layer Fe$_3$O$_4$-rGO@EP/GF and a reflecting layer CF/EP was designed, its electromagnetic parameters measured by the above-mentioned VNA are used to simulate and design the thickness matching of each layer in the double-layer composite and the influence of the contents of absorbing functional particles on absorbing performance of composite through FEKO, so as to obtain the composite have the best absorbing performance in X-band by adjusting its thickness of each layer and the contents of functional particles.

Through genetic algorithm, it is finally determined that when the absorbing layer is 12 wt% Fe$_3$O$_4$-rGO@EP/GF with a thickness of 3.3 mm and the reflecting layer CF/EP with a thickness of 0.2 mm, the double-layer composite has the best EMW absorption performance in X-band, as shown in figures 7(a) and (b), which has effective absorption from 8.33 to 12.34 GHz and $R_{\text{Lmin}}$ of $-35.99$ dB at 10.20 GHz. However, although the broadband absorption performance in X-band is obtained by matching the thickness of the absorbing layer and the reflective layer, its absorbing performance is still not ideal because the maximum absorbing intensity is still not high enough. According to formula 4, the input impedance of the multi-layer absorbing layer with pure reflective metal as the base can be obtained.

$$Z_n = \frac{\eta_n Z_{n-1} + \eta_n t h(\gamma_n d_n)}{\eta_n + Z_{n-1} t h(\gamma_n d_n)}$$ (4)

Figure 7. FEKO simulation and model diagrams of the best double-layer absorbing composite (a), (b) and triple-layer absorbing composite (c), (d) in X-band.
Among them:

\[ \eta_n = \sqrt{\frac{\mu_n}{\varepsilon_n}} = \sqrt{\frac{\mu_n' - j\mu_n''}{\varepsilon_n' - j\varepsilon_n''}} \]  

(5)

\[ \gamma_n = \frac{2\pi f}{c} \sqrt{(\mu_n' - j\mu_n'')(\varepsilon_n' - j\varepsilon_n'')} \]  

(6)

Here: \( n \) is the number of layer of material, \( \eta_n \) is the characteristic impedance of the \( n \)th layer of material, \( \gamma_n \) is the propagation constant of the \( n \)th layer material, \( d_n \) is the thickness of the \( n \)th layer, and \( Z_{n-1} \) is the input impedance of the \( n-1 \)th layer material, \( f \) is the frequency of the incident EMW, and \( c \) is the speed of light.

Matching the impedance with the intrinsic impedance of the air is very important for the design of microwave absorbing composites, which can be achieved by adjusting the dielectric constant of the absorbing material or designing multi-layer absorbing material \[1\]. By adjusting the dielectric constant of the surface layer, the impedance of the whole multi-layer absorber can be adjusted, then the reflection caused by the sudden change of the dielectric of the surface layer can be reduced, the incidence of EMW can be increased, and the absorbing performance to EMW of composites can be improved \[41\]. Therefore, the above-designed wave-absorbing layer of the double-layered structure is further subdivided into multiple functional layers, and while keeping the bottom absorbing layer unchanged, then the dielectric constant of the upper absorbing layer can be reduced, which can reduce the surface reflection to EMW and then have absorbing performance improved, so as to obtain a composite with higher absorbing ability.

Therefore, the structure of the composite is further optimized by genetic algorithms. For the thickness of the single-layer glass fiber cloth is 0.25 mm, the simulation value of the thickness of each layer of the absorbing layer is set to an integral multiple of 0.25. The optimal structure of composite obtained through FEKO simulation is: the surface layer is 10 wt% Fe\(_3\)O\(_4\)-rGO@EP/GF with a thickness of 0.5 mm, the middle layer is 12 wt% Fe\(_3\)O\(_4\)-rGO@EP/GF with a thickness of 2.8 mm, and the bottom layer is still CF/EP with a thickness of 0.2 mm. Figure 7(d) is the FEKO modeling diagram of the designed wave-absorbing composite, and figure 7(c) is its modeling wave-absorbing performance. It can be seen that by adjusting the dielectric properties of the surface, although the effective absorption bandwidth of the composite does not change much (8.38–12.33 GHz), its RL\(_{\text{min}}\) increases to \(-60.35\) dB at 10.25 GHz.

Figure 8 is the comparisons of experimental and simulative RL-f of two-layer (a) and three-layer (b) absorbing structure composites. It can be seen that the frequencies corresponding to RL\(_{\text{min}}\) from experiments of the two composites are all close to their simulation values, especially for the three-layer composite system; their RL\(_{\text{min}}\) measurement values are higher than the simulation values, and the three-layer composite has the relatively larger increase. The ideal thickness of each layer is designed to achieve accurate impedance matching. However, the thicknesses of the manufactured absorbing composites slightly deviate from those of their simulations due to the tiny change in the thickness of each layer caused by the hot pressing process. However, all the errors are small. Specifically, for the double-layer absorption structure composite, its frequency corresponding to RL\(_{\text{min}}\) from experiment is 10.50 GHz, possessing a small change compared with the simulation value 10.20 GHz, RL\(_{\text{min}}\) increases from \(\approx 35.99\) dB of simulation to \(-28.31\) dB of experiment, and the effective absorption bandwidth, 8.65–12.40 GHz from experiment, changes little too. For the three-layer absorption structure composite with the frequency corresponding to RL\(_{\text{min}}\) of 10.37 GHz from experiment, the change is also small compared to the simulated value, its RL\(_{\text{min}}\) is increased to \(-34.60\) dB and the effective absorption bandwidth is 8.43–12.40 GHz from experiment. Based on these, it can be considered that the simulation in this study is scientific and accurate.
4. Conclusions

In brief, experimental data, theoretical researches and FEKO simulation are effectively combined to improve the developing efficiencies and properties of microwave absorbing structure composites. Through the preparation of high-performance absorbing functional particles and the combination of their filling amounts, composite structure and thickness of each layer, the design to the EMW absorbing capability of structural composite is realized. The pure magnetite Fe₃O₄ in the wave-absorbing functional particle Fe₃O₄-rGO prepared by the co-precipitation method almost completely covers on the surfaces of rGO sheets and is also formed between its sheets, which help to improve the dispersion uniformity of rGO and Fe₃O₄; its RLₘᵢᵦᵢₐᵦᵦ is −35.95 dB and effective absorption can cover most the whole X-band and Ku-band. The addition of absorbing functional particles improves the electromagnetic balance of composite EP/GF and increases its EMW absorbing ability. With the increase of Fe₃O₄-rGO filling amount, the polarized groups and defects in rGO and the interface between Fe₃O₄ and rGO all increase, resulting in a large number of interfacial polarization and strong dipole polarization, and therefore higher dielectric relaxation and polarization relaxation. However, single-layer composite Fe₃O₄-rGO@EP/GF has a poor absorbing performances, so the matching thickness and absorbing functional particle content of each layer in double-layer and three-layer composites are designed by FEKO simulation, then a multi-layer structure composite is prepared according to the structure of composite with the best EMW absorption performances obtained by FEKO simulation, which has RLₘᵢᵦᵦᵦ of −34.60 dB, and effective absorption bandwidth of 8.43–12.40 (3.97) GHz, almost covering the whole X-band. The experimental results are basically consistent with those from FEKO simulation. Therefore, a structure composite possessing the outstanding wave absorbing performance is obtained with high efficiency, especially with a simple preparation process.

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References

[1] Choi JH, Nam Y W, Jang M S and Kim C G 2018 Characteristics of silicon carbide fiber-reinforced composite for microwave absorbing structures Compos. Struct. 202 290–5
[2] Eun S W, Choi W H, Jang H K, Shin J H, Kim J B and Kim C G 2015 Effect of delamination on the electromagnetic wave absorbing performance of radar absorbing structures Compos. Sci. Technol. 116 18–25
[3] Hu T, Wang J and Wang J 2015 Electromagnetic interference shielding properties of carbon fiber cloth based composites with different layer orientation Mater. Lett. 158 163–6
[4] Duan S C, Zhu D M, Jia H Y and Zhou W C 2018 Enhanced mechanical and dielectric properties of SiC/SiC composites with silicon oxycarbide interphase Ceram. Int. 44 131–7
[5] Nam Y W, Choi J H, Lee W J and Kim C G 2017 Fabrication of a thin and lightweight microwave absorber containing Ni-coated glass fibers by electroless plating Compos. Sci. Technol. 145 165–72
[6] Gao X H, Wu X Y and Qiu J 2018 High electromagnetic waves absorbing performance of a multilayer-like structure absorber containing activated carbon hollow porous fibers-carbon nanotubes and Fe₃O₄ nanoparticles Adv. Electron. Mater. 4 1700565
[7] Zhang K L, Zhang J Y, Hou Z L, Bi S and Zhao Q L 2019 Multifunctional broadband microwave absorption of flexible graphene composites Carbon 141 608–17
[8] Song W L, Zhang K L, Chen M J and Hou Z L 2017 A universal permittivity-attenuation evaluation diagram for accelerating design of dielectric-based microwave absorption materials: a case of graphene-based composites Carbon 118 86–97
[9] Estevé D, Qin F X and Luo Y 2019 Tunable negative permittivity in nano-carbon coated magnetic microwave polymer metacomposites Compos. Sci. Technol. 171 206–17
[10] Liu P Y, Wang L M, Cao B, Li L C, Zhang K L, Bian X M and Hou Z L 2017 Designing high-performance electromagnetic wave absorption materials based on polymeric graphene-based dielectric composites: from fabrication technology to periodic pattern design J. Mater. Chem. C 5 6745–54
[11] Micheli D, Pastore R and Delfini A 2018 Electromagnetic characterization of advanced nanostructured materials and multilayer design optimization for metrological and low radar observability applications Acta Astronaut. 134 33–40
[12] He F, Hou Z L and Bi S 2017 Lightweight ferroferric oxide nanotubes with natural resonance property and design for broadband microwave absorption J. Mater. Sci. 52 8258–67
[13] Liu P Y, Li L C, Wang L M, Huang T and Zhao Q L 2017 Broadening electromagnetic absorption bandwidth: design from microscopic dielectric-magnetic coupled absorbers to macroscopic patterns Phys. Status Solidi A 214 1700589
[14] Liu X D, Hou Z L, Zhang B X, Zhan K T, He P, Zhang K L and Song W L 2016 A general model of dielectric constant for porous materials Appl. Phys. Lett. 108 102902
[15] Zhang K L, Hou Z L, Bi S and Fang H M 2017 Modeling for multi-resonant behavior of broadband metamaterial absorber with geometrical substrate Chin. Phys. B 26 127802
[16] Zou J P, Wang Z Z, Yan M Q and Bi H 2014 Enhanced interfacial polarization relaxation effect on microwave absorption properties of submicron-sized hollow Fe3O4 hemispheres J. Phys. D: Appl. Phys. 47 275001
[17] Zhang N, Huang Y and Wang M Y 2018 3D ferromagnetic graphene nanocomposites with ZnO nanorods and Fe3O4 nanoparticles co-decorated for efficient electromagnetic wave absorption Compos. Part B-Eng. 136 135–42
[18] Zong M, Huang Y, Zhao Y and Sun X 2013 Facile preparation, high microwave absorption and microwave absorbing mechanism of RGO-Fe3O4 composites RSC Adv. 3 23638
[19] Wang L N, Jia X L, Li Y F, Yang F, Zhang L Q, Liu L P, Ren X and Yang H T 2014 Synthesis and microwave absorption property of flexible magnetic film based on graphene oxide/carbon nanotubes and Fe3O4 nanoparticles J. Mater. Chem. A 2 14940
[20] Fu M, Jiao Q Z, Zhao Y and Li H S 2014 Vapor diffusion synthesis of CoFe2O4 hollow sphere/graphene composites as absorbing materials J. Mater. Chem. A 2 735–44
[21] Sun X, He J P, Li G X, Tang J, Wang T, Gao Y X and Xue H R 2013 Laminated magnetic graphene with enhanced electromagnetic wave absorption properties J. Mater. Chem. C 1 765–77
[22] Chen T, Qu J H, Zhu K J and Che Y C 2014 Enhanced electromagnetic wave absorption properties of polyaniline-coated Fe3O4/reduced graphene oxide nanocomposites J. Mater. Sci-Mater. El. 25 3664–73
[23] Zhao Y T, Liu L, Han J N, Wu W H and Tong G X 2017 Effective modulation of electromagnetic characteristics by composition and size in expanded graphite/Fe3O4 nanoring composites with high Snoek’s limit J. Alloys Compd. 728 100–111
[24] Wu H, Wang L D and Wu H J 2014 Synthesis, characterization and microwave absorption properties of dendrite-like Fe3O4 embedded within amorphous sugar carbon matrix Appl. Surf. Sci. 390 588–97
[25] Liu Q C, Zi Z F, Zhang M, Pang A B, Dai J M and Sun Y P 2013 Enhanced microwave absorption properties of carbonyl iron/Fe3O4 composites synthesized by a simple hydrothermal method J. Alloys Compd. 561 65–70
[26] Zhang K C, Zhang Q, Gao X B and Chen X F 2016 Magnetic reduced graphene oxide nanocomposite as an effective electromagnetic wave absorber and its absorbing mechanism J. Mater. Chem. B 4 3701–8
[27] Min D D, Zhou W C, Luo F and Zhu D M 2017 Facile preparation and enhanced microwave absorption properties of flake carbonyl iron/Fe3O4 composite J. Magn. Magn. Mater. 435 26–32
[28] Li Z X, Li X H, Zong Y, Tan G G, Sun Y, Lan Y Y and Zheng X L 2017 Solvothermal synthesis of nitrogen-doped graphene decorated by superparamagnetic Fe3O4 nanoparticles and their applications as enhanced synergistic microwave absorbers Carbon 115 493–502
[29] Qiao M T, Lei X F and Zhang Q Y 2018 Application of yolk–shell Fe3O4@N-doped carbon nanochains as highly effective microwave-absorption material Nano Res. 11 1560–19
[30] Huang Y M, Qi Q and Liu X B 2016 Facile preparation of octahedral Fe3O4/RGO composites and its microwave absorption properties J. Mater. Sci-Mater. El. 27 9577–83
[31] Li Y H, Qin F X and Quan L 2019 Vertical interphase endurable tunable microwave dielectric response in carbon nanocomposites Carbon 153 447–57
[32] Quan L, Qin F X and Estevez D 2019 The role of graphene oxide precursor morphology in magnetic and microwave absorption properties of nitrogen-doped graphene J. Phys. D: Appl. Phys. 52 305001
[33] Huang Y, Ding X, Li S, Zhang N and Wang J G 2016 Magnetic reduced graphene oxide nanocomposite as an effective electromagnetic wave absorber and its absorbing mechanism Ceram. Int. 42 17116–22
[34] Wu J M, Ye Z M, Liu W X and Chen J 2017 The effect of GO loading on electromagnetic wave absorption properties of Fe3O4/reduced graphene oxide hybrids Ceram. Int. 43 13146–53
[35] Liu W, Tan S J, Yang Z H and Ji G B 2018 Hollow graphite spheres embedded in porous amorphous carbon matrices as lightweight and low-frequency microwave absorbing material through modulating dielectric loss Carbon 138 143–53
[36] Naidu M K, Ramji K and Santhoshi B V S R N 2018 Influence of NiFe alloy nanopowder on electromagnetic and microwave absorption properties of MWCNT/Epoxy composite Adv. Polym. Technol. 37 622–8
[37] Chen Y J, Zhang A B, Ding L C, Liu Y and Lu H L 2017 A three-dimensional absorber hybrid with polar oxygen functional groups of MWNTs/graphene with enhanced microwave absorbing properties Compos. Part B-Eng. 108 386–92
[38] Quan B, Zhang B S and Li A H 2018 Constructing multi-interface Mo7C/Co@C nanorods for a microwave response based on a double attenuation mechanism Dalton T 47 14767–73
[39] Pang W H, Pang H, Zhang B and Ren N 2018 Excellent microwave absorption properties of the h-BN-GO-Fe3O4 ternary composite J. Mater. Chem. C 6 11722–30
[40] Bora P J, Porwal M, Vinoy K J and Madras G 2018 Industrial waste fly ash cenosphere composites based broad band microwave absorber Compos. Part B-Eng. 134 151–63
[41] Liu Y, Su X L and Qu Y H 2017 Enhanced electromagnetic and microwave absorption properties of carbonyl iron/Ti3SiC2/epoxy resin coating J. Mater. Sci-Mater. El. 29 2500–8