Electromagnetic interference shielding MWCNT-Fe₃O₄@Ag/epoxy nanocomposites with satisfactory thermal conductivity and high thermal stability

Lei Wang, Hua Qiu, Chaobo Liang, Ping Song, Yixin Han, Yixuan Han, Junwei Gu, Jie Kong, Duo Pan, Zhanhu Guo

A R T I C L E   I N F O

Hierarchical composite nanoparticles of multiwall carbon nanotube (MWCNT)-Fe₃O₄@Ag combining electrical conductivity and magnetism were obtained from acyl-amine reaction between carboxylation of Fe₃O₄@Ag (Fe₃O₄@Ag-COOH) nanoparticles and amino functionalized MWCNTs (MWCNTs-NH₂). Finally, the MWCNT-Fe₃O₄@Ag/epoxy nanocomposites were fabricated via blending-casting method. When the mass ratio of MWCNTs-NH₂ to Fe₃O₄@Ag-COOH was 9:1 (MF-10), the corresponding epoxy nanocomposites presented an optimal electrical conductivity and electromagnetic interference (EMI) shielding effectiveness (SE). Furthermore, the MF-10/epoxy nanocomposites with 15 wt% MF-10 presented a satisfying EMI SE of 35 dB and high electrical conductivity of 0.280 S/cm, satisfactory thermal conductivity (thermally conductive coefficient, \( \lambda \) of 0.46 W/mK), outstanding Young’s modulus of 4.60 GPa & hardness value of 0.26 GPa and excellent thermal stability \( \Delta H_{fri} \) of 183.4 °C. The introduction of Fe₃O₄@Ag nanoparticles not only enhanced the interaction among MF-10, so as to promote the formation of conductive networks, leading to higher \( \lambda \) and EMI SE value, but also contributed to hysteresis loss of electromagnetic waves, and offered more interfaces to reflect and reabsorb electromagnetic waves, resulting in highly improved attenuation of electromagnetic waves.

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1. Introduction

With the rapid development of modern aviation electronic technology, the transmission power of the mission system is getting larger, and the corresponding influences on other systems and workers become more and more serious [1,2]. Under this background, it would be significant for the development of aviation weapons & equipments to design & investigate aircraft structures with electromagnetic interference (EMI) shielding performance.

Compared to conventional metal-based EMI shielding materials, polymeric composites present potential applications in EMI shielding fields, owing to their lightweight, excellent corrosion resistance and easy processing & fabrication, etc. [3–5]. Generally, polymer-based EMI shielding materials are divided into two types: intrinsic type and compound type. However, the poor mechanical and processing properties of intrinsic type electrically conductive polymers have restricted their applications in EMI shielding [6]. While the compound type EMI shielding polymeric composites present the advantage of one-time molding process. And

[Note: The rest of the text is not shown due to the page limitation.]
incorporating fillers into polymeric matrix is considered to be one of the most effective ways to fabricate the EMI shielding materials (compound type), due to their easy processing and adjustable EMI shielding performance by changing the filler content [7]. Silver, copper, nickel and carbon materials [8] are generally used as the conductive fillers. Herein, carbon nanotubes (CNTs) with excellent elastic modulus, electrical and thermal conductivity, have presented promising applications in EMI shielding fields. For example, Huang et al. [9] prepared single-walled CNTs (SWCNTs)/epoxy composites, and the EMI shielding effectiveness (SE) of the obtained 5 wt% SWCNTs/epoxy composite reached 15−20 dB (500 MHz−1.5 GHz). Furthermore, Li et al. [4] reported the maximum EMI SE of the SWCNTs/epoxy composites reached 24 dB at X-band (8−12 GHz) by introducing SWCNTs into epoxy matrix. Liu et al. [10] improved the dispersion of CNTs in epoxy matrix by fluorinated modification, and the obtained EMI SE of the CNTs/epoxy nanocomposites reached 28 dB (1 GHz−8 GHz).

However, it remains challenging to achieve the targeted EMI SE only by addition of CNTs [9]. So far, hybrid fillers of CNTs and magnetic nanoparticles (such as Fe [11], Ni [12], Co ferrites [13] and their multi-component ferrites like Fe3O4 [14], MnO2 [15], CrO2, etc.) were synchronously introduced to fabricate the EMI shielding nanocomposites. Herein, the Fe3O4 nanoparticles are functionalized with amino groups and used magnetic nanoparticles [16]. Combining CNTs with Fe3O4 nanoparticles will further broaden their applications [17] for strengthening the magnetic hysteresis loss of the obtained composites. Fu et al. [18] coated CNTs with Fe3O4 nanoparticles via solvothermal method. The loss for electromagnetic waves was significantly improved, which was strongly dependent on the magnetic coating structure. Chaudhary et al. [19] fabricated the conductive paper by synchronously introducing carbon microspheres, Fe3O4 and CNTs. The obtained EMI SE of the conductive paper was increased by nearly 50% with the introduction of Fe3O4 nanoparticles. However, the introduction of Fe3O4 nanoparticles often leads to a decrease in electrical conductivity. According to the previous researches [20,21], coating the Fe3O4 nanoparticles with silver could be in favor of improving the electrical conductivity. Sun et al. [22] reported the increased conductivity from 2.5 × 10−3 to 64.7 S/cm by overlaying of Fe3O4 with silver. However, to our knowledge, adopting hybrid fillers of CNTs and Fe3O4@Ag nanoparticles to fabricate the electromagnetic shielding polymeric nanocomposites has hardly been reported till now.

As one of high performance thermosetting resins, epoxy resins possess excellent comprehensive properties (high mechanical properties [23] & adhesion strength [24], good electrical insulation [25], excellent dimensional & thermal stabilities [26], high solvent resistance [27], and ease of processing [25], etc.), and have been widely applied as the matrix of coatings, adhesives and composites. Herein, we proposed a novel approach to prepare epoxy EMI shielding nanocomposites. The Fe3O4@Ag-COOH core-shell nanoparticles were firstly synthesized by functionalizing the Fe3O4 nanoparticles with silver and 11-mercaptoundecanoic acid (MUA) [28,29]. Meanwhile, MWNTs-NH2 were also obtained by amino functionalization of MWNTs. And the hierarchical composite nanoparticles of MWNT-Fe3O4@Ag combining with electrical conductivity and magnetism were then obtained from the acylamine reaction between Fe3O4@Ag-COOH nanoparticles and MWNTs-NH2 (as shown in Scheme 1). Finally, the MWNT-Fe3O4@Ag/epoxy EMI shielding nanocomposites were then fabricated via blending-casting method. The corresponding structures and morphologies of the Fe3O4@Ag-COOH, MWNTs-NH2 and MWNT-Fe3O4@Ag were explored, and characterized by transmission electron microscope (TEM), thermal gravimetric analyses (TGA), Fourier transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS) and Raman spectrum, etc. The optimum ratio of Fe3O4@Ag-COOH to MWNTs-NH2 was determined according to EMI SE value of the obtained epoxy nanocomposites. Furthermore, the effects of the MWNT-Fe3O4@Ag contents on the EMI SE, electrical conductivity, thermal conductivity, mechanical and thermal properties of the obtained MWNT-Fe3O4@Ag/epoxy nanocomposites were discussed and investigated.

2. Experiment section

2.1. Materials

MWNTs (~50 μm in length, 98% purity) were obtained from Chengdu Organic Chem. Co. (Chengdu, China). FeCl2·4H2O, tetramethylammonium hydroxide pentahydrate (TMAOH), sodium citrate, diisopropylethylamine (DIEA), NaBH4 and NH2OH·HCl were all purchased from Alfa Aesar (Shanghai, China). Sodium citrate, N-methylpyrrolidone (NMP), FeCl3·6H2O and AgNO3 were all received from Macklin (Shanghai, China). Polyethyleneimine (PEI, w.t. 600), 11-mercaptoundecanoic acid (MUA), diisopropylethylamine (DIEA) and N-[[(dimethylamino)methylene]-1H-1,2,3-triazolo-[4, 5-b]-pyridin-1-ylmethylene]-N-methylmethanaminium hexafluorophosphate (HATU) were all purchased from Macklin (Shanghai, China). Bisphenol F epoxy (Epon 862) and curing agent of 2,4-diethyl-6-methylbenzene-1,3-diamine (EK 3402) were both provided by Hexion Inc (Columbus, USA).

2.2. Preparation of MWNT-Fe3O4@Ag 2.2.1. preparation of Fe3O4@Ag-COOH nanoparticles

The synthesis of Fe3O4@Ag-COOH core-shell nanoparticles was similar to our previous work [30], despite the oxidation of Fe3O4 to Fe3O4 and AgNO3 instead of HAUCl4, the dosage of the other chemicals was the same.

2.2.1. Preparation of MWNTs-NH2

Carboxylation of MWNTs (MWNTs-COOH) was prepared by refluxing 1 g pristine MWNTs in a mixed acid of H2SO4/HNO3 (1:3 by volume) at 90°C for 90 min. The obtained products were collected by vacuum filtering and washed with deionized water until the pH value reached 7, and dried in vacuum at 60°C for 12 h. Then 100 mg MWNTs-COOH, 200 mg HATU and 200 mg DIEA were added into 30 mL N-Methyl-2-pyrrolidone (NMP) solution, and sonicated for 2 h. Subsequently, 10 mL NMP solution containing 300 mg PEI was added. The above mixtures were maintained and reacted at 130°C under refluxing for 4 h, followed by vacuum...
filtered and washed with methanol. Finally, the obtained products were dried in vacuum at 60 °C for 12 h. 2.2.3 Preparation of MWCNT-Fe3O4@Ag

30 mg Fe3O4@Ag-COOH, 200 mg HATU and 200 mg DIEA were added into 30 mL NMP solution, and then sonicated for 2 h. Consequently, the obtained mixtures were then added dropwise into NMP solution containing different loadings of MWCNTs-NH2. The above mixtures were kept reaction at 130 °C for 4 h, followed by centrifugation with methanol for three times and dried in vacuum at 60 °C for 12 h. The obtained product was named as MF for neat MWCNT-Fe3O4@Ag, whereas MF-5, MF-10, MF-15 and MF-20 named for 5, 10, 15, and 20 wt% of Fe3O4@Ag-COOH loading in MWCNT-Fe3O4@Ag, respectively.

2.3. Preparation of MWCNT-Fe3O4@Ag/epoxy electromagnetic shielding nanocomposites

Epon 862 and appropriate MWCNT-Fe3O4@Ag were mechanically stirred for 2 h at room temperature, followed by adding EK 3402. The above mixtures were stirred uniformly at 70 °C, degassed in a vacuum vessel to remove air bubbles, and then poured into the preheated mold. Finally, the obtained mixtures above were cured at 120 °C for 5 h and cooled down to room temperature naturally, finally the MWCNT-Fe3O4@Ag/epoxy electromagnetic shielding nanocomposites were obtained.

2.4. Characterizations

TEM images were collected on a Talos F200X/TEM microscope (FEI Company) operated at 200 kV. XPS analyses of the samples were performed on a PHI5400 equipment (PHI Co., England). The magnetic properties of the samples were investigated using a vibrating sample magnetometer (VSM) at room temperature. All the UV–Vis spectra were performed on a Shimadzu UV-2550 spectrophotometer. Raman spectrum was collected on a Renishaw micro-Raman with a Ti-Safire laser, tuned at 785 nm. TGA of the samples were carried out using STA 449F3 (Netzsch C Corp., Germany) at 10 °C/min (air condition), over the entire temperature range (40–900 °C). X-ray diffraction (XRD) crystallography was obtained on a PhilipsPW3040-MPD diffractometer (copper K-radiation, λ = 1.5418 Å). FTIR spectra of the samples were captured on a Bruker Tensor 27 equipment (Bruker Co., Germany) with thin films on KBr. The nanoindentation technique was employed to evaluate the samples’ mechanical properties (modulus, hardness, and creep behavior). The indentation experiment was performed with a G200 nanoindenter from Agilent. The peak indentation load was set as 9 mN with the fixed loading and unloading rates of 300 and 450 mN/s, respectively. The dwell time at the maximum load was 5 s. To avoid the interference among the different indents, the intervals among any neighboring indents were greater than 100 mm. To get statistically significant results, at least 36 indents were conducted on each sample. The electrical conductivity of the samples was measured by a four-probe method at room temperature. S-paramaters of the samples, which corresponded to the reflection (S11 and S21) and transmission (S12 and S21) of transverse electromagnetic waves, were measured by a VNA (MS4644A, Anritsu) using the wave-guide method in the X-band frequency range (8.2–12.4 GHz) according to ASTM D5568-08, and the corresponding specimen dimension was 22.86 mm × 10.16 mm × 2 mm.

3. Results and discussion

3.1. Fe3O4@Ag-COOH nanoparticles

FTIR spectra of Fe3O4 and Fe3O4@Ag-COOH nanoparticles are depicted in Fig. 1(a). It was clear that the peaks at 3413 cm−1 and 1626 cm−1 were ascribed to the characteristic absorption of -OH group. During the chemical co-precipitation, some hydroxyl groups covered the surfaces of magnetite in an aqueous environment [31]. The peak at 583 cm−1 was assigned to the characteristic absorption of Fe-O group [32]. For Ag coated by MUA, the bands appeared at 2916 cm−1 and 2846 cm−1 were assigned to the characteristic absorption peaks of ν (CH2) and νs (CH2) modes of MUA [33], and the peak at 1642 cm−1 was ascribed to the characteristic absorption of C=O group, which confirmed the successful introduction of MUA onto the surface of Fe3O4@Ag nanoparticles. Fig. 1(b) presented the wide-scan XPS spectrum of Fe3O4 nanoparticles. The peaks at 54.0 eV, 711.0 eV and 724.0 eV were corresponded to the characteristic doublets of Fe 3P3/2, Fe 2P3/2 and Fe 2P1/2, consistent with the reported values for Fe3O4 [34]. For Fe3O4@Ag-COOH nanoparticles, all the characteristic peaks of Fe disappeared, and the new peaks at 368.0, 374.0 and 229.0 eV were ascribed to Ag 3d5/2, Ag 3d3/2 and S 2s [35], indicating that the MUA had been deposited on the surface of Fe3O4@Ag nanoparticles. As shown in Fig. 1(c) and (c′), the spherical Fe3O4 nanoparticles synthesized via co-precipitation method presented a uniform average size about 10.3 ± 1.8 nm, and aggregated due to magnetic force. After coated with Ag, the size was increased to 13.3 ± 2.4 nm. Results of Kolmogorov-Smirnov tests revealed that the corresponding nanoparticle sizes conformed to a normal distribution. And the HRTEM image of Fe3O4@Ag-COOH NPs was also shown in Fig. 1(c′). It confirmed the Fe3O4@Ag-COOH NPs possessed the core-shell structure, and the corresponding particle size of the Fe3O4 core was about 10.7 nm and the thickness of silver shell was about 2.7 nm.

Furthermore, the dispersion of Fe3O4@Ag-COOH nanoparticles in water was also improved obviously. The UV–vis absorption spectra of Fe3O4 and Fe3O4@Ag-COOH nanoparticles are shown in Fig. 1(d). The as-prepared Fe3O4@Ag nanoparticles presented obvious plasmon peak in the range of 350–450 nm [36], while Fe3O4 nanoparticles exhibited no absorption peak over the entire range from 300 to 800 nm, which was attributed that Fe3O4 nanoparticles were coated with Ag shell. Fig. 1(e) shows the XRD patterns for Fe3O4 and Fe3O4@Ag-COOH nanoparticles. Six characteristic peaks (2θ = 30.1, 35.5, 43.1, 53.4, 57.0, and 62.6°) were observed in the XRD pattern of Fe3O4 nanoparticles, marking their indices ((220), (311), (400), (422), (511), and (440)), in accordance with those reported in previous literature [37]. And in the XRD pattern of Fe3O4@Ag-COOH nanoparticles, the four new appeared peaks were attributed to the indices (111), (200), (220), and (311) of silver [38]. Furthermore, the magnetic properties of Fe3O4 and Fe3O4@Ag-COOH were studied by vibrating sample magnetometer.
NH2 was assigned to the nitrogen element of PEI. Fig. 2(d) shows the wide-scan XPS spectra of MWCNTs and MWCNTs-NH2. It could be seen that the MWCNTs with heavy agglomeration presented a relatively larger length/diameter ratio. After the surface treatment by mixed acid and functionalization with PEI, the length/diameter ratio of MWCNTs-NH2 was decreased and the dispersibility in ethanol for MWCNTs-NH2 was improved obviously, mainly ascribed to rich COOH [40] and -NH2 groups on the surface of the MWCNTs-NH2 [41]. Fig. 2(c) shows the FTIR spectra of MWCNTs and MWCNTs-NH2. There was no absorption peak for MWCNTs, while MWCNTs-NH2 presented four new absorption peaks at 3410, 1703, 1560 and 1203 cm\(^{-1}\), corresponded to the stretching vibration of amide group [42], -C=O [43], primary amine [44] and C-N groups, respectively. It confirmed that the PEI had been grafted onto MWCNTs successfully. Fig. 2(d) shows the wide-scan XPS spectra of MWCNTs and MWCNTs-NH2, and the corresponding XPS results are shown in Table 1. Compared to that of MWCNTs, the appearance of N 1s peak at 400.0 eV [45] of MWCNTs-NH2 was assigned to the nitrogen element of PEI. Fig. 2(d’) and Fig. 2(2d’’) show the high resolution of the Cls XPS spectra of MWCNTs and MWCNTs-NH2, respectively. And detailed information about peak fitting is summarized in Table 2. Compared to that of MWCNTs-NH2, the proportion of C=O (284.4 eV) ascribed from MWCNTs and C-O/C-N (285.4 eV) of MWCNTs-NH2 was decreased, and there were three new peaks at 286.8 eV, 287.8 eV and 289.21 eV, ascribed to C-O/C-N, C=C and COO/CON, respectively. Results further confirmed that PEI had been successfully grafted onto MWCNTs.

3.2. MWCNTs-NH2

Fig. 2(a) presents the Raman spectra of the MWCNTs. It could be observed that the peak at 130 cm\(^{-1}\) and 180 cm\(^{-1}\) was ascribed to the semiconductor-like and metallic carbon nanotubes [39], respectively. It indicated that the purchased MWCNTs were composed of semiconductor-like and metallic carbon nanotubes. Fig. 2(b) shows the TEM images of MWCNTs and MWCNTs-NH2, and the corresponding information about peak fitting is shown in Table 3. Compared to that of MWCNTs-NH2, the proportion of C=O (284.4 eV) decreased, and C-C (285.4 eV) increased with the addition of Fe3O4@Ag-COOH nanoparticles on the surface of MWCNTs-NH2 for MF-5, while some aggregations were formed for MF-15 and MF-20. Compared with that of MWCNTs-NH2 (Fig. 3(b)), all the MF-5, MF-10, MF-15 and MF-20 showed the absorption peaks of V (CH2) and Vs (CH2) patterns, revealing the successful introduction of Fe3O4@Ag-COOH nanoparticles on the surface of MWCNTs-NH2. Moreover, all the peaks corresponded to amide, -C=O, primary amine and -NH groups, are mainly ascribed to the reaction between Fe3O4@Ag-COOH nanoparticles and MWCNTs-NH2. Fig. 3(c) and (d) present the XPS spectra and TGA curves of MF-5, MF-10, MF-15 and MF-20, and the obtained results are summarized in Table 3. Fig. 3(c) shows the wide-scan XPS spectra of MF-5, MF-10, MF-15 and MF-20 from 450.0 eV to 350.0 eV. The increase of Ag element and decrease of N element also proved the acyl-amine reaction between Fe3O4@Ag-COOH nanoparticles and MWCNTs-NH2. The high resolution of the Cls XPS spectra of MF-5, MF-10, MF-15 and MF-20 is also shown in Fig. 3(c’), Fig. 3(c’’), Fig. 3(c’’) and Fig. 3(c’’’), respectively. The corresponding information about peak fitting is shown in Table 4. Compared to that of MWCNTs-NH2, the proportion of C=O (284.4 eV) ascribed from MWCNTs and C-O/C-N (286.5 eV) decreased, and C=C (285.4 eV) increased with the addition of Fe3O4@Ag-COOH nanoparticles. The Fe3O4@Ag NPs could not be thermally degraded, while the MWCNTs-NH2 would be oxidized and volatilized in high temperatures. The residue of the MF-5, MF-10, MF-15 and MF-20 reached about 4.1 wt%, 9.0 wt%, 13.4 wt% and 17.9 wt%, respectively. It indicated that more Fe3O4@Ag-COOH NPs reacted with MWCNTs-NH2 with the addition of Fe3O4@Ag-COOH nanoparticles. There were few Fe3O4@Ag-COOH nanoparticles on the surface of MWCNTs-NH2 for MF-5, while some aggregations were formed for MF-15 and MF-20. Fig. 3(a) shows the TEM images of MF-5, MF-10, MF-15 and MF-20. The content of the Fe3O4@Ag-COOH nanoparticles on the surface of MWCNTs-NH2 was normally increased with increasing the

### Table 1

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### Table 2

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3.3. MWCNT-Fe3O4@Ag

Fig. 3(a) shows the TEM images of MF-5, MF-10, MF-15 and MF-20. The content of the Fe3O4@Ag-COOH nanoparticles on the surface of MWCNTs-NH2 was normally increased with increasing the
increasing addition of Fe3O4@Ag-COOH NPs. The above analyses and results further proved that more Fe3O4@Ag-COOH nanoparticles were decorated on the surface of MWCNTs-NH2.

3.4. MWCNT-Fe3O4@Ag/epoxy nanocomposites

Fig. 4 (a) depicts the electrical conductivity of epoxy nanocomposites filled with MWCNTs, MWCNTs-NH2, MF-5, MF-10, MF-15 and MF-20. The electrical conductivity of epoxy nanocomposites filled with 5 wt% MWCNTs-NH2 was decreased from 0.0186 S/cm (5 wt% MWCNTs) to 0.0158 S/cm, mainly ascribed to the structural damage and produced disordered sites of MWCNTs after carboxylation treatment by strong acids [46]. For a given filler loading (5 wt% and 10 wt%), the electrical conductivity of the MWCNT-Fe3O4@Ag/epoxy nanocomposites was all higher than that of MWCNT/epoxy nanocomposite, except MF-20/epoxy nanocomposite. Herein, MF-10/epoxy nanocomposites with 10 wt% MF-10 presented the maximum electrical conductivity value of 0.226 S/cm. On one hand, the improved interfacial compatibility between MWCNT-Fe3O4@Ag and epoxy matrix could be in favor of increasing the dispersion of MWCNT-Fe3O4@Ag inner epoxy matrix [47], also beneficial to the rapid formation of conductive networks. On the other hand, compared with that of single MWCNTs, the addition of Fe3O4@Ag on the side-wall of the MWCNTs was more likely for the contacting possibility between MWCNT-Fe3O4@Ag, which was conducive to the formation of conductive networks. Meanwhile, the magnetic properties of the MWCNT-Fe3O4@Ag were also enhanced with the introduction of Fe3O4@Ag-COOH, which could help the contact of MWCNT-Fe3O4@Ag. Electrons could not only transfer by contact between MF, but also form electric current by electron transition. As a result, the electrical conductivity was improved after the introduction of Fe3O4@Ag-COOH nanoparticles.

In our work, MWCNTs played the main role in the conductive networks. In fact, the mass fraction of the MWCNTs was decreased with the increasing content of Fe3O4@Ag NPs, and the corresponding ability to transfer electrons was also weakened. Therefore, the electrical conductivity of MF-15/epoxy nanocomposite and MF-20/epoxy nanocomposite were both dropped down. Fortunately, the epoxy nanocomposites with 10 wt% MF-20 still maintained the same electrical conductivity value with that of epoxy nanocomposites with 10 wt% MWCNTs.

Fig. 4(b and c) illustrates the EMI SE for epoxy nanocomposites at X-band filled with MWCNTs, MWCNTs-NH2, MF-5, MF-10, MF-15 and MF-20 (5 wt% for (b) and 10 wt% for (c), respectively). For a given filler loading (5 and 10 wt%), all the MWCNT-Fe3O4@Ag/epoxy nanocomposites presented relatively higher average EMI SE values in comparison to those of the MWCNTs/epoxy and MWCNTs-NH2/epoxy nanocomposites. The epoxy nanocomposites with 10 wt% MF-10 presented the maximum EMI SE value of 26 dB, increased by 51% compared to that of MWCNTs/epoxy nanocomposite (17 dB for 10 wt% MWCNTs). When incident waves stroked the shield, a portion of the waves was reflected back and absorbed via interacting with surface charges. The transmitted waves would be further multiply reflected and reabsorbed. One hand, MWCNT-Fe3O4@Ag/epoxy nanocomposites possessed higher conductivity than those of MWCNTs/epoxy nanocomposites, which would discourage the impedance matching. Therefore, it could cause more electromagnetic waves to be reflected back and reabsorbed, resulting in the improvement of the EMI SE. On the other hand, the addition of Fe3O4@Ag nanoparticles could contribute to the hysteresis and dielectric loss for electromagnetic waves, thus improving the attenuation of the electromagnetic waves [48]. As a result, the MWCNT-Fe3O4@Ag/epoxy nanocomposites showed relatively higher average EMI SE values in comparison to those of the MWCNTs/epoxy and MWCNTs-NH2/epoxy nanocomposites.

Furthermore, for the MF-10/epoxy nanocomposites with the optimal electrical conductivity, MWCNTs also played the leading role in absorbing electromagnetic waves. With the increasing addition of Fe3O4@Ag nanoparticles, the relative content of MWCNTs was decreased. Excessive addition of Fe3O4@Ag nanoparticles not only decreased the conductivity of the MF-10/epoxy nanocomposites, but also decreased the ability of absorb electromagnetic waves for MWCNTs. Therefore, there would be a balance point of content between the Fe3O4@Ag nanoparticles and MWCNTs. Results revealed that MF-10 was this equilibrium point. It not only enhanced the conductive networks of the MF-10/epoxy nanocomposites, but also presented the strongest attenuation to electromagnetic waves by hysteresis and dielectric loss. Therefore, the optimal EMI SE value was obtained for the MF-10/epoxy nanocomposite, which was slightly higher than that of MF-15/epoxy nanocomposite and MF-20/epoxy nanocomposite. In addition, the obtained EMI SE MWCNTs/epoxy nanocomposite at f = 12 GHz was slightly higher than the MF-20/epoxy nanocomposite due to the fluctuation of EMI SE curves.

3.5. MF-10/epoxy nanocomposites

To our knowledge, the percolation theory [9] was more applicable to guide and verify our system. Fig. 5(a) shows the electrical conductivity of MF-10/epoxy nanocomposites as a function of MF-10 content. The electrical conductivity of the epoxy nanocomposites was increased with increasing the addition of MF-10. The MF-10/epoxy nanocomposites with 15 wt% MF-10 possessed the maximum electrical conductivity of 0.280 S/cm, and the corresponding conductivity percolation phenomenon was occurred near 1 wt% MF-10.

The total EMI SE (SEf, Fig. 5(b)), absorption SE (SEA, Fig. 5(c)) and reflection SE (SER, Fig. 5(d)) values of the MF-10/epoxy nanocomposites were also compared and analyzed. With increasing the addition of MF-10, both SEf and SEA values were increased.

### Table 3

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<th>N (%)</th>
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### Table 4

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<td>62.92</td>
<td>13.81</td>
<td>1.38</td>
<td>8.66</td>
</tr>
<tr>
<td>MF-20</td>
<td>11.66</td>
<td>61.74</td>
<td>11.31</td>
<td>1.80</td>
<td>8.29</td>
</tr>
</tbody>
</table>
obviously, while the $S_E$ values were increased slowly. The corresponding $S_E$ value of the MF-10/epoxy nanocomposites with 15 wt% MF-10 was enhanced to 35 dB, far above that of MWCNTs/epoxy nanocomposites (15 wt% MWCNTs), also higher than that of target value needed for commercial applications (20 dB). It was also observed that the $S_A$ values were much higher than that of $S_E$ values, which indicated that $S_A$ played a leading role in the loss of electromagnetic waves [49]. The differences between $S_A$ and $S_E$ values with increasing the addition of MF-10 were ascribed to the interfacial polarization of MF-10/epoxy system [50]. The primary mechanism of EMI shielding was usually a reflection of the electromagnetic radiation incident, due to the interaction of EMI radiation with free electrons on the surface of the shield [51]. The absorption was usually the secondary mechanism of EMI shielding. The electric dipoles in the shield interacted with the electromagnetic fields in the radiation [52]. With increasing the addition of MF-10, the conductive networks were gradually developed, resulted in the increased electrical conductivity and improved EMI $S_E$ values. Moreover, the increased frequency of reflection, absorption and hysteresis loss between $\text{Fe}_3\text{O}_4@\text{Ag}$ and CNTs could improve the attenuation of electromagnetic waves in the MF-10/epoxy nanocomposites.

A comparison with previously reported polymeric composites with similar composition by the blend-compounded method is presented in Table 5. Compared with other works, the obtained MF-10/epoxy nanocomposites with 15 wt% MF-10 in our work presented relatively higher electrical conductivity (0.280 S/cm) and $S_E$ value (35 dB) with the same thickness and/or lower thickness. It indicated that MF-10 was a good candidate for the promising EMI shielding. The reason was that the introduction of $\text{Fe}_3\text{O}_4@\text{Ag}$-COOH nanoparticles not only contributed to hysteresis and dielectric loss to electromagnetic waves, but also strengthened the connection between MWCNTs, promoting the formation of conductive networks. As a result, the corresponding EMI $S_E$ value in the X-band was improved.

Fig. 6 presents the mass fraction dependence of MF-10 on the thermally conductive coefficient ($\lambda$) and thermal diffusivity ($\alpha$) values of the MF-10/epoxy nanocomposites. Higher $\lambda$ and $\alpha$ values of the MF-10/epoxy nanocomposites could be achieved with higher MF-10 content. And the $\lambda$ and $\alpha$ values of the epoxy nanocomposites with 15 wt% MF-10 were increased to 0.46 W/mK and 0.27 mm$^2$/s, increased by 129.6% and 43.0% for that of pure epoxy matrix ($\lambda$ of 0.22 W/mK and $\alpha$ of 0.19 mm$^2$/s), respectively. The reason was mainly attributed to the enhanced touching & connecting probability of the MF-10 [59], in favor of forming more effectively thermally conductive channels [60], finally to increase the $\lambda$ and $\alpha$ values of the MF-10/epoxy nanocomposites.

![Fig. 5. (a) Log electrical conductivity vs mass fraction of MF-10; EMI SE for MF-10/epoxy nanocomposites at X-band: (b) $S_E$, (c) $S_A$, (d) $S_E$. (A colour version of this figure can be viewed online.)](image1)

![Fig. 6. Mass fraction of MF-10 affecting the $\lambda$ and $\alpha$ values of the MF-10/epoxy nanocomposites. (A colour version of this figure can be viewed online.)](image2)

![Fig. 7. Mass fraction of MF-10 on the hardness and Young’s modulus of the MF-10/epoxy nanocomposites. (a) The representative load-displacements; (b) Hardness and Young’s modulus. (A colour version of this figure can be viewed online.)](image3)

<table>
<thead>
<tr>
<th>Filler</th>
<th>Matrix</th>
<th>Content</th>
<th>Thickness (mm)</th>
<th>Conductivity (S/cm)</th>
<th>EMI SE (dB)</th>
<th>Frequency (GHz)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag Nanowires</td>
<td>PS</td>
<td>2.5 vol%</td>
<td>0.8</td>
<td>0.19</td>
<td>33</td>
<td>8.2–12.4</td>
<td>[53]</td>
</tr>
<tr>
<td>Graphite</td>
<td>PE</td>
<td>18.7 vol%</td>
<td>3</td>
<td>0.10</td>
<td>21</td>
<td>8.2–12.4</td>
<td>[54]</td>
</tr>
<tr>
<td>RGO/Fe$_3$O$_4$</td>
<td>Epoxy</td>
<td>15 wt%</td>
<td>2.5</td>
<td>10$^{-6}$</td>
<td>18</td>
<td>8.2–12.4</td>
<td>[55]</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Epoxy</td>
<td>15 wt%</td>
<td>2</td>
<td>0.20</td>
<td>25</td>
<td>8.2–12.4</td>
<td>[56]</td>
</tr>
<tr>
<td>MWCNTs/Fe$_3$O$_4$/Fe</td>
<td>Epoxy</td>
<td>10 wt%</td>
<td>2</td>
<td>0.26</td>
<td>35</td>
<td>8.2–12.4</td>
<td>[57]</td>
</tr>
<tr>
<td>MF-10</td>
<td>Epoxy</td>
<td>15 wt%</td>
<td>2</td>
<td>0.28</td>
<td>35</td>
<td>8.2–12.4</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^*\text{- values not provided.}$
Effects of mass fraction of MF-10 on the hardness and Young's modulus of the MF-10/epoxy nanocomposites are presented in Fig. 7. The decreased indentation depth (Fig. 7(a)) of the MF-10/epoxy nanocomposites revealed their enhanced ability to resist the indentation with increasing the addition of MF-10 [61]. In Fig. 7(b), compared to that of MF-10/epoxy nanocomposites with 1 wt% MF-10, the Young's modulus of the MF-10/epoxy nanocomposites with 15 wt% MF-10 was increased from 4.28 to 4.60 GPa, and the corresponding hardness was also enhanced from 0.23 to 0.28 GPa. There was a strong interaction between the MF-10 and the epoxy due to the existence of reactive groups on the MF-10. Therefore, the hardness and Young's modulus of the MF-10/epoxy nanocomposites were improved with the addition of MF-10. As a result, the addition of MF-10 was in favor of increasing the Young's modulus and hardness of the MF-10/epoxy nanocomposites.

Fig. 8 depicts the TGA curves of MF-10/epoxy nanocomposites at air condition, and the corresponding characteristic thermal data were shown in Table 6. The thermal decomposition of the all above epoxy nanocomposites took place in two stages. Epoxy resins was broken down in the first stage from 300 to 400 °C, and benzene rings in the epoxy backbone were degraded in the second stage from 450 to 600 °C. All the \( T_5 \), \( T_{30} \) and \( T_{50} \) values were increased with increasing the addition of MF-10, and the \( T_{III} \) value of the MF-10/epoxy nanocomposites with 15 wt% MF-10 was obviously increased from 167.7 °C for MF-10/epoxy nanocomposites with 1 wt% MF-10 to 183.4 °C. It confirmed that the thermal stabilities of the MF-10/epoxy nanocomposites were gradually increased with increasing the addition of MF-10.

\[
T_{Heat-resistance\ index} = 0.49(T_5 + 0.6(T_{30} - T_5))
\]  \hspace{1cm} (1)

\( T_5 \) and \( T_{30} \) is corresponding decomposition temperature of 5% and 30% weight loss, respectively.

### 4. Conclusions

The novel hierarchical composite nanoparticles of MWCNTs-Fe3O4@Ag combining electrical conductivity and magnetism were firstly obtained from the acyl-amine reaction between Fe3O4@Ag-COOH nanoparticles and MWCNTs-NH2. TEM, TGA, FTIR, XPS and Raman analyses revealed that the nanoparticles of Fe3O4@Ag-COOH, MWCNTs-NH2 and their compound of MWCNTs-Fe3O4@Ag were obtained successfully. When the mass ratio of MWCNTs-NH2 to Fe3O4@Ag-COOH was 9:1 (MF-10), the corresponding MWCNTs-Fe3O4@Ag/epoxy nanocomposites presented the optimal electrical conductivity and EMI SE. Furthermore, the MF-10/epoxy nanocomposites with 15 wt% MF-10 presented the excellent EMI SE of 35 dB and high electrical conductivity of 0.280 S/cm, satisfactory \( \lambda \) of 0.46 W/mK, outstanding Young's modulus of 4.60 GPa & hardness value of 0.26 GPa and excellent thermal stability (THRI of 183.4 °C). The excellent comprehensive properties make the obtained MWCNT-Fe3O4@Ag/epoxy nanocomposites suitable for broad applications such as medical equipment, industrial electronic equipment, wireless base stations and aviation equipment.

### Acknowledgments

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### References


