Multiple cooperative systems obtained by powder metallurgy-like processing method: Adenine containing phthalonitrile/graphene/Fe₃O₄ high-performance composites with ultra-high EMI shielding

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Abstract. Adenine containing phthalonitrile (ADCN)/graphene/Fe₃O₄ composites with excellent EMI performance, outstanding thermal, thermo-oxidative stability, and heat resistance are introduced. The interactions between ADCN and nanofillers combined with high-energy ball milling-molding sintering processing method ensure the uniform dispersion of nanofillers in the matrix. The EMI shielding effectiveness (EMI SE) of ADCN/G/Fe₃O₄ is up to 50 dB with only 0.5 mm thickness, which is one of the best EMI performance compared with previous reports on conductive polymer composites (CPCs). The high-performance ADCN polymer introduces outstanding thermal, thermo-oxidative stability and heat resistance into the composites. The $T_{5\%}$ in the air of composites could still maintain more than 491 °C, and the EMI value of composites after flame retardancy test could reach 40 dB. The results prove that ADCN/G/Fe₃O₄ composite is a promising candidate that could be used in the aerospace industry and under extreme working conditions.

Keywords: polymer composites, electromagnetic interference, heat resistance, adenine containing phthalonitrile, homogeneous dispersion system

1. Introduction

With the development of communication technology and the electronics industry, the resulting electromagnetic pollution has become an inevitable issue. A series of electromagnetic shielding materials such as metals and conductive polymer composites (CPCs) has been developed to curb electromagnetic pollution [1–6]. Conductive polymer composites (CPCs), as a class of electromagnetic shielding materials with broad development prospects, have received extensive attention due to their versatility and designability [7–11]. With the rapid development of the aerospace industry, extreme working conditions need higher standards for the performance of electromagnetic

shielding materials. Single-function EMI materials rarely meet the development needs. For example, the electromagnetic shielding materials used in navigation equipment of aerospace aircraft are required both qualified EMI and high-temperature stability [12]. To the best of our knowledge, electromagnetic shielding materials with high-temperature stability, suitable mechanical properties, and excellent EMI performance are urgently needed but rarely reported [13–18]. The electromagnetic shielding mechanism of most conductive polymer composites is mainly based on the absorption of electromagnetic waves, supplemented by reflection. The absorption strategy of electromagnetic waves can be roughly divided into three

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categories: conductive loss, hysteresis loss, and dielectric loss [19–21]. Based on the conductive loss strategy, as a 2D carbon nanomaterial, graphene is regarded as a high-quality absorbing and electromagnetic shielding composite filler [22–25] due to its excellent electrical conductivity (~ 6000 S/cm) and high specific surface area. For example, Shen *et al.* [26] reported a graphene film with excellent electromagnetic shielding performance; the electromagnetic shielding performance could reach 20 dB. Based on the hysteresis loss strategy, Fe_3O_4 nanoparticles are also regarded as high-quality EMI material fillers due to their low toxicity, good biocompatibility, and high saturation magnetization [27–30]. For example, Chen *et al.* [31] reported an EMI material (30 dB) developed by blending ferric oxide nanoparticles with thermally-annealed graphene oxide/polystyrene. The incorporation of Fe_3O_4 nanoparticles can effectively avoid the skin effect that is likely to occur when highly conductive fillers are incorporated [32]. Furthermore, because of the high resistivity, Fe_3O_4 nanoparticles make the entry of electromagnetic waves more efficient. The co-doping of graphene and Fe_3O_4 magnetic nanoparticles could achieve the joint improvement of conduction loss and hysteresis loss ability of composites, thereby significantly improving the electromagnetic shielding performance.

However, nanofillers such as graphene and Fe_3O_4 nanoparticles are prone to agglomeration [32], and the dispersion of nanofillers in the polymer matrix, to a large degree, determines the electromagnetic shielding performance of the material [33, 34]. At present, the related literature mostly adopts the synthesis of Fe_3O_4 @graphene hybrid to handle the issue of agglomeration [31, 32]. This method has been reported to avoid the agglomeration of graphene and Fe_3O_4 magnetic particles effectively, but the processing process is relatively complicated. Among the physical dispersion methods, high-energy ball milling is reported to be a processing method that could achieve uniform dispersion of nanofiller and the polymer powder. It has the advantages of simple processing technology, suitable for large-scale mass production and environmental protection. For example, Tang *et al.* [35] achieved good dispersion of RGO in epoxy by high energy ball milling. Besides, compared with the conventional melting process, which may lead to the agglomeration of nanofillers, our previous work proved that the molding sintering processing (MSP) method could maintain the dispersion state of the

components inside the material during the curing process. The good dispersion state of the filler after high energy ball milling could be maintained without recurrence agglomeration [36]. In summary, it is speculated that the high-energy ball milling-molding sintering processing method could achieve uniform dispersion of the nanofiller in the matrix and thereby improve the electromagnetic shielding performance.

Phthalonitrile, as a typical high-performance cross-linked polymer, has been widely used in aerospace engineering and military engineering due to its high glass transition temperature, good thermal and thermo-oxidative stability, excellent flame retardancy, radiation resistance and outstanding mechanical properties [37]. The bio-based adenine containing phthalonitrile monomer (ADCN) reported in our previous work [36] not only has the characteristics of CN resin, but the introduction of adenine structure further enhances the thermal and thermomechanical properties. So far, it is speculated that using ADCN as the polymer matrix of composites could introduce its excellent mechanical properties, thermal and thermo-oxidative stability into composites. It makes possible the development of electromagnetic shielding materials with high-temperature resistance and superior mechanical properties. Besides, the adenine structure has great prospects in various applications because of its unique aromatic heterocyclic structure and various interactions (such as hydrogen bonding, π - π interaction, *etc.*). Therefore a new system based on physical interaction was developed by our group to achieve a good dispersion of graphene: the non-covalent bond interaction between the functional group of rGO/GO, and the adenine structural units was enhanced by π - π interaction and hydrogen bond interaction. These interactions improve the graphene dispersion in organic solvents [38–40]. Furthermore, adenine structure could even improve the efficiency of graphene exfoliation in solution [41]. Besides, we found that the active site of Fe^{2+} with adenine-containing monomer is located on the adenine fragment by exploring the interaction mechanism [42]. This is similar to the mechanism of synthesizing graphene@ Fe_3O_4 hybrids to anchor iron ions on graphene sheets to avoid the agglomeration of Fe_3O_4 nanoparticles [31]. It can be speculated that the introduction of adenine structure can prevent the agglomeration of Fe_3O_4 nanoparticles through the interaction with iron ions. Besides, previous studies have shown that

phthalocyanine rings can generate iron phthalocyanine with iron ions, which also confirms that ADCN interacts with Fe_3O_4 nanoparticles [43, 44].

In summary, blending adenine-containing phthalonitrile (ADCN) with graphene and Fe_3O_4 nanoparticles could achieve a good dispersion of the filler in the matrix to obtain a better EMI performance. Simultaneously, the two fillers could improve the EMI performance of the composite through different wave absorption mechanisms. The high-energy ball milling-molding sintering processing method could achieve high EMI performance by achieving good dispersion of the filler in the matrix. On the other hand, the prepared porous structure could increase the multiple reflections of the electromagnetic wave inside the material to improve the electromagnetic shielding performance. Inspired by this, in this paper, graphene and Fe_3O_4 nanoparticles were blended with ADCN through high-energy ball milling and then made into adenine-containing phthalonitrile/graphene/ Fe_3O_4 nanoparticles (ADCN/G/ Fe_3O_4) electromagnetic shielding materials by molding-sintering processing method. The cooperative system endows the composite with excellent electromagnetic shielding properties. The introduction of ADCN endows the composite with outstanding thermal properties and qualified mechanical properties. Ultra-thin (less than 1 mm) porous structure could be achieved by the high-energy ball milling-molding sintering processing method. This work will provide some guidance for the preparation and application of high-performance composites with ultra-high EMI shielding.

2. Experimental

2.1. Materials

Adenine was purchased from Chengdu Best Reagent Co., Ltd (Chengdu, China), purity:99%. 4-Nitrophthalonitrile was purchased from Jinan Wedo Chemical Corporation (Jinan, China), purity:99%. Magnetic Fe_3O_4 Nanoparticles were purchased from Nanjing Emperor Nanomaterials Co. Ltd (Nanjing, China), purity: >99%, average particle size: 20 nm, specific surface area: >60 m^2/g , color: black, shape: spherical particle, density: 4.8–5.1 g/cm^3 , molecular weight: 231.54, melting point: 1867.5 K(1594.5 °C). Anhydrous ethanol was purchased from Shanghai Youshi Co., Ltd (Shanghai, China), purity: $\geq 99.5\%$. Graphene was purchased from Guangzhou Angstrom Graphene Co., Ltd (Guangzhou, China),

purity: >97%, particle size distribution: 0.1–1.0 μm , thickness: <1 nm, color: black, specific surface area: 400–600 m^2/g , carbon content: >95%. The graphene was prepared by an oxidation-reduction method. Chemicals above were used as received except 4-Nitrophthalonitrile. 4-Nitrophthalonitrile was purified by the recrystallization method with absolute ethyl alcohol before use.

2.2. Characterizations and methods

EMI shielding characteristics of the ADCN/G/ Fe_3O_4 composites and ADCN/G/ Fe_3O_4 composites after the flame test reported here were collected by PNA-X N5247A network analyzer (Agilent Technologies Inc., Shanghai, China). Samples with a 15 mm diameter and 0.51–0.97 mm thickness were placed in the specimen holder. Scattering parameters (S_{11} and S_{21}) in the frequency range of 8.2–12.4 GHz (X-band) were obtained and used to calculate the EMI shielding effectiveness (EMI SE). The scattering parameters (S_{11} and S_{21}) of the Graphene/ADCN composites in the total EMI shielding effectiveness (SE_{Total}) is the sum of microwave reflection (SE_R) from the material surface, microwave absorption(SE_A), and microwave multiple internal reflections (SE_M) of electromagnetic radiation. SE_R is related to the impedance mismatch between air and absorber; SE_A can be regarded as the energy dissipation of the electromagnetic microwave in the absorber. The EMI SE (SE_T), the ability of the material to shield an electronic device from electromagnetic radiation, is calculated by Equation (1) [61, 62]:

$$SE_T [\text{dB}] = 10 \lg \frac{P_i}{P_T} \quad (1)$$

where P_i is the incident power, and P_T is the transmitted power. Generally, electromagnetic waves are attenuated by three mechanisms: absorption (SE_A), reflection (SE_R), and multiple reflections (SE_M). SE_M is negligible when EMI SE is larger than 15 dB, and SE_T simplifies to Equation (2):

$$SE_T = SE_R + SE_A \quad (2)$$

In a two-port vector network analyzer, SE_T can be determined by the calculation of reflectance (R), transmittance (T), and absorbance (A) coefficients, which can be correlated to scattering parameters (S_{11} , S_{12} , S_{21} , S_{22}) as shown by Equations (3)–(5):

$$T = |S_{12}|^2 = |S_{21}|^2 \quad (3)$$

$$R = |S_{11}|^2 = |S_{22}|^2 \quad (4)$$

$$A = 1 - R - T \quad (5)$$

SE_R and SE_A can be written according to Equations (6) and (7):

$$SE_R = 10 \lg\left(\frac{1}{1-R}\right) = 10 \lg\left(\frac{1}{1-|S_{11}|^2}\right) \quad (6)$$

$$SE_A = 10 \lg\left(\frac{1-R}{T}\right) = 10 \lg\left(\frac{1-|S_{11}|^2}{|S_{21}|^2}\right) \quad (7)$$

SE_T can be deduced from equation SE_R and SE_A as given by Equation (8):

$$SE_T = 20 \lg(|S_{21}|) \quad (8)$$

X-ray diffraction (XRD) patterns of samples were obtained by an X-ray diffractometer (Ultima IV). The Raman spectra were measured by a DXRxi spectrometer (Thermo Fisher Scientific, Waltham, USA) with a laser emitting at 532 nm. Thermogravimetric analysis (TGA) was performed using a Q500 thermogravimetric analyzer (TA Instruments, Shanghai, China) at a heating rate of 20 °C/min in nitrogen and air atmospheres, respectively, at a flow rate of 60 ml/min. The electrical conductivity of samples was investigated using an RTS-9 type double electric test four-probe tester (China Guangzhou Four Probe Technology Co., Ltd. Guangzhou, China). The diameter (15 mm) and thickness (0.51–0.97 mm) measured by slide caliper of samples were input parameters of the test system. Then the conductivity was measured using a four-probe tester. The electrical conductivity was calculated according to Equation (9) [63]:

$$\text{conductivity} = \frac{1}{4.53 \cdot \frac{V}{I} \cdot d} \quad (9)$$

where I = current in Amperes, V = voltage in Volt and d is the measured thickness (meter) of the sample. Scanning electron microscope (SEM) images were determined by a Quanta 250 field-emission SEM (FEI, Oregon, USA). The specimen was coated with Au before observation. The high energy ball milling process was carried out by using a QM-3SP2 planetary ball mill (NanDa Instrument Plant, Nanjing, China) under the condition of 250 rpm (revolutions per minute) rotation speed, a ball-to-powder mass

ratio of 10:1, and balls (10 mm in diameter)-to-balls(5 mm in diameter) mass ratio of 1:1. Raman images were collected by using a Laser Microscope Raman Imaging Spectrometer, DXRxi (Thermo Fisher Scientific, Waltham, USA). Multivariate curve resolution MCR images are analyzed by the multivariate curve resolution included in the instrument. A random zone of the cross-section in each sample was selected. The size of each area is 200 μm × 200 μm; the step size is 5 μm and integration time is 1 s. The excitation source is a 514.5 nm laser with a power of ~1 mW. The spot size of the laser at the sample is ~1 μm with a 50× objective (NA = 0.5), and the probed volume is ~1 μm with a confocal optical system. The magnetic properties of the samples were investigated using a BHV-55 vibrating sample magnetometer (VSM) (Riken Corundum CO., LTD, Miyamae, Japan) at room temperature. Infrared reflection spectra were measured on a Nicolet-460 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, USA) between 4000 and 400 cm⁻¹ in air. The sample was ground thoroughly and mixed with dried potassium bromide in an agate mortar. After full grinding, the mixture was put evenly into a pressing mold and molded under 15 MPa pressure for 2 minutes to get a translucent sample. The sample was tested in transmission.

2.3. Synthesis of ADCN and preparation of ADCN/G/Fe₃O₄ composites

For the synthesis steps of ADCN refer to our previous work; the structure characterization results are shown below [36]:

¹H NMR (300 MHz, DMSO-*d*₆, ppm), 8.87–8.88 (d, J = 2.2 Hz, 1H), 8.85 (s, 1H), 8.69–8.73 (dd, J 1 = 2.2 Hz, J 2 = 8.6 Hz, 1H), 8.36–8.39 (d, J = 8.6 Hz, 1H), 8.29 (s, 1H), 7.57 (s, 2H).

FTIR (KBr, cm⁻¹) 3457s, 3305m (N–H), 3082w (Ar–H) 2235m (C≡N), 1653s, 1600s (C=N), 1554s, 1521s, 1471s (C=C), 1437m, 1373m (C–N).

Elem. Anal. Calc. for ADCN (C₁₃H₇N₇): C, 59.77; H, 2.70; N, 37.53%. Found: C, 59.65; H, 2.90; N, 37.39%.

ADCN and graphene were added to absolute ethanol and ultrasonically dispersed for two hours at room temperature, and the slurry was taken out for mechanical stirring for 30 minutes (60 rpm). Then the Fe₃O₄ magnetic nanoparticles were added to the slurry and sonicated at room temperature for 1 hour. Using high-energy ball milling method to disperse

Table 1. The size and filler content of four samples.

Sample	Diameter [mm]	Thickness [mm]	Graphene content [wt%]	Fe ₃ O ₄ NPs content [wt%]
A	15.0	1.0	0.0	0.0
B	15.0	1.0	2.5	2.5
C	15.0	0.7	5.0	5.0
D	15.0	0.5	7.5	7.5

the slurry (rotation speed 250 rpm, ball-to-material weight ratio 10:1, 10 mm ball: 5 mm ball = 1:1), the ball milling time was 6 hours, and the slurry is mechanically stirred every half hour for 5 minutes. After the ball milling, the slurry was vacuum dried for 12 hours, and the absolute ethanol is removed at a temperature of 100 °C to obtain a powder. The powder was press-molded (15 MPa, 3 minutes) to make a disc with a diameter of 15 mm and a thickness of 0.5–1 mm. Then put the disc into the muffle furnace to heat it (heating program: 325 °C for 5 hours, 375 °C for 5 hours).

3. Results and discussion

The process flow of porous ADCN/G/Fe₃O₄ composites is shown in Figure 1. Ultrasonic dispersion in the early stage could preliminarily achieve uniform distribution of the filler in the matrix. Meanwhile, during the ball milling process, the agglomeration of nanofillers is suppressed by mechanical friction and shear force. The matrix and nanofillers are

fully contacted and mixed during the ball milling process, leading to a uniform dispersion of nanofillers in the matrix. After that, the molding-sintering processing (MSP) method could maintain the dispersion state of each component. A good dispersion state could make composites obtain a better EMI performance at a lower filler content by establishing a conductive path. Furthermore, this processing method is versatile and simple that could achieve industrial-level mass production, which can provide a reference for the preparation of a similar type of material. Table 1 shows the specific parameters of the samples produced in this work, including the diameter, thickness, graphene dosage, and Fe₃O₄ NPs dosage of each sample.

Figure 2 shows the Raman spectrum of pure-graphene and ADCN/G/Fe₃O₄ composite materials. Both samples have two distinct absorption peaks in the spectrum: D band (1332–1355 cm⁻¹) and G band (1558–1587 cm⁻¹). D band is attributable to the vibrational mode of a tetrahedral sp³ configuration which is used to characterize the defects and disorders structure of graphite lattice. G band is caused by in-plane vibration of sp² carbon, which characterizes the ordered structure of graphite lattice [45–47]. Therefore, the integrated area ratio (*R*) of D and G was used to judge the degree of disorder in carbon material. The integrated area ratio (*R*) of D and G was calculated by Gaussian peak fitting method from Raman spectrum,

Figure 1. Schematic for the fabrication procedure of porous ADCN/G/Fe₃O₄ with uniform distribution structure.

Figure 2. Raman spectra of graphene and ADCN/G/Fe₃O₄.

I_D/I_G (Graphene) = 1.023, I_D/I_G (ADCN/G/Fe₃O₄) = 1.239. It indicates the increase of disorder and defects of the graphite lattice. The reason for this result may be attributed to the destruction of the graphene sheet structure caused by the ball milling process, leading to more defects occurring on the graphene sheet. Besides, the introduction of N in the adenine fragment of the polymer matrix may also affect the charge distribution and properties of graphene and cause more defects [48–51].

As mentioned in the introduction, cyano resin could react with iron ions to form an iron-phthalocyanine structure during the curing process. To analyze the influence of interaction on the composite structure, FTIR was used to observe the evolution of the structure. To verify whether the Fe₃O₄ nanoparticles reacted with the phthalocyanine ring formed in PADCN during the curing process, ADCN monomer, Fe₃O₄ nanoparticles, ADCN blended graphene cured sample, and ADCN/G/Fe₃O₄ composite were tested. It is known from the results shown in Figure 3 that PADCN and PADCN/Graphene show absorption peaks at 1010 cm⁻¹, indicating that phthalocyanine rings are formed during the monomer curing process, and the introduction of graphene does not affect the formation of phthalocyanine rings. From the FTIR spectrum of Fe₃O₄ nanoparticles, the emergence of a characteristic diffraction peak at 588 cm⁻¹ belongs to Fe₃O₄ nanoparticles, consistent with related reports [52]. In the infrared results of ADCN/G/Fe₃O₄, a new peak was observed at 727, 1080, 1117, and 1649 cm⁻¹, which is attributed to iron phthalocyanine [53]. It indicates a chemical reaction process between ADCN and Fe₃O₄ during the curing process,

Figure 3. FTIR spectra of the ADCN, Fe₃O₄, cured ADCN/Graphene and ADCN/G/Fe₃O₄ composite.

and this phenomenon may be beneficial to the dispersion of Fe₃O₄ nanoparticles in the matrix.

The XRD results shown in Figure 4 demonstrated that all samples present characteristic diffraction peaks at $2\theta = 26.69^\circ$. It belongs to the characteristic diffraction peak of few-layer graphene (FLG) [54]. According to the JCPDS 19-629 (JCPDS = Joint Committee on Powder Diffraction Standards), The characteristic diffraction peak of Fe₃O₄ nanoparticles could be attributed to (220), (311), (400), (422), (511), (440), and (533) reflections [55].

The unique structure of graphene makes it possible to obtain a higher electrical conductivity at lower concentrations than other conductive fillers. However, in the case of a large concentration, graphene would be stacked with each other in the matrix, which will greatly affect the composite performance and a waste of graphene as well. Raman mapping based on Raman scattering is an effective method for characterizing the dispersibility of fillers in the matrix [54]. Figures 5a–5c show the results of Raman mapping MCR of three samples with different filler contents. It can be seen that the filler in each sample is basically uniformly dispersed in the matrix resin, there is no distinct agglomeration occurs. As the filler content increases, the area of fillers in the photo also increases. It can be seen from the picture of low filler content that continuous chain conductive channels were not formed completely, and there is a large distance between the graphene sheets. With the increasing filler content, the graphene sheets were gradually connected to each other; a continuous and complete conductive network was formed in the matrix. This

Figure 4. (a) XRD patterns of ADCN/G/Fe₃O₄ (5%, 10%, 15%). (b) XRD patterns of ADCN, graphene and Fe₃O₄ NPs.

Figure 5. Raman multivariate curve resolution images of ADCN/G/Fe₃O₄ composites with filler concentration at a) 5 wt%, b) 10 wt%, c) 15 wt%, red part represents ADCN, blue and green parts represent Graphene and Fe₃O₄ NPs. Raman peak height images of ADCN/Graphene/Fe₃O₄ composites with filler concentration at d) 5 wt%, e) 10 wt%, f) 15 wt%, Red and yellow parts represent graphene, green and blue parts represent ADCN.

trend is also consistent with the trend of electrical conductivity and EMI performance data. From Figures 5d–5f, the distribution of each component was determined by calibrating the absorption peak in the scanning area. Based on this data, the approximate dispersion of components could be observed. The result indicates that in the randomly selected scan area, graphene has good dispersibility without distinct agglomeration. Besides, with the increase of filler content, the internal conductive network is gradually formed, the trend is consistent with the electrical conductivity and EMI results.

SEM test was employed to further analyze the distribution of fillers in the matrix and morphology of composites. The interconnected micrometer-sized pores could be found in Figure 6a. This is because there are intervals between monomer particles, and monomer did not melt significantly during the curing process, so the intervals between particles are retained to form pores. The porous structure is conducive to extending the propagation path of the incident wave and increasing the probability of reflection and diffraction inside the composites. So the incident wave could eventually be dissipated by transferred to heat loss, leading to the improvement of electromagnetic shielding performance of composites [56]. Figures 6a–6d highlighted the approximate distribution areas of graphene and Fe_3O_4 NPs, respectively. It can

be seen that graphene and Fe_3O_4 NPs did not undergo large-scale agglomeration; the fillers were roughly uniformly dispersed in the polymer matrix. Combined with the results of Raman mapping, it can be speculated that the filler has achieved uniform dispersion in the matrix. Furthermore, the graphene sheets maintain the original lamellar structure after the processing procedure. The uniform dispersion of graphene in the matrix makes it easier to form a conductive network in the resin matrix, which is conducive to the enhancement of conductivity, which is more conducive to the enhancement of conductivity. Figures 6e and 6f showed the BSE SEM images of the sample. It could be observed that there is no obvious agglomeration of Fe_3O_4 NPs. Figures 6g and 6h showed the morphology of pristine graphene and pristine Fe_3O_4 NPs

Figure 7 shows the electrical conductivity of samples with different filler content and pure ADCN. The conductivity of each sample was tested three times at different areas, the final results were obtained by calculating the arithmetic average. The conductivity of the pure ADCN is so low that it exceeds the test range ($<10^{-5}$ S/cm), while the conductivity of the 5% sample increases exponentially compare with the pure ADCN. According to the percolation theory [57], the percolation threshold of composites should be between 0–5% filler content. The fillers

Figure 6. (a–d) SEM images of ADCN/G/ Fe_3O_4 composites (filler content graphene: 7.5 wt%, Fe_3O_4 : 7.5 wt%, ADCN: 85 wt%) after curing process. (a): 10 000 $\times$, (b): 20 000 $\times$, (c): 50 000 $\times$, (d): 100 000 $\times$. The yellow dashed circle highlights the graphene distribution area, the blue dashed circle highlights the Fe_3O_4 NPs distribution area. (e, f): BSE SEM images of ADCN/G/ Fe_3O_4 composites (filler content graphene: 7.5 wt%, Fe_3O_4 : 7.5 wt%, ADCN: 85 wt%) after curing process. (e): 100 000 $\times$, (f): 200 000 $\times$. (g): SEM image of pristine graphene, 10 000 $\times$. (h): SEM images of pristine Fe_3O_4 , 10 000 $\times$.

Figure 7. Electrical conductivity of samples.

content of three samples prepared in this paper have all exceeded the percolation threshold; the electrical conductivity of samples was beyond the mutation value, which indicates the successful construction of the internal conductive network inside the composite. The electromagnetic shielding performance is strongly related to electrical conductivity. The changing trend of the electrical conductivity is also positively associated with the direction of the electromagnetic shielding performance data, consistent with related reports [58].

The magnetic properties of the composite materials were tested by vibrating sample magnetometer (VSM) at room temperature; the magnetic field range is -20 –20 kOe (Figure 8). Compared with the saturation magnetization of pure Fe_3O_4 NPs: 60 emu/g [31], the saturation magnetization of the highest filler content was reduced by 36.3 emu/g. The saturation magnetization increased with the increase of Fe_3O_4 content. In addition, the magnetization curves

show reversible, nonlinear characteristics with no significant coercivity after removing the applied magnetic field, indicating that the material has superparamagnetic characteristics. As the filler content increased from 5 to 15%, the saturation magnetization of the composite material increased from 5.4 to 23.7 emu/g. From the relevant formula: $B = \mu_0(H + M)$, $W = K_1 B_m^n f$ (M : magnetization, W : hysteresis loss per unit volume) [59], it can be seen that the saturation magnetization of the material is a positive correlation to the hysteresis loss. Thus, the hysteresis loss capacity of the material increases with the increase of the filler content. This result is also consistent with the electromagnetic shielding performance data trend, shown in Figure 8b. It can be seen that the sample shows the characteristics of fast driving when contacting the permanent magnet and shows a strong attraction to the static magnetic field. Figure 9a shows the electromagnetic shielding performance values of four samples, of which ADCN (0%) as a blank control group shows the electromagnetic shielding performance (5 dB) of the polymer matrix without the introduction of fillers. With the addition of fillers, the EMI performance of the composite has been rapidly improved. When the filler content is only 5 wt% (graphene: Fe_3O_4 = 1:1 the composite has been increased to 30 dB. As the filler content increases, the EMI performance is further improved to reach 40 and 50 dB when the filler content is 10 and 15%, respectively. It is also worth noting that when the filler content reaches 15%, the EMI performance of the material is still steadily improving, and there is no phenomenon of the growth trend slows down or decreases instead. This indicates the

Figure 8. Superparamagnetic porous ADCN/G/ Fe_3O_4 composites: (a) Magnetization of the composites with different graphene/ Fe_3O_4 loading; (b) composites can be actuated by an external magnetic field.

Figure 9. (a) SE_{Total} ; (b) SE_A ; (c) comparison of total EMI shielding effectiveness (SE_{Total}), $SE_{Total}/thickness$ value, microwave absorption (SE_A), and microwave reflection (SE_R) at a frequency of 8.0–12.0 GHz; (d) SE_R .

processing method reported in this article could achieve uniform dispersion even at high filler content. The thickness of materials is also a factor that affects the electromagnetic shielding performance. Therefore, the $SE_T/thickness$ EMI value of each sample could better reveal the actual EMI performance. Comparing the SE_T line chart with the SE_T specific thickness chart (Figures 9a and 9c), the property of EMI improve to a greater extent as the filler content increase. Figures 9b and 9d show the absorption and reflection efficiency values of the four samples. The EMI performance of the three samples with fillers is dominated by absorption. The fillers are mainly increasing the absorption efficiency of the material to improve electromagnetic shielding performance. As discussed in the introduction, composition and structure play important roles in the EMI performance of polymer-based composites. Thus, based on the characterization of structure, conductivity, and magnetic properties, a mechanism on high EMI performance of ADCN/G/Fe₃O₄ was proposed in Figure 10. The increase of impedance matching caused by the introduction of Fe₃O₄ is conducive to the entrance

of incident waves, and leading to a decrease of reflection. When the incident waves enter the composites, on the one hand, the porous structure processed by the molding-sintering method provided a large pore-matrix interface area. The incident waves could be reflected and scattered between interfaces, and hard to escape from composites [32]. On the other hand, the important factor in improving the microwave absorption capacity is to enhance the attenuation of electromagnetic waves, which depends on the conductive loss and hysteresis loss, synergy between magnetic dipoles in Fe₃O₄, and the increased conductivity of graphene results in high attenuation of

Figure 10. the ideal model of EMI shielding mechanism.

EM radiation. Although, the skin effect determines that electromagnetic waves can only be attenuated at a certain depth on the surface of the material [60]. Meanwhile, the agglomeration of functional nanofiller such as graphene and Fe_3O_4 NPs happens frequently during the curing process, resulting in a decrease in EMI performance and waste of nanofillers. Related reports overcome the agglomeration by using a chemical modification to anchor Fe_3O_4 NPs on graphene sheets [31, 32, 35]. Although the agglomeration issue has been handled, it has also increased the process and preparation costs of composites. Based on the results of Raman multivariate curve resolution images, SEM photos, FTIR, and our previous works [38, 42], the ball milling-molding-sintering process and interaction between adenine fragment and nanofillers can restrain the strong magnetic attraction between the Fe_3O_4 and weaken aggregation of graphene without chemical modification. The increased interconnected conductivity network and interfacial polarization formed by the graphene, which strengthens the interaction with incoming waves. As demonstrated in Figure 10, the porous structure could reflect and scatter the incident electromagnetic waves, increasing their propagation paths, which could further enhance the absorbing ability. Based on the effect of the factors mentioned above, excellent EMI performance was obtained.

The electromagnetic shielding performance of the composites introduced in this article was compared with polymer composites of the same fillers in terms of filler content, sample thickness, test frequency range, and corresponding electromagnetic shielding performance (Table 2). As we all know, the thickness of the sample will greatly affect the electromagnetic shielding performance. Therefore, the value obtained by dividing the value of SE_T by the thickness of the sample is more meaningful, and it is closer to the actual electromagnetic shielding performance of the material as well. From Table 3, when the filler content <10%, the ADCN/G/ Fe_3O_4 (5%) sample reported in this paper has the best electromagnetic shielding performance, and its SE_T /thickness performance is three times higher than the performance of second-best composites in the table. When the filler content exceeds 10%, the electromagnetic shielding performance of the ADCN/G/ Fe_3O_4 (10%) and (15%) samples reported in this paper is also among the top. Among them, the ADCN/G/ Fe_3O_4 (15%) sample achieved a nearly double improvement in SE_T /thickness performance by increasing the filler content by only 5% (1086.9 dB/cm, ADCN/G/ Fe_3O_4 (10%): 571.4 dB/cm). The comparison of electromagnetic shielding performance data shows that the composite introduced in this article have ultra-high electromagnetic shielding performance, and the thickness can also be processed to a relatively thin level in the field

Table 2. EMI shielding performance of the samples in comparison with conductive polymer electromagnetic shielding materials.

Components	Filler concentration [wt%/vol%]	Thickness [mm]	SE [dB]	Frequency [GHz]	SE/thickness [dB/cm]	Ref.
EP/TAGA@ Fe_3O_4	2.7	3	35	8–12	116.7	[34]
PS/TGO@ Fe_3O_4	2.24	—	30	9.8–12	—	[33]
EP/GO@ Fe_3O_4	8.97	2	13.45	8.2–12.4	67.2	[34]
SR/G@ Fe_3O_4 @BaTiO ₃	16	2	35	1–20	175	[31]
RGO/ Fe_3O_4	—	1	50	8.4–12	—	[22]
EP/GNP@ Fe_3O_4	14	2	25	8–12	125	[3]
PU/GNS-IL@ Fe_3O_4	22	0.6	27.5	8–12	458.3	[10]
ADCN/G/ Fe_3O_4	5	0.95	30	8–12	315.8	This work
ADCN/G/ Fe_3O_4	10	0.70	40	8–12	571.4	This work
ADCN/G/ Fe_3O_4	15	0.46	50	8–12	1086.9	This work
PS/rGO-MoS ₂ @CNTs	20	1	35	12–18	350	[31]
PDMS/FRS ^a	10.7	2	24	14–20	120	[1]
PU-SH/MGMF ^b	8	—	30	8–18	—	[61]
Fe_3O_4 @N-rGO/epoxy	15	1	20	2–8	200	[14]

^aFRS: Ferrous ferric oxide (Fe_3O_4) decorated reduced graphene oxide (RGO)/single wall carbon nanohorn (SWCNH).

^bMGMF: MWNT/rGO@MoS₂@ Fe_3O_4 .

Figure 11. (a) TGA curve of ADCN and cured composites in air; (b) TGA curve of ADCN, graphene, Fe_3O_4 , and cured composites in N_2 .

Table 3. Thermal parameters: Atmosphere, $T_{5\%}$, $T_{10\%}$ and char yield of the ADCN/G/ Fe_3O_4 (5%, 10%, 15%).

Sample	Atmosphere	$T_{5\%}^a$ [°C]	$T_{10\%}^b$ [°C]	Char yield ^c [%]
ADCN/G/ Fe_3O_4 (5%)	N_2	537	600	68
ADCN/G/ Fe_3O_4 (10%)	N_2	558	602	69
ADCN/G/ Fe_3O_4 (15%)	N_2	560	603	69
ADCN/G/ Fe_3O_4 (5%)	Air	469	555	11
ADCN/G/ Fe_3O_4 (10%)	Air	480	564	6
ADCN/G/ Fe_3O_4 (15%)	Air	491	571	5

^a $T_{5\%}$: the temperature when the weight loss rate reached 5%.

^b $T_{10\%}$: the temperature when the weight loss rate reached 10%.

^cChar yield: the residual quality when the temperature reached 800 °C.

of sheet materials, which also in line with the trend of thin material in this field.

TGA was employed to analyze the thermal and thermo-oxidative stability of composites. Figure 11a showed the TGA results of three samples and the control group in air. It confirms that composites have outstanding thermo-oxidative stability; $T_{5\%}$ air of three samples reached 469, 480, and 491 °C, respectively. Figure 11b showed the TGA results of three samples, pure ADCN, graphene, and Fe_3O_4 NPs in N_2 condition. Compare with the control group (pure ADCN), the thermal stability of the three samples improved. The $T_{5\%}$ of pure samples reached 491 °C, while the $T_{5\%}$ of the three samples reached 550 °C (5%), 564 °C (10%) and 566 °C (15%) respectively. Compared with pure ADCN, the $T_{5\%}$ of samples with fillers increased by 50 °C. In addition, the addition of fillers also increased the char yield of the material from 61 to 70% at 800 °C. This could be attributed to the excellent thermal properties of graphene and Fe_3O_4 nanoparticles, verifying that the introduction of ADCN as the polymer matrix successfully introduces outstanding thermo-oxidative

stability into the system. Meanwhile, giving outstanding thermal and thermo-oxidative stability.

Flame retardancy test was carried out for two minutes; the sample disk did not burn throughout the test. And there were no droplets or smoke found during the experiment (Figure 12a). Moreover, the sample basically maintained the original shape that indicates the excellent heat resistance property of ADCN/G/ Fe_3O_4 composite (Figure 12b). Figure 12c shows the results of the EMI test between the original sample and the sample after the flame test. Compared with the original sample, the EMI value of the sample after the flame test decreased about 10 dB. But it still maintained at a relatively high level. The EMI results of the sample before and after the flame test are indicating that the composite could remain the excellent EMI performance even at high-temperature working conditions.

4. Conclusions

In this paper, a multiple cooperative dispersion system processed by powder metallurgy-like processing method was introduced. The ADCN/G/ Fe_3O_4

Figure 12. a) Flame retardancy test of ADCN/G/Fe₃O₄ (15%) composite from 0 to 120 s. (b) The diameter of sample before and after the flame retardancy test. (c) The EMI performance of sample before and after flame test.

high-performance composites have excellent electromagnetic interference performance. Due to the high-energy ball milling-molding sintering processing method and interaction between ADCN and graphene and Fe₃O₄ NPs, the fillers achieving uniform dispersion in the polymer matrix. Based on the conductive loss strategy, the establishing of a continuous conductive path caused by uniform dispersion of fillers leading to a good EMI property. Based on the hysteresis loss, the introduction of magnetic nanofiller caused the improvement of hysteresis loss by enhancing the saturation magnetization. The EMI

performance of the sample with graphene content (7.5 wt%) and Fe₃O₄ NPs (7.5 wt%) reached 50 dB with 0.5 mm thickness. Furthermore, it is proven that composites have outstanding thermal, thermo-oxidative stability, excellent heat resistance, and qualified mechanical property, indicating the application potential of ADCN/G/Fe₃O₄ in the field of the aerospace industry and military engineering.

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