MWCNT/CuO/Fe₃O₄/Polyaniline Nanocomposites with Remarkable Microwave Attenuation and Broad Frequency Band by Tuned Composition

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Abstract

Novel quaternary MWCNT/CuO/Fe₂O₄/PANI nanocomposites were synthesized with three different weight ratios of CuO/Fe₂O₄/PANI to MWCNT (1:3), (1:4), and (1:5), in a way, all its components were synthesized separately and then combined with certain weight ratios. TEM image of CuO/Fe₂O₄/PANI proved that most of the nanoparticles were in a form of CuO/Fe₂O₄ hybrids with narrow size distribution which were uniformly dispersed in a polymer background. TEM and SEM of MWCNT/CuO/Fe₂O₄/PANI nanocomposite indicated that MWCNT was covered with a uniform thickness of CuO/Fe₂O₄/PANI. All three samples of nanocomposites exhibited excellent microwave attenuation performance via both aspects of reflection loss and absorption bandwidth. Minimum reflection losses were 45.7, 58.7 and 85.4, 87.4 dB for MWCNT/CuO/Fe₂O₄/PANI nanocomposites (1:3), (1:4) and (1:5), respectively. Absorption bandwidths (RL ≤ -10 dB) were 6, 7.6 and 6 GHz, for MWCNT/CuO/Fe₂O₄/PANI nanocomposites (1:3), (1:4) and (1:5), respectively.

1. Introduction

Carbon is widely used in many applications due to its good electrical and thermal conductivity, low density, as well as good corrosion resistance, low thermal expansion, and low elasticity. Carbon is used as a resistive element to convert input microwaves into heat. Most of the carbon allotropes exhibit excellent capability of microwave absorption due to the response of electric dipoles created inside them to the alternating electric field of input waves [1, 2]. Magnetic materials are also capable to absorb the magnetic field of the microwave by an analogous process. Among the wide range of magnetic materials, magnetite (Fe₂O₄) is highly attractive for its usage as a magnetic dissipater and improver of the microwave attenuation property of carbon nanotubes or carbon-based materials because of low toxicity, good compatibility, high unpaired spin density, and strong spin polarization at room temperature [3–5]. Carbon/ferrite-based composites provide a better balance between electrical conductivity and magnetic susceptibility than individual magnetic or carbonaceous absorbents, so they are promising as electromagnetic wave absorbers [6]. In addition, there are numerous reports that confirm the use of other metal oxides in combination with magnetite can improve the absorption properties of the resulting hybrid nanoparticles. The use of metal oxide hybrids in magnetic materials leads to the development of conduction loss mechanisms, residuals, interfacial polarization, electron spin resonance, and resonant domain wall, which can directly increase the microwave absorption properties [7–9].

Many reports indicate that hybridized magnetite/metallic, magnetite/semiconductor nanoparticles embedded in a conductive polymer or loaded on carbon materials, especially carbon nanotubes, is an effective strategy in producing microwave absorber composites with sound absorption performance [11–13].

Copper oxide (CuO), a semiconductor with a narrow gap, was used to decorate carbon material such as carbon fibers to fabricate efficient microwave absorbing composites [10, 11]. Microwave absorption properties of hybridized copper oxide with magnetite, carbon nanotubes, and graphene, have not yet been studied, but we speculated that it could improve both dielectric and magnetic absorption.

On the other hand, the use of conductive polymers that have good microwave absorption properties as a coater of magnetic surface, not only causes a better impedance matching but also hinders the nanoparticles' aggregation, corrosion, and magnetic phase transformation via heat generation during the microwave absorption process.

Polaraniline is the most important polymer in the category of conductive polymers. It exhibits good environmental stability, which is easy to synthesize, inexpensive, lightweight, having high electrical conductivity with high
polarizability (due to the presence of strong chemical bonds or localized charges), polarization relaxation, and conductive loss, was applied to synthesize highly effective microwave absorber composites.

Polymers can also cause a better dispersion of NPs and lead to enhance interfacial area and multiple interfacial reflections between individual nanoparticles. Polyaniline can uniformly conjugate with CNT’s surface and other substrates, by representing surface tension and chemical reactive sites to bind with functional groups of CNTs, which results in further increment in interfacial area [14, 15]. Polyaniline also can greatly optimize the impedance matching of EW. So, polyaniline can improve the electromagnetic wave absorption performance via several mechanisms [17–22].

In this study, a novel quaternary MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposite was synthesized using a step-by-step method so that the CuO/Fe$_3$O$_4$ hybrid nanoparticles were prepared by optimum protocol to attain suitable magnetic property and uniform size distribution. Then aniline was polymerized at the surface of CuO/Fe$_3$O$_4$ hybrid NPs by using in situ polymerization and CuO/Fe$_3$O$_4$/PANI nanocomposite was produced. Then CuO/Fe$_3$O$_4$/PANI was loaded on the surface of the MWCNT with the weight ratios of three, four, and five times to MWCNT and MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4) and (1:5) nanocomposites have been achieved. These nanocomposites were characterized via the following methods:

The crystalline phases of the CuO and Fe$_3$O$_4$ were identified by an X-ray diffraction pattern. Successful polymerization of aniline on the surface of nanoparticles was confirmed by FT-IR. The Morphology of CuO/Fe$_3$O$_4$/PANI and MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites were investigated by scanning and transmission electron microscopy (SEM & TEM). SEM and TEM images show a uniform distribution of CuO/Fe$_3$O$_4$ nanoparticles, embedded in the polymer and a uniform loading of MWCNT with CuO/Fe$_3$O$_4$/PANI nanocomposite.

Vibrating sample magnetometer (VSM) analysis presented the superparamagnetic properties of MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites with high saturation magnetizations (40–60 emu/g).

Electromagnetic parameters of nanocomposites were calculated in the range of 8–18 GHz using a vector network analyzer. The curve of reflection losses versus frequency was plotted at the basis of electromagnetic parameters for all samples with different thicknesses. The results showed that all samples cause high reflection loss which varied between ~ 50 to -87 dB and broad absorption band was over 6 GHz.

2. Experimental

Herein, the novel MWCNT/CuO/Fe$_3$O$_4$/PANI quaternary composite was prepared with a controllable method that includes three steps process. As the constituents of the composite were prepared under controlled conditions and then combined with an optimum weight ratio to prepare the final nanocomposite. First, CuO/Fe$_3$O$_4$ hybrid nanoparticle was synthesized with optimal protocol to have the best superparamagnetic property. Then nanoparticles were used as an initiator to polymerize aniline and form CuO/Fe$_3$O$_4$/PANI nanocomposite. Finally, the MWCNT was used as a substrate for carrying and stabilizing CuO/Fe$_3$O$_4$/PANI nanocomposite.

2.1 Materials

MWCNTs with diameters and lengths ranged from 20 to 40 nm and 5–15 µm, respectively, and a minimum purity of 95% was provided by neutrino Co. Ltd. Other raw materials including FeCl$_2$.4H$_2$O, FeCl$_3$.6H$_2$O, Cu(NO$_3$)$_2$ (Purity > 98%), HCl and NaOH (>= 97%) were purchased from Sigma Aldrich. Aniline and ammonium persulfate (APS) were purchased from Merck.
2.2 Preparation of CuO/Fe₃O₄ hybrid nanoparticles

1.51 g of copper nitrate and 2.31 g of iron oxide were mixed with 40 mL of deionized water and were stirred to obtain a homogeneous solution. 0.1 mole of NaOH was added drop by drop until the pH of the solution reached 13. Finally, the productions were collected with a magnet and washed and dried at 40°C.

2.3 Synthesis of CuO/Fe₃O₄/PANI nanocomposites.

CuO/Fe₃O₄/PANI nanocomposite was prepared via in situ polymerization of aniline on the O-H functional groups CuO/Fe₃O₄ NPs. Polyaniline was synthesized from the chemical oxidation of aniline by ammonium persulfate in an acidic medium. First, 1.5 g of prepared CuO/Fe₃O₄ NPs and 0.75 g of aniline monomer (1:2 ratio of aniline to CuO/Fe₃O₄) were dissolved in 20 mM aqueous HCl solution. Then the mixture was exposed to ultrasonic waves for 30 minutes to disperse the NPs (separate nanoparticles in the clusters). The polymerization reaction must be performed at a temperature less than 4°C. Then 0.8 g of ammonium persulfate (oxidizing agent) was dissolved in 30 mL of deionized water and added dropwise to the mixture. Adding the first oxidizing droplets leads to the appearance of a green-blue color indicating the beginning of polymerization. When the polymerization was completed, the products were collected by a magnet and the solution was washed to remove the residual aniline and reach neutral pH.

2.4 Preparation of MWCNT/CuO/Fe₃O₄/Polyaniline nanocomposite

To prepare the final nanocomposite, 0.5 g of CuO/Fe₃O₄/PANI nanocomposite and 0.1 g of MWCNT (weight ratio of MWCNT to CuO/Fe₃O₄/PANI was 1:5)) were separately dispersed in 100 mL of deionized water. Then two suspensions were added together and sonicated for 30 min. The sediment was then separated from the liquid by centrifugation. Finally, the black precipitate was dried in an oven at 50 °C. Similar nanocomposites were prepared with the 1:4 and 1:3 weight ratios of MWCNT to CuO/Fe₃O₄/PANI.

2.5 Characterizations

Successful preparation of MWCNT/CuO/Fe₃O₄/PANI nanocomposite was confirmed by determination of its chemical bonding and crystalline planes thorough FT-IR (Nicolet IS10) and X-ray diffraction (XRD), model PANalytical, respectively. The magnetic behavior of products was investigated at room temperature in the presence of a magnetic field using a vibrating sample magnetometer (VSM JDM-13). Transmission electron microscopy (TEM) technique was used to study the morphology of CuO/Fe₃O₄/PANI and MWCNT/CuO/Fe₃O₄/PANI nanocomposites using MIRA3 TESCAN and Tecnai. The electromagnetic properties and microwave absorption ability of composite were recorded via Agilent vector network analyzer (VNA) E8364B using transmission/reflection waveguide method in the frequency range of 8.2–18 GHz.

3. Results And Discussions

3.1 Material characterization

The FT-IR spectra of CuO/Fe₃O₄/PANI and MWCNT/CuO/Fe₃O₄/PANI nanocomposites were prepared by KBr tablet method. According to Fig. 1, in the spectrum of CuO/Fe₃O₄/PANI, a broad signal at 3441 cm⁻¹ is related to the presence of O-H groups and the carboxylic acid (C = O and C-O) functional groups of CNT presented at 1562 and 1150 cm⁻¹. The absorption band at 1562 cm⁻¹ also corresponds to the tensile vibration of C = N corresponding to the quinoid ring in the polyaniline structure. The characteristic peak of carbon nanotubes at 1638 cm⁻¹ is related to the symmetrical expansion vibration of the C = C bonds. The absorption band at 1479 cm⁻¹ is attributed to the C = C
functional groups in the benzenoid rings in the polyaniline structure [29]. The absorption band at 1296 cm$^{-1}$ shows the tensile vibration of the C-N bonds and the absorption band at 1131 cm$^{-1}$ shows the bending vibration of the C-H bonds, which is a characteristic of polyaniline bonds [23]. The absorption band at 800 cm$^{-1}$ belongs to the Fe-O functional groups and the absorption band at 559 cm$^{-1}$ belongs to the Cu-O functional groups. Peaks in the range of 800 cm$^{-1}$ are characteristic of the substitution of aromatic rings, which indicates the formation of the polymer [24]. The absorption band at 3435 cm$^{-1}$ is related to the tensile vibration of N-H bonds in polyaniline. The absorption band at 1570 cm$^{-1}$ is due to the tensile vibration of the C= N bonds corresponding to the quinoid ring. The absorption bands at 1119 cm$^{-1}$ and 1030 cm$^{-1}$ show the C-N bonds in the expansion state and the bending vibration of the C-H bonds, respectively.

Figure 1

The crystalline structure of MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposite was determined by the X-ray diffraction pattern. As shown in Fig. 2, the scattering peaks are around 2$\theta$ = 30.3°, 35.6°, 43.4°, 53.5°, 57.3° and 62.7°, are related to the Bragg plates (220), (311), (400), (422), (511) and (440), respectively, which are completely consistent with the diffraction patterns of magnetite (Fe$_3$O$_4$), according to the JCPDS Card 19–0629, this pattern is related to the face center cubic structure (FCC) of Fe$_3$O$_4$, no additional peaks are observed to indicate the presence of impurities [25]. The peak of the carbon nanotube was observed at an angle of 2$\theta$=25.9° corresponding to the (002) of graphite’s hexagonal structure [25]. The peak 2$\theta$=39.4° belongs to the (200), (111) planes and the peak at 2$\theta$=32.5° relates to (110) plane which indexed to the monoclinic structure of CuO (JCPDS Card 48-1548) [26, 27].

Figure 2

Field emission scanning electron microscopy (FESEM) was used to study the morphology of the synthesized powder of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3) and (1:5). FESEM images of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3) and (1:5) (Fig. 3, a & b) show that during the polymerization process, OH groups of CuO/Fe$_3$O$_4$ NPs act as an initiator for aniline polymerization. So, a layer of the polymer created on the surface of CuO/Fe$_3$O$_4$ NPs, resulting in the separation of nanoparticles in the polymer matrix. The activation energy required to form a polymer on the surface of CuO/Fe$_3$O$_4$ NPs is much less than in the absence of such surface, so aniline tends to start spontaneously polymerization on such surfaces. The initial diameter of purchased nanotubes was 20 nm, after the polymerization process, the average diameter has increased to 40 and 42 nm for MWCNT/CuO/Fe$_3$O$_4$/PANI (1:4) and (1:5) nanocomposite (Fig. 3, a & b) indicating an almost uniform coating of CuO/Fe$_3$O$_4$/PANI nanocomposite on the MWCNT’s surface. The number of OH and COOH functional groups at the ends of the nanotubes are higher than other parts of their surfaces, which interact via hydrogen bonding to amino groups of aniline. Therefore, in FESEM images, few small clusters can be seen at the end of the CNTs.

Electron diffraction spectroscopy (EDS), was performed to determine the type of elements present in a 9 µm$^2$ surface area of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:4) nanocomposites’ thin film (Fig. 3, c). EDS diagram shows that the weight percentage of carbon, iron, nitrogen, oxygen, and copper are 52.6, 21.7, 16.3, 8.2, and 1.2, respectively.

TEM image of CuO/Fe$_3$O$_4$/PANI nanocomposite (Fig. 4, a) demonstrates that CuO/Fe$_3$O$_4$ hybrid NPs have a spherical shape, mostly are core-shell with black core and gray are observed are embedded in the polymer matrix with narrow size distribution (4–6 nm). Few single CuO NPs (gray) and Fe$_3$O$_4$ NPs (black) are also observed. TEM images of MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposite (1:3) & (1:5) (Fig. 4, b & c) show that, the whole surface of nanotubes was covered with a uniform thickness of about 40 nm with CuO/Fe$_3$O$_4$/PANI nanocomposite, as the nanotubes were buried
under the polymeric shell. The polymer enhances the specific surface area of the nanotubes with proper adhesion and facilitates the surface tension at the interface, in addition to chemical bonding to functional groups of CNT. These features lead to uniform adhesion of CuO/Fe$_3$O$_4$/PANI on MWCNT.

No obvious aggregation of nanoparticles was observed in the TEM images. Interconnected polymer chains not only increase the solubility of nanotubes in the reaction medium but also prevent them from merging and clustering without using the surfactant. As a result, coating polymer on the surface of CuO/Fe$_3$O$_4$ NPs causes uniform deposition of CuO/Fe$_3$O$_4$ NPs on the outer surface of CNTs as shown in the TEM images (Fig. 4, b & c).

Figures 4&5

4. Magnetization And Microwave Absorption Properties

Vibrating Sample Magnetometer analysis (VSM) of different samples of MWCNT/CuO/Fe$_3$O$_4$/PANI was performed at room temperature (25°C) in the range of -15000 to 15000 Oe and in the saturation magnetization ($M_s$) range of ± 60 emu/g which is shown in Fig. 5. A closed-loops of hysteresis was observed for MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites (remanences are lower than 5 emu/g and coercivities are below 15 Oe) indicating the presence of superparamagnetic CuO/Fe$_3$O$_4$ NPs. Saturation magnetization of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4), (1:5) are 38.61, 47.5, and 60 emu/g, respectively. It was quite expected that, as the weight ratio of magnetic CuO/Fe$_3$O$_4$ NPs increased, the magnetic saturation would be increased [39,40].

Figure 5

4.1 Electromagnetic parameters

Electromagnetic (EM) parameters of MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites were calculated to determine the absorption capability of MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites. For this purpose, each nanocomposite was homogeneously dispersed in paraffin with a filler content of 25 wt%. The real and imaginary parts of electrical permittivity ($\varepsilon'$ & $\varepsilon''$) and the real and imaginary parts of magnetic permeability ($\mu'$ & $\mu''$) of MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites were achieved by a network vector analyzer (Anritsu.37269D) in the 8.2–18 GHz frequency range, presented in Fig. 6.

Complex permittivity ($\varepsilon$) and complex permeability ($\mu$) are EM parameters, which are an intrinsic property of each absorbent material, and determine the ability of a matter to absorb waves. The real part of permittivity and permeability $\varepsilon'$ and $\mu'$ which show the degree of the polarizability of absorbent material, is a measure of the ability to store electrical and magnetic energy. $\varepsilon''$ and $\mu''$, known as dielectric and magnetic loss are in regards to attenuation of electric and magnetic energy of incident wave within the mater [29, 30]. $\varepsilon''$ and $\mu''$, the imaginary parts, related to polarization relaxation and spin rotation relaxation (aligning dielectric and magnetic dipole with alternative electric and magnetic fields of incident waves). $\varepsilon''$ originated from various polarization such as electron, nuclei, dipoles and interfacial polarization relaxation (space accumulated charge polarization). Here, space-charge polarization is the major factor in dielectric loss. Because other polarizations take place at higher frequency ranges [31, 32]. Interfacial polarization is caused by space-charge accumulation at the interface of materials that have different dielectric constants. For conductive materials, $\varepsilon''$ usually originates from conduction loss as well as polarization relaxation [32].

From Fig. 6, it is clear that nanocomposite (1:3) has the highest values of $\varepsilon''$ (6.2–8.5). Characteristic of a high amount of CNT that has high values of $\varepsilon'$ and $\varepsilon''$. Nanocomposite (1:4) has slightly lower values of $\varepsilon''$ and has the same trend.
as nanocomposite (1:3). nanocomposite (1:5) shows the lowest amount of $\varepsilon$ because the weight percentage of CNT is the lowest one.

$\varepsilon$ values of all samples of nanocomposites, almost are the same. In our composite, $\varepsilon$ was resulted from several factors: (i) charge accumulation created at the interface of CuO and Fe$_3$O$_4$ in hybrid form, CuO or Fe$_3$O$_4$ single form, and polyaniline, CuO/Fe$_3$O$_4$ and polyaniline, polyaniline and CNT [33, 34]. Dispersion of nanoparticles within the polymer leads greatly to increase joint surface of the nanoparticles with the polymer. Also, the surface of the nanotube is covered with a layer of polymer. Due to the surface-to-volume ratio of the nanotubes, a large interface is created between the nanotubes and the polymer. It is known that the larger the area of the interface, the higher the amount of space charge and polarization relaxation [35]. The presence of a conductive loss in polyaniline and CNT is another phenomenon that has a significant contribution in the $\varepsilon$ of nanocomposites. It seems that polarization relaxation of space charge at the interface of NPs/PANI which is created at high frequency (> 14 GHz) and conductive loss of PANI, are dominant mechanisms. In addition, multiple reflections occurred between separated CuO/Fe$_3$O$_4$ NPs cause more incident wave dissipation [36, 37]. As a result, the nanocomposite (1:5) with the highest amount of CuO/Fe$_3$O$_4$/PANI nanocomposite represents the highest $\varepsilon$ and dielectric tangent loss (tan$\delta_\varepsilon$) at a higher frequency range. As Fig. 6 shows, $\mu_\parallel$ curves of all samples are similar to each other. Except, at the end of the frequency range, $\mu_\parallel$ values of nanocomposites (1:4) and (1:5) almost are equal, and $\mu_\parallel$ values of the nanocomposite (1:3) are slightly lower. This observation referred to the higher amount of Fe$_3$O$_4$ NPs in nanocomposites (1:4) and (1:5) than (1:3). $\mu_\parallel$ demonstrates the possibility of magnetic dipoles in the matter. Since magnetic dipoles can only occur in magnetic materials with unpaired spin, by increasing the amount of magnetite, $\mu_\parallel$ values increased. $\mu_\parallel$ was related to spin rotation relaxation that originally corresponds to natural resonance in ferromagnetic, domain wall resonance which occurs in lower frequencies (< 100 MHz), exchange resonance, and eddy current [38]. Present nanocomposites, contained CuO/Fe$_3$O$_4$, with single domain superparamagnetic nanoparticles. So, exchange resonance and eddy current loss are involved in magnetic dissipation, which occurs at high frequencies (> 13 GHz) [32]. Since ferrites have a relatively high electrical resistance [39], they have a weak dielectric loss and low eddy current loss. However, introducing CuO, a semiconductor with a narrow bandgap, to form CuO/Fe$_3$O$_4$ hybrid, may improve conductivity and therefore, increase eddy current loss. An increment in $\mu_\parallel$ values and magnetic tangent loss (tan$\delta_\mu$) of nanocomposite (1:5) over 13 GHz, was quite predictable. Generally, tan$\delta_\varepsilon$ is higher than tan$\delta_\mu$ for all samples, indicating dielectric loss has a larger contribution in microwave dissipation which has often been observed [40].

The relaxation (especially polarization relaxation) is an important dielectric loss mechanism in the absorption of EM waves. The relaxation process can be expressed with the Cole-Cole model (Fig. 7). Debye relaxation model is used to interpret $\varepsilon$ scattering mechanisms. In this model, the Cole-Cole curve is presented in the shape of semicircles. Each semicircle represents a separate Debye relaxation. The radius of the semicircle exhibits relaxation time. The larger the radius, the longer the rest time.

Long relaxation time corresponds to relaxation with higher periodicity and lower frequency [41]. So, for these relaxations, resonance occurs at lower frequencies; And vice versa, for the shorter radius of semicircle (short relaxation time) resonance, occurs at higher frequencies.

In all three composites, one or two semicircles are observed indicating multiple relaxation processes occur for the composites which proves the contribution of the Debye relaxation in increasing the dielectric dispersion of the composites [42]. Cole-Cole curve of nanocomposite (1:3) consists of large and small semicircles and is evidence of three relaxation resonances which belong to two long relaxation times and a short one. Nanocomposite (1:4), shows two large semicircles (with a higher radius than that of nanocomposite (1:3)) and a very small one which indicates two long relaxation times and a short one. Nanocomposite (1:5) shows two medium semicircles and two equal relaxation
times. According to what was said above, polarization relaxation is one of the dominant factors in the attenuation of the incident wave. The resonance peaks in the RL diagram depend on these relaxation frequencies. So, for nanocomposite (1:4) with the largest relaxation frequency, the minimum reflection loss is placed at the lowest frequency, and for nanocomposite (1:3) to (1:5), in which the relaxation frequency is increasing, the minimum reflection loss moves towards higher frequencies.

Figures 6&7

4.3 Reflection losses and absorption bandwidths

The reflection loss values were calculated using the EM parameters for different sample thicknesses:

\[ Z_{in} = Z_0 \sqrt{\frac{\mu_r}{\epsilon_r}} \tanh \left( \frac{2 \pi fd}{c} \sqrt{\epsilon_r \mu_r} \right) \]

\[ RL(dB) = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \]

where \( Z_{in} \) is the input impedance of the microwave absorbing material, \( Z_0 \) is the impedance of free space, \( j \) is the imaginary unit, \( d \) is the thickness of the absorbent, \( f \) is the microwave frequency, \( c \) is the velocity of light, and \( RL_{\text{min}} \) is the reflection loss.

The reflection losses of MWCNT/CuO/Fe\(_3\)O\(_4\)/PANI (1:3), (1:4), and (1:5) versus frequency in the range of 8.2–18 GHz are shown in Fig. 8. The results show that all MWCNT/CuO/Fe\(_3\)O\(_4\)/PANI samples exhibit excellent MA behavior. The thickness of the absorber has a large effect on the microwave absorption properties. The \( RL_{\text{min}} \) peak gradually moves to a lower frequency with increasing absorbent thickness, which follows the formula \( f_m = \frac{c}{2 \pi \mu \mu' d} \), where \( f_m \) is the frequency adapted to \( RL_{\text{min}} \), and \( d \) is the sample thickness. For all samples, double strong absorption peaks have appeared for 3 mm thickness of the sample.

In \( RL_{\text{min}} \) curve of nanocomposite (1:3), both reflection loss and bandwidth decrease by increment in the thickness of the sample except for the thickness of 2.2 and 3 mm. A minimum reflection loss is -47.5 dB for the absorbent thickness of 2.2 mm at 14.3 GHz by absorption bandwidth of about 6 GHz (12.2–18 GHz). For nanocomposite (1:4), the reflection loss decreases by increasing the sample thickness. For thicknesses of 3 mm, minimum reflection losses reach -85.4 and -58.7 dB at 10.6 and 9.8 GHz, respectively, with an effective bandwidth of 3 GHz (8.8–11.8 GHz). The broadest bandwidth is 7.6 GHz (10.4–18 GHz) for 2.2 mm absorbent.

In nanocomposite (1:5), \( RL_{\text{min}} \) is higher than 87.4 dB at 16.2 GHz with the broadest absorption band of 6 GHz (12–18 GHz) for 2.2 mm thickness of absorbent. Double strong peaks with \( RL_{\text{min}} \) -45 and -43 dB appeared at 10.3 and 11.8 GHz, respectively, with the absorption band of 4.4 GHz (9.8–14.2) for 3 mm absorbent. For all thicknesses of absorbent, the absorption bandwidths are over 3 GHz.

Figure 8
Figure 9 shows the loss constant ($\alpha$) as the main effective factor on the range of microwave absorption. The loss constant ($\alpha$) is used to evaluate the ability of absorption integral loss which is calculated by the following formula:

$$\alpha = \frac{\sqrt{2} \pi f}{c} \left( \epsilon^{\prime} \mu^{\prime} - \epsilon^\prime \mu^\prime \right) + \sqrt{\left( \epsilon^\prime \mu^\prime - \epsilon^\prime \mu^\prime \right)^2 + \left( \epsilon^\prime \mu^\prime + \mu^\prime \epsilon^\prime \right)^2}$$

The higher values ($\alpha$) indicate the more powerful magnetic and dielectric loss if the microwave can reach the inner space of the absorber. The magnetic and dielectric loss tangent are two key factors efficient on the absorption efficiency of an absorber. The higher values of loss tangent indicate the high ability to convert electromagnetic waves to other forms of energy. The attenuation constant was significantly increased in the frequency range of 10–18 GHz, Meanwhile, the (1:5) exhibited a larger attenuation constant, which was also well consistent with the results of RL curves.

Figure 9

Several mechanisms of absorption mentioned in section 4.1 led to the remarkable absorption capability of the MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposites, which are much higher than the results obtained by similar composites as reported in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Filler</th>
<th>Matrix</th>
<th>Loading (wt%)</th>
<th>Thickness (mm)</th>
<th>Minimum RL (dB)</th>
<th>Broadest bandwidth (GHz) RL &lt; -10 dB</th>
<th>Frequency range (GHz)</th>
<th>Ref.</th>
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<td>9.2–14.5</td>
<td>16</td>
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<td>MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3)</td>
<td>paraffin</td>
<td>25</td>
<td>2.2</td>
<td>-47.5</td>
<td>6</td>
<td>12.2–18</td>
<td>This work</td>
</tr>
<tr>
<td>MWCNT/CuO/Fe$_3$O$_4$/PANI (1:4)</td>
<td>paraffin</td>
<td>25</td>
<td>2.2</td>
<td>-85.4</td>
<td>7.6</td>
<td>10.4–18</td>
<td>This work</td>
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<tr>
<td>MWCNT/CuO/Fe$_3$O$_4$/PANI (1:5)</td>
<td>paraffin</td>
<td>25</td>
<td>3</td>
<td>-87.4</td>
<td>6</td>
<td>12–18</td>
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5. Conclusions

A new quaternary MWCNT/CuO/Fe$_3$O$_4$/PANI nanocomposite was prepared using a multi-step method. First, CuO/Fe$_3$O$_4$ hybrid NPs with narrow size distribution were prepared by a simple co-precipitation route. Then, O-H functional groups presented on the surface of the CuO/Fe$_3$O$_4$ NPs as initiator led to the polymerization of aniline on the surface of CuO/Fe$_3$O$_4$ NPs, then CuO/Fe$_3$O$_4$/PANI nanocomposite was produced. Finally, MWCNTs were loaded by different weight ratios (1:3), (1:4), and (1:5) of CuO/Fe$_3$O$_4$/PANI nanocomposite via simple physical agitation. The FESEM and TEM images showed that the CuO/Fe$_3$O$_4$ nanoparticles were dispersed with an almost uniform size distribution in the polyaniline background. These images also showed that MWCNTs were covered with an almost constant thickness of CuO/Fe$_3$O$_4$/PANI nanocomposite. Results showed all samples of MWCNT/CuO/Fe$_3$O$_4$/PANI had a superparamagnetic property with high saturation magnetization that varies from 38 to 60 emu/g. All samples of MWCNT/CuO/Fe$_3$O$_4$/PANI exhibited excellent absorption properties from both aspects of reflection loss and absorption bandwidth. Minimum reflection losses are 45, 58.7 and 85.4, 87.4 dB (2.2 mm absorbent) and 80 dB (3 mm absorbent) for MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4), and (1:5), respectively. The broadest absorption bandwidths are 6, 7.6 GHz (2.2 mm absorbent) and 6 GHz (2.6 mm absorbent) for MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4), and (1:5), respectively.

Abbreviations

MWCNT
multi walled carbon nanotube

CNT
carbon nanotube

PANI
Polyaniline

EM
Electromagnetic

EW
Electromagnetic wave

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Figures
Figure 1

FT-IR spectra of CuO/Fe$_3$O$_4$/PANI and MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3).
Figure 2

XRD pattern of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3).
Figure 3

FESEM images of: (a) MWCNT/CuO/Fe₃O₄/PANI (1:3) and (b) (1:5). EDS pattern of: (c) MWCNT/CuO/Fe₃O₄/PANI (1:3)
Figure 4

TEM images of: (a) CuO/Fe₃O₄/PANI, (b) MWCNT/CuO/Fe₃O₄/PANI (1:3) and (c) MWCNT/CuO/Fe₃O₄/PANI (1:5).
Figure 5

Magnetization versus applied magnetic field (Oe), at room temperature, for MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4) and (1:5).
Figure 6

Up: Real and imaginary parts of permittivity and dielectric tangent losses of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4), (1:5). Down: real and imaginary parts of permeability and magnetic tangent losses of them.

Figure 7

Typical Cole-Cole semicircles of: (a) MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (b) (1:4) and (c) (1:5).
Figure 8

Reflection loss of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4) and (1:5) versus frequency for different absorbent thickness (2D, 3D).
Figure 9

Attenuation constant ($\alpha$) of MWCNT/CuO/Fe$_3$O$_4$/PANI (1:3), (1:4) and (1:5) versus frequency.