Novel Microwave Absorber of Ni$_x$Mn$_{1-x}$Fe$_2$O$_4$/Carbonized Chaff (x = 0.3, 0.5, and 0.7) Based on Biomass

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ABSTRACT: A novel magnetic nanocomposite of Ni$_x$Mn$_{1-x}$Fe$_2$O$_4$/carbonized chaff (x = 0.3, 0.5, and 0.7) has been synthesized successfully via the co-carbonization and hydrothermal method. The microstructure, morphology, complex permittivity and permeability, and microwave absorbing properties were systematically studied by X-ray diffraction, scanning electron microscopy, and a vector network analyzer. Compared to the pure Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$ NPs, the Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ composite exhibits an optimal microwave absorption property at 4 mm as the mass percent of carbonized chaff is 10 wt %, the maximum reflection loss of which can reach $-14.58$ dB at 1.91 GHz with the $-10$ dB frequency bandwidth in the range of $1.46-2.41$ GHz (0.95 GHz). The enhanced electromagnetic wave absorbing performance is ascribed to the good synergistic effect among laminated structures, better impedance matching condition, strong natural resonance loss, Debye dipolar relaxation to some extent, and so forth. Most importantly, this study provides a novel way to prepare easily degradable, environment-friendly, and high-efficiency electromagnetic wave absorbers by utilizing the structural property of renewable biomaterials.

1. INTRODUCTION

For several decades, the fast development of advanced electronic equipment for military and commercial applications, for example, radar detection systems, wireless network systems, satellite detection, data communication, and so forth, has led to many problems such as electromagnetic interference and electromagnetic compatibility. These problems can affect the military security of strategic weapon, the normal running of electronic equipment for military and commercial applications, among laminated structures, better impedance matching condition, strong natural resonance loss, Debye dipolar relaxation to some extent, and so forth. Therefore, much attention has been paid toward the improvement of electromagnetic wave absorption performance in biomass by compositing them with other materials to overcome these deficiencies. Lee et al. investigated the microwave absorption properties of rice husk ash (RHA) composited with carbon nanotubes (CNTs). It was observed that the content of CNTs can influence the $\varepsilon’$ and $\varepsilon''$ values of the as-prepared composites, and the RHA/CNTs composite with the CNTs content of 5 wt % exhibited an optimal microwave absorption property, whose maximum reflection loss (RL) reached $-27$ dB at 11.7 GHz. Lan et al. fabricated the bio-based helical ferromagnetic particles via the Ni–Fe alloy electroplating process; the complex permittivity and permeability of coated spirulina were measured by a vector network analyzer (VNA). These results showed that the samples after heat treatment displayed an optimal microwave absorbing properties, and the maximum RL values are $-10.6$ dB at 15.2 GHz for 1 mm and $-10.2$ dB at 8.8 GHz for 1.5 mm. Oka et al. found that the microwave absorption
characteristics of the half-carbonized wood with Mn–Zn ferrite coating could be adjusted by controlling the processing temperature. Moreover, both the bending strength and the matching frequency can achieve the proper value under the treatment of 250 °C. Zhu et al. synthesized a novel composite with the surface of CBC coated by Ni nanoparticles, which forms a three-dimensional network structure. It can be found that the CBC/Ni nanocomposite exhibits the higher microwave absorption effect than the pure CBC in 0.6−13.2 GHz frequency range. Similarly, Ren et al. synthesized CBC decorated with CoFe₂O₄ nanocrystals by a solvothermal method; the composite exhibited excellent microwave absorption performance with a maximum RL of −45 dB at 8.6 GHz (2 mm) as the mass content of CBC/CoFe₂O₄ is 10 wt %. Kwon et al. investigated the effect of carbonization temperature on the electromagnetic shielding effectiveness, resistivity, and mechanical performance of carbonized medium density fiber (MDF). The results indicated that the MDF carbonized below 700 °C shows the limited electromagnetic shielding values; however, it shows the high electromagnetic shielding values as the carbonization temperature is in the range of 900−1500 °C.

Overall, the above investigations point out that the microwave absorbing property of the biomaterials can be enhanced after compositon with other materials, in which ferrites are good choices for its chemical and thermal stability, high Curie temperature, excellent magnetic loss ability, and so on. MFe₂O₄ (M = Ni, Mn etc.) nanoparticle has been widely used in many fields, for example, magnetic recording media, magnetic fluids, magnetic resonance imaging, and microwave absorption. On the other hand, the carbonized chaff is an excellent biomaterial with good dielectric loss properties, low density, biodegradable and recyclable utilization, corrosion resistance, low cost, specific structures, and so forth. Therefore, combining carbonized chaff with MFe₂O₄ nanoferrites may be a feasible strategy to enhance the microwave absorption properties of this biomaterial.

Furthermore, the operating frequency band of many radars has been extended to the low frequency now. Thus, the detection frequency of modern metrewave radar is mainly located in the low-frequency range of the 2−18 GHz, thus the microwave absorbing performance of which will be much worse to the low-frequency electromagnetic wave. This brings forward a strong requirement to design new MAMs with good electromagnetic wave absorbing properties in low-frequency band. Therefore, in this study, the NiₓMn₁₋ₓFe₂O₄/carbonized chaff (x = 0.3, 0.5, and 0.7) composites with different amounts of carbonized chaff have been prepared via the hydrothermal synthesis method. The crystal structures, morphologies, relative permittivity and permeability, and electromagnetic wave absorbing properties of as-prepared NiₓMn₁₋ₓFe₂O₄/carbonized chaff composites were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and VNA. The results of investigation displayed that the NiₓMn₁₋ₓFe₂O₄/carbonized chaff-N₂ composite exhibited an optimal electromagnetic wave absorbing performance in the low-frequency range of 0.1−3.0 GHz when the mass content of carbonized chaff is 10 wt %, which can be used as a novel electromagnetic wave absorbing candidate in this band.

2. CHARACTERIZATION

The crystalline structure of the as-prepared composites was characterized by the DX-2700 X-ray diffractometer with Cu Kα radiation (XRD, German Bruker D8, λ = 0.154 nm). The microstructure of the composites was studied by the SEM (Hitachi S-8020). The hybrid with a tantamount mass content of the composite and paraffin was pressed into circular rings (Resist: 7.00 mm, Resist: 3.04 mm, thickness: 2−5 mm) for the detection of S-parameters, that is, S_{11} and S_{12}, by VNA (TIANDA TD3618C) in 0.1−3.0 GHz frequency range. Thus, the electromagnetic parameters and microwave absorbing properties can be calculated based on the measured S-parameters and the theory of Nicolson and Ross.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Analysis. The XRD patterns of NiₓMn₁₋ₓFe₂O₄/carbonized chaff (x = 0.3, 0.5, and 0.7) composites are shown in Figure 1. The diffraction peaks at 2θ = 30.5°, 35.8°, 43.6°, 57.2°, and 62.9° are corresponded to the (220), (311), (400), (511), and (440) planes of the spinel structure NiₓMn₁₋ₓFe₂O₄. The diffraction peak around 2θ = 44.9° is assigned to the (111) plane of nickel because a small amount of Ni²⁺ was reduced to pure nickel in ethylene glycol solution at high temperature. Moreover, the diffraction peak of carbonized chaff cannot be observed in the XRD pattern, which may be attributed to the less content and existence form of amorphous state.

3.2. Micromorphology Observation. The microstructures of NiₓMn₀.₃Fe₂O₄ NPs and NiₓMn₁₋ₓFe₂O₄/carbonized chaff (x = 0.3, 0.5, and 0.7) composites are shown in Figure 2. Figure 2a shows that the NiₓMn₀.₃Fe₂O₄ NPs present the bonded ball-like granules, and Figure 2b−e displays the NiₓMn₀.₃Fe₂O₄/carbonized chaff composites with different contents of the carbonized chaff, which indicates that the NiₓMn₀.₃Fe₂O₄ NPs also present a bonding growth morphology and form a coarse, poriferous, and lax structure. Only a little carbonized chaff can be seen in the elliptical area shown in Figure 2b for the very small amount in the composite; however, with the increased content of carbonized chaff, it is shown in Figure 2c that the NPs were adhered well on the surface of carbonized chaff as the content is 10 wt %. Moreover, it can also be seen that the surface of carbonized chaff is not coated well with the NPs for excess amount of

Figure 1. XRD patterns of NiₓMn₁₋ₓFe₂O₄/carbonized chaff, NiₓMn₀.₃Fe₂O₄/carbonized chaff, and NiₓMn₀.₃Fe₂O₄/carbonized chaff composites.
carbonized chaff; some area of carbonized chaff is bared as the content added to 15 wt % as shown in Figure 2d, which is not conducive to enhance the microwave absorbing performance of the composite. Especially, in Figure 2e, when the carbonized chaff content is added to 20 wt %, irregularly stacked lamellar microstructures of carbonized chaff can be clearly seen in the square area. Thus, we can conclude that the appropriate mass content of carbonized chaff is about 10 wt %, and the surface of carbonized chaff can be coated well just enough. In addition, the morphologies of the Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff 10 wt % and Ni$_{0.7}$Mn$_{0.3}$Fe$_2$O$_4$/carbonized chaff 10 wt % are shown in Figure 2f,g, which is quite similar with the Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff 10 wt %. Besides, the macromorphology of the as-prepared hybrid is shown in Figure 2h; the hybrid presents the characteristic of paramagnetic materials, which can be attracted by the magnet for being coated by ferrite nanoparticles.

### 3.3. Electromagnetic Characteristics

Generally, it is well known that the electromagnetic wave absorbing performance of the composites is related to the complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) and permeability ($\mu = \mu' - j\mu''$). The real part of permittivity and permeability represents the storage capabilities of the electromagnetic wave energy, as well as the dissipation capabilities can be represented by the imaginary part in general.\textsuperscript{30}–\textsuperscript{32} It can be seen from Figure 3a that the $\varepsilon'$ values of the composites are higher than the pure Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ when the mass content of the carbonized chaff is less than or equal to 10 wt %, indicating that a moderate amount of carbonized chaff can enhance the $\varepsilon'$ values in the composites. However, the $\varepsilon'$ values will reduce in the whole range with the further increase of carbonized chaff content. Besides, the $\varepsilon'$ values of all samples decrease gradually with the enhancement of frequency in the measurement range. The imaginary parts of permittivity are shown in Figure 3b, and the $\varepsilon''$ values of Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composites with the 5 and 10 wt % content of carbonized chaff are increased first and then decreased slightly, while the composites with 15 and 20 wt % content of carbonized chaff keep on increasing with increasing frequency. The Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composite exhibited the highest $\varepsilon''$ value when the mass content of carbonized chaff was 5 wt %, the maximum value
reached 0.97 dB at 1.84 GHz. The enhanced $\varepsilon'$ values can be explained by the multiple polarization originated from the special structures of carbonized chaff, and electron polarization originated from electron exchange between Fe$^{3+}$ and M$^{2+}$ (M = Ni and Mn). This implies a relatively stronger storage capability and dissipative ability for EM wave energy.

The frequency-dependent real and imaginary parts of complex permeability are shown in Figure 3c,d. It can be noted that the real part and the corresponding imaginary part of permeability in Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composites with different carbonized chaff contents suggest an increasing trend with the variation of frequency. On the other hand, the $\mu'$ and $\mu''$ values of the Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composites are higher than those of pure Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ when the mass content of carbonized chaff was less than 10 wt%, resulting from the appropriate amount of carbonized chaff which can provide enough carrying surface to prevent the aggregation of Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ NPs, which is conducive to enhance the small size effect of NPs. However, the $\mu'$ and $\mu''$ values will decrease when the mass content of carbonized chaff further increased because of the magnetic inertness of carbonized chaff. In addition, the $\mu''$ values of all samples were higher than their $\varepsilon''$ values because of the excellent magnetic properties of Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ NPs.

As we all know, the microwave attenuation of the absorber mainly generates from the dielectric and magnetic loss. In order to investigate this property of the as-prepared composites, the dielectric loss tangents (tan $\delta_\varepsilon$ = $\varepsilon''$/ $\varepsilon'$) and magnetic loss tangents (tan $\delta_\mu$ = $\mu''$/ $\mu'$) have been calculated and shown in Figure 4. It can be found that the values of tan $\delta_\varepsilon$ in all samples are very close to each other within the 0.1–3.0 GHz frequency range shown in Figure 4a, and the tan $\delta_\mu$ of composites with 5 and 10 wt% content of carbonized chaff are slightly larger than others in average. Compared to pure Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ NPs, the tan $\delta_\mu$ values of Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composites are improved with the increasing content of carbonized chaff in a suitable range. This might be attributed to the structural synergy of different components. The tan $\delta_\mu$ values of all samples increase at the beginning and then reduce with the enhancement of frequency. The Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff 10 wt% composites show the highest tan $\delta_\mu$ value of 1.4 at 2.0 GHz as shown in Figure 4b, which exhibits a strong magnetic loss effect. Moreover, for all Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composites, the tan $\delta_\mu$ values are higher than the tan $\delta_\varepsilon$ values, indicating that the magnetic loss plays the primary role in the electromagnetic wave absorbing process over the whole frequency range.

3.4. Microwave Absorption Properties. Generally speaking, the electromagnetic wave absorbing property of composites is expressed by the microwave RL, which can be calculated based on the transmission line theory by using the complex permittivity and permeability at a given thickness of absorber.

$$Z_m = Z_0 \left( \frac{\mu'}{\varepsilon'} \right) \tan\left( \frac{2\pi fd}{c} \right)$$

Here, $Z_0$ is the impedance of free space, $Z_m$ the input characteristic impedance, $\varepsilon'$ and $\mu'$ the complex permittivity and permeability of the absorber, $f$ the frequency, $d$ the thickness of the absorbent, and $c$ the velocity of light in free space. Thus, the microwave RL can be expressed as

$$RL(dB) = 20 \log \left( \frac{Z_m - Z_0}{Z_m + Z_0} \right)$$(2)

The effective absorption bandwidth is defined as the corresponding frequency range of RL < −10 dB because more than 90% of electromagnetic energy can be dissipated if the RL of absorber is below −10 dB. Figure 5 shows a comparison of the calculated RL curves for Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff composites with different carbonized chaff contents at a thickness of 4 mm.
frequency range of 2.17–2.93 GHz (0.76 GHz), which may be ascribed to the preferable synergetic effect of dielectric and magnetic components within the nanoscale and the porous structure of carbonized chaff. Moreover, the carbonized chaff provided excellent carrier for Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$ NPs, which can prevent the compact agglomeration of Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$ particles to some extent, which may benefit for improving the microwave absorption property.

In order to investigate the effect of thickness on the microwave absorbing performance of absorber, the RL curves of the Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff 10 wt % composite at different thicknesses are illustrated in Figure 6. It suggests that the RL value of $-12.43$ dB at 2.61 GHz obtained previously at 4 mm is the optimum performance of this composite. Moreover, the absorption peaks of Ni$_{0.5}$Mn$_{0.5}$Fe$_2$O$_4$/carbonized chaff 10 wt % composite gradually shifts to the lower-frequency range with the increase of absorber layer thickness, which can be explained by the quarter wavelength mechanism:

$$ f = \frac{nc}{4d\sqrt{\varepsilon\mu}} $$

The results indicate that the electromagnetic wave absorbing performance of the composite can be tuned effectively by changing its thickness.

Figure 7 displays the RL value of the Ni$_{x}$Mn$_{1-x}$Fe$_2$O$_4$/carbonized chaff ($x = 0.3, 0.5$, and $0.7$) prepared in different atmospheres ($d = 4$ mm). It can be obviously observed that the peak values of RL are enhanced with the increase of manganese ratio in ferrites. The Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff composite presents an optimal electromagnetic wave absorbing properties. The maximum RL reached $-13.46$ dB at 2.2 GHz and the effective bandwidth covers from 1.8 to 2.7 GHz (0.9 GHz). Furthermore, it can be seen that the carbonization atmospheres do play a crucial role in the determination of surface properties and microwave absorption performance. There is a better microwave absorbing property in Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff composite prepared in the inert nitrogen atmosphere than that of those composites prepared in air, and an optimal RL of $-14.58$ dB at 1.91 GHz with an effective absorption frequency between 1.46 and 2.41 GHz (0.95 GHz) can be obtained. This is owing to that the more microstructural morphologies of chaff can be retained as carbonized in nitrogen atmosphere, which is beneficial to enhance microwave absorption for the microstructure effect. Besides, detailed microwave absorption mechanisms will be further explained in the following section. Moreover, the comparison of electromagnetic wave absorption performance between Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ and other ferrite composites reported in recent literature has been listed in the Table 1.$^{31-49}$ It can be noted that the microwave absorption performance of ferrites in the GHz range can be improved by compositing them with other materials processing different loss mechanisms; however, the frequency position of absorbing peak corresponding to the Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ composite prepared here is obviously the lowest.

### 3.5. Microwave Absorption Mechanism.

The better impedance matching between the free space and absorber can make more electromagnetic wave enter into the absorber to be dissipated. In general, the impedance characteristic can be expressed by the following formula,$^{50}$

$$ Z = Z_{\infty}/Z_0 = \left(\frac{\mu}{\varepsilon}\right) $$

where $Z_{\infty}$ and $Z_0$ are the impedance values of the absorber and the free space, respectively. Figure 8 shows the impedance matching ratios of the as-prepared samples with the change of frequency. It can be observed that the $Z$ values of Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ composite with a layer thickness of 4 mm are more closer to the free space at the frequency of 1.97 GHz, which is attributed to the good matching relationship between complex permeability and permittivity at this range. Furthermore, it can also be found that the frequency ranges of $Z_{\infty}/Z_0$ approached to 1 in all samples indicates the locations of absorption peaks just right, which reflects the importance of impedance matching property in the microwave absorption of composites.

The another possible reason that may significantly affect the magnetic loss of the composite in GHz range is the eddy current loss, which can be given by the following equation,$^{51}$

$$ C_0 = \mu^2 (\mu')^{-2} f^{-1} = \frac{2\mu_0 \sigma d^2}{3} $$

where $\mu_0$ is the permeability in vacuum, $\sigma$ the electrical conductivity, and $d$ the thickness of the absorber. The eddy current loss is the main reason for magnetic loss if the $C_0$ maintains the constant as the frequency is changed. Figure 9 shows the $C_0$ curves of composites at the thickness of 4 mm, as shown in the graph, and the $C_0$ vary with change of frequency in the whole measurement range, indicating that the eddy current loss does not play a major role in the magnetic loss. Therefore, the magnetic loss here may be caused by the natural resonance loss and so forth.

Moreover, the relaxation process of heterogeneous interface polarization can be presented by the Cole–Cole semicircle,
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dipolar polarization, Maxwell semicircle implies the existence of other mechanisms, such as Wagner relaxation, conductive loss, and so on, which made a significant contribution for improving the dielectric loss of microwave absorption.

Except for the absorption mechanisms mentioned above, the laminated structures of Ni$_{x}$Mn$_{1-x}$Fe$_2$O$_4$/carbonized chaff ($x = 0.3, 0.5$, and $0.7$) composites may cause the multiple reflection of microwave in the absorber by increasing the propagation path of microwave among the layers, which can further enhance the microwave absorption ability of the as-prepared composites. Overall, we can clearly find that the carbonized chaff has a great potential in the development of easily degradable, environment-friendly, and high-efficiency MAMs.

4. CONCLUSIONS

In summary, the Ni$_{x}$Mn$_{1-x}$Fe$_2$O$_4$/carbonized chaff ($x = 0.3, 0.5$, and $0.7$) composites with different contents of carbonized chaff were synthesized successfully via the co-carbonization and hydrothermal method, and their microwave absorption properties were also researched in the low-frequency range of 0.1–3 GHz. The results show that the electromagnetic wave absorbing property of the as-prepared composite can be manipulated by adjusting the mass content of carbonized chaff in hybrid. Compared to the pure Ni$_{0.8}$Co$_{0.2}$Fe$_2$O$_4$ NPs, the Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ hybrid exhibits an optimal electromagnetic wave absorbing performance at 4 mm when the mass content of carbonized chaff is 10 wt %, and the maximum RL can reach −14.58 dB at 1.91 GHz with the effective absorption bandwidth covering from 1.46 to 2.41 GHz (0.95 GHz). This work reports a novel way to prepare easily degradable, environment-friendly, and high-efficiency electromagnetic wave absorbers by taking the advantages of renewable biomaterials.

5. EXPERIMENTAL SECTION

5.1. Materials. The chaff was purchased from Zhejiang Chenxi Organic Feed Factory, China. Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) was purchased from Hefei BASF Biotechnology Co. Ltd., China. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O), manganous chloride tetrahydrate (MnCl$_2$·4H$_2$O), sodium acetate trihydrate (NaAc), and polyethylene glycol were purchased from Chengdu Kelong Chemical Reagent Co. Ltd., China. Ethylene glycol was purchased from Sinopharm Chemical Reagent Co. Ltd., China. All reagents used in the experiment were of analytical grade and used as received without further purification.

5.2. Preparation of Carbonized Chaff. The chaff was washed by deionized water to remove impurities and then impregnated in 10 wt % hydrochloric acid for 2 h to remove a small amount of K, Ca, and other metal ions. Then, the chaff

Table 1. Comparison of Microwave Absorbing Properties between Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/Carbonized Chaff and Other Ferrite Composites Reported in Recent Years

| materials                                      | thickness (mm) | minimum RL (dB) | position (GHz) | RL < −10 dB (GHz) | refs |
|------------------------------------------------|----------------|-----------------|----------------|-------------------|------|
| Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ | 4              | −14.58          | 1.91           | 1.46–2.41          | this work |
| Co$_{0.3}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$/MWCNTs          | 2.5            | −37.7           | 10.2           | 10.0–10.5          | 38   |
| CoFe$_2$O$_4$/graphene                                | 2.5            | −42.0           | 12.9           | 11.2–15.8          | 39   |
| Ni$_{0.3}$Co$_{0.3}$Fe$_2$O$_4$/Ni–C                   | 2.3            | −84.9           | 17.0           | 10.6–18.0          | 40   |
| Fe$_3$O$_4$/GNPs–NH–PANI                               | 2.6            | −40.3           | 10.3           | 7.9–17.5           | 41   |
| Li$_{0.3}$Ni$_{0.3}$Fe$_2$O$_4$/PANI                    | 2.0            | −57.5           | 13.8           | 11.0–16.5          | 42   |
| Fe$_3$O$_4$/carbon nanofiber                            | 2.5            | −47.0           | 10.0           | 7.0–13.0           | 43   |
| Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$/polyaniline             | 2.5            | −39.6           | 11.0           | 9.6–12.5           | 44   |
| HMG/Ni$_{0.5}$Zn$_{0.3}$Fe$_2$O$_4$/PT                  | 3              | −13.8           | 10.5           | 9.4–12.0           | 45   |
| Co$_{0.3}$Ni$_{0.3}$Zn$_{0.3}$Fe$_2$O$_4$/rGO           | 2.5            | −49.5           | 16.9           | 12.0–18.0          | 46   |

Figure 8. Frequency-dependent $Z_a/Z_0$ values of Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-air and Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ with 10 wt % carbonized chaff.

Figure 9. Eddy current loss curves of Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-air and Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ with 10 wt % carbonized chaff.

which has an important influence on the dielectric loss behaviors of electromagnetic wave absorbing materials. According to the Debye dipolar relaxation theory, the complex permittivity can be expressed as follows

$$
\epsilon'(\omega) = \frac{\epsilon_s + \epsilon_m}{2} + \left(\epsilon_s - \epsilon_m\right)^2 + \frac{2\omega \tau}{\omega^2 + \omega^2 \tau^2}
$$

where $\epsilon_s$ is the static dielectric constant and $\epsilon_m$ is the dielectric constant at infinite frequency. The $\epsilon'$–$\epsilon''$ curves of the Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff are shown in Figure 10; however, one semicircle can be observed in each sample, indicating the existence of only one Debye dipolar relaxation during the EM wave absorption process. In addition, the Ni$_{0.3}$Mn$_{0.7}$Fe$_2$O$_4$/carbonized chaff-N$_2$ composite displays the largest radius among all the samples, and the deformed semicircle implies the existence of other mechanisms, such as dipolar polarization, Maxwell–Wagner relaxation, conductive

Figure 10. $\epsilon''$ vs. $\epsilon'$ curves of the Ni$_{x}$Mn$_{1-x}$Fe$_2$O$_4$/carbonized chaff-N$_2$ composite materials and their $\epsilon''$ vs. $\omega^2 \tau$ curves.
was washed to a pH of 7 and dried at 40 °C. Later, the preceding chaff was added into 300 mL solution 1.0 M NiCl₂·6H₂O for 24 h. Finally, the preprocessed chaff was heated to 700 °C at a heating rate of 10 °C·min⁻¹ in a horizontal tube furnace and then maintained the temperature for 5 h to carbonize.

5.3. Preparation of NiₓMn₁−ₓFe₂O₄/carbonized chaff (x = 0.3, 0.5, and 0.7) Composites. Because the NPs of ferrite prepared by hydrothermal method have the advantages of good grain integrity, controllable particle size, uniform distribution, low cost, easy to get suitable stoichiometry, and crystal shape. Here, the NiₓMn₁−ₓFe₂O₄/carbonized chaff composite was synthesized via a typical hydrothermal method, and the brief synthesis process of the composites is shown in Figure 11. First, 2.7 g of ferric chloride hexahydrate, 0.5 g of MnCl₂·4H₂O, and 0.6 g of NiCl₂·6H₂O were dissolved in 80 mL of ethylene glycol with continuous stirring to form the homogeneous solution. Second, 9.6 g of NaAc, 2 g of polyethylene glycol, and carbonized chaff with different masses were consecutively added into the preceding solution with continuous stirring and ultrasonic dispersion for 45 min. Third, the obtained mixed solution was transferred into a 150 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h. Fourth, after the autoclave was cooled down to room temperature, the precipitation was separated from the solution and washed by ethanol for several times. Finally, the precipitation was dried at 60 °C for 12 h and the target product was obtained. Moreover, the NiₓMn₁−ₓFe₂O₄/carbonized chaff composite with different ion ratios can be prepared by changing the molar ratio of Ni²⁺ to Mn²⁺ (i.e., γ = 1:1, 3:7, and 7:3). In order to investigate the influence of carbonized chaff content on the microwave absorption performance of composites, samples with contents of carbonized chaff are 5, 10, 15, and 20 wt % were prepared through the same method as mentioned above.

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Notes
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