Double-layer Electromagnetic Wave Absorber Based on Carbon Nanotubes Doped with La(NO₃)₃ and Fe₃O₄ Nanoparticles

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Double-layer structure absorbing materials based on the impedance matching principle and transmission line theory can effectively improve the electromagnetic wave absorbing properties. In this paper, the electromagnetic wave absorbing properties of double-layer absorbers (2 mm thickness), where multiwall carbon nanotube (MWCNT)-La(NO₃)₃/polyvinyl chloride (PVC) and MWCNT-Fe₃O₄/PVC composites had been taken turns as the absorption layer and matching layer, were investigated in 2–18 GHz range. The absorbing properties of single- and double-layer structure and different each-layer thickness with two types of combinations were compared. The results showed that the design of double-layer structure for composites could effectively broaden the absorption frequency area, and increase the absorption intensity. When MWCNT-La(NO₃)₃/PVC composite were used as absorption layers with 0.6 mm thickness, the absorption bandwidth (≤ −15 dB or > 97 %) of double-layer composite was the widest, reaching a maximum of about 3.36 GHz, and the absorption peak value was also the lowest about −46.02 dB at 16.24 GHz.

Keywords: multiwall carbon nanotubes, La(NO₃)₃, Fe₃O₄, electromagnetic wave absorbing properties.

1. INTRODUCTION

With mounting electromagnetic pollution, electromagnetic wave absorbing materials have been paid much attention in recent years [1–6]. Many absorbing composites containing carbon fibers [7], carbon nanotubes (CNTs) [8, 9], graphene [10, 11], carbon spheres [12], ferrite [13, 14], carbonyl iron [15], etc. have been most extensively studied. In addition, previous research has found that the absorbing bandwidths of these materials are relatively narrow and weak. Therefore, multilayer absorbing composites with gradient impedance, in which relatively more electromagnetic waves can be absorbed by impedance matching, are fabricated in order to broaden the absorbing bandwidths, enhance the absorbing intensity and improve the absorbing performance. Electromagnetic wave absorbing composites with a suitable absorption performance are usually designed with an appropriate matching layer. It is possible to achieve suitable impedance matching allowing incidents of electromagnetic waves to reach the absorbing layer with the free space [16–18]. Danlée et al. [19] presented that a novel multilayer arrangement of polymer nanocomposites composed of alternating films of dielectric polymer and conducting layers, which consisted of either polycarbonate nanoparticle films with CNTs or a very thin CNTs coating deposited on insulating polymer from a CNT waterborne ink, was able to very effectively absorb electromagnetic wave over a broad frequency range or selectively reflect desired wavelengths. Das et al. [20] found that the double-layer CoZn-ferrite/TiO₂ (−24.3 dB), where ferrite powders were substituted using Zinc MCo₃Zn₀.₅Fe₃O₄ (Me = Co, Mn and Ni) had been prepared by the sol-gel auto-combustion, possessed lower reflection loss than the single-layer NiZn-ferrite (−11.2 dB) of the same total thickness at 12.02 GHz. Ni et al. [21] presented that the magnetic, dielectric and reflection loss value of double-layer nanocomposites consisted of barium titanate (BTO)/CNT 30 wt.% (r) and BTO 30 wt.% (matching layer) thickness were improved compared to single-layer BTO/CNT 30 wt.% nanocomposites. The bandwidth (≤ −10 dB) covered a wide frequency area from 12.1 to 13.8 GHz when the absorption and matching layer thickness were respectively 1.0 and 0.3 mm, and the minimum reflection loss achieved −63.7 dB (over 99.9999 % absorption) at 13.7 GHz.

In a certain total thickness, each-layer thickness and layer-permutation have exerted great influence on the absorbing properties of double-layer composites. Therefore, we used MWCNTs doped with Fe₃O₄ and La(NO₃)₃ as an absorbent and insulating resin (PVC) as a matrix to fabricate double-layer composites for high-performance absorbing microwave. The reflection loss of electromagnetic absorbers with various layer permutation and thickness was theoretically estimated by the calculation according to the single- or double-layer absorbers model. Electromagnetic parameters (ε′= ε′′, μ′ = μ′′) of as-prepared composites were measured by space method in the required frequency range.

2. EXPERIMENTAL

2.1. Materials

MWCNTs were treated with a concentrated acid mixture of H₂SO₄/HNO₃ (3:1 v/v) for 4 h for increasing their activity and purity, and were then ball-milled. MWCNTs doped with Fe₃O₄ or La(NO₃)₃ with optimal
microwave absorbing properties were fabricated according to our previous reports: (1) The acid-treated MWCNTs were agitated ultrasonically with 6 wt.% of La(NO₃)₃ for 1 h, dried out and ground. Then the black MWCNT-La(NO₃)₃ powder was prepared by a simple method [22]; (2) The acid-treated MWCNTs (100 mg) were ultrasonically dispersed in a mixture solution (250 mL) of FeCl₃/FeSO₄ (molar ratio = 2:1, FeSO₄ concentration = 0.02 mol/L) for 0.5 h. This solution was heated to 50 °C, while this temperature was maintained for 0.5 h with stirring under N₂ protection, followed by a further heating at 65 °C for 1 h at pH > 12 (adjusted with 6 mol/L NaOH). The solution was added slowly with sodium dodecyl sulfate (SDS, 0.25 g) at 85 °C and cooled until room temperature was achieved. Black precipitates from the solution had been collected by filtration, washed by deionized water to neutral, dried out and milled. Then soft magnetic MWCNT-Fe₃O₄ hybrid materials were obtained via magnetic separation [23].

2.2. Characterization

The samples were prepared by 8 mass % MWCNT-La(NO₃)₃ or MWCNT-Fe₃O₄ hybrid materials that were homogeneously dispersed in PVC matrix (MWCNT-La(NO₃)₃/P or MWCNT-Fe₃O₄/PVC), and then made into a rectangular waveguide that has a length of 22.86 mm, a width of 10.16 mm for electromagnetic measurements. The sample complex permittivity and permeability were carried out using a network analyzer (Agilent technologies E8362B: 10 MHz–20 GHz).

2.3. Calculation of reflection loss

According to the transmission theory [24], the formulas of calculation for double-layer absorber were given to determine the reflection loss as follows [25, 26]:

\[
R(\text{dB}) = 20 \log_{10} \left| \frac{Z_m - Z_0}{Z_m + Z_0} \right|,
\]

\[
Z_m = Z_{in} + Z_i \tanh(j2\pi\mu d/c) \sqrt{\frac{\mu_z\varepsilon_z}{c}},
\]

\[
Z_{in} = Z_i \tanh(j2\pi\mu d/c) \sqrt{\frac{\mu_z\varepsilon_z}{c}},
\]

where \(Z_m\) is the input impedance at the material interface and free space, \(Z_{in}\) is the interface impedance between absorbing layer and matching layer, \(Z_i\), \(Z_0\), \(Z_0\) are the characteristic impedance of absorbing layer, matching layer and a vacuum, respectively, \(\varepsilon_i\) and \(\mu_i\) are the relative complex permittivity and permeability, respectively, \(j\) is the electromagnetic wave frequency in vacuum, \(d\) is the layer thickness, and \(c\) is the light velocity in vacuum.

3. RESULTS AND DISCUSSION

Fig. 1 shows the complex permittivity (\(\varepsilon'\), \(\varepsilon''\)) (a, b) and permeability (\(\mu'\), \(\mu''\)) (c, d) spectra for MWCNT, MWCNT-La(NO₃)₃, and MWCNT-Fe₃O₄ vs frequency

While a small fluctuation is observed in the real part of complex permittivity of MWCNT-Fe₃O₄/PVC composite, which can be ascribed to the dielectric relaxation of the sample interface under the action of the
external electromagnetic wave. A vibration is observed at the corresponding frequency region of the imaginary part. This phenomenon is obviously characteristic for nonlinear dielectric resonance [27]. From Fig. 1 c and d, it can be found that the real part of complex permeability of MWCNT-La(NO$_3$)$_3$/PVC composite is lower than that of MWCNT/PVC composite, and the imaginary parts did not appear to be much different. This is mainly because La$^{3+}$ ions could be complex with C = O, –COOH and –OH located on MWCNT surface to enhance magnetic anisotropy and coercivity. The real part and imaginary part of complex permeability of MWCNT-Fe$_3$O$_4$/PVC composite are the lowest. This may be due to MWCNTs not only have a unique chiral structure but also a lot of dangling bonds. Electrons can quickly exchange between MWCNTs and Fe$_3$O$_4$ nanoparticles to strengthen Fe$_3$O$_4$ conductivity and eddy current effect in 8.2–12.4 GHz. Eddy current creates the magnetic field that opposes the original magnetic field, which leads to a decrease in the complex permeability.

Multiple resonance peaks are detected in the imaginary-part high-frequency region. They are mainly caused by natural resonance, domain wall resonance and the eddy current loss arising from intrinsic damping [28].

![Reflection losses of single-layer absorbers for MWCNTs, MWCNTs-La(NO$_3$)$_3$ and MWCNTs-Fe$_3$O$_4$ vs frequency](image)

Fig. 2 indicates the reflection losses of single-layer absorbers for MWCNTs, MWCNTs-La(NO$_3$)$_3$, and MWCNTs-Fe$_3$O$_4$ with 2 mm thicknesses in 2–18 GHz. Among all of the samples, MWCNT/PVC composite has the highest minimum reflection loss (−9.84 dB, 11.28 GHz) and no absorbing bandwidth (<15 dB, >97 %), while MWCNT-Fe$_3$O$_4$/PVC composite, in contrast, has the lowest minimum reflection loss (−29.60 dB, 16.64 GHz) and the widest absorbing bandwidth at about 2.88 GHz (<15 dB, >97 %) from 15.12 to 18 GHz. This is mainly due to the magnetic loss and frequency dispersion on permeability of Fe$_3$O$_4$ nanoparticles caused by the natural resonance in the high frequency region. In addition, exchange energy caused by exchange effect can be significantly enhanced owing to the nanoscaled size and high surface anisotropy of Fe$_3$O$_4$ nanoparticles. Accordingly, exchange resonance may also contribute to the magnetic loss [29]. For MWCNT-La(NO$_3$)$_3$/PVC composite, the dielectric loss is enhanced with adding La(NO$_3$)$_3$, so the absorption properties are also strongly improved. As the absorption mechanism of La(NO$_3$)$_3$ is not the same as that of magnetic Fe$_3$O$_4$, the absorption band is also different. And the electromagnetic parameter changes lead to the interference condition change, the absorption peak shift to the low frequency region.

![Reflection losses of double-layer absorbers consisting of absorption layer (d$_1$) filled with MWCNTs-La(NO$_3$)$_3$ and (d$_2$) matching layer filled with MWCNTs-Fe$_3$O$_4$ vs frequency](image)

The reflection losses of double-layer absorbers with MWCNT-La(NO$_3$)$_3$/PVC composites as absorption layer and MWCNT-Fe$_3$O$_4$/PVC composite as matching layer versus frequency in 2–18 GHz are shown in Fig. 3, and the reflection losses of double-layer absorbers with MWCNT-Fe$_3$O$_4$/PVC composites as absorption layer and MWCNT-La(NO$_3$)$_3$/PVC composite as matching layer versus frequency in 2–18 GHz are shown in Fig. 4. According to Maxwell equations, electromagnetic wave propagation characteristics in materials are determined by the complex permittivity and permeability. Using the double-layer structure of the composite, electromagnetic wave in space enters into the absorption layer as much as possible by the double-layer matching function and is absorbed by the absorption layer. Electromagnetic wave absorption peak minimum shifts to a higher frequency area with the absorbing layer thickness decreases. When the thickness of absorption layer and matching layer are 0.6 mm and 1.4 mm, respectively, the peak value achieves a minimum of about –46.02 dB at 16.24 GHz, which means that two layers matching is the best. And absorption bandwidth is about 3.36 GHz (<−15 dB or >97 %) ranging from 14.64 GHz to 18 GHz. Compared to the single-layer composite as shown in Fig. 2, the double-layer composites are more efficiency for electromagnetic wave absorption in 2–18 GHz. Whereas, when MWCNT-Fe$_3$O$_4$/PVC and MWCNT-La(NO$_3$)$_3$/PVC composites are respectively used as absorption and matching layer (Fig. 4), and the peak value achieves a minimum about –40.71 dB at 14.32 GHz, with the narrow bandwidth about 2.72 GHz (<−15 dB or >97 %). The effective absorption band lies in the relatively low frequency region, and the electromagnetic wave absorption peak minimum shifts to the lower frequency region with the absorbing layer thickness decreases. Two different variation trends are attributed to the different attenuation properties of the dielectric and magnetic materials. Compared to MWCNT-Fe$_3$O$_4$/PVC and MWCNT-La(NO$_3$)$_3$/PVC composites. This implies that MWCNT-Fe$_3$O$_4$/PVC composite would be more suitable for impedance matching with free space, resulting in the overall impedance of double-layer absorber relatively closer to the ideal impedance matching ($Z_m = Z_0$).


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