Electrical properties and applications of carbon nanotube composites

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Abstract: Many types of electromagnetic (EM) absorbers have been developed to convert EM energy into heat and to absorb EM wave. However, multilayer EM absorbers are complicated to design, fabricate, and dispose of. In this work, we present a simple and scalable design method to achieve a single-layer electromagnetic absorber with a high absorption coefficient in a wide range of frequency bands. On the basis of the design, we develop two types of nonwoven fabrics with high porosity in which the fibers are coated with multi-walled carbon nanotubes (MWCNTs). The absorption coefficients exceed 0.9 for the 5-mm-thick MWCNT-coated nonwoven fabric measured in the 50-67 GHz rang. An absorption coefficient of 0.94 at 5.8 GHz is expected to be obtained by using 50-mm MWCNT-coated fabric with a lower MWCNT content. The present MWCNT-coated nonwoven fabrics will be useful materials for high performance EM absorbers.

Keywords: Carbon nanotube, multi-walled carbon nanotube, nonwoven fabric, composite, conductivity, permittivity, electromagnetic absorber, electromagnetic interference problems

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1 Introduction

Carbon nanotubes (CNTs) have been attracting much attention due to their excellent electrical, mechanical, and thermal properties [1]. Inclusion of CNTs into base materials improves the performance of the materials and even produces additional functions for them. The extremely high conductivity and large aspect ratio of CNTs are very effective for filler in conductive composite materials. The application areas of these materials include transparent conductive sheets, battery electrodes, and electromagnetic (EM) absorbers. As wireless equipment has become more convenient, electromagnetic interference (EMI) problems have become more serious. Many types of EM absorbers have been developed to convert EM energy into heat and to absorb EM wave. In the design of commonly used multilayer EM absorbers with metal backplanes, the thickness, permittivity, and/or conductivity of each layer must be adjusted to achieve high absorbance at a target frequency [2]. CNT composites are effective to achieve wide ranges of permittivity and conductivity [3-9] and to widen design flexibility of EM absorbers. A high conductivity of more than 10^3 S/m has been reported for both single-walled (SW) [10] and multi-walled (MW) [11] CNT composites, while a large real permittivity of 200 at 18 GHz has been observed for MWCNT/cellulose composite paper [12]. However, multilayer EM absorbers are complicated to design, fabricate, and dispose of. Therefore, the purpose of this work is to present CNT composites with the complex permittivity required to achieve a single-layer absorber with a high absorption coefficient.

2 Experimental details

2.1 Material design

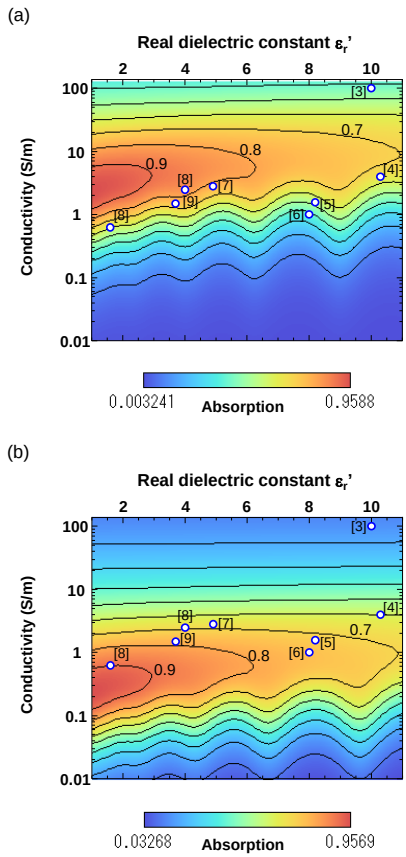
The coefficients of transmission *T*, reflection *R*, and absorption *A* for a single-layer conductive material were calculated by taking into account the multiple reflections at both surfaces of the material [13] (see Appendix A). The permeability of the material was assumed to be equal to that of vacuum, while the complex permittivity in the material was expressed as

$$\varepsilon = \varepsilon_0(\varepsilon_r' - j\varepsilon_r'') = \varepsilon_0(\varepsilon_r' - j\frac{\sigma}{\omega\varepsilon_0}) \tag{1}$$

Here, ε_0 is the permittivity of vacuum, σ is the conductivity, and ω is the angular frequency. Figure 1(a) shows a contour plot of the calculated absorption coefficient in the ε_r'-σ plane for the normal incident to the material (thickness d=5 mm) at 60 GHz. The

calculation result indicated that an absorption coefficient of 0.95 can be achieved with only a single layer when ε_r' is close to that of the free space and σ is around 3 S/m. This design method is simple and scalable. When used in 5.8 GHz ISM (Industry-Science-Medical) band (e.g. electronic toll collection systems in Japan), the thickness *d* should be increased to ~50 mm and the conductivity σ should be decreased to 0.3 S/m (keeping ε_r" constant). This is clearly shown in Figure 1(b). In Figure 1(a) and (b), the values of ε_r' and σ reported for the CNT composites [3-9] are plotted, although they were not measured at 5.8 or 60 GHz. The reported CNT composites seemed to be unsuitable for the single-layer absorbers with sufficient absorption coefficients at both frequencies. It is difficult to obtain CNT composites with ε_r' close to 1.0 using dense base materials such as silica, ceramic, and even polymer, because their dielectric constants are larger than 2. CNT composites using porous materials (e.g. nonwoven fabrics with high porosity) as base materials seem to very effectively achieve the ε_r' and σ required to achieve high absorption coefficients [13].

Figure 1 Contour plots of calculated absorption coefficient in ε_r'-σ plane for single-layer conductive materials with thicknesses of (a) 5 mm at 60 GHz and (b) 50 mm at 5.8 GHz. Open circles: reported values of ε_r' and σ for CNT composites measured at 1 GHz [3], 12 GHz [6], 18 GHz [5, 9], and 40 GHz [4, 7, 8]



2.2 Fabrication and evaluation methods

Two types of MWCNT-coated nonwoven fabrics were fabricated: one (fabric I) for 60 GHz use and the other (fabric II) for 5.8 GHz use. The MWCNTs used for fabrics I and II were produced by Nanocyl S.A. and CNano Technology Ltd., respectively. The basic fabric was polyester thermally bonded nonwoven fabric (Nishikawa Rose, specific gravity=0.093 g/cm^3). A sheet of nonwoven fabric was dipped into the MWCNT-water suspension, wrung by a mangle machine, and dried in a hot-air oven at 90 ºC to obtain MWCNT-coated nonwoven fabric [13]. The MWCNT contents of fabrics I and II were respectively 2.4 and 0.6 wt%. The porosity of both MWCNT-coated fabrics was 95%.
The fabricated absorbers were evaluated using a vector network analyzer (Agilent, E8361C) and materials measurement software (Agilent, 85071E) on the basis of a free space method (see the inset of Figure 2). Two horn antennas (Schwarzbeck, BBHA9120C) were used in 3-18 GHz, while two standard gain horn antennas (Millitech, SGH-15) were used in 50-67 GHz. The distances between the two antennas were 16 and 20 cm for 3-18 GHz and 50-67 GHz measurements, respectively. The two-port system was calibrated by using the gated reflect line calibration method. All the absorbers were 21 x 21 cm. In this measurement setup, the absorber was large enough to avoid any environment effects. The absorption coefficients were calculated as $1-|S_{11}|^2-|S_{21}|^2$ from measured scattering parameters (S_{11} and S_{21}). The complex permittivity values of the absorbers were extracted from the measured scattering parameters by using the materials measurement software. The accuracy of the free space measurement system had been confirmed by comparing the measured results with those measured with a waveguide method in the 50-67 GHz band [13]. See the website of Keysight Technologies [14] for more details about the measurement method.

3 Results and discussion

Figure 2 shows the measured absorption coefficient of fabric I with a thickness of 5 mm. High absorption coefficients larger than 0.9 were achieved in the 50-67 GHz frequency range. The dashed line in Figure 2 was calculated by Eqs. (A1)-(A4), where the complex permittivity of fabric I was approximated by the Maxwell-Garnett and Drude-Lorentz models (see Appendix B). Good agreement between measured and calculated absorption coefficients was obtained in the 50-67 GHz frequency range. In contrast, the calculations deviated from the measurements in the 3-18 GHz frequency range. To investigate the reason for the discrepancy in the 3-18 GHz frequency range, we examined the permittivity of fabric I extracted from measured scattering parameters by using the materials measurement software. Figure 3 compares measured and calculated relative permittivity (real part ε_r' and imaginary part ε_r"). The calculations using the Maxwell-Garnett (M-G) model closely matched the measured permittivity in the 50-67 GHz frequency range. Although the M-G model fairly reproduced the measured ε_r', it failed to reproduce ε_r" in the 3-18 GHz frequency range. The substitution of Eq. (B5) into Eq. (B1) reveals that ε_r' and ε_r" approach $\varepsilon_i\{N+f(1-N)\}/N/(1-f)$ and 0, respectively, at 0 Hz. Since ε_r" approaches 0 when the frequency diverges to infinity, ε_r" is convex upward as shown in Figure 3. The decreased ε_r" in the M-G model was the major reason for the difference between measured and calculated absorption coefficients in the 3-18 GHz frequency range.

Then we examined the often used Birchak model (see Appendix B). The dotted lines in Figure 3 were calculated by using the Birchak model. Although the Birchak model monotonically decreases both ε_r' and ε_r" as the frequency increases, the deviation from the measured values were large. The dashed-dotted lines for ε_r" in Figure 3 were

calculated by Eq. (1) with two conductivity values. Development of an appropriate model describing the permittivity at lower frequency region remains for future work.

Figure 2 Measured and calculated absorption coefficients of fabric I. Inset shows the measurement setup.

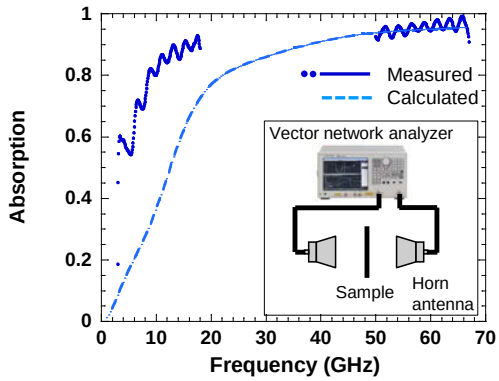


Figure 3 Measured and calculated relative permittivity of fabric I. Solid lines: measured. Dashed lines: calculated using Maxwell-Garnett (M-G) model. Dotted lines: calculated using Birchak model. Dashed-dotted lines: calculated by $\sigma/(\omega\varepsilon_0)$ with σ = 2.1 and 1.3 S/m

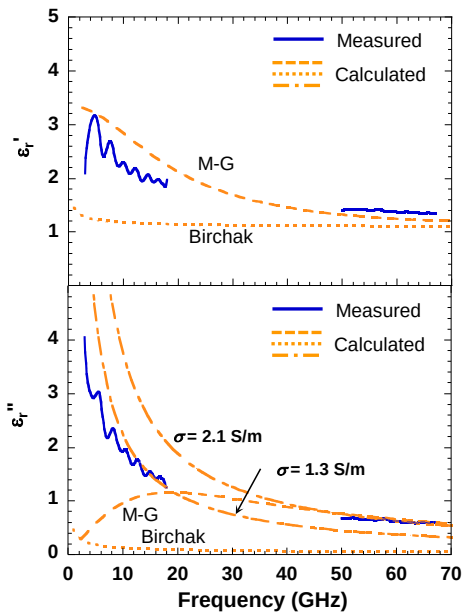
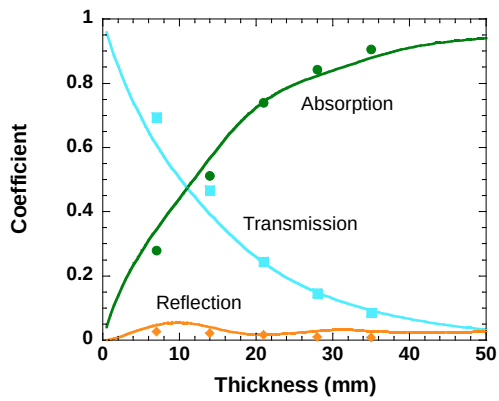


Figure 4 shows the dependences of absorption, transmission, and reflection coefficients on thickness for fabric II measured at 5.8 GHz. The solid lines were calculated using the measured permittivity of ε_r'=1.42 and ε_r"=0.69. A good agreement

was obtained between measured and calculated coefficients. The AC conductivity ($\sigma=\omega\varepsilon_r''\varepsilon_0$) was 0.22 S/m. The achieved ε_r' and σ were close to the optimum values shown in Figure 1(b). An absorption coefficient of 0.94 was expected to be obtained by using 50-mm MWCNT-coated fabric.describing the permittivity at lower frequency region remains for future work.

Figure 4 Dependences of absorption, transmission, and reflection coefficients on thickness for fabric II at 5.8 GHz. Symbols: measured. Lines: calculated.



4 Conclusions

In this work, we presented a simple and scalable design method to achieve a single-layer electromagnetic absorber with a high absorption coefficient in a wide range of frequency bands. On the basis of the design, we developed two types of nonwoven fabrics with high porosity in which the fibers were coated with MWCNTs. The absorption coefficients exceeded 0.9 for the 5-mm-thick MWCNT-coated nonwoven fabric measured in the 50-67 GHz range, which was in agreement with the calculations. An absorption coefficient of 0.94 at 5.8 GHz was expected to be obtained by using 50-mm MWCNT-coated fabric with a lower CNT content. The MWCNT-coated nonwoven fabrics opened up a new region in the ε_r'-σ plane. The present MWCNT-coated nonwoven fabrics will be useful materials for high performance electromagnetic absorbers.

Appendix A

The coefficients of transmission T, reflection R, and absorption A for a three-layer system are given by

$$T = tt^*, R = rr^*, A = 1 - T - R, \tag{A1}$$

where

$$t = \frac{t_{12}t_{23}\exp(-j\Delta)}{1 + r_{12}r_{23}\exp(-2j\Delta)} \tag{A2}$$

and

$$r = \frac{r_{12} + r_{23}\exp(-2j\Delta)}{1 + r_{12}r_{23}\exp(-2j\Delta)} \tag{A3}$$

with

$$\Delta = k_0 n_2 d \cos\theta_r .$$

Here, t^* and r^* are respectively the complex conjugates of t and r, r_{mn} and t_{mn} are respectively the reflection and transmission ratios of the complex electric field amplitudes (from medium m to n), k_0 is the wave number in the free space, n_2 and d are respectively the complex index of refraction and the thickness of Medium 2, θ_r is the refraction angle calculated by Snell's law, and $j = \sqrt{-1}$. The ratios r_{mn} and t_{mn} for perpendicular polarization are given by

$$r_{mn} = \frac{\eta_n \cos\theta_i - \eta_m \cos\theta_r}{\eta_n \cos\theta_i + \eta_m \cos\theta_r} \text{ and } t_{mn} = r_{mn} + 1 \tag{A4}$$

with the wave impedances η_m and η_n of Medium m and n [15]. A single-layer absorber was examined by treating Media 1 and 3 as air.

Appendix B

According to the Maxwell-Garnett model, the effective permittivity of CNT composites is given by [16]

$$\varepsilon_{eff} = \varepsilon_i \frac{[N + f(1-N)]\varepsilon_{CNT} + (1-N)(1-f)\varepsilon_i}{N(1-f)\varepsilon_{CNT} + (fN + 1 - N)\varepsilon_i} . \tag{B1}$$

Here, ε_i is the dielectric constant of a base material, f is the filling factor (CNT content), and N is the geometrical factor expressed as

$$N \approx \frac{r^2}{a^2} \ln\frac{a}{r} \tag{B2}$$

for CNTs with a length of $2a$ and a radius of r. The dielectric constant ε_i of a porous base material with a porosity of p is expressed as

$$\varepsilon_i = \varepsilon_{air} p + \varepsilon_d (1-p) , \tag{B3}$$

where ε_d is the dielectric constant of solid base material, and ε_{air}=1. The filling factor f in Eq. (B1) is approximated by

$$f = (1-p)v , \tag{B4}$$

where v is the volume fraction of CNTs. The dielectric constant of CNTs was approximated by the Drude-Lorentz model as in the work of Jeon et al. [16]

$$\varepsilon_{CNT} = \varepsilon^{\infty} - \frac{\omega_p^2}{\omega^2 - j\Gamma\omega} + \frac{\omega_{pl}^2}{\omega_l^2 - \omega^2 + j\Gamma_l\omega} . \tag{B5}$$

The parameter values deduced from terahertz time-domain spectroscopy measurements for SWCNTs [16] were used in the calculation. They were $\varepsilon^{\infty} = 3.24$, $\omega_p/2\pi$= 5.4 THz, $\Gamma/2\pi$= 1.17 THz, $\omega_{pl}/2\pi$= 6.19 THz, $\omega_l/2\pi$= 2.4 THz, and $\Gamma_l/2\pi$= 4.56 THz. Although they were deduced for SWCNTs, these parameter values well reproduced the measured permittivity of fabric I in the 50-67 GHz frequency region.

The Birchak model gives the effective permittivity of CNT composites as

$$\varepsilon_{eff}^{\beta} = f\varepsilon_{CNT}^{\beta} + (1-f)\varepsilon_i^{\beta} \tag{B6}$$

with β=1/2 [17].

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