Electromagnetic wave absorption property of carbon microcoils in 12–110 GHz region

S. Motojima, Y. Noda, and S. Hoshiya
Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan
Y. Hishikawa
CMC Technology Development Co. Ltd., Techno Plaza 4-179-1 Sue-cho, Kakamigahara City, Gifu 509-0180, Japan

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The electromagnetic (EM) wave absorption properties in the gigahertz region (12–110 GHz) of carbon microcoils (CMCs) with a three-dimensional-helical/spiral chiral structure (1–10 μm coil diameter and 0.1–10 mm coil length) were examined using the open space method. It was found that the target value of reflection loss, over −20 dB (above 99% absorptivity) necessitated for commercial applications, could be obtained for EM absorption composites of only 1–2 wt % addition of CMCs in a polyurethane matrix for the 30–35, 50–55, 75–80, and 95–100 GHz bands. A CMCs addition of more than 3 wt % resulted in a decrease of the EM wave absorptivity, because of the increase in the reflection of the EM waves. Multilayer absorption composites showed a higher EM absorptivity than that of single-layer composites. The longer the coil length, the higher the absorptivity could be obtained. The absorption mechanism of the EM waves by CMCs is discussed.


I. INTRODUCTION

In recent years, application using electromagnetic (EM) waves, especially gigahertz (GHz) regions, has significantly expanded. These band regions are further apt to shift to higher frequency regions with the development of information technology as well as electronic devices. For example, the EM waves of 0.8–1.2 GHz for mobile phones, 2.45 GHz for electronic ranges, 5.6–8.2 GHz (G band) for synthetic aperture radar (SAR) or microwave communications on the ground, 8.2–12.4 GHz (X band) for SAR or electron spin resonance apparatus, 50–75 GHz (V band) for intelligent transportation systems, etc., are often used. However, so-called “EM pollution” problems, such as EM wave interference (EMI) of electronic devices and instruments, missed actions in the transportation systems of railways, airplanes, or medical instruments, etc., by the EM waves have appeared along with the increasing use of the EM waves in the GHz regions. Conductive metal films are generally used for shielding the EM waves in the megahertz (MHz) regions. Ferrites, carbon powders, metal-coated carbon fibers or synthetic organic fibers are also used for the shielding/absorbing of the MHz and lower frequency EM waves in the GHz regions. Many researchers have studied the EMI properties of carbon powders, straight carbon fibers (CFs) or metal-coated CFs in the 1–3 GHz regions.1–6 Shielding materials have no absorption properties of EM waves while they can effectively reflect and shield EM waves, and thus the EM pollution problems are not solved radically by conventional shielding materials. Furthermore, there are currently no ef-
II. EXPERIMENT

As the source CMCs, the as-grown CMCs obtained using a Ni catalyst at 700–800 °C and the CMCs partially oxidized in air at 650 °C were evaluated. The detailed preparation procedure and morphology are shown in Ref. 12. The CMCs were mixed with a polyurethane precursor solution at room temperature and molded in a 150×150 mm² frame placed on an Al plate (1 mm thickness). The thickness of the sample (absorption layer) was 4–7 mm. To examine the effect of the multilayer absorption composites with different absorption layers, different layers with different absorption materials were successively stacked on the Al plate. The reflection loss (absorptivity) of the EM waves was measured using the free space microwave measurement system (JFCC-HVS). The measured EM band regions were 12.4–110 GHz. A schematic of the measurement apparatus is shown in Fig. 1. The measurement sample of 150×150 mm²/Al(1 mm) was placed between two antennas, and the complex dielectric constant ($S_{11}$, $S_{21}$) from the reflected EM wave was obtained. The complex reflection loss ($|S_{11}|$) of the EM waves was calculated by the following equation:

$$|S_{11}| = 20 \log_{10} \sqrt{S_{11}^2 + S_{21}^2} [\text{dB}].$$

The reflection loss of $-20 \text{ dB}$ indicates that 99% of the introduced EM waves are absorbed, and this value is the target value to be attained for the EM absorbers from an industrial point of view.

III. RESULTS AND DISCUSSION

Figure 2 shows the representative scanning electron microscopy image of the used CMCs. The CMCs have a 3D double helical/spiral chiral morphology generally with a coil diameter of 2–10 μm, a coil length of 0.1–3 mm, and no coil gap. The diameter of the carbon fibers constituting the CMCs is 0.03–1.0 μm. The bulk electrical resistivity of the bulk (powder) CMCs is 10–0.1 Ω m, depending on the bulk density.

A. Single-layer EM absorption composites

Figure 3 shows the reflection loss of the CMCs and various carbon materials as reference materials. The carbon materials were embedded into the polyurethane matrix to form a 3 wt % single-layer EM absorption composite. The layer thickness of the EM absorption composite ("thickness" hereafter) was 3.5–4.6 mm. The three kinds of carbon powders (carbons A–C) were supplied from three different carbon makers. The CMCs, carbon powders, and vapor grown carbon fibers (VGCFs) of the straight form have a coil length of 0.3–1 mm, grain size of 1–10 μm, and fiber length of 50–100 μm, respectively. It can be seen that the reflection loss of the carbon powders is below $-5 \text{ dB}$ over the 12–100 GHz regions, indicating no absorptivity. The VGCFs also show a poor reflection loss below $-10 \text{ dB}$ at 52–110 GHz while they show a high reflection loss over $-20 \text{ dB}$ at 23 GHz. On the other hand, the CMCs show high reflection loss over

![FIG. 2. Representative morphology of carbon microcoils.](image)

![FIG. 3. Reflection loss of different carbon materials. Matrix: polyurethane, added amount of carbon microcoils in matrix: 3 wt %, thickness of absorption layers: 3.5–4.6 mm. (a) Carbon microcoils, (b) vapor grown carbon fibers with straight form VGCFs, (c) carbon powder-A, (d) carbon powder-C, and (e) carbon powder-B.](image)
FIG. 4. Effect of the added amount of carbon microcoils on the reflection loss.

-20 dB at 32 and 55 GHz, and over -15 dB at 80 and 100 GHz. That is, the CMCs have an excellent absorptivity in the higher GHz regions while the carbon powders or straight form VGCFs show poor EM absorptivities in the higher GHz regions. Figure 4 shows the effect of the addition amount of the CMCs to the polyurethane matrix in which the thickness was 4.1–5.4 mm. It is found that the samples with a low CMC addition of only 1–2 wt % show very high reflection losses over -20 dB at 55, 75–80, and 96–100 GHz, while the samples with the lower CMC amounts of 0.1–0.5 wt % or above 3 wt % show a low reflection loss of below -10 dB. The needed addition amount of the absorbers to conventional absorbers, such as ferrites, carbon powders, etc., in matrix is usually 20–80 wt % for obtaining a higher reflection loss. The higher addition amount of the EM absorbers in the matrix generally results in the degradation of the mechanical properties and increased density. The low addition of only 1–2 wt % to the matrix is of very high merit for the preparation of light EM absorption composites applicable for the higher GHz regions. Figure 5 shows the effect of the coil length of the CMCs on the reflection loss, in which the addition of the CMCs to a polyurethane matrix was 3 wt % and the thickness was 3.8–4.8 mm. It can be seen that the longer the coil length, the higher the reflection loss.

B. Multilayer EM absorption composite

Making multilayers and thus matching the impedance of the absorption layers is generally used to prepare the EM wave absorption composites for obtaining a higher reflection loss. The CMCs were uniformly mixed with three different carbon sources to form a single-layer composite with the thickness of 6.1 mm, in which the addition amount of the respective carbon materials to the polyurethane matrix was 2 wt %. On the other hand, the CMC layer (addition amount: 2 wt %, thickness: about 1.7 mm) was prepared on the Al plate (1 mm thick) as the first layer and then a carbon-A layer (carbon-A, 2 wt %, about 1.7 mm thick) was prepared on the first CMC layer as the second layer, and then carbon-B and carbon-C layers were successively prepared to form four absorption layers. The total thickness of the multilayers was about 7 mm. The effect of the single and multilayer absorptions on the reflection loss is shown in Fig. 6. It can be seen that for the multilayer sample, the reflection loss of over -20 dB is obtained in 26.5, 35.4, 52.4, and 92.4–110 GHz, while for a single layer sample, the reflection loss of over -20 dB was obtained at only 29.1 GHz. That is, the absorption band and absorptivity can be increased by making multilayers of the absorption composites, probably caused by the matching of the impedance of the respective absorption layers. Figure 7 shows the reflection loss of different multilayer composites with a 2 wt % addition. Of the different

FIG. 5. Effect of coil length on the reflection loss. Coil length: (a) 0.15–0.3, (b) 0.6–0.15, (c) <0.09, (d) 0.3–0.5, (e) 0.5–1.0, and (f) >1 mm.

FIG. 6. Difference in EM reflection loss between single layer and s. Added amount of CMCs: 2 wt %. (a) s (Al/CMC/carbon-A/carbon-B/carbon-C), total thickness: 7 mm. (b) Single layer (CMC and three carbon powder was uniformly mixed), thickness: 6.1 mm.
multilayer composites, sample (a) (Al/Cmcs/Carbon-A/Carbon-B/Carbon-C) showed the highest reflection loss at various bands. On the other hand, sample (c) (VGCF/Carbon-A/Carbon-B/Carbon-C), in which straight VGCFs are used as substitutes of the CMCS scarcely absorb the EM waves. These critical differences in the EM absorption between the two kinds of carbon fibers; coiled fiber (CMC) and straight fiber (VGCF) may be caused by the difference in the interaction with EM waves as will be discussed later.

C. Reproducibility of absorption property

It was sometimes observed that the reproducibility of the reflection loss of the absorber, which was prepared using the same materials and same preparation procedure of the composite, was different from sample to sample. Figure 8 shows the reflection loss of the three samples of the single-layer CMC composites (addition amount: 1.5 wt%) prepared using the same preparation procedure. It can be seen that the absorption bands and the strength are different for the three samples. One reason may be that, in this study, the thickness of the sample, which affects the dielectric constant and thus the reflection loss, was not strictly controlled as a constant value. Another reason may be the different dispersibility of the CMCS in the polyurethane matrix from sample to sample. The latter is mainly caused by the poor chemical activity and wettability of the CMCS in the polyurethane matrix. It is well known that the carbon substances can be partially oxidized to increase their chemical activity and wettability by organic solvents or polymers. The CMCS were partially oxidized in air at 650 °C for 30 min and three samples of the CMCS addition amount of 1.5 wt% in the polyurethane were prepared. The reflection loss of the partially oxidized CMCS is shown in Fig. 9, the high reproducibility of the reflection loss can be seen. The difference in the absorption band of the partially oxidized CMCS is 3.9 GHz (for 55.8–59.7 GHz) –7.7 GHz (for 76.6–84.3 GHz), while 5.6 GHz (for 55-61.1 GHz) –11.5 GHz (for 76.5–88.0 GHz) for the as-grown CMCS (see Fig. 8). This effect may be caused by the uniform dispersion of the CMC in the matrix. Figure 10 shows the reflection loss of the partially oxidized CMCS at 650 °C for 60 min. It can be seen that by 60 min oxidation the reproducibility of the absorption band and the absorptivity are decreased, in comparing to that of the 30 min oxidation.

The reflection loss of the same sample was measured after just its preparation, and after 120, 240, and 300 days exposure in the atmosphere (Fig. 11), in which the sample is the multilayer composite material with the Al/Cmcs/Carbon-A/Carbon-B/Carbon-C stacking layers and the added amount is 2 wt%. The thickness of the sample slightly decreased from 7.0 mm just after the preparation to 5.8 mm after 240
and 300 days. It can be seen that the absorption band shifts by 9.2–11.6 GHz to a higher frequency with the increasing exposure times and attained a constant band after 240 days, and also the reflection loss increases with the increasing exposure times for the 51–80 GHz band.

D. Absorption mechanism

Materials generally absorb the EM waves by the three mechanisms, i.e., dielectric loss, conductive loss and magnetic loss. The CMCs are typical chiral materials with a microcoiling morphology and shows different interactions from unchiral materials against EM waves. Tsuda et al. have found that an electromotive force was induced when the CMCs were exposed to the alternative EM waves of 1–1000 Hz.\textsuperscript{21} Accordingly, it is reasonably considered that when EM waves are irradiated on CMCs, the CMCs will act as chiral microcoils (microsolenoid) and an inductive electromotive force and thus an inductive current is induced in the CMCs according to the Faraday’s law. For the most effective generation of an inductive current, the coiling-chiral morphology of the fibers is considered to be a more favorable form than that of the straight or powder-like form.

The EM waves irradiated on CMCs are effectively polarized to form straight and/or circular polarized waves; right-handed (RCP) or left-handed (LCP) waves, and are also reflected or dispersed at the same time, resulting in being sharply attenuated as shown in Fig. 12. Varadan et al. extensively studied on the interaction of EM waves with the chiral materials, especially on the EM wave polarization phenomena by the chiral materials.\textsuperscript{22–28} They proposed the relationship between the speed of introduced EM waves and the speed of EM waves polarized by the irradiated materials as follows:

for the coiling-chiral materials,
\[ \nu_{\text{LP}} \neq \nu_{\text{LCP}} + \nu_{\text{RCP}}, \quad \nu_{\text{LCP}} \neq \nu_{\text{RCP}}, \]
for the nonchiral materials, \[ \nu_{\text{LP}} = \nu_{\text{LCP}} + \nu_{\text{RCP}}, \]
where \( \nu_{\text{LP}} \), \( \nu_{\text{LCP}} \), and \( \nu_{\text{RCP}} \) is the speed of the linear polarized wave (LP), right-handed polarized wave (RCP) and left-handed polarized wave (LCP), respectively. These equations suggest that the EM waves can be attenuated much more effectively by the coiling-chiral materials such as CMCs than by the nonchiral materials. Furthermore, the CMCs are oriented in different directions and thus can effectively attenuate EM waves even if EM waves are irradiated from any direction. The CMCs can effectively absorb the EM waves of the 12–110 GHz bands as already shown. The coil diameter of the CMCs is 2–10 μm and the coil length is 0.1–3 mm, while the wavelength of the EM waves of 10 GHz is 3 cm and of 100 GHz is 0.3 mm. That is, the CMC can absorb EM waves with wave length of two or three orders of magnitude greater than that of the CMCs dimensions. The CMCs used in this study have almost the same number of right-handed and left-handed coiling morphologies. The correlation of the coiling chirality of the CMCs with EM waves is not well known. However, it is considered that the EM absorption materials must have a chiral structure and high chiral parameters to obtain an effective absorption ability in the GHz regions. In the case of the materials with a 3D-helical/spiral structure, the optimum relationship between the coil diameter (\( D_c \)), coil pitch (\( P \)), and fiber diameter (\( D_f \)) are \( D_f / D_c = 0.1–0.2 \) and \( P / D_c = 3 \).\textsuperscript{23} The ratio of the \( P / D_c \) of the used CMCs is smaller than these values. Accordingly, the CMCs have a better larger coil pitch, coil diameter, and coil length for obtaining a higher absorption property.

IV. CONCLUSION

High-performance EM absorbers applicable to the EM waves in the GHz regions were developed. It was found that the target value of the reflection loss over 20dB (above 99% absorption) in 30–35, 50–55, 75–80, and 95–100 GHz for commercial applications can be attained using a sample of only 1–2 wt % (carbon coils)/polyurethane. The CMCs addition amount of more than 3 wt % resulted in a decreased EM absorptivity, because of the increase in the reflection of the EM waves. Multilayer absorbers showed a higher EM absorptivity than that of a single absorber. The longer the
coil length, the higher the absorptivity could be obtained. The absorption mechanism of the EM waves by the CMCs is discussed. The high reproducibility of the reflection loss can be obtained by the partial oxidation of the CMCs.

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