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Microwave absorption of carbon nanotube/photopolymer composites

Houmin Li, Yuanyuan Zhang, Kaiqiang Zhu, Xixi Feng, and Hou-Jun Sun

A novel additive manufacturing approach can be used to fabricate samples in any shape and is a promising methodology for the design of microwave-absorbing material structures.

In recent years, the problems of electromagnetic interference and electromagnetic compatibility (caused by the excessive use of electromagnetic devices) have seriously affected wireless communications and human health. High-performing microwave-absorbing materials (MAMs) have therefore become particularly important in both military and civilian applications.¹⁻³ In previous studies, carbon nanotubes (CNTs) have been used as a promising dopant, together with many kinds of polymer matrix materials, to form composite MAMs.^{4,5} MAMs can be classified as either electric-loss or magnetic-loss materials. The former class typically contain dopants such as nanoconductive graphite powder, silicon carbide fiber, or CNTs, whereas the latter group typically contain nanoferrite powder, magnetic metal powder, or magnetic fibers.⁶ In practice, the microwave-absorbing capabilities of conventional MAMs are limited by their 2D sheet geometry. To maximize microwave absorption and prevent unwanted interference, 3D shapes that fit specific project space limitations are greatly desired.

Additive manufacturing (AM) is an innovative technology with which objects can be manufactured through the accumulation of successive layers of materials (e.g., 3D printing). Compared with traditional MAM fabrication methods (e.g., conventional sheet manipulation processes), 3D printing offers the advantages of fast shaping and fitting to almost any 3D shape requirements. By including as much microwave-absorbing composite material as possible into a project's allowed space, the overall microwave-absorbing capability can be greatly improved. To date, metal, ceramic, and carbon nanomaterials have been incorporated into several AM technologies that include laser sintering, fused filament fabrication, and stereolithography (SLA). With these AM approaches, the properties of the final fabricated parts are greatly affected by the addition of nanostructured materials.^{7,8}



Figure 1. Free-space time-domain reflectivity measurements from the carbon nanotube (CNT)/photopolymer composites. The reflection difference results are shown as a function of CNT content for samples with different thicknesses (i.e., 3, 6, and 9mm) at frequencies of (a) 4-8GHz, (b) 8-12GHz, and (c) 12-18GHz.

In our study,³ we have used a novel AM procedure to fabricate a composite MAM. In our SLA approach we mixed acrylic ester and CNTs to form the liquid photopolymer resin. After a controlled

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exposure the resin solidified and formed the computed shape, i.e., with a 40 \times 60mm cross section and a thickness of 3, 6, or 9mm. We were thus able to investigate the microwave-absorption properties of the CNT/photopolymer resins (with CNT content of 0.5, 1.0, and 1.5wt%) that we produced. To achieve uniform dispersion of the CNTs in the acrylic ester matrix—which is critical for achieving appropriate printing and improved absorption properties⁹—we used an AD200S-H homogenizer (for 15 minutes, before printing) to homogenize the CNT/photopolymer resin. In addition, the printing concentration threshold of the MiiCraft 3D printer that we used with our CNT/photopolymer resin was 1.6wt% CNTs.

After completing the fabrication process, we measured the reflectivity of our CNT/photopolymer composites over the 4–18GHz frequency range. To make these measurements we used a microwave anechoic chamber, with an Anritsu MS2028B vector network analyzer (VNA) and the free-space method with a time-domain grating. Our measured free-space time-domain reflectivity results are shown in Figure 1. In general, we find that the reflectivity decreases with increasing CNT content and with the thickness of the composites (in the



Figure 2. The (a) imaginary (ε'') and (b) real (ε') parts of the permittivity of the CNT/photopolymer composites (with 0.5, 1.0, and 1.5wt% CNTs), shown as a function of frequency.

4–8GHz range). In the 8–12GHz range, the maximum absorption we achieved was 15.98dB for the 6mm-thick composites with a 1.5wt% CNT content. For the 9mm-thick composites with 1.5wt% CNTs, the samples exhibited less absorption at 12–18GHz than at 8–12GHz.

As part of our study, we also used an Agilent E8363B VNA, a 7mm Agilent 85051 air coaxial verification kit, and the Agilent 85071E material-property testing software to measure the permittivity of our composites (from 4–18GHz). To do this, we prepared coaxial cylinder samples (with inner diameter of 3mm, outer diameter of 7mm, and height of 5mm) of our photopolymer composites. We then fitted the cylinders in the 85051 kits and used the VNA to measure the reflection coefficients. Lastly, we used the software to calculate the corresponding electromagnetic parameters.

The real (ε') and imaginary (ε'') permittivity results we obtained (from 4 to 18GHz) are shown in Figure 2. These results exhibit a positive correlation between ε' or ε'' and the CNT content of the samples. This means that the absorption of microwaves increases as the conductive filler content increases. In particular, we find that as the CNT content increases from 0.5 to 1.5wt%, ε' increases from 2 to 6 and ε'' increases from 0.2 to 0.8. For the composites that contain 0.5wt% CNTs, the ε'' curves fluctuate in the low-frequency range and there is one absorbing peak at 17.6GHz. The ε'' curves for the 1.0 and 1.5wt% CNT composites, however, include two absorption peaks in the 4-18GHz range. Although there are a number of fluctuations at the low-frequency range, the overall variation of permittivity in the samples is small and these fluctuations do not change our overall conclusion that both ε' and ε'' vary as a function of CNT content. Our results thus confirm that the CNT/photopolymer composites can be classified as dielectric-loss materials.

In summary, we have investigated the microwave-absorbing properties of CNT/photopolymer composites with different thicknesses that we fabricated using a novel AM procedure. Our fabrication method can be used to form the composite material into any shape and is a promising future method for the design of MAM structures. Our results also indicate that the polarization relaxation of the CNT/photopolymer is a wideband absorption effect. Although the fabricated structure we have studied is still planar (for the ease of investigation and measurement), it is possible to produce any 3D-shaped MAM composite structure with our proposed AM method. To fully utilize this absorption effect, we recommend the use of broadband matching structures (e.g., pyramidal cones) and project-specific volume shapes to maximize composite volume for optimum absorption performance. In our future work we will aim to increase the CNT content of the composites and to further improve the uniform distribution of the CNTs within the matrix.

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Author Information

Houmin Li, Yuanyuan Zhang, Kaiqiang Zhu, Xixi Feng, and Hou-Jun Sun

Beijing Institute of Technology Beijing, China

Houmin Li received his PhD from Auburn University in 2011 and then joined the faculty of the Beijing Institute of Technology. His research interests include advanced electromagnetic materials, low-loss broadband microwave and millimeter-wave circuits, and advanced manufacturing of microwave and millimeter-wave components (3D-printed circuits).

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