Journal of Applied Polymer Science

Effect of Low-Content Carbon Nanotubes on the Dielectric and Microwave Absorption Properties of Graphite/Polymer Nanocomposites

A. A. Khurram,[1] Sobia A. Rakha,[1] Naveed Ali,[1] Peiheng Zhou,[2] Arshad Munir[1,3]

[1]Experimental Physics Labs, National Centre for Physics, Islamabad 45320, Islamic Republic of Pakistan

[2]School of Micro-Electronics and Solid-State Electronics, University of Electronic Science and Technology of China, North Jianshe Rd, Chengdu 610054, People's Republic of China

[3]Centre of Excellence in Science and Advance Technologies, Islamabad 45320, Islamic Republic of Pakistan

Correspondence to: S. A. Rakha (E-mail: sobiaqau@gmail.com)

ABSTRACT: Honeycomb cores (HCs) coated with graphite and multiwalled carbon nanotubes (MWCNTs) filled in a thermoplastic resin are proposed as microwave absorbers. The MWCNT contents varied from 0.2 to 0.6 wt % in a graphite-filled (15 wt %) thermoplastic resin. The HCs were coated with three different types of coating materials for the sake of comparison: graphite, MWCNTs, and graphite plus MWCNTs. The dielectric properties [the real and imaginary parts of complex permittivity (ε' and ε'', respectively)] and reflection loss (RL) of all of the coated HCs were measured and compared. We observed that the permittivities and RL increased significantly with increased weight percentage of the MWCNTs in the graphite-filled thermoplastic resin. The RL measurements showed a maximum loss of −20 dB around 7 GHz and a bandwidth of 2.7 GHz at −10 dB in the HCs coated with the 0.4 wt % MWCNT plus graphite. There was also a shift in the RL peak position from the x band to the c band after the increase of MWCNT content. We also observed from the measurements that a combination of graphite and MWCNTs resulted in a broadband microwave absorber; a bandwidth of 13 GHz was observed for 80% RL when the MWCNT content increased to 0.6 wt % in the graphite-incorporated resin. The possible mechanism that increased RL with the incorporation of MWCNTs in the graphite-mixed thermoplastic resin is discussed. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40891.

KEYWORDS: applications; dielectric properties; graphene and fullerenes; morphology; nanotubes

Received 9 January 2014; accepted 21 April 2014

DOI: 10.1002/app.40891

INTRODUCTION

Radar-absorbing structures (RASs) are lightweight multifunctional structures, which not only absorb the incoming microwaves from radar but are also used for load-bearing applications. They often replace the higher density structural material of a traditional aircraft and result in much lighter structures.[1] Honeycomb core (HC) as a RAS is widely used because of its high strength-to-weight ratio and stiffness; this provides low-density support for absorbing materials. The advantage of honeycomb RAS is the depth without additional weight.[2] A honeycomb RAS consists of a top skin that is transparent to microwaves and a lower skin made of a carbon fiber/epoxy composite, which acts as a perfect reflector. The cores of the honeycomb between these two skins are coated with an absorbent material (uniformly coated or with a gradient in the thickness of the coating). The microwaves, once they have entered the coated honeycomb, are barely able to come out because of internal reflections and subsequent absorption. In the available literature, honeycomb-based microwave absorbers have been prepared with carbon black,[3] metal magnetic particles (MMPs),[4] a mixture of MMPs and carbonyl iron/nickel fibers,[5] and a carbon slurry filled in the HCs.[6] In a report,[3] HCs coated with carbon black mixed in various chemicals resulted in maximum attenuation of −20 dB. HCs coated with MMPs[4] up to 90 wt % resulted in a maximum reflection loss (RL) of −45 dB but a very narrow bandwidth. In a similar work,[5] HCs were filled with MMPs and carbonyl iron/nickel fibers at 40 wt %; the resulting RL was −10 dB over a very narrow frequency range. HCs coated with lossy dielectric or magnetic fillers incorporated in polymer composites are one of the most useful structural materials for the fabrication of parts of modern war planes.[7,8]

Research has focused on polymer composites filled with nanoparticles for quite a long time and their microwave absorption properties in the frequency region of 2–18 GHz.[9,10] The use of carbon-based nanofillers in polymeric matrices has arisen during the last decade with tailored electromagnetic properties, particularly in the microwave range. Among various carbon-based

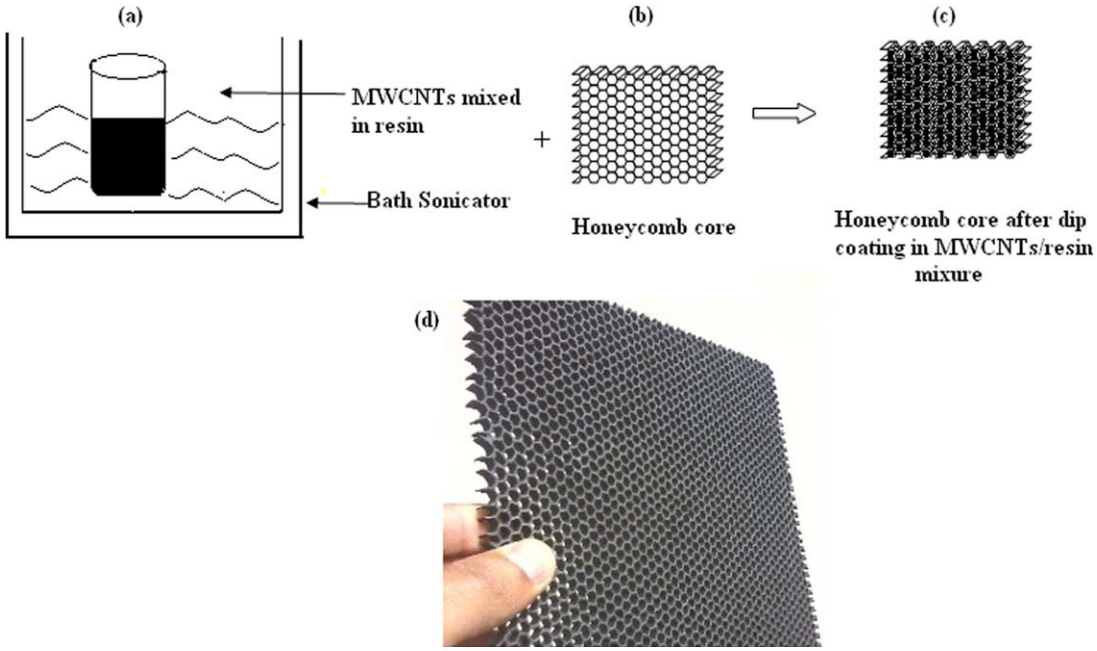

Figure 1. Manufacturing process of the honeycomb coating with thermoplastic resin filled with MWCNTs and graphite: (a) mixing of the MWCNTs in the resin, (b) HCs, (c) coating of the honeycomb by a dipping method, and (d) photograph of the coated honeycomb after drying and curing in the oven for 7 h at 105°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanostructures, multiwalled carbon nanotubes (MWCNTs) have become very attractive for the development of novel polymer composites because of their enormous mechanical strength and higher electrical and thermal conductivities.[11] MWCNTs have the tendency to form percolated networks,[12] and these network-like structures aid in the improvement of the electrical properties of the composites. However, network structures cannot be achieved with a very low concentration of MWCNTs. Attempts to use binary fillers in the polymer matrix have been made to improve network structures and hence to achieve a better performance in composites.[13,14] In previous studies, RASs have been developed through the incorporation of MWCNTs as dielectric fillers in woven glass fiber/epoxy composites. These structures were in the form of multilayers, Salisbury screens with a dielectric spacer, and composites with the uniform filling of the MWCNTs.[15] In that approach, the concentration of MWCNTs was varied to achieve the desired level of the complex permittivity for maximum microwave absorption. The disadvantage of these structures is their thickness (2–5 mm or even more), and this results in an increase in the weight.

In this study, three different types of coated HCs were prepared: graphite-coated, MWCNT-coated, and graphite plus MWNCTs. The objective of the use of a combination of MWCNTs and graphite was to use MWCNTs as an enhancer of the dielectric properties (complex permittivity) of the graphite coating.

EXPERIMENTAL

Materials and Methods

The MWCNTs were purchased from Chengdu Organic Chemicals Co., Ltd. (China). The outer diameter of the tubes was 15 nm, the length was 10–200 μm, and the purity was greater than 95%. High-purity graphite powder with a particle size of less than 20 μm was purchased from Sigma Aldrich (Germany). The graphite powder was mixed in a thermoplastic resin in 15 wt % with a high-speed mixer for 1 h. MWCNTs in 0.2, 0.4, and 0.6 wt % were dispersed in the graphite-mixed resin by sonication for 1 h. Nomex honeycombs (core size = 5.5 mm) with a 5-mm thickness were purchased from Armicore (China). Three different types of coated HCs were prepared: graphite-coated, MWCNT-coated, and graphite plus MWNCTs. These three groups of honeycombs were labeled as honeycomb–graphite (HC–G), honeycomb–carbon nanotubes (HC–CNTs), and honeycomb–graphite–carbon nanotubes (HC–GCNTs), respectively. Figure 1 shows the schematic of the manufacturing process. The coated HCs were then left overnight at room temperature. Further curing was done under a heating cycle at 105°C for 7 h in an oven. The coated honeycombs were used in sandwich panels. These panels were prepared with a carbon-fiber-reinforced epoxy composite as a reflector plate at the bottom and a glass-fiber-reinforced epoxy composite as a transmission layer on the top. The carbon fiber/epoxy and glass fiber/epoxy composite sheets were prepared with vacuum-assisted resin-transfer molding. The thickness of both composite sheets was 1 mm.

Characterization

The RL in the 2–18-GHz frequency range was measured by a free-space method with an NRL Arch reflectivity test setup [Figure 2(a)]. The scattering parameter (S11) of the panels was measured backed by an aluminum plate as a perfect reflector. The samples were tested for the measurements of the complex permittivity with a vector network analyzer in the frequency range 8–12 GHz with the free-space method without a perfect electrical conductor plate [Figure 2(b)]. The standard size of the sample specimens for the holder was 190 × 190 mm^2. The system used spot-focusing horn lens antennas to minimize

Figure 2. Free-space measurement system: (a) RL measurements and (b) complex permittivity measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

diffraction effects. The surface morphology of the hybrid nanocomposites was investigated with scanning electron microscopy (SEM; JED 2300). The direct-current (dc) conductivity of the coated samples was measured with a four-probe method in linear geometry with a Keithley 2401 source and measurement unit. Rectangular plates with dimensions of 50 × 25 mm^2 were prepared.

RESULTS AND DISCUSSION

HC–GCNT Series

The dc electrical conductivity measurements of the honeycomb coating as a function of the carbon nanotube (CNT) content is shown in Figure 3. As shown, the conductivity increased with increasing MWCNT content in the graphite-filled thermoplastic resin. At a 0.6 wt % MWCNT content, there was a sudden increase in the conductivity (ca. 72%); this was an indication of the formation of a conductive network between the graphite grains by the MWCNTs.

There were four different honeycomb samples: HC–G, HC–GCNT (0.2), HC–GCNT (0.4), and HC–GCNT (0.6). The ε measurements and tangent loss of HC–G, HC–GCNT (0.2), HC–GCNT (0.4), and HC–GCNT (0.6) are shown in Figure 4(a–c), respectively. The number in the parenthesis indicates the concentration of MWCNTs. Eor example, HC-GCNT (0.2) indicates 0.2 wt. % MWCNTs concentration in the resin. The imaginary permittivity (ε''), which is the dielectric loss factor, contributed toward the absorption of the microwaves. As shown, both the real part of the complex permittivity, or the effective permittivity (ε'), and the ε'' significantly increased with increasing MWCNT content in the graphite coating. The tangent loss, which is a measure of the loss of microwaves in the HCs, also increased with increasing MWCNT content. The factors taking part in the increase of ε' and ε'' are discussed separately in the following.

In our system, MWCNTs played the role of dielectric media. In an applied field, mobile charge carriers in dielectric material migrate, but their motion is restricted at the surfaces or at grain boundaries. The accumulation of charge carriers at the interfaces between the MWCNTs and the host matrix resulted in the polarization known as *interfacial or space charge polarization*. In our system, nanotube polymer interfaces were abundant; this resulted in significant interfacial polarization. The lattice imperfections of the MWCNTs also had strong effects on the dielectric properties[16] and, hence, on the microwave absorption properties of the composite. In our samples, lattice imperfections, that is, twisted and interconnected MWCNTs [as can be seen from the SEM image of as received MWCNTs in the inset of Figure 5(a)] and foreign impurity atoms (as observed from the X-ray diffraction spectrum of the as-received nanotubes not shown here) collectively played the role of defects. These defects acted as tiny dipoles or polarized centers under the electromagnetic field and contributed toward the increase in ε'. Therefore, polarizations due to defects and interfaces were present in our system and gave rise to the increase in ε'. By increasing the MWCNTs concentration, we increased the number of tubes, and as a result, both types of polarizations that is, interfacial and defect polarizations also increased.

The increase in ε'' with the addition of MWCNTs was also due to two factors, that is, defects present in MWCNTs and the

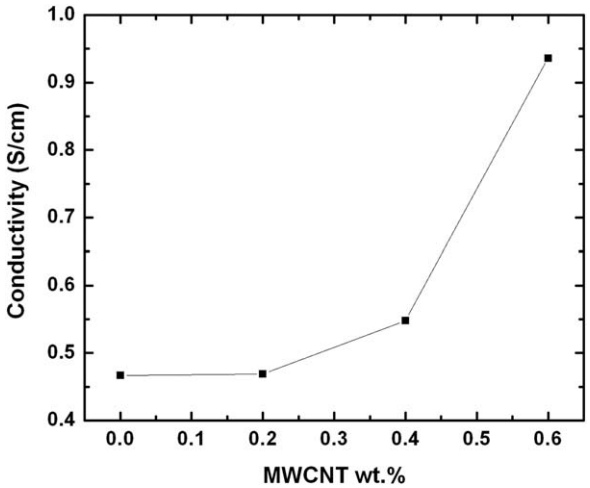

Figure 3. dc electrical conductivity measurements as a function of the MWCNT content in the graphite-filled polymer.

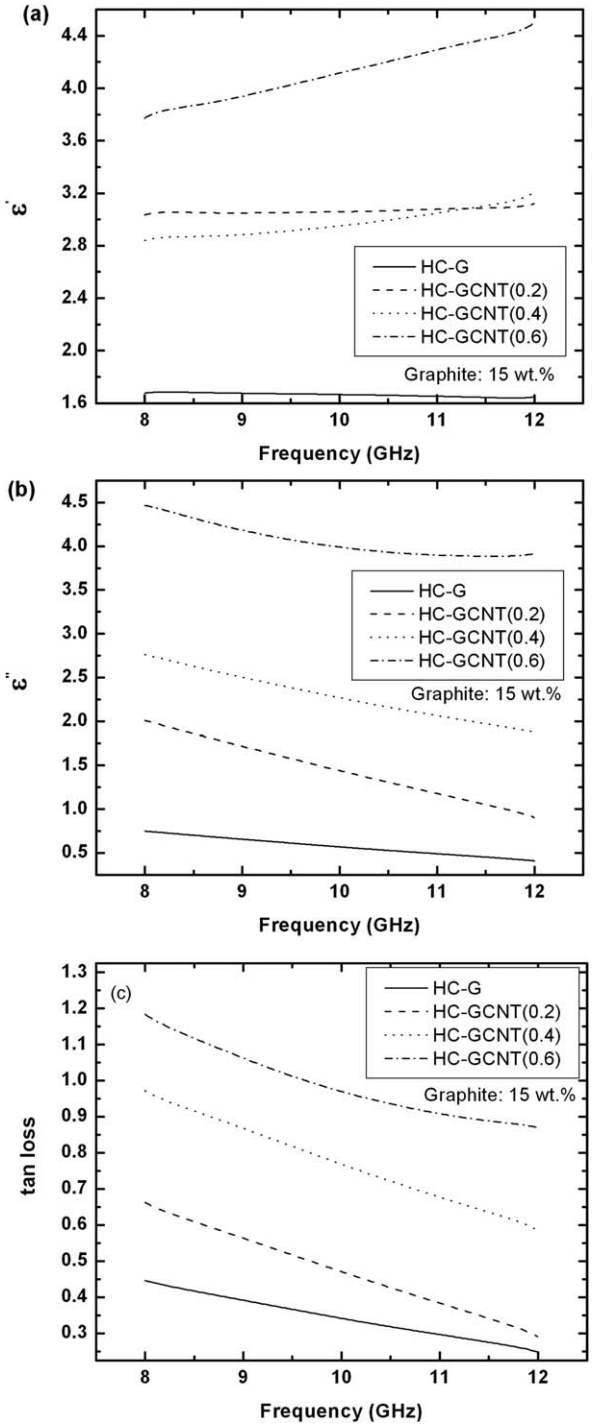

Figure 4. Complex permittivity of the MWCNT-added, graphite-coated HCs as a function of the measured frequency: (a) ε', (b) ε'', and (c) tangent loss.

increase in the conductive networks through the formation of interconnected networks among graphite sheets. It was reported in the literature that in the defected MWCNTs, the transport mechnaism was controlled by the migration of electrons in the MWCNT walls and by hopping electrons distributed in the lattice-imperfect region.[16] Lattice imperfections, that is, twisted and interconnected MWCNTs, and the presence of foreign impurity atoms were the type of defects present in our MWCNTs. According to the theory, these defects collectively took part in the creation of additional energy states near Fermi level,[17] and electromagnetic energy was absorbed by the transition from these localized states to the Fermi level when the electromagnetic radiations were incident on the absorber surface. The sufficient creation of such states resulted in increased conduction by electron motion to such states, and hence, ε'' increased.

In the HCs coated with MWCNTs and graphite, resistive loss was dominant because a relatively large amount of graphite already produced a conducting network in the polymer. The addition of MWCNTs enhanced this network (as was obvious from the increase in conductivity) by bridging the graphite sheets [Figure 5(c)]. These network or interconnections interacted with incident radiation and led to a higher electromagnetic absorption. Because of the small concentration of nanotubes, there was a rare chance for the nanotubes to form their own networks. Hence, MWCNTs, because of their higher aspect ratio and electrical conductivity and the presence of defects contributed to microwave absorption in three ways: by the formation of interfaces (interfacial polarization), by the resistive losses through conducting network of CNTs, and by the presence of defects (taking part in increasing both ε' and ε'').

The SEM micrographs of the coated honeycomb HC–GCNT (0.6) are shown in Figure 5(a,b). The SEM image of the MWCNTs used in this study is also shown in the inset of Figure 5(a). Debonding between the matrix and graphite sheets (the word *sheet* is used because of the microstructure of the graphite grains) at different locations was also observed, as indicated by an arrow in Figure 5(a). This revealed the dense structures composed of many graphite sublayers. Although the graphite sheets were dispersed in the matrix in the form of bundles, the degree of dispersion was, in general, satisfactory. These graphite sheets immersed in the polymer matrix are shown at high magnification in Figure 5(b); this allowed the formation of the electrical conducting network within the matrix. The MWCNTs were also observed in the matrix connecting the sheets through the epoxy matrix, as indicated by the circle and arrow. The circle highlighted the region where a nanotube bridged the graphite sheet through the polymer matrix. A possible reason for the increase in the conductivity with the small incorporation of MWCNTs was the formation of network among the disconnected graphite sheets enhanced by the MWCNT bridging. The MWCNTs were favored in the vicinity of the graphite sheets because of the π–π interaction between the MWCNTs and graphite sheets. The schematic in Figure 5(c) shows that the mechanism of such interconnections between the graphite sheets through the MWCNTs in the polymer matrix. The effect of this interconnection was also observed from the increase in the dc electrical conductivity with increasing MWCNT content [Figure 3].

The RL measurements in the 2–18-GHz range of all four samples are shown in Figure 6. The HCs coated only with graphite showed only a very small RL in the whole frequency range: −6.37 dB (77%) was the maximum RL with a very narrow

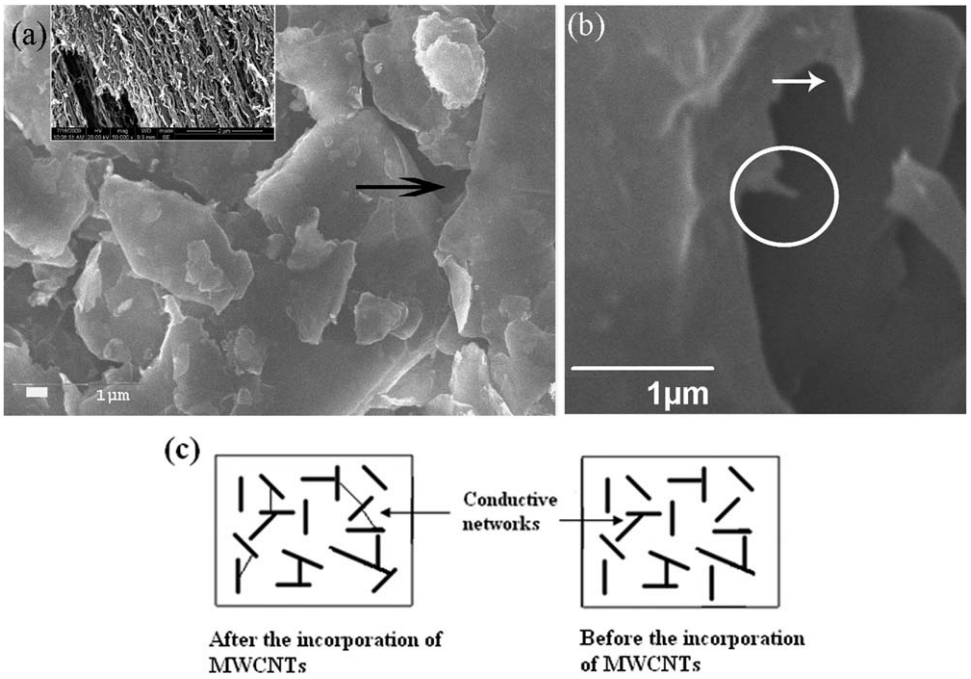

Figure 5. SEM micrographs of HC–GCNT (0.6) with (a) low magnification and (b) higher magnification. (c) Schematic showing the possible interconnects formed between graphite sheets by the MWCNTs: (a) MWCNTs + graphite and (b) graphite.

bandwidth. However, the addition of the MWCNTs in the graphite resulted in a large increase in the RL and the bandwidth. Moreover, all of the MWCNT-coated samples showed two matching frequencies, one around 6.5 GHz and the second around 11 GHz. The maximum RL in all of the MWCNT-coated HCs appeared around 6.5 GHz (C band). The magnitude of RL and the −10 dB (90% attenuation) bandwidth increased with increasing MWCNTs up to 0.4 wt % (RL = −20 dB, −10 dB bandwidth = 2.7 GHz). These values decreased to −16.8 dB and 2.46 GHz, respectively, in the HCs coated with 0.6 wt % MWCNTs, whereas the highest bandwidth (13 GHz) for 80% RL was observed in the HCs coated with 0.6 wt % MWCNTs. The matching frequency also shifted to a lower frequency for all of the samples after the addition of the MWCNTs in the coating matrix. The results of the RL measurements are summarized in Table I. The decrease in the maximum reflection loss $[(RL)_{max}]$ with increasing MWCNTs above 0.4 wt % could be explained by the following equation:

$$(RL)_{max} = 20 \log [1 - 4/(2 + \varepsilon''(\tan \delta + 1/\tan \delta))] \quad (1)$$

Equation (1) shows that the optimized ε'' and loss tangents were required to achieve the maximum RL; a very large value of ε'' led to reflection instead of absorption, and a very small ε'' did not favor absorption.[18] This was the possible reason that the honeycomb with highest ε'' showed a lower absorption as compared to that filled with 0.4 wt % MWCNTs. Similarly, the filler concentration also influenced the absorption bandwidth.[19] The variations in the MWCNT content could be used to manipulate the absorption bandwidth. These results show that 0.6 wt % of the MWNCTs resulted in a higher bandwidth of 13 GHz for the 80% RL of the microwaves. This work resulted in the enhanced microwave absorption properties of HCs as compared to the previous results of similar work in which HCs were coated or filled with lossy magnetic/dielectric materials in high weight percentages through complicated and longer processes.[7–10]

HC–CNT Series

The ε' measurements and tan loss of the HC–CNTs for 0.4 ad 0.6 wt % in 8–12 GHz (x band) are shown in Figure 7(a–c). The results of the 0.2 wt % MWCNT-coated honeycomb are not included because it was difficult to coat with such a small concentration and the results were also not reproducible. The HCs coated with a higher concentration of MWCNTs in the resin had higher values of ε' and ε''. The tangent loss ($\varepsilon'/\varepsilon''$), which ultimately determined the microwave losses, was also higher for the HCs coated with 0.6 wt % MWCNTs. It was observed in both samples that ε' and ε'' had a maximum at a certain frequency because we tested ε' for the sample; this

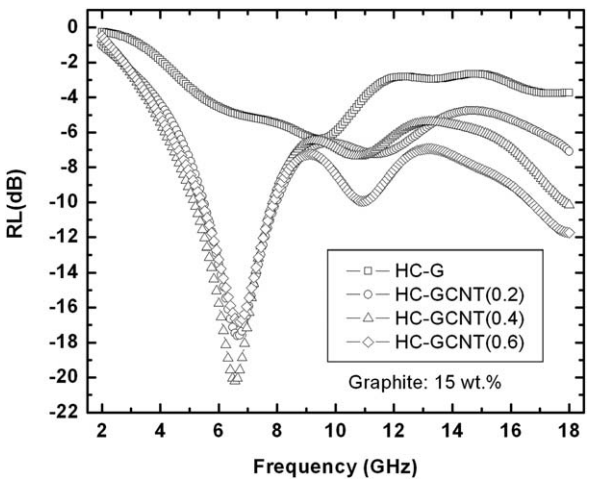

Figure 6. Results of the RL measurements of the HCs coated with the MWCNTs and graphite-filled polymer resin.

Table I. Summary of the Results of the Complex Permittivity and RL Measurements of the MWCNTs and the Graphite-Coated HCs

MWCNT (wt %)	f_1 (GHz)	RL (at f_1)	f_2 (GHz)	RL (at f_2)	Bandwidth (GHz) for 90% RL	Bandwidth (GHz) for 80% RL
0	9.44	−6.37	13.36	−3	—	—
0.2	6.64	−17.61	11.44	−7.22	2.46	4
0.4	6.56	−20.2	10.8	−7.36	2.7	4.25
0.6	6.72	−16.8	10.96	−9.94	2.46	13

f_1 and f_2 are the matching frequencies where the first and second maximum of reflection losses appear.

included the honeycomb frame, absorbing coating, and air holes. It was possible to have electric resonance because of the magnetic (H) field or electric (E) field or both field oscillations induced by their spatial distribution in the sample. The HCs coated only with MWCNTs had lower values of the complex permittivity compared to those coated with a mixture of graphite and MWCNTs. The probable reason was that at this smaller MWCNT concentration, the formation of the insulating polymer layer between the MWCNTs decreased the tunneling conductivity, and this resulted in in a smaller ε''.[20] The case for ε' was similar; this was higher in HC–GCNTs because of the combined effects of the MWCNTs and micrometer-sized graphite.

The electron micrograph of HC–CNT (0.6) is shown in Figure 8(a). As shown, the CNTs were uniformly dispersed in the thermoplastic resin. The reason for the smaller complex permittivity and RL in the HCs coated only with MWCNTs was the nonuniformity of the coating. As shown in the schematic in Figure 8(a), small islands of MWCNTs were formed; they could not provide conducting networks. The RL measurements are also shown in Figure 8(b). The RL increased by 0.6 wt % to −4.25 dB. The matching frequency was observed around 10 GHz. Because the matching frequency and the magnitude of RL both depended on the dielectric loss factor and the tan loss, the smaller RL in the HC–CNT honeycombs was obvious.

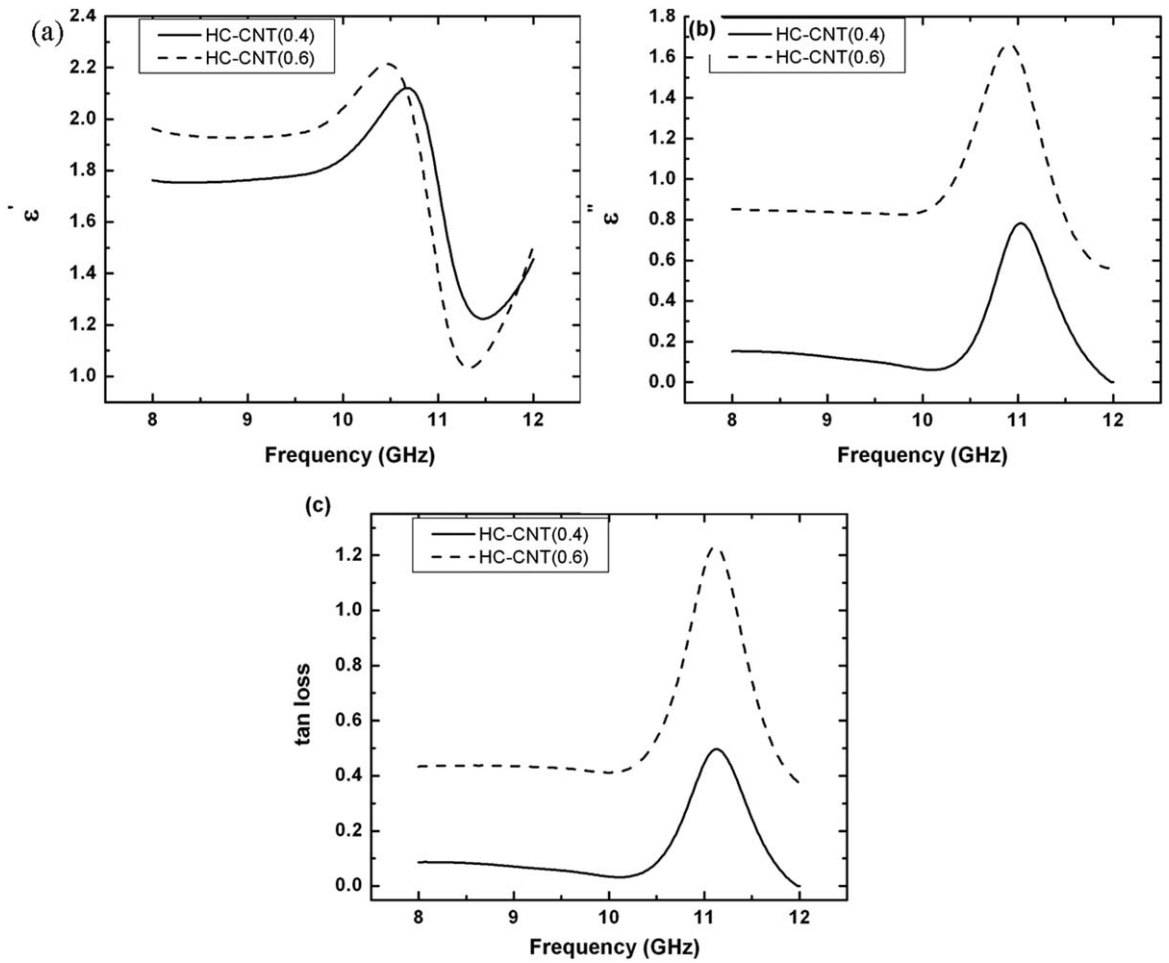

Figure 7. Complex permittivity of the MWCNT-coated HCs as a function of the measured frequency: (a) ε', (b) ε'', and (c) tangent loss.

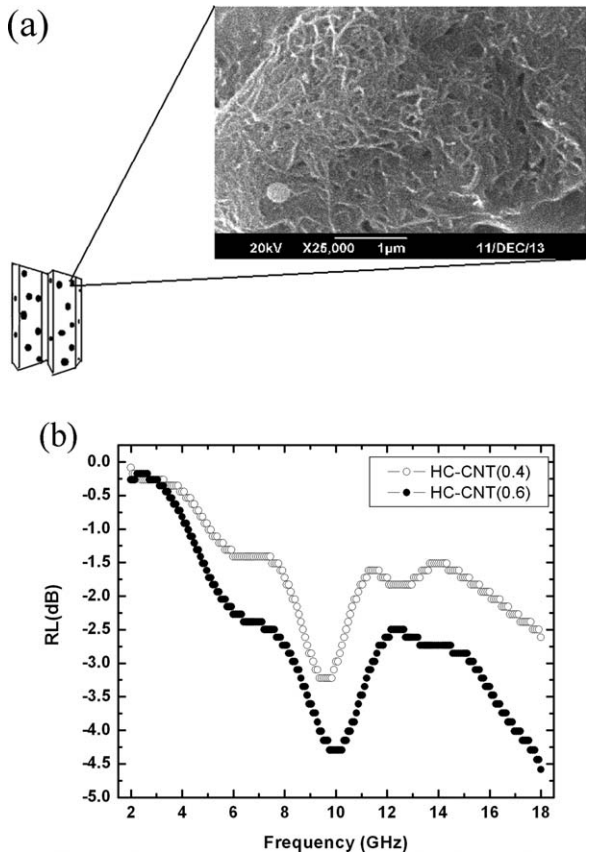

Figure 8. (a) SEM micrograph of the HC–CNT (0.6) honeycomb sample. (b) Results of the RL measurements of the HCs coated with the MWCNT-filled polymer resin.

CONCLUSIONS

In this study, we used the MWCNTs and graphite powder for honeycomb coating through a very simple and fast process for electromagnetic absorption. We optimized the MWCNT content, that is, less than 1% when added in the graphite-filled resin to achieve the maximum RL and higher bandwidth. The −20-dB RL and 2.7-GHz bandwidth for −10 dB were achieved with 0.4 wt % MWCNTs. The large RL of −20 dB with just 0.4 wt % was a pronounced result and highlighted the importance of MWCNTs for the enhancement of microwave properties of honeycomb absorbers, whereas the further addition of MWCNTs to 0.6 wt % resulted in the increase of the absorption bandwidth for 80% RL of microwaves. The absorption bandwidth, RL, and matching frequency were all found to be dependent on the concentration of MWCNTs in the coating material. We suggest that the enhanced microwave absorption properties by the small incorporation of MWCNTs were due to their roles in the formation of interconnected networks among the graphite sheets, which gave rise to direct tunneling between adjacent sheets in the composite. The results presented here indicate that such structures may be used as effective microwave absorption materials for structural applications.

ACKNOWLEDGMENTS

The authors thank Zhang Guorui of the School of Micro-Electronics and Solid-State Electronics, University of Electronic Science and Technology of China, for his efforts to measure the scattering parameters in the 2–18-GHz frequency range. The cooperation of Dr. Iftikhar H. Gul from School of Chemical and Materials Engineering, NUST, Islamabad is gratefully acknowledged for SEM experiments.

REFERENCES

1. Wu, L.; Wang, Q.; Tang, Z. In Proceeding of Environmental Electromagnetics Asia-Pacific Conference (CEEM); Shanghai, China, **2012**; p 309.
2. Bollen, P.; Quievy, N.; Detrembleur, C.; Thomassin, J. M.; Bailly, C.; Pardoen, T.; Huynen, I. In Proceedings of IEEE International Symposium on Electromagnetic Compatibility (EMC EUROPE); Rome, Italy, **2012**; pp 1.
3. Zhou, P.; Huang, L.; Jianliang, X.; Difei, L.; Lu, H.; Longjiang, D. *IEEE Trans. Anten. Propag.* **2012**, *60*, 3679.
4. He, Y.; Gong, R.; Cao, H.; Wang, X.; Zheng, Y. *Smart Mater. Struct.* **2007**, *16*, 1501.
5. He, Y.; Gong, R.; *Eur. Phys. Lett.* **2009**, *85*, 58003.
6. Williams, R. B. U.S. Pat. 7345616 B2 (**2008**).
7. Johansson, M.; Holloway, C. L. *IEEE Trans. Anten. Propag.* **2005**, *53*, 728.
8. Eggermont, S.; Bollen, P.; Quievy, N.; Detrembler, C.; Molenberg, I.; Thomassin, J. M.; Monnereau, L.; Urbanczyk, L.; Bailly, C.; Pardoen, T.; Huynen, I. In Proceedings of the IEEE 5th European Conference on Antennas and Propagation; Rome, Italy: **2012**; p 2201.
9. Masahiro, H.; Miyuki, H. Y.; Michael, T. H.; Dinesh, K. A.; Kazuhiro, N. *ISIJ Int.* **2011**, *51*, 1766.
10. Singh, B. P.; Veena, C. H.; Parveen, S.; Shailaja, P.; Singh, V. N.; Mathur, R. B. *J. Nanopart. Res.* **2013**, *15*, 1554.
11. Saleh, M. H.; Sundararaj, U. *Carbon* **2009**, *47*, 2.
12. Hollertz, R.; Chatterjee, S.; Gutmann, H.; Geiger, T.; Nüesch, F. A.; Chu, B. T. *Nanotechnology* **2011**, *22*, 125702.
13. Shin, Y. Y.; Wei, N. L.; Yuan, L. H.; His, W. T.; Jeng, Y. W.; Chen, C. M.; Yu, S. W. *Carbon* **2011**, *49*, 793.
14. Kim, M.-S.; Yan, J.; Joo, K.-Y.; Pandey, J. K.; Kang, Y.-J.; Ahn, S.-H. *J. Appl. Polym. Sci.* **2013**, *130*, 3947.
15. Kim, P. C.; Lee, D. G. *Compos. Struct.* **2009**, *87*, 161.
16. Watts, P. C. P.; Hsu, W. K.; Barnes, A.; Chambers, B. *Adv. Mater.* **2003**, *15*, 600.
17. Wei, L. S.; Mao, S. C.; Zhi, L. H.; Xiao, Y. F.; Xiao, L. S.; Jie, Y. *Appl. Phys. Lett.* **2009**, *94*, 233110.
18. Qin, F.; Brosseau, C. *J. Appl. Phys.* **2012**, *111*, 061301.
19. Liu, Z. F.; Bai, G.; Huang, Y.; Li, F. F.; Ma, Y. F.; Guo, T. Y.; He, X. B.; Lin, X.; Gao, H. J.; Chen, Y. S. *J. Phys. Chem. C* **2007**, *111*, 13696.
20. Sun, X. G.; Gao, M.; Li, C.; Wu, Y. Carbon Nanotubes—Synthesis, Characterization, Applications; Yellampalli, S., Ed.; InTech, Croatia: **2011**; p 2265.