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카본블래랙과 탄소섬유를 포함하는 에폭시 복합체의 마이크로파 흡수 특성

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Microwave Absorbing Characteristics of Epoxy Composites Containing Carbon Black and Carbon Fibers

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Abstract: In this study, the composites containing carbon black(CB) or carbon fibers were prepared, and the microwave absorbing properties and the absorption mechanism of them were investigated and discussed in the frequency range of 2−18 GHz, respectively. The optimum mass fraction of CB has been found as 6%, and the carbon fibers were discovered to absorb radar wave either under parallel or vertical polarization, the suitable gap distance between each bundle of which was 5 mm. According to the results of the single constitute absorber samples, the structured composites with the two kinds of absorbers combination were fabricated and studied at 2−18 GHz. The top layer absorbers affect the absorption performance a lot; the maximum reflection loss of composites with CB as top layer absorbers was −31.8 dB with the frequency range of 2.4 GHz below –10 dB, and the other type with CFs as the top layer absorbers obtained the reflection loss peak value of −31.4 dB with 2 GHz below−10 dB.

Keywords: radar absorbing structure, composites, carbon black, carbon fiber.

Introduction

Radar wave absorbing technology has been a very important issue for both business and military purposes. The most effective way to avoid the radar detection is to minimize the reflected microwave from the targets, which can be achieved by the control of radar cross section (RCS). Now there are mainly two ways to reduce the RCS, i.e., shaping the aircrafts and employing the radar absorbing materials (RAM) or radar absorbing structures (RAS). Especially, the RAM and RAS have attracted considerable attention for these years.[1]

In general, RAM is such a kind of composite consisting magnetic or dielectric loss fillers. The magnetic loss fillers such as ferrites have great advantages of microwave absorbing. However, the high specific gravity usually limits their application from aircraft assembly. Whereas the dielectric loss fillers have attracted more attentions in recent years, especially in the filed of RAS, which could both absorb the microwave and bear the force. Recently, the multi−layered RAS[2−4] has also showed a most promising way of microwave absorption.

Concerning the dielectric loss fillers, the carbon family including carbon fibers (CFs), carbon black (CB)[5,6] and carbon nanotubes[7−9] have often been considered. CF can be used in RAS due to its high mechanical performance and its unique electrical resistance. The absorbing mechanism of CF depends on its size and arranging style,[10−15] as well as CB and carbon nanotubes. Hence, via combining the different form of dielectric loss fillers, composites with high reflection loss in a wide microwave band can be expected.

In this study, epoxy composites containing CB or CFs were prepared firstly, and microwave absorbing characteristic of those composited were tested. Furthermore, multi−layer structured composites containing both CB and CFs were

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then fabricated and their electromagnetic performance was characterized.

Experimental

Materials. The CB (acetylene black) used in this study, purchased from Huji Co. (China). Epoxy resin matrix (EPOXY-128), curing agent (polyamide solidified agent, 593); acetone and glass fabric were supplied by Tibin Co. (China). The rayon-based carbon fibers with a conductivity of 24.1 S/m were made in our lab.

Fabrication of CB-Filled Epoxy Composite. The CBs were firstly added into acetone, ultrasonic treatment for 30 min, and then mixed with epoxy through mechanical stirring for 15 min and ultrasonic treatment for another 30 min. After the mixture prepared, the curing agent with the mass ratio of epoxy/curing agent=4/1 was added and stirred for 15 min, and then paved uniformly onto the glass fabrics layer by layer. Subsequently, the CB-filled fabric composites were press-cured at room temperature under a certain pressure for 4 h. The samples were denoted as CB2, CB4, CB6 and CB8 for CB mass ratio of 2, 4, 6 and 8%. All the specimens were 4 mm thick and were cut to the size of 180 mm×180 mm.

The resistance and dielectric characteristics of the CB composites were measured using a KEITHLEY 236 source measure unit.

Fabrication of Composites Containing Parallel-Arranged CFs. Firstly the epoxy resin was blended uniformly with the curing agent in a mass ratio of 4/1, then the polymer matrix, the CFs and glass fabrics was cast into layered composites just as described in Figure 1. Here the embedded CFs were parallel to the surface of the sample and aligned in equidistance. Molding for those composites was carried out in the same way of CB composites, resulting in the specimens of 180 mm (width)×180 mm (length)×4 mm (thickness).

According to the different gap distance between two nearby bundles of carbon fiber, the manufactured composite samples were classified into two categories, as shown in Table 1.

Fabrication of CB/CF Filled Composites. In order to combine the merits of two kinds of absorbers discussed above and obtain the materials with better absorption properties, we applied the CB and CFs to fabricate the absorber with two-layer structure, in which one layer contained 6 wt% of CB, and the other was embedded by parallel-arranged CF bundles with a gap of 5 mm. The CB/CF filled samples were also shaped into a dimension of 180 mm×180 mm×4 mm.

Figure 1. The cross section of composite.

Table 1. Specimen Denotation of CF Composites

Denotation	Gap between carbon fiber (mm)	Carbon fiber layers
A1	10	1
A2	10	2
A3	10	5
A4	10	8
B1	5	1
B2	5	2
B3	5	5
B4	5	8

Table 2. Denotation of the Two-Layer Composites

Denotation	1st layer		2nd layer	Polarization
I-Type	2mm-CB	+	2-layer CFs	P/C
	2mm-CB	+	4-layer CFs	P/C
	2.8mm-CB	+	2-layer CFs	P/C
	2.8mm-CB	+	4-layer CFs	P/C
II-Type	2-layer CFs	+	2mm-CB	P/C
	4-layer CFs	+	2mm-CB	P/C
	2-layer CFs	+	2.8mm-CB	P/C
	4-layer CFs	+	2.8mm-CB	P/C

According to the thickness of CB layer and the cascades of CFs layer, two types of samples were prepared and illustrated in Table 2. All the samples were tested both under parallel and vertical polarization according to the orientation of the CFs and electric field, where P presents parallel polarization and C presents vertical polarization.

Absorption Performance Measurements. The absorption performance of all composites were investigated by using a network analyzer (HP8722ES), the samples were placed on an aluminum panel (180 mm×180 mm) and the microwave reflection loss were recorded within a band ranged between 2 and 18 GHz.

Compared with CB composites, CF composites obtained in this study would show anisotropic absorption manner because of the oriented arranging of the CF bundles. Therefore, absorption measurements for CF composites were carried out in two orthogonal directions, which were named parallel and vertical polarizations, respectively.

Moreover, depending on the up or down placement of multilayered composites, CB/CF filled epoxy would show different absorption performance. Taking the first sample in Table 3 for instance, if CB layer was up placed under parallel polarization, the sample would be named as 2 mm+2 P, otherwise it would be named as 2P+2mm if being placed inversely.

Results and Discussion

Basic Electromagnetic Characteristics and Microwave Absorbing Properties of CB Composites. The microstructure of the epoxy mixed with CB was captured by scanning electron microscopy (SEM). Figure 2 (a to d) shows the SEM images of CB2 to CB8, from which we can see that the CBs were well dispersed.

Figure 3 showed the resistivity of CB composites as a function of CB concentration. It was observed that the resistivity of composites would decay when CB load was increased because more conductive pathway would form under a high CB fraction. Especially when the weight fraction of CB was 6%, the resistivity would fall in a range of 10^3~10^4(Ω·cm), which was regarded as the perfect resistivity range for microwave absorbing materials.[16]

The dielectric characteristics of the CB composites were shown in Figure 4. The real and imaginary parts of the permittivity increased obviously with the increasing CB content but decreased with the increasing frequency, and the magnitude of change in lower frequency range was larger than

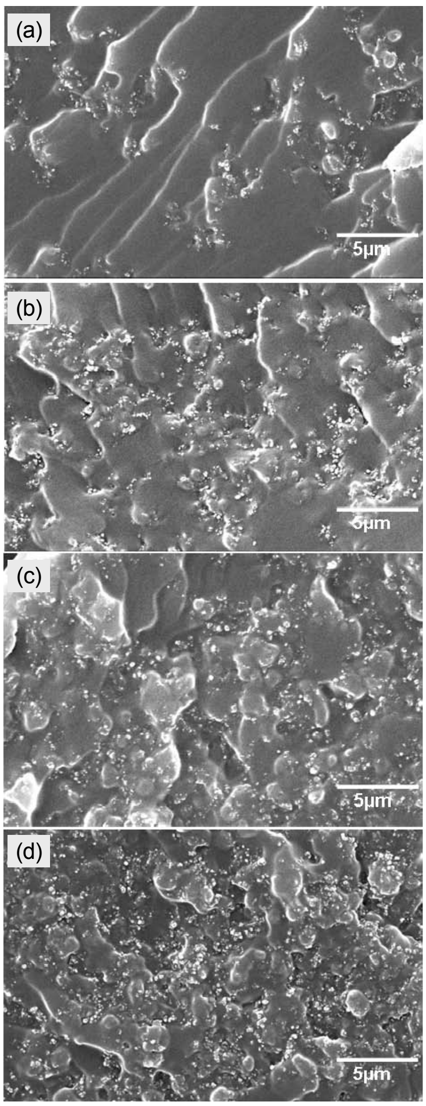

Figure 2. SEM images of CB composite: (a) 2CB; (b) 4CB; (c) 6CB; (d) 8CB.

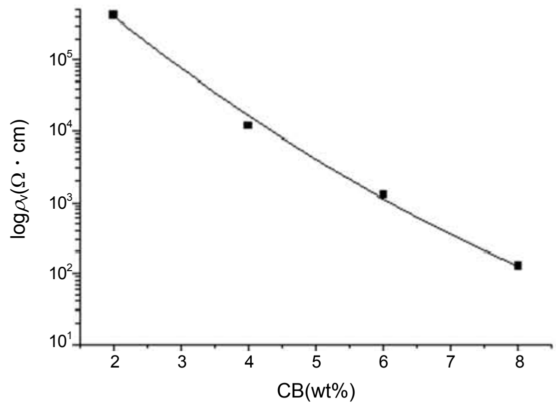

Figure 3. Resistivity of CB composites.

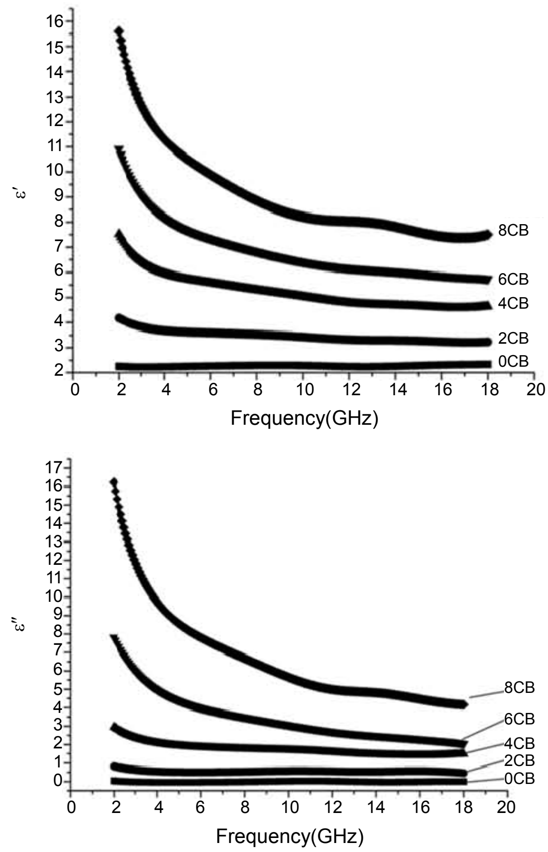

Figure 4. Relative permittivity of CB/epoxy composites with frequency.

that in the higher frequency range. The theoretical analysis of the complex permeability and permittivity was carried out in Ref.[17] and similar phenomena were reported in Ref.,[18] where they were considered to be due to eddy current loss. On the other hand, the magnetic loss of these composites in the frequency range from 8 to 18 GHz was negligible because magnetic permeability testing would always give $\mu'=1$, $\mu''=0$ for each sample.

Based on the measured data of electromagnetic parameters, the reflection loss (RL) of a single layer absorber usually can be evaluated by the following equations:[19]

$$R_L=-20\ \log_{10}[|(Z-Z_0)/(Z+Z_0)|], \tag{1}$$

$$Z=Z_0(\mu_r/\varepsilon_r)^{1/2}\tanh[(-j2\pi/c)(\mu_r/\varepsilon_r)^{1/2}fd] \tag{2}$$

where c is the velocity of light, d is the thickness of absorber, $\varepsilon_r=\varepsilon'-j\varepsilon''$ is the complex permittivity, $\mu_r=\mu'-j\mu''$ is the complex magnetic permeability, and Z_0 is the impedance of free space. For microwave absorbing application, when RL is less than −20 dB, we can say that Z_{in} and Z_0 are matched. When the impedances are matched, the frequency and the absorber thickness are termed as "matching frequency" and "matching thickness", respectively.

For the purpose of demonstration, Figure 5 illustrates the calculated maximum reflection loss and corresponding frequency depending on the thickness of each blend. It can be seen from Figure 5(a) to 5(c) that the maximum reflection loss increases due to the increasing content of CB powders, and the approximately same tendency existing between the maximum reflection loss and the thickness of samples. But observed from Figure 5(d), the reflection loss diminished even with increased thickness because the reflection wave from the back interface was not enough to destruct the surface reflection wave due to excessive absorption in transiting wave even though surface reflection wave was increased, as compared to former three samples.

On the other hand, the characteristics of microwave reflection loss of the single-layered CB composites with the varied CB contents and the fixed thickness of 4 mm were investigated and compared with the calculated RL values. Figure 6 shows the measured and calculated reflection

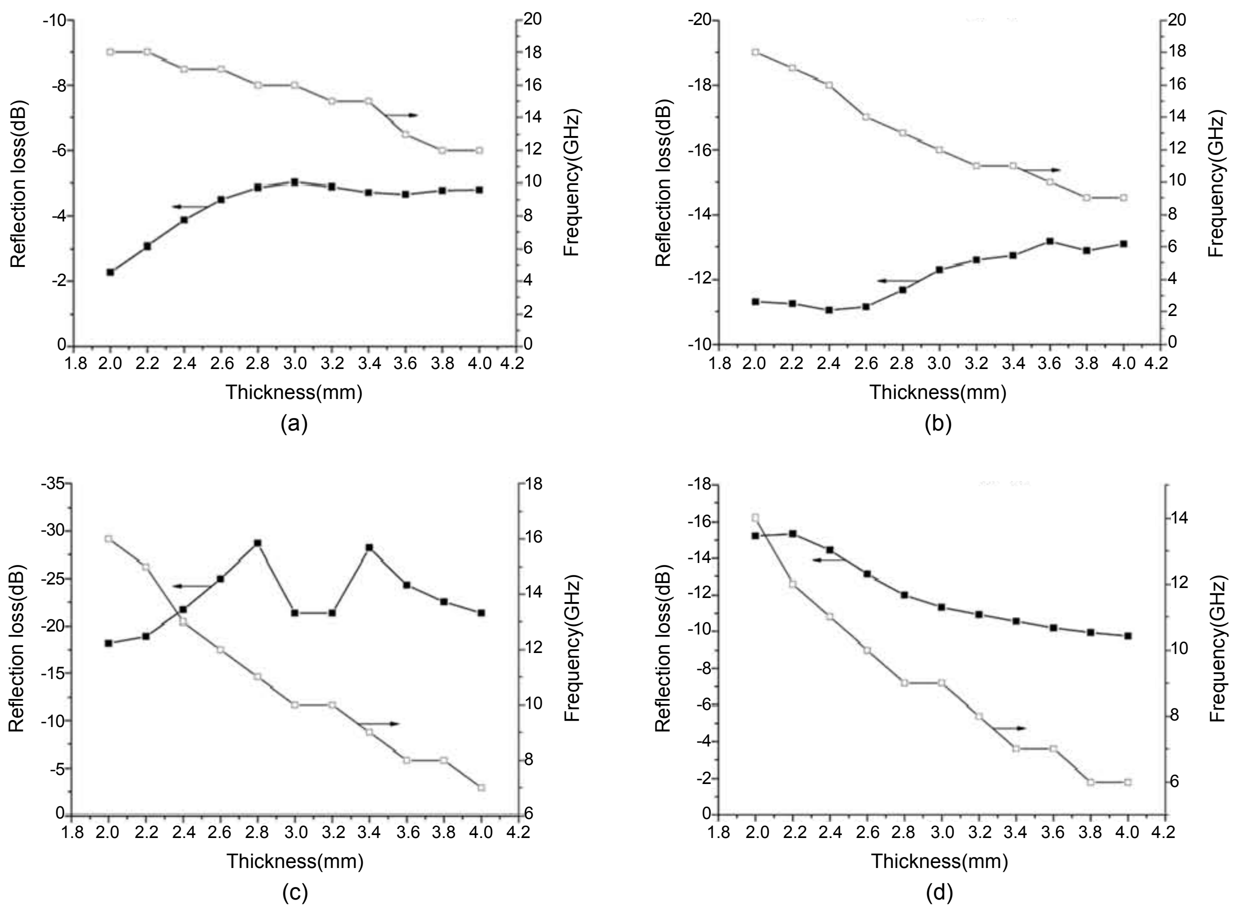

Figure 5. Variation of reflection loss and corresponding frequency with respect to thickness of each blend: (a) 2% CB(wt); (b) 4% CB(wt); (c) 6% CB(wt); (d) 8% CB(wt).

losses of CB composites. It can be seen that the calculated values using eq. (2) agree well with the measured values at 2−18 GHz. The reflection loss increases up from CB0 to CB6, but decreased in some extent by the case CB8. The CB powder used in this study is a conductive material, of which the conductivity is 2.5×10^{-2} $\Omega\cdot$cm, and does not show dielectric properties by itself. However, if it is en-capsulated with insulation materials, it shows a dielectric property.[20] The microwave absorption in the system of the conductive material mixed with the non-conductive material is related to the interfacial polarization. Interfacial, or Maxwell-Wagner type, polarization occurs in heterogeneous dielectrics where one component has a higher electrical conductivity than the other, in which dipoles can be induced by an electric field.[21] By blending into the non-conductive matrix some CB powders, the microwave entering the com-posites was absorbed by CB powders. The more CB in the composites, the more microwave absorbed. On the other hand, the higher the CB content in the composites, the lower the resistivity is (Figure 2), and that could make the com-posites exhibit metallic properties like reflecting electro-magnetic radiation. In the course that the CB content in-creased in the composites, two trends were in competition: one was that the microwave absorbing capacity of the com-posites increased and the other was that the metallic pro-perty was also intensified. At the initial stage when the CB content increased from 0%, the former trend was dominant. However, the latter one continuously grew when the CB content increased in the composites. So there must exist an optimum CB content for the composites to absorb as much as possible the microwave energy. From the results above, the CB amount of 6% by weight could be regarded as the optimal one. The measured reflection loss less than −10 dB could be obtained in the frequency range of 5.4−7.3 GHz. The impedance matched frequency is 6.2 GHz and the reflection loss shows a minimum value of −23.4 dB. So at the following stage, we studied the microwave absorbing characteristics of the composites with the fixed CB weight fraction of 6%.

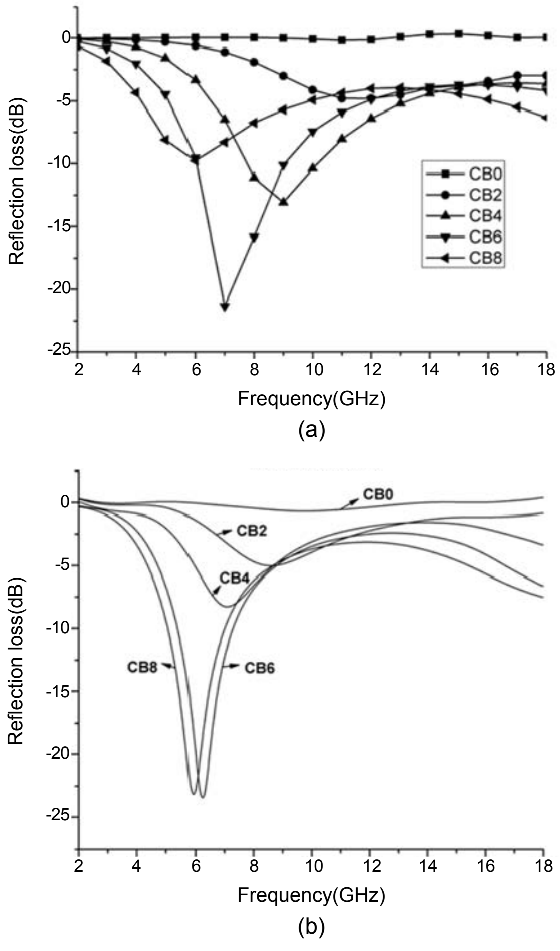

Figure 6. Reflection loss of CB composites: (a) calculated; (b) measured.

Figure 7 shows the reflection loss of CB6 as a function of the thickness at 2−18 GHz. The frequency of the impedance matching point was shifted to a low frequency with increasing sample thickness. A measured reflection loss less than −10 dB was obtained within 10.9−12.5 GHz at 2 mm, within 6.8−8.8 GHz frequency range at 2.8 mm, and within 5.7−7.2 GHz at 4 mm of sample thickness.

We could see that some difference exists between opti-mized and measured curves. It may be caused by errors in permittivity and reflectivity measurement and by absorber preparation, and the different matrix of composites.

Absorption Properties of CF Composites under Parallel and Vertical Polarization. The absorption performance of the CF composites at the 2−18 GHz at parallel polarization is shown

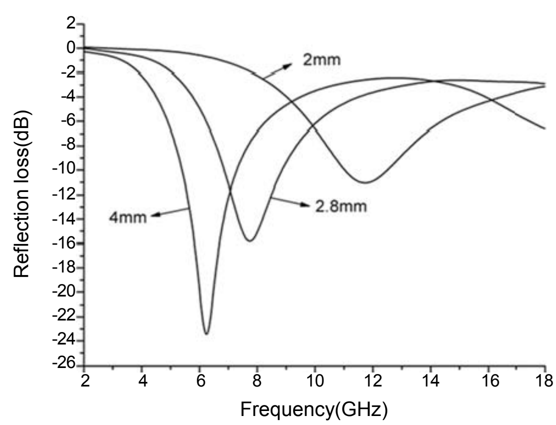

Figure 7. Reflection loss of composite containing 6%(wt) CB with different thickness.

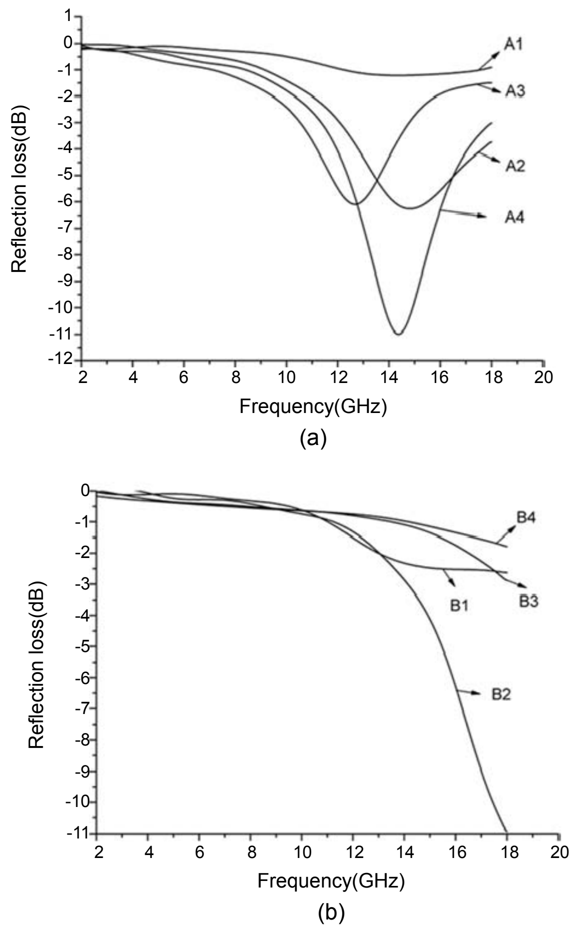

Figure 8. Microwave absorption properties of the composite specimens under parallel polarization: (a) A1−A4; (b) B1−B4.

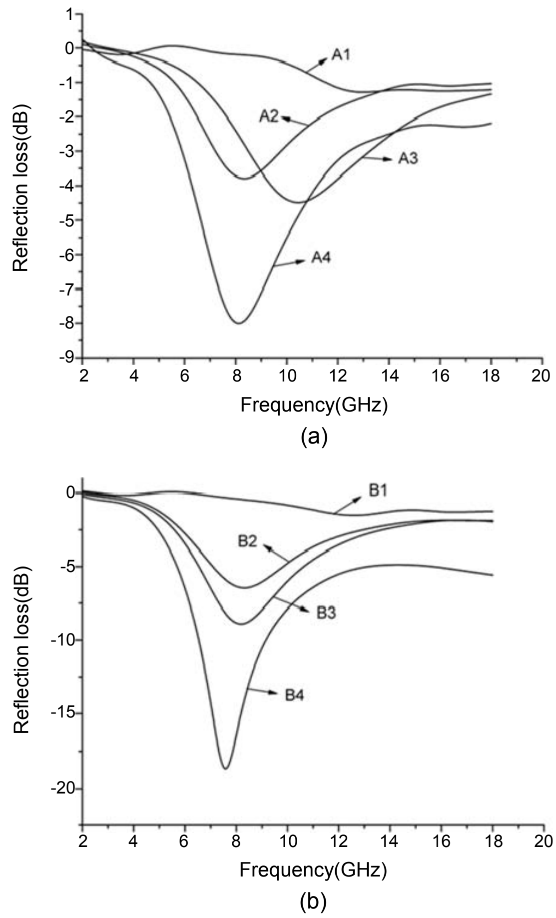

Figure 9. Microwave absorption properties of the composite specimens under vertical polarization: (a) A1−A4; (b) B1−B4.

in Figure 8. It could be seen that with the increment of CF layers, the absorption value became higher, and the bandwidth below −10 dB occurs. The absorption peak value of A4 reaches −10.97 dB at 14.46 GHz. While the absorption peak value of B4 reaches −10.89 dB at 17.96 GHz.

Taking note of Figure 8(b), it can be seen that the peak value of B series does not display in the existing frequency range. This suggests that the absorption performances of B series were not good as that of A series in such a frequency range, or the corresponding peak frequency (f_0) will move to higher value as the gap between CF bundles become narrower.

Based on the theory of electromagnetism, when the conductor was polarized in parallel electric field, there will be electric current emerged on the surface of the conductor, which was called volute current. In this case, the carbon fibers play the role of the conductor. It could be expected that more surface current will emerge while the CF amount increase and polarization frequency becomes higher. In this way more resistance power loss could be obtained and contribute to the absorption properties of composite. On the other hand, the induced current occurs along the CFs, which made the CFs display the feature of metal, and that may cause numerous wave reflections from the fiber. As the CFs got denser at the surface, the reflection effect was stronger, by which it can be interpreted that the B series were poorer.

It can be seen from Figure 9 that under vertical polarization the layer number of CFs influences the absorption property of the composite greatly. With the increment of CFs layer, the peak value of absorption increases, and the bandwidth below −10 dB appears. It is observed that the reflection loss of B4 reaches −18.7 dB at 7.6 GHz, and the bandwidth less than −10 dB is over 2.6 GHz which covers the frequency range of the radar wave. It was also found that the peak reflection losses of all composites appear at almost the same frequency about 7.5−8.0 GHz. The locations of the peak frequency do not change with both the content of CF and gap of CF bundles arranged.

Comparing Figure 8 with Figure 9, we could find that the composites of B series presented better absorption characteristics under vertical polarization. According to the theory of electromagnetic field, when an arbitrary included angle exists between the incident electric field direction and fiber orientation (Figure 10), the reflected field is not parallel with the incident electric field, and the component which is vertical to incident electric field occurs. The incident electric field along the direction of X_1 could be decomposed as two components: one is parallel to the fiber called $Ei_{||}$, and the other is vertical to the fiber called $Ei_{\perp}$. These two components acting on the carbon fiber give birth to their reflected field components $Er_{||}$ and $Er_{\perp}$, respectively. Then the reflected electric field composed by $Er_{||}$ ($Er_{||} \approx Ei_{||}$) and $Er_{\perp}$ ($Er_{\perp} \ll Ei_{\perp}$) could not be parallel to the incident electric field. In the case θ=0°, there could be the following relationship: $Ei_{||}$=Ei, $Ei_{\perp}$=0. Contrarily, $Ei_{||}$=0, $Ei_{\perp}$=Ei when θ=90°. Therefore, $Er_{90°}$ is far less than $Er_{0°}$. In addition, as the CFs amount rose, the effects get more distinct, and that is why the B series have greater reflection loss and peak value increases with the larger layer number.

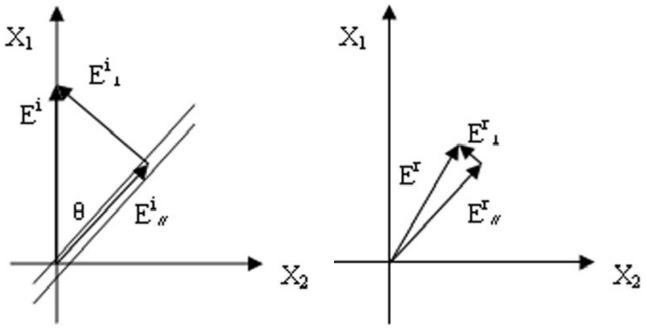

Figure 10. Reflected electric field at fibers not parallel to the incident electric field.

Absorption Properties of the Composites Combining CB and CF Absorbers. Figure 11 and Figure 12 display the absorption curves of the composites under parallel and vertical polarization, respectively. From Figure 11(b), it informed that the composites with embedded CFs acting as the first layer show the similar absorption performances with the samples of B series talked above. At this moment, the adding of CB was no use for the microwave absorbing. The incident wave was reflected from the top of the sample rather than entered them due to the metal conductor-like carbon fibers. However,

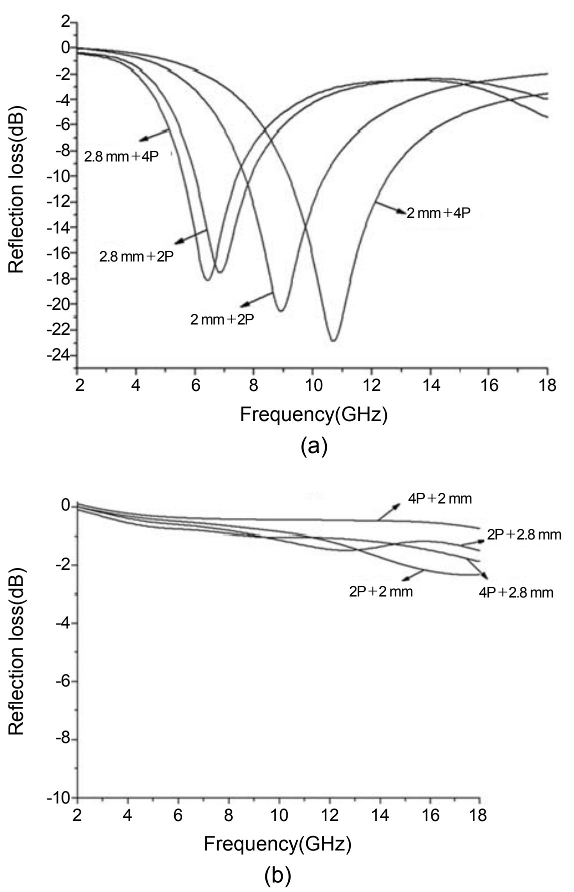

Figure 11. Reflection loss of two-layered composite under parallel polarization: (a) I-type; (b) II-type.

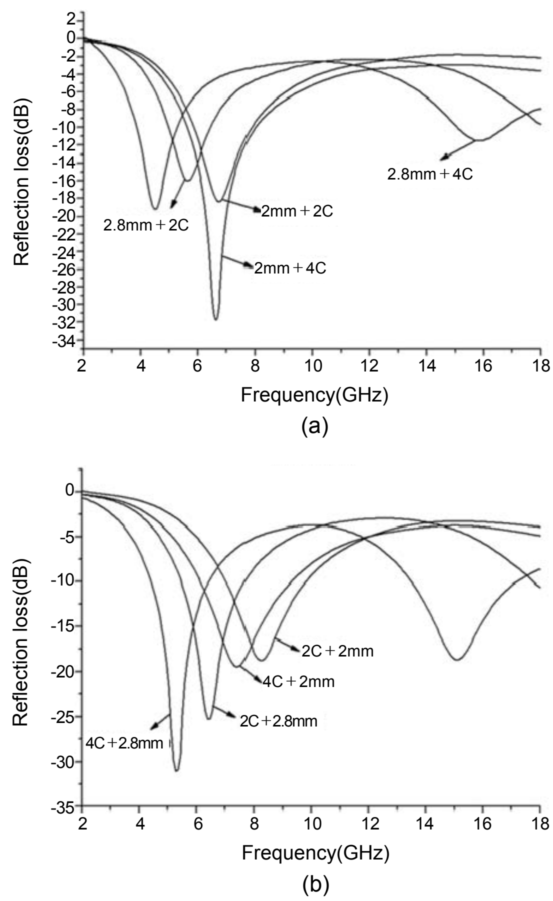

Figure 12. Reflection loss of two-layered composite under vertical polarization: (a) I-type; (b) II-type.

when CB used in the 1st layer of the composites (Figure 11(a)), the samples presented large reflection loss, especially with the case that the CB−layer is 2 mm thick. Compared to I−type, the CB−layer can be regarded as the matching layer to the free space impedance. If only in such a circumstance, the entrance of electromagnetic wave into composites can help it be consumed subsequently. In addition, the energy of electromagnetic wave was weakened while passing through the CB−layer, and the left part reaching the CFs−layer could not cause the reflectivity as large as that of the top layer like I−type. Therefore, the eddy current loss caused by CFs act with CB absorbers together, making the II−type samples show a better absorption performance than any other sample containing only one absorber discussed above. Besides, as the layers of parallel−arranged CFs increased, the microwave absorbing characteristics of the samples could be more satisfied. The reflection loss of sample 2 mm+4 P reached −22.8 dB at 10.7 GHz, with the bandwidth below −10 dB of 3.5 GHz.

While under vertical polarization, both type I and II present good microwave absorbing properties, seen from Figure 12, the maximum reflection loss was over −30 dB, which exceeded that of the samples under parallel polarization. The mech−anism of combined absorbers should abide by the theory mentioned in the previous section, but the optimal reflection loss differs depending on different structure. Obviously the accordant tendency concluded that the increment of CFs was positive to reduce the electromagnetic wave reflection. However, the best thickness of CB−layer was distinct due to the different structure. When the CB used in the top layer, 2 mm thick CB layer with 4−layer embedded CFs seem to be a good option for the composites, which had the peak value of −31.8 dB with the frequency range below −10 dB of 2.4 GHz. While in type−II with 4−layered CFs used in the top, the CB−layer with the thickness of 2.8 mm presents better properties. The peak value of I−4 is −31.4 dB around 5.3 GHz with the frequency range of 2 GHz below −10 dB. This is also likely because the microwave having passed through the top layer was changed, making the impedance of the next layer and the electromagnetic field energy match with each other, and consequently the absorption properties were improved.

Particularly, I−4 and II−4 both have a second absorbing peak of −11.5 dB and −18.7 dB, and the frequency range below −10 dB are 1.7 GHz and 3.8 GHz, respectively. A possible explanation is that the microwave was reflected into the inside of the material by the back sheet, which can probably cause a reflection loss again.

Conclusions

(1) The composites containing CB can obtain a good re−flection loss of with the mass content of 6% and the thick−ness of 4 mm. Additionally, when the CFs acts as the absor−bers, the composites showed a well absorption properties, especially under vertical polarization with the gap distance between each two bundles of 5 mm. The increment of CFs layers is propitious for microwave absorption.

(2) The combination of CB and CFs absorbers can improve the microwave absorption performance of the composites greatly, particularly in vertical polarization circumstances. The largest reflection loss obtained by sample was −31.8 dB with the frequency range of 2.4 GHz below −10 dB.

(3) In the situation of absorbers combination, the thick−ness of CB layer depend the different structure. When such layer played the role of top layer, 2 mm could be a best choice. While in the other structure, the CB layer should be 2.8 mm.

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