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Mechanical and Dielectric Properties of Short-Carbon-Fibers/Epoxy-Modified-Organic-Silicone-Resin as Heat Resistant Microwave Absorbing Coatings

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ABSTRACT: Heat resistant microwave absorbing coatings were prepared by brushing and thereafter heat treatment, using epoxy modified organic silicone resin as binding material, short carbon fibers (C_{sf}) as absorbers, talcum powder and glass powder as filling materials. The mechanical and dielectric properties of the coatings before and after heat treatment at 600°C for 10 mins were studied. The results showed that the adhesive power after heat treatment enhances remarkably, both the real (ε') and imaginary (ε'') parts of the permittivity of the coatings increase with increasing C_{sf} content in the frequency range of 8.2–12.4 GHz. The calculation value of the reflection loss as single layer absorber indicates that epoxy modified organic silicone resin coatings containing short carbon fibers could be a promising radar absorbing material applied at high temperature. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1392–1398, 2013

KEYWORDS: fibers; dielectric properties; mechanical properties; resins; coatings

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INTRODUCTION

Recent years, much attention has been paid to microwave absorption materials due to their potentials both in military and civil applications, such as the radar cross section (RCS) reduction and electromagnetic interference (EMI) shielding.[1,2] Typical microwave absorption materials are composed of resin matrix and magnetic lossy absorbers, such as short polycrystalline iron fibers,[3] carbonyl iron powders and ferrites.[4–7] These absorbers possess favorable absorption performance and are widely used in the applications aforementioned, but they can be used only at room temperature. Another kind of microwave absorption coatings, which is composed of matrix and dielectric absorbers, such as short carbon fibers,[8–11] carbon black,[12,13] and carbon nanotube,[14–17] could be used at high temperatures. However, the application of this kind of coatings in the high temperature environment is still challenged taking account of the weak adhesion between the coating and the metal substrate caused by the thermal expansion coefficient mismatch and the unsatisfactory absorption performance as compared to the coatings containing magnetic lossy absorbers. Therefore, the coatings with good adhesion strength and absorption performance are preferred.

Epoxy modified organic silicone resin is a good binder candidate for high temperature coatings because of its high strength, good thermal stability, excellent chemical resistant, and strong adhesion on substrates.[18,19] Low melting point glass powders can be also used as binding additives to strengthen the epoxy modified organic silicone resin coatings. The glass powders melt at high temperature and the viscous liquid bridges the filling particles and also adheres the coating to the substrate. Carbon fiber is a kind of conventional dielectric absorber and an ideal reinforcement to fabricate high-performance composites, which possesses the properties of high strength, high stiffness, high specific modulus, low-expansion coefficient, high electric conductivity, and light-weight.[20,21]

Carbon fiber/epoxy resin composites and carbon black/resin materials have been widely investigated and applied in industry.[11,22] Nevertheless, C_{sf}/epoxy modified organic silicone resin coatings on metal substrate, used as high temperature microwave absorption material, have been reported rarely. According to the available data,[8,12,13,23] the coatings with lower content short carbon fiber can obtain the same complex permittivity as the coatings with a large number of carbon black and carbon nanotube. The better frequency dependence of the coatings with C_{sf} also favors the absorption performance. Moreover, fiber-like constituent incorporation can improve the mechanical properties of the coatings. Therefore, C_{sf}/epoxy modified organic silicone resin coatings on high temperature alloy substrates were

Table I. Physical Properties of T300 Carbon Fiber

Name	T300
Diameter (μm)	7.8
Carbon content (wt %)	96
ρ (g·cm^{-3})	1.78
σ_b (MPa)	3100
E (GPa)	230
Resistivity (Ω·cm)	1.6×10^{-3}

prepared in this work. The adhesive power, impact strength, dielectric properties, and microwave absorption in the frequency range of 8.2–12.4 GHz (X-band, military radar band) of the coatings were discussed.

EXPERIMENTAL

Materials and Sample Preparation

Epoxy modified organic silicone resin and polyamide resin were used as binder and curing agent, respectively. The fillers used in the experiment were glass powders (softening point is about 550°C), organic soil, and talcum powders. The glass powders also play the role of the binder at high temperature. Short carbon fibers with the length of 3 mm were incorporated into the coatings as microwave absorber. The physical properties of the short carbon fibers are listed in Table I.

The coatings were prepared by following steps. Talcum powders, glass powders, organic soil, binder, and curing agent were proportionally weighed and mixed uniformly. Then the short carbon fibers were added into the above mixture with a mass fraction of 0.5, 1, and 1.5 wt %, respectively (samples without C_{sf} skipped this step). The dimethylbenzene was gradually added until the viscosity of the slurry was appropriate for ball milling. The slurry after ball milling was brushed layer-by-layer on the grit-blasted high temperature alloy substrates until the total thickness of the coating was 2 mm and the sample is used to measure the mechanical properties of the coatings. Another group samples were prepared with the same composition and progress on aluminum foil to measure dielectric properties for it was easy to peel off the coatings from the foil. The coatings were cured at 120°C for 4 h in oven at last. The coatings were heat treated at 600°C for 10 minutes and air cooled in the furnace. The mechanical properties and complex permittivity of coatings were measured before and after heat treatment.

Microstructure Observation

The morphology of the coatings was observed by JSM-6360LV scanning electron microscope (SEM).

Mechanical Measurements

Impact strength measurement of the coatings was carried out in QCJ type paint film impactor and the adhesive power in Posi Test Adhesion tester.

Dielectric Measurements

The complex permittivity of the samples was tested by network analyzer (Agilent Technologies E8362B). The samples peeled off from the aluminum foils were cut into a plate with the size of $22.86 \times 10.16 \times 2$ mm^3 and put them into the brass holder ($22.86 \times 10.16 \times 2.00$ mm^3) to measure the complex permittivity, which is based on the measurements of the reflection and transmission module between 8.2 and 12.4 GHz, in the fundamental rectangle wave-guide mode TE10.

Microwave Absorption of the Coatings

The calculation of the reflection loss was carried out to obtain the microwave absorption property of the coatings. According to the transmission line theory, the theoretical reflection loss for the coatings can be calculated by the following formula[15]:

$$\mathrm{RL(dB)} = 20\log\left|(Z_{\mathrm{in}} - Z_0)/(Z_{\mathrm{in}} + Z_0)\right| \tag{1}$$

where Z_0 is the impedance of the free space; Z_m is the input impedance of the coatings, which can be expressed as the following equation[15]:

$$Z_{\mathrm{in}} = Z_0(\mu_r/\varepsilon_r)^{1/2}\tanh\left[j(2\pi fd/c)(\mu_r\varepsilon_r)^{1/2}\right] \tag{2}$$

where μ_r and ε_r are the relative permeability and permittivity of the coatings, respectively; j is the imaginary unit; f is the frequency of the electromagnetic (EM) wave; d is the thickness of the coatings; c is the velocity of light in free space. Here, the real and imaginary part of μ_r could be taken as 1 and 0, respectively, for the weakly magnetic property of the coatings.

RESULTS AND DISCUSSION

Mechanical Properties of the Coatings

Effect of Talcum Powder Content on Mechanical Properties of the Coatings. As high temperature binding material, glass powders play an important role in the microstructure development and properties of the coatings at high temperature. Therefore, five groups of samples with different contents of glass powders and talcum powders were prepared to optimize the performance of the coatings. At the same time, in order to obtain good processing properties of the coatings at room temperature, 23.6 wt % organic silicone resin was added into all the samples and the curing agent content was kept for 5.9 wt %, correspondingly. The constituents of the samples are showed in Table II.

The effect of the talcum powder weight content on the adhesive power of the coatings before and after high temperature treatment is presented in Figure 1(a). It shows that at room

Table II. The Constituents of the Coatings

	Constituents of the coatings (wt %)				
Sample no.	Organic silicone resin	Talcum powders	Glass powder	Curing agent	Organic soil
1	23.6	0	70	5.9	0.5
2	23.6	15	55	5.9	0.5
3	23.6	25	45	5.9	0.5
4	23.6	35	35	5.9	0.5
5	23.6	45	25	5.9	0.5

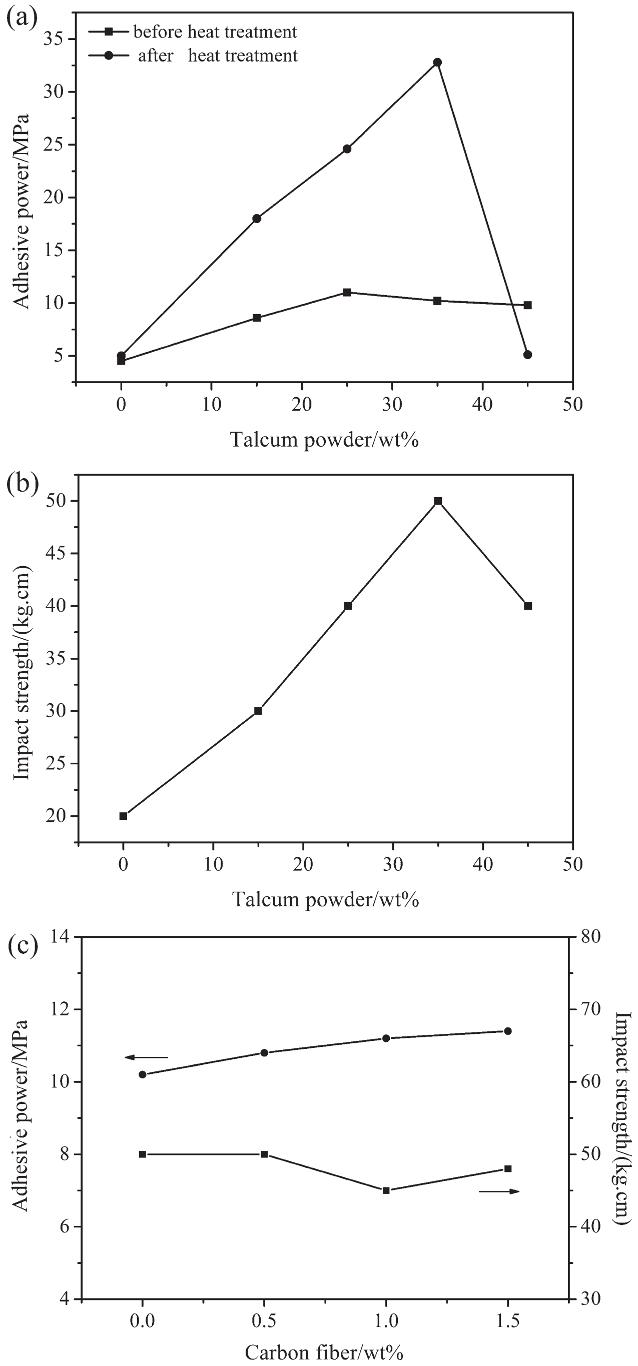

Figure 1. Mechanical properties of the coatings (a) adhesive power versus talcum powder content, (b) impact strength versus talcum powder content, and (c) mechanical properties versus C_{sf} content.

temperature the adhesive power of the coatings increases from 4.5 to 11 MPa as the content of talcum powders increases from 0 to 25 wt %. Further addition of talcum powders causes slight decrease of the adhesive power. It is reasonable that excessive talcum powder addition makes the epoxy modified organic silicone resin insufficient to bind the solid fillers and adhere the coatings on the substrates firmly. The adhesive power of the coatings after heat treatment at 600°C for 10 min greatly increases from 5 to 32.8 MPa with the content of talcum powders increases from 0 to 35wt % and then turns to decrease sharply with 45 wt % talcum powders. The reason is that the flaky talcum powder can enhance the flexural rigidity of the coatings, as a result, the adhesive power increases with the increasing flaky talcum powder content. However, more talcum powder addition implies lower content of glass powders being incorporated into the coatings, this means that the amount of the viscous melting glass formed at high temperature decreases. In this article, the melting glass was used as binder to strengthen the bonding among talcum flakes and the adhesion between the coating and the substrate, so the decrease of the binder content inevitably lead to the decrease of the adhesive power of the coatings. In addition, it is evident that the maximum of the adhesive power after heat treatment increases to almost three times as compared with the value before the heat treatment. It is attributed to the melting glass powders liquid formed at high temperature and the good wettability among melting glass powders, talcum powders, and substrate.

Figure 1(b) exhibits that the impact strength of the coatings before heat treatment increases from 20 to 50 kg cm when the talcum powders content increases from 0 to 35 wt %. Talcum powder is flake-like mineral, which is beneficial to improve the impact strength of the coatings by lamellar distribution during brushing. The impact strength of the coating decreases to 40 kg cm when the talcum powders content reaches 45 wt %. The reason should be that the bonding among fillers is poor due to the relative reduction of glass powders content reduced its impact strength.

Effect of C_{sf} Content on Mechanical Properties of the Coatings. Results shown above demonstrate that sample 4 presented the best mechanical performance of the five samples shown in Table I. Therefore, extra 0.5, 1, and 1.5 wt % short carbon fibers were added into sample 4, respectively, then the coatings containing short carbon fibers were prepared as described in section “Materials and Sample Preparation.”

Figure 1(c) shows that the addition of short carbon fibers has little influence on the room temperature adhesive power and impact strength of the coatings. The reason is that the content of the short carbon fibers in the coatings was very low.

Dielectric Properties of the Coatings

Effect of C_{sf} Content on Dielectric Properties of the Coatings. Figure 2 shows the morphology of the coatings before and after heat treatment. The short carbon fibers were marked with red dotted line rings in Figure 2. It is found that the short carbon fibers in the coatings are directionally distributed due to the brushing method and the fillers combine compactly [seen from Figure 2(a)]. And, a lot of small pores are observed in the coating after heat treatment [seen from Figure 2(b)]. They should be generated from the decomposition and pyrolysis of the organic silicone resin during heat treatment, carbon, and silicon elements in the resin were oxidized into CO, CO_2, and SiO_2, respectively. CO and CO_2 escaped out of the coatings and left the small pores.

Complex permittivity ε_r is a key parameter for microwave absorbing materials. Real part (ε') is an expression of the

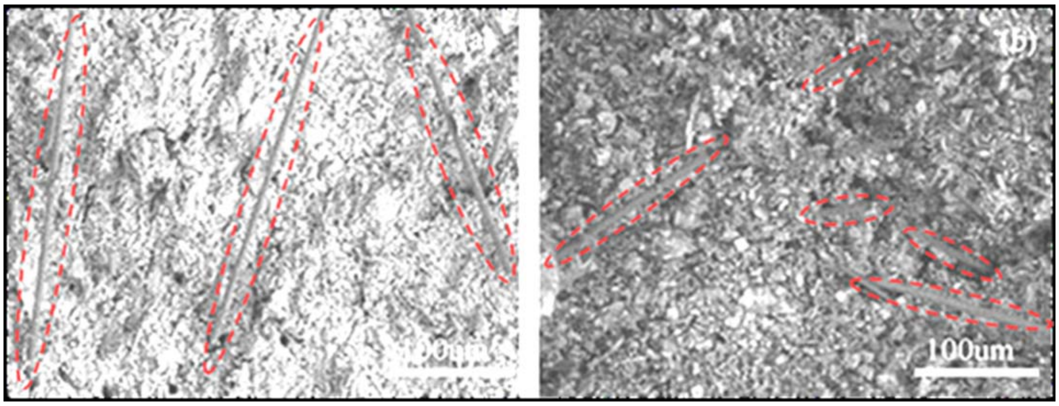

Figure 2. SEM photographs of the coatings (a) before and (b) after heat treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polarization ability of a material and imaginary part (ε'') is an expression of the capacity of dielectric loss in the microwave frequency.[1]

Figure 3 shows the complex permittivity of the coatings in X-band before heat treatment. Obviously, the complex permittivity of the coatings is closely correlated with the content of short carbon fibers. It indicates that the values of both ε' and ε'' remarkably increase with the increasing carbon fiber content. Both the ε' and ε'' reach their maximum values when the carbon fiber content is 1.5 wt %, which are 26–24 and 16.5–10.5, respectively.

It can be ascribed to the fact that electron relaxation polarization would occur as a response to the electromagnetic field in the carbon fibers because the free electrons in the carbon fibers respond rapidly to an alternating electromagnetic field. In this case, relaxation polarization is enhanced as carbon fibers content increases. Therefore, it is reasonable that ε' increases with the increasing carbon fiber content. In comparison with other carbon materials, such as carbon nanotube[16] and carbon blacks,[24] less constituent of short carbon fibers in the coating can match the real part of the complex permittivity of the materials containing such kinds of carbon constituents. The reason is that in addition to the response of free electrons to alternating electromagnetic field, resonance generated by the short carbon fibers as half-wave harmonic oscillators also contributes to ε'. The imaginary part is mainly dependent on two different factors: electrical conductivity and resonance electric current. The effect of the first factor can be expressed by the following equation[1]:

$$\varepsilon'' \approx \varepsilon''_{\text{relax}} + \sigma/(\varepsilon_0\omega) \tag{3}$$

where $\varepsilon''_{\text{relax}}$ is relaxation polarization, σ is the electrical conductivity, ε_0 is the dielectric constant in vacuum, and ω is the angular frequency. According to eq. (3), we can see that ε'' will boost with the carbon fiber content increase. Simultaneously, the resonance electric current in the short carbon fibers also causes severe absorption and makes ε'' increase.

Effect of Heat Treatment on Dielectric Properties of the Coatings. The complex permittivity of the coatings in the X-band after heat treatment is shown in Figure 4. Both ε' and ε'' increase obviously with the increasing carbon fiber content, the variation tendency with the C_{sf} content is similar to the coatings before heat treatment. Both ε' and ε'' reach the maximum values when the content of the carbon fiber is 1.5 wt %, which are

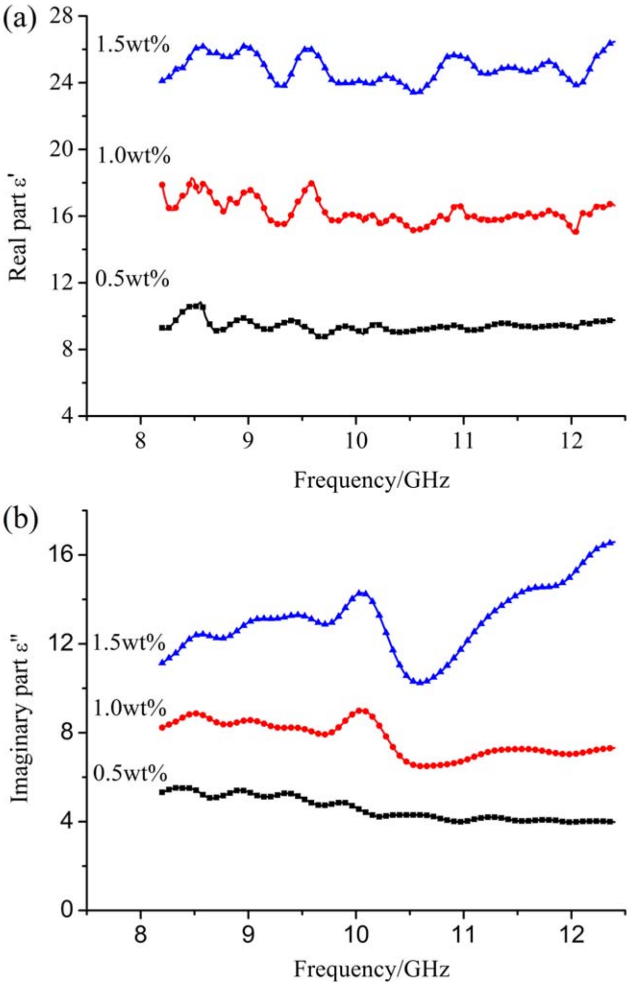

Figure 3. (a) ε' and (b) ε'' of the coatings before heat treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

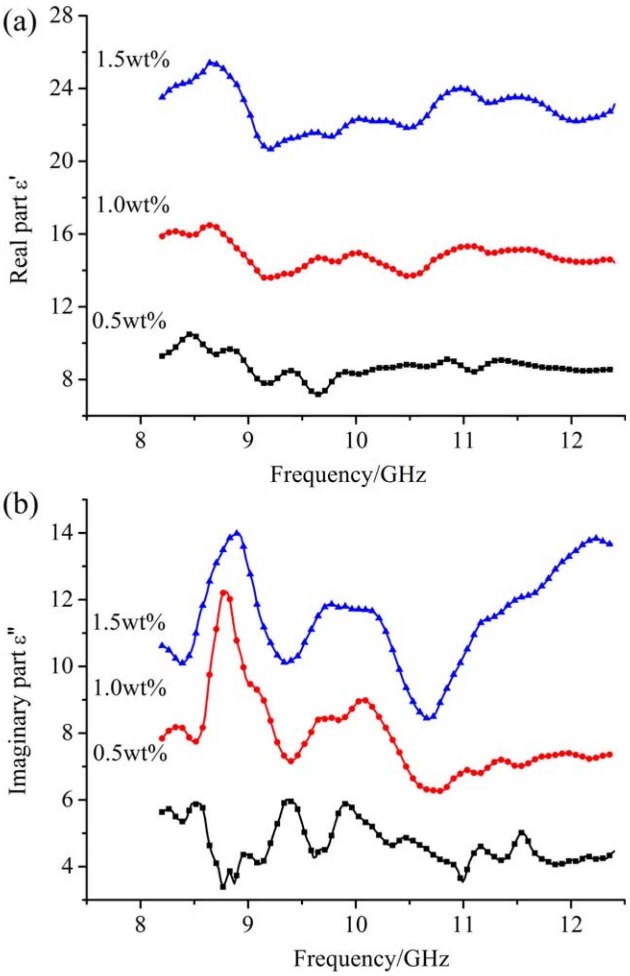

Figure 4. (a) ε' and (b) ε'' of the coatings after heat treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

25–21 and 14–9.0, respectively. Compared with the results obtained before heat treatment of the coatings, seen from Figures 3 to 4, ε' slightly decreases and ε'' keeps almost constant after treatment at 600°C for 10 mins. The decrease of the real part after heat treatment mainly results from the existence of the pores seen from Figure 2(b).

Microwave Absorption Properties of the Coatings

Effect of C_{sf} Content on Microwave Absorption Properties of the Coatings. Figure 5 shows the calculation value of reflection loss, according to formula ((1)), ((2)) and measured ε' and ε'' in the frequency of 8.2–12.4 GHz, for all coatings containing C_{sf} before heat treatment with different thicknesses. It is worth nothing that the reflection loss values $\leq$10 dB were obtained in the 8.2–12.4 GHz range for all the coatings. Moreover, the coating containing 0.5 wt % C_{sf} with thickness of 2.4 mm and the coating containing 1.0 wt % C_{sf} with thickness of 1.8 mm exhibited that the reflection loss exceeds −6 dB all over 8.2–12.4 GHz range, and the minimum reflection loss values are −25.3 and −17.3 dB, respectively. When compared with the results showed in Ref. [24], which added carbon black as absorbing fillers, better microwave absorption performance was obtained with less carbon fiber content and smaller thickness of the coating in the present work. It is observed that the reflection loss of the coatings depended on the C_{sf} content and the thickness of the coating. The minimum reflection loss peak shifts toward lower frequency with the increasing coating thickness for all C_{sf} contents. There is an optimal thickness of the

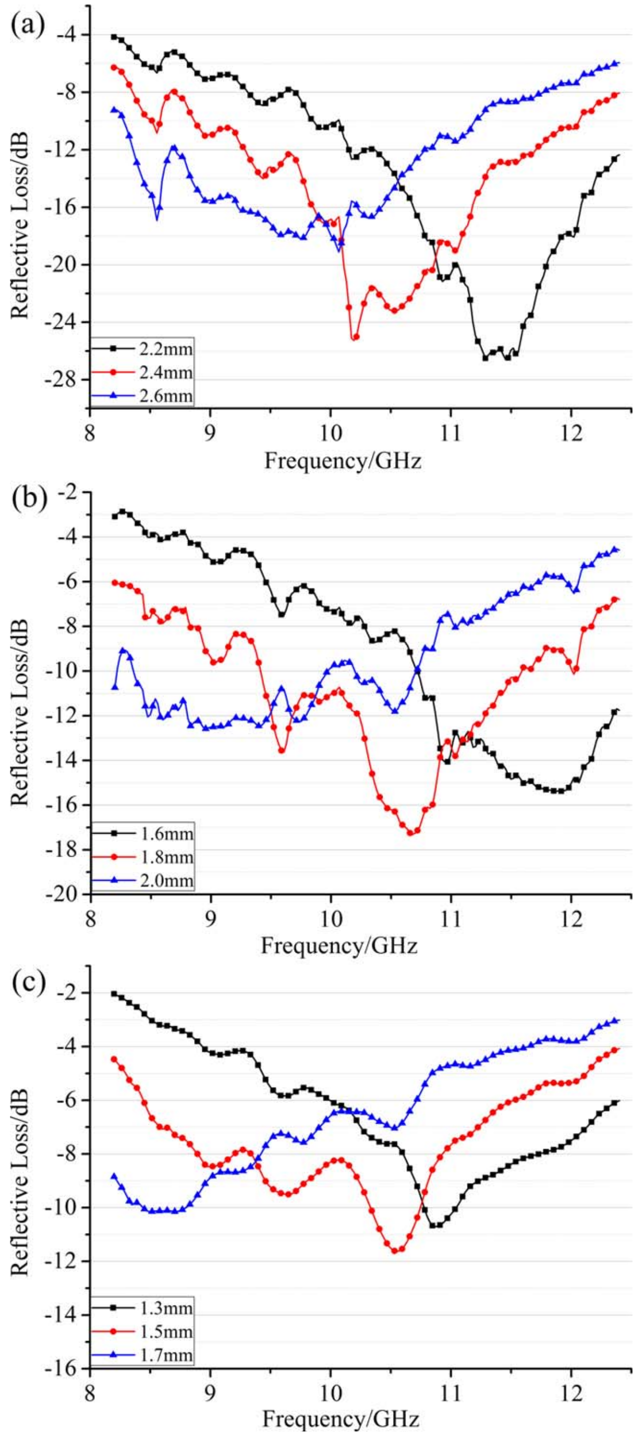

Figure 5. The reflection loss of the coatings with different thickness: (a) 0.5 wt % C_{sf}, (b) 1.0 wt % C_{sf}, and (c) 1.5 wt % C_{sf}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

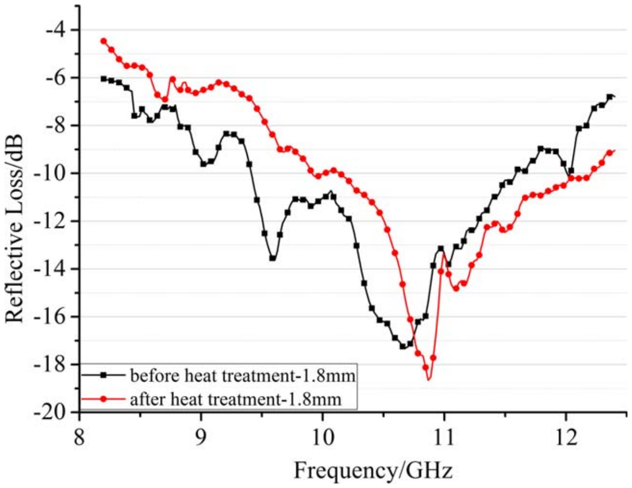

Figure 6. The reflection loss of the coating containing 1.0 wt % with the thickness of 1.8 mm (a) before and (b) after heat treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coatings with optimal attenuation for different C_{sf} contents. The optimal thickness of the coatings decreases with increasing C_{sf} content. The results are considering that the main mechanism of microwave absorption of the coatings is that the conductive fillers of short carbon fibers in the coatings transform EM wave energy into heat energy. Therefore, it can be concluded that it is not enough to dissipate effectively the incident EM wave when the amount of C_{sf} is too small, but if the amount is too much the coating will become an EM wave reflector. On the other hand, from formula ((1)) and ((2)), it can be seen that the variation of thickness of the coating changes the impedance matching situation between free space (Z_0) and the coating (Z_{in}). As a consequence, the variation of the impendence matching conditions leads to the variation of reflection loss of the coating.

Effect of Heat Treatment on Microwave Absorption Properties of the Coatings. Figure 6 shows the calculation value of reflection loss of the coatings containing 1.0 wt % C_{sf} before and after heat treatment with thickness of 1.8 mm. It is clearly found that the minimum reflection loss keeps almost unchanged. The results indicate that the microwave absorption properties of the coatings are fairly stable before and after heat treatment and it could be a good candidate for microwave absorbing material used at high temperature for 10 mins.

CONCLUSIONS

The coating with high adhesion and impact strength was obtained by using glass powders, talcum powders, short carbon fibers, and epoxy modified organic silicone resin as raw materials. The complex permittivity of the coating can be regulated with addition of short carbon fibers. Both ε' and ε'' remarkably increased as the carbon fibers content increased from 0.5 to 1.5 wt %, the complex permittivity of the coatings kept almost unchanged before and after the heat treatment. Microwave absorption property was remarkably influenced by the thickness of the coatings and short carbon fiber content. The energy transform effect caused by C_{sf} in the coating and impedance matching conditions would be responsible for the influence of the short carbon fiber content and the thickness of the coating on the microwave absorption property, respectively. The results indicate that the coatings could be a good candidate for microwave absorbing material used at high temperature for 10 mins.

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