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Smart absorbing property of composites with MWCNTs and carbonyl iron as the filler

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ABSTRACT

A smart absorbing composite was prepared by mixing silicone rubber, multi-walled carbon nanotubes (MWCNTs) and flaky carbonyl iron particles (CIPs) in a two-roll mixer. The complex permittivity and permeability of composites with variable compression strain was measured by the transmission method and dc electric conductivity was measured by the standard four-point contact method, then the reflection loss (RL) could be calculated to evaluate the microwave absorbing ability. The results showed that the applied compression strain made the complex permittivity decrease but not obviously due to the broken original conductive network. The enforcement of the strain on the complex permeability was attributed to the orientation of flaky CIPs. With the compressing strain applied on the composites with thickness 1 mm or 1.5 mm, the RL value decreased (minimum −13.2 dB and −25.1 dB) and the absorbing band (RL < −10 dB) was widened (5.2–10.6 GHz and 4.0–8.4 GHz). While as the composite thickness decreased caused by the compression strain, the RL value still decreased (minimum −12.4 dB and −18.6 dB) and the absorbing band was also broadened (6.5–10.7 GHz and 4.4–10.0 GHz). Thus the smart absorbing property was effective on preparing absorbers with wide absorption band and high absorption ratio.

1. Introduction

The emerged electromagnetic interference (EMI) and electromagnetic compatibility (EMC) problems have attracted people's attention. Fabricating absorbing materials provides an effective way to overcome these problems due to their attenuation on microwave energy. The metal ferromagnetic particles have been extensively studied as absorbents due to the unique dielectric and magnetic properties. Recently many researchers gradually pay more attention to the carbon/metal hybrid material especially the MWCNTs, such as CNTs/$CoFe_2O_4$ [1], raw MWCNTs/Fe catalyst [2], Fe/CNTs [3], etc. These absorbents have a superior absorbing property caused by the dielectric loss property of carbonous materials and magnetic loss property of the metal absorbents. However, the wide use of these hybrid composites is limited for the complicated technological conditions, preparation processes and rare production. Nowadays, it is well accepted that a good absorbing material should satisfy two important conditions: (1) the intrinsic impedance of the absorbing materials is made equal to that of the free space (matching characteristics), and (2) the incident electromagnetic (EM) wave must enter and get rapidly attenuated through the material layer (attenuation characteristics). The promising absorbing materials should be in thin thickness, wide absorption band, light weight and high absorption ratio, but the conventional absorbing materials are often limited due to the electromagnetic characteristics of the absorbent. For example, in order to achieve a thin thickness with wide absorption ratio, the volume content of the absorbent should increase which made the composite density enlarged simultaneously. While to attain a high absorption ratio and a wide absorption band with constant volume content of the absorbent, the thickness should be increased usually. So, in order to achieve an excellent absorbing property, the fabrication process of the absorber was gradually taken into account. Previous research had reported that the orientation of the absorbents could improve the permittivity and permeability of the composites [4–6]. Therefore, preparing the piezo-absorbing composites could be a practicable way to enhance the microwave absorbing property of the absorbers due to the variable conductivity, dielectric and magnetic constant, which were sensitive to the loaded pressure. The piezo-resistive property of rubber composites (MWCNTs/rubber composites [7], carbon black/rubber composites [8], etc.) had been studied previously as well as their dielectric properties. At the same time, mixing carbonous materials and ferromagnetic metals could also improve the absorbing property of the metal/rubber absorbers [2,6,9]. Therefore, given the viscoelastic property of the rubber composite, mixing CNTs and ferromagnetic metals might be an efficient way to prepare smart absorbing composites of good performance under the compressing load.

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The objective of this work is to prepare smart absorbers with the MWCNTs and flaky CIPs as the filler, and the main focus was on the electromagnetic property of the absorbers with the loaded strain.

2. Experiment

2.1. Materials preparation

Methyl vinyl silicone rubber was used as the matrix and 2,5-dimethyl hexane was used as vulcanized assistants, and both were supplied by LaiZhou Jintai Silicon Industry Co. Ltd., China. Raw commercial flaky CIPs were supplied by Shenyang Hangda Technology Co. Ltd., China, which were fabricated by a mechanical milling process using the spherical CIPs. The MWCNTs were purchased from Anhui Gold Sun Nano Techonology Co. Ltd., China. The average diameter of spherical CIPs was 3 μm, the diameter of flaky CIPs was about 5 μm and the thickness was about 0.5 μm, diameter of the MWCNTs was 10–30 nm with length 1–2 μm. The morphology of the two particles is shown in Fig. 1.

As more MWCNTs or CIPs added to the silicone rubber, the elasticity of the absorbing rubber composites would decrease. So, in order to maintain a proper elasticity, 0.5 wt% MWCNTs relative to the silicone rubber weight and 45 vol% flaky CIPs relative to the silicone rubber were chosen in the experiment. As a result, the elasticity could be guaranteed, which would be convenient for the EM parameter testing experiment. The silicone rubber and the two absorbents were mixed in a two-roll mixer, the MWCNTs were added to the silicone rubber firstly, and then the vulcanized assistants and flaky CIPs were added. The uniform dispersion could be ensured for the mixer led a shearing force on the mixture which could overcome the intermolecular van der Waals force of the particles [10,11]. The standard testing sample for complex permittivity and permeability measurements was a toroidal shape with outer diameter 7.0 mm, inner diameter 3.04 mm and thickness 4 mm. In order to measure the two parameters of composites with variable compressing strains, the inner diameter of the prepared samples was established 3.04 mm, three different outer diameters less than the standard outer diameter 7 mm were selected, and the corresponding thickness was established to maintain the same volume with the standard sample. The nominal strain relative to the standard sample was established as the ratio of the reduction thickness to the original thickness of each testing sample. The feature size of each testing sample is shown in Table 1. Then all the samples were vulcanized at 180 °C under pressure 10 MPa for 5 min on a vulcanizing machine.

2.2. Testing method

The morphology of the particles was observed using a scanning electron microscope (SEM CamScan CS-3400). The dc electric conductivity was measured on pressed rectangular of the composites prepared at room temperature by the standard four-point contact method. The effective complex dielectric permittivity and magnetic permeability of the absorbing composites were measured using the transmission method with an AV3627 vector network analyzer and coaxial transmission line in the frequency range of 4–12 GHz. Then the calculated RL could be established, for a single-layer absorbing material, the RL of normal incident EM wave at the absorber surface is given by [12]:

$$RL = 20\lg|(Z_{in} - Z_0)/(Z_{in} + Z_0)| \tag{1}$$

$$Z_{in} = \sqrt{\mu_r\mu_0/(\varepsilon_r\varepsilon_0)}\tan h(2\pi dj\sqrt{\mu_r\varepsilon_r}/\lambda) \tag{2}$$

where Z_{in} is the normalized input impedance of the microwave absorbing composites, $Z_0 = \sqrt{\mu_0/\varepsilon_0} = 120\pi\Omega$ is the intrinsic impedance of free space, ε_r, μ_r and ε_0, μ_0 are complex permittivity and complex permeability of absorption materials and free space, respectively, λ is the microwave wavelength, and d is the thickness of the absorbing composite.

3. Results and discussion

3.1. Complex permittivity and permeability of the composites added MWCNTs/CIPs

Fig. 2 shows the complex permittivity (ε) and complex permeability (μ) of the composite with variable strains depending on the frequency. Firstly, the real part of permittivity (ε') decreased as the compressing strain increased, ε' of the normal composite was the maximum with the average value 21, and it decreased to the average value 13 as the strain reached to 20.1%. The imaginary part of the permittivity (ε'') of each composite had a fluctuating changing tendency, but the changing magnitude of ε'' with each

Table 1
Feature size of each testing sample.

Outer diameter (mm)	Inner diameter (mm)	Thickness (mm)	Strain (%)
7.0	3.04	4.0	0
6.8	3.04	4.30	6.9
6.7	3.04	4.46	10.2
6.4	3.04	5.01	20.1

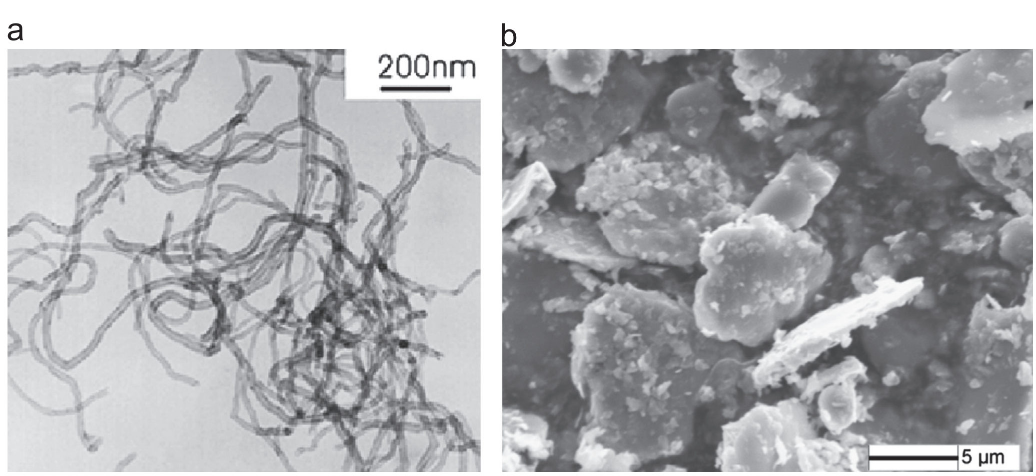

Fig. 1. SEM images of the particles, (a) MWCNTs and (b) flaky CIPs.