Diamond & Related Materials 77 (2017) 53–56

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Electromagnetic microwave absorption properties of carbon nanocoils/tissue

Ruixue Cui[a], Lujun Pan[a,*], Dongmei Zhang[a], Habib Nasir[b]

[a] School of Physics, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian 116024, China
[b] School of Natural Sciences, National University of Sciences and Technology, H-12 Sector, Islamabad, Pakistan

ARTICLE INFO

Keywords:
Carbon nanocoils
Tissue
Microwave absorption property

ABSTRACT

An economic electromagnetic wave absorber with carbon nanocoils (CNCs)/tissue and paraffin has been successfully synthesized and exhibits excellent microwave absorption property. The CNCs/tissue composite was obtained by growing spring-like CNCs on the tissue substrate with $Fe_2(SO_4)_3/SnCl_2$ catalyst in a chemical vapor deposition method. It is found that the absorbers containing 10 wt% and 20 wt% CNCs/tissue show strong microwave absorption in a frequency range of 2–18 GHz. For the composite with 10 wt% CNCs/tissue, the maximum reflection loss (RL) of − 46.36 dB at 14.72 GHz and the bandwidths of 7.44 and 5.68 GHz respectively corresponding to RL below − 10 and − 20 dB can be obtained. In addition, the composite with 20 wt% CNCs/tissue can also gain broad bandwidth corresponding to reflection loss below − 10 dB, which is as high as 7.52 GHz. It is revealed that the composite with 10 wt% CNCs/tissue owns suitable real part of permittivity, which helps to obtain better impedance match and lower reflection coefficient to enhance the absorption of electromagnetic wave.

1. Introduction

With high-speed development of modern science and technology, the electromagnetic radiation problem that comes along cannot be underestimated. Among numerous electromagnetic shielding and absorbing materials, the carbon materials, such as carbon nanotubes (CNTs), carbon fibers (CNFs) and graphite, have obtained extensive attentions and researches owing to their light weight, good structure stability and excellent electromagnetic properties [1–7]. Fan et al. prepared and characterized the CNTs/polymer composites for microwave absorption applications in the range of 2–18 GHz. They found that 4 wt% CNTs/PET and 8 wt% CNTs/varnish composites can achieve maximum reflection loss (RL) of − 17.61 dB and − 24.17 dB at 7.6 GHz and 15.3 GHz, respectively [8]. Zhang et al. synthesized a macroscopic 3D graphene foam with ultrahigh compressibility [9]. This kind of graphene foam under 90% compressive strain can achieve 60.5 GHz absorption bandwidth (RL ≤ − 10 dB) and the microwave absorption performance can be tuned by physically compression.

Compared with the above carbon materials, carbon nanocoils with 3D helical chiral structure own more excellent electromagnetic properties and then would obtain high performance of microwave absorption shown in many previous reports [10–12]. The carbon microcoils synthesized by Motojima et al. in a polyurethane matrix with 1–2 wt% addition can get 99% absorptivity of electromagnetic microwave at 30–35, 50–55, 75–80 and 95–100 GHz bands [13]. Tang's group have researched microwave absorption properties of carbon coils with various morphologies [14–17]. They found that the twin carbon nanocoils synthesized by decomposing acetylene over nickel nanoparticles own the maximum RL of − 36.09 dB and bandwidth (RL ≤ − 10 dB) of 6.43 GHz [16]. Liu et al. also studied the microwave absorption properties of carbon fibers grown with carbon coils, and obtained the maximum RL of − 41.2 dB and the bandwidth (RL ≤ − 10 dB) of 9.6 GHz for the single-CNCs–CFs composite [18,19].

In our previous work, high yield of spring-like CNCs have been successfully synthesized on various substrates using $Fe_2(SO_4)_3/SnCl_2$ catalyst by a thermal chemical vapor deposition (CVD) method [20–24]. These spring-like carbon nanocoils possess larger size of coil diameter and pitch, which can enhance the dielectric loss and cross polarization effect to improve the microwave absorption property. Despite all this, the purification of the CNCs is still a labor-intensive and time-consuming process, leading to a relative high cost. In this work, we directly use the commercially available tissue as substrates to grow CNCs and directly add these as-grown CNCs/tissue composites into paraffin in different wt% to detect their microwave absorption properties.

---

[*] Corresponding author.
E-mail address: lpan@dlut.edu.cn (L. Pan).

http://dx.doi.org/10.1016/j.diamond.2017.05.014
Received 12 April 2017; Received in revised form 16 May 2017; Accepted 22 May 2017

2. Experimental

The CNCs/tissue samples were prepared by a CVD method. Firstly, the tissue substrate was calcined at 710 °C for 30 min in an argon atmosphere with a flow rate of 480 sccm. Afterwards the calcined tissue substrate was dipped into the $Fe_2(SO_4)_3 \cdot 9H_2O$ and $SnCl_2 \cdot 5H_2O$ deionized water solution for 10 min and then calcined again in an argon atmosphere. The CNCs/tissue samples were obtained by inletting acetylene and argon gases with flow rates of 30 and 450 sccm at 710 °C for 30 min, respectively. The detailed process can be referred to our previous work [23]. Then the CNCs/tissue composite was grinded until the carbonized fibers with about 50 μm length. Next, the microwave absorption materials were achieved by mixing paraffin with 2, 5, 10, 20 and 30% mass percent of the CNCs/tissue. Then the composites were compressed into a toroid with 7 mm outer diameter, 3 mm inner diameter and 2 mm thickness.

At last, the complex permittivity and permeability of the composites can be measured by Agilent-N5230A network analyzer in a frequency range of 2–18 GHz. The CNCs/tissue samples were characterized by a field-emission scanning electron microscope (FE-SEM, NOVA NanoSEM 450). The RL curves were calculated from the relative permittivity and permeability according to the transmission line theory, as follows:

$$\boldsymbol{Z_{in}} = \sqrt{\frac{\mu_r}{\varepsilon_r}} \tanh\left(\frac{j2\pi f d\sqrt{\mu_r \varepsilon_r}}{c}\right) \tag{1}$$

$$\mathrm{RL} = 20\log\left|\frac{Z_{in}-1}{Z_{in}+1}\right| \tag{2}$$

where f is the frequency of electromagnetic wave, d is the thickness of the absorber, c is the velocity of light, and Z_{in} is the input impendence of the absorber.

3. Results and discussion

After the CNCs/tissue sample was crushed down, the structure is shown in Fig. 1(a). It is observed that two kinds of structures are found, containing the broken carbonized fibers with CNCs and carbon layer grown on them and the falling CNCs displayed in Fig. 1(b) and (c), respectively. The average diameter of original carbon fibers in tissue substrate is 8.6 μm and it becomes larger after the growth process. The average coil diameter of the CNCs on tissue substrate is 560 nm displayed in Fig. 1(c) [23]. And the TEM image of a single CNC is inserted in Fig. 1(c). From the previous research by our group, it is confirmed that the structure of CNC is polycrystalline-amorphous [25,26]. Such kind of composite structure work together to absorb electromagnetic microwave.

Then the permittivity and permeability parameters of the CNCs/tissue sample were tested by the coaxial line method. The real and imaginary parts of permittivity have been respectively shown in Fig. 2(a) and (b). It is observed from Fig. 2(a) that the samples with lower contents, 2, 5 and 10 wt%, of CNCs/tissue own relatively stable real part of permittivity. In contrast, when the CNCs/tissue composite is added to 20 and 30 wt%, the real part of permittivity decreases obviously with the increasing of frequency, especially for the 30 wt%. Moreover, the conductivity of absorbing materials is enhanced by adding more CNCs/tissue, because of the fact that the increasing of CNCs and carbon fibers can provide more conductive path. The changes of imaginary part of permittivity have been displayed in Fig. 2(b). It is found that with the increasing of CNCs/tissue content, the imaginary part of permittivity also increases, indicating the improvement of dielectric loss of the absorbing materials. Fig. 2(c) shows that the complex permeability for the composite sample containing different content of CNCs/tissue varies among the frequency range of 2 to 18 GHz. It is observed that the real and imaginary parts of permeability respectively fluctuate around 1 and 0 for all the samples except for that with 30 wt% of CNCs/tissue. The permeability of composite with 30 wt% of CNCs/tissue is greatly influenced by the change of frequency and the imaginary part reaches up to 0.3, which is may be resulted from the gradual appearance of the magnetism of Fe-containing catalyst. Nevertheless, compared with the permittivity result, the magnetic loss is much weaker than the dielectric loss.

The dielectric tangent loss ($\tan\delta_E = \varepsilon''/\varepsilon'$) of composites with different contents of CNCs/tissue has been exhibited in Fig. 3. It is observed that with the increase of CNCs/tissue content, the $\tan\delta_E$ value also increases. When the content reaches 30 wt%, the $\tan\delta_E$ value achieves a really high value. However, the excess $\tan\delta_E$ would increase the reflection of electromagnetic wave. The absorption materials only own suitable can obtain a high absorption efficiency.

Fig. 4 shows RL curves of paraffin composites with different CNCs/tissue concentrations calculated by Eqs. (1) and (2). It is observed that the RL is greatly influenced by the content of CNCs/tissue. For the composites with 2 and 5 wt% CNCs/tissue, they own the weak absorption properties, whose reflection loss are all above − 10 dB. However, with the increase of mass ratio, the reflection loss peak increases sharply and shifts to lower frequency. Especially for the 10 wt% CNCs/tissue content, the peak value reaches a maximum of − 46.36 dB at 14.72 GHz and the bandwidths corresponding to the reflection loss below − 10 and − 20 dB (namely 90 and 99% microwave absorption) are respectively 7.44 and 5.68 GHz. Another broad bandwidth corresponding to reflection loss below − 10 dB, which is as high as 7.52 GHz, can be obtained from the composite with 20 wt% CNCs/tissue.

The excellent microwave absorption property would benefit from the following facts. The CNCs/tissue composite contains not only good conductive CNCs but also poor conductive carbonized fibers and carbon layers, which leads the composite to own lower permittivity than the purified CNCs. It is reported that for the dielectric-loss absorbers, the relatively low permittivity can provide a balance between permeability and permittivity, resulting in better impedance match and lower reflection coefficient [18]. It is verified by the composite containing 10 wt% CNCs/tissue, which owns lower permittivity and finally gets an excellent RL. Furthermore, the interconnections among the CNCs and

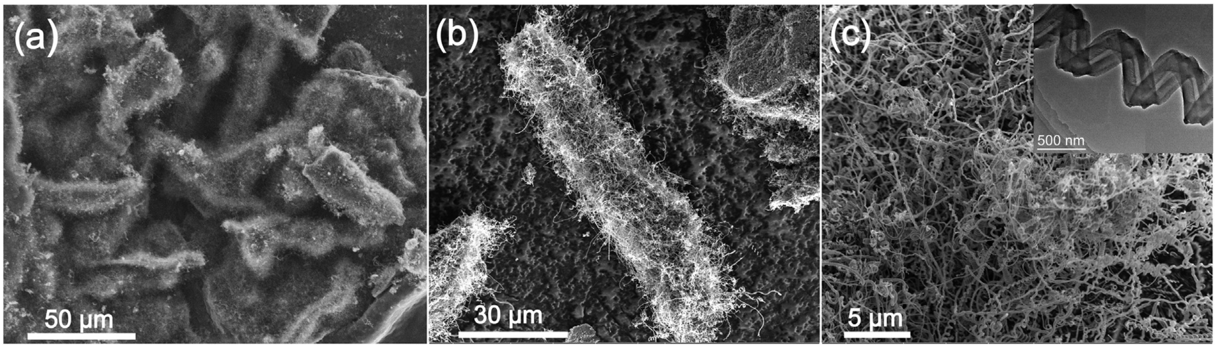

Fig. 1. SEM images of (a) CNCs/tissue, (b) carbonized fibers, and (c) the falling CNCs. The inset in (c) is the TEM image of a single CNC.