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Effects of diameter and hollow structure on the microwave absorption properties of short carbon fibers

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Abstract

A series of polyacrylonitrile (PAN)-based solid or hollow carbon fibers were prepared with outer diameters ranging from sub-micrometer to two hundred micrometers. They have similar compositions and intrinsic conductivities. Their electromagnetic parameters and microwave reflections were measured and compared. It was found that both the real and imaginary parts of the complex permittivity increased with decreasing diameter, especially at around 1.0 μm. The microwave absorption peaks moved to lower frequencies as well. However, some different properties were observed among the hollow carbon fibers with similar outer diameters. For example, the imaginary part of the complex permittivity increased much more gently and the microwave absorption peak located at the lower frequency had a stronger absorption. A connected network was finally proposed to understand these diameter-dependent properties. That is, a finer diameter means more fibers and a denser network, which produces a higher increase of the complex permittivity, especially for its imaginary part. Hollow structures could accelerate the increasing rate of the real part while lowering that of the imaginary part. It can be concluded that decreasing diameter and introducing a hollow or porous structure are both beneficial to the strong absorption at lower frequencies.

Keywords: Microwave absorption property; Carbon fiber; Hollow fiber; Short fiber

1. Introduction

Radar absorbing materials (RAMs) are widely used in many civil and military applications, which see more and more demands nowadays due to the progressive uses of microwaves. Ideally, RAMs should have strong radar wave absorption properties over a wide frequency range and need to be thin with light weight, especially for the use in the stealth technology of aircrafts [1–4]. However, it is extremely difficult to meet all the requirements using one material. What is more important is to adjust their microwave absorption characteristics as needed [1].

Carbon-based materials, such as carbon black powders, carbon fibers, carbon nanotubes, graphite and more recently graphene, were firstly used in this field and still play a majority role nowadays [3–15]. Take carbon fibers for example, they have been widely used as RAMs in reducing backscattering from objects or radar targets, electromagnetic interference suppressors and paints [2,7–11]. Their electromagnetic parameters can be tailored by adjusting intrinsic conductivities through compositions, graphitization and microstructures. These effects have been extensively studied based on the commercially available polyacrylonitrile (PAN)-based carbon fibers [9–11].

On the other hand, their microwave absorption properties can also be tuned by adjusting the length, diameter, or porosity of the short carbon fibers, which is a kind of size-dependent issue. For instance, small-diametered solid carbon fibers and large-diametered hollow carbon fibers were prepared and their microwave absorption properties were evaluated [12–14]. However, researches in this aspect are very limited due to the limited samples as well as the differences in the intrinsic conductivity among the samples [15].

In this paper, solid and hollow carbon fibers of various diameters were prepared through various spinning techniques. They had similar compositions as well as intrinsic

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conductivities, which were controlled by varying the processing conditions. Effects of the diameter and hollow structure on the electromagnetic parameters and the microwave reflections were investigated.

2. Experimental procedures

2.1. Preparation of PAN precursor fibers

Micro or sub-micro PAN fibers were prepared using an electrospinning process, of which both solid and hollow structures could be obtained selectively using one spinneret or a coaxial spinneret, as described in [16,17]. Hollow-porous PAN fibers, with a dual-layer finger-like porous structure on the cross-section and a diameter as high as >200 μm, were spun by a dry-wet spinning process using a coaxial spinneret, as described in [15,18]. Solid PAN fibers with several micrometers in diameter were purchased from Sinosteel Jili Carbon Co. Ltd., China, and used as received.

2.2. Oxidation and carbonization

Commercial solid PAN fibers were oxidized at 523 K for 60 min in air, carbonized at 1073 K for 120 min in nitrogen. The heating rate for oxidation and carbonization were 1.0 and 3.0 K min^{-1}, respectively. The intrinsic volume conductivity of the final solid carbon fibers was about 2.0×10^3 S m^{-1} with a carbon purity of 86 wt%. In order to maintain the similar chemical composition and the similar intrinsic conductivity, electrospun micro and sub-micro PAN fibers and the hollow-porous PAN fibers were oxidized and carbonized at different conditions, as shown in Table 1. After carbonization, the obtained carbon fibers were labeled according to their diameter and hollow structure, *i.e.*, D7.4 μm, D1.40 μm, D1.08 μm, D0.72 μm, H1.10 μm, H210 μm, respectively.

2.3. Characterization

The morphologies were studied using a scanning electron microscopy (SEM, JEO210, Japan) and the average diameter were calculated from SEM images with more than 50 fibers being collected. The carbon fiber samples were mashed into powders and compressed into a plate shape then the intrinsic volumetric conductivity was measured using the Keithley 2000 digital multimeter by the four-probe method [14]. The elemental composition of N, O, and C were checked by the Leco TCH-600 N/H/O and Leco CS-600 C/S analyzers.

According to an assumed mass ratio, 33 wt%, the same mass amounts of carbon fibers were cut into millimeter long using a fiber cutter (XQD140, Dandong Machine Factory, China), dispersed separately into paraffin wax, and molded into a coaxial template. The transmission/reflection (T/R) coaxial line was used to determine the electromagnetic parameters [19]. The measurement setup consisted of an Agilent 8720ET vector network analyzer with a synthesized sweep oscillator source and an S-parameter test set. A gold-plated coaxial air line with a precision 7 mm connector interface was used to hold the samples. The relative complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ (ε' and ε'' are the real and imaginary parts of the complex permittivity, respectively) of the samples was calculated from the measured T/R coefficients over the frequency range of 2–18 GHz. Reflectivities were calculated based on the electromagnetic parameters using a RAMCAD software [20], during which the thickness was fixed as 3 mm.

The scattering of electric field of the single short carbon fiber was simulated according to the three-dimensional finite element (FEM) algorithm based on Ansoft HFSS simulation platform. Plane wave excitation, tetrahedral edge element mesh, radiation boundary conditions and the adaptive iterative algorithm of matrix equations were used [21]. Parameters are assumed as follows: conductivity, 2.0×10^3 S m^{-1} (3 S m^{-1} for H210 μm); length, 1.0 mm; thermal expansion coefficient, -0.7×10^{-6} K^{-1}; modulus, 230 GPa.

3. Results and discussion

3.1. Morphology

SEM morphologies of the carbon fibers with different outer diameters are shown in Fig. 1.

Deep axial stripes could be observed on the surfaces of commercially derived carbon fibers, (f) D7.4 μm. On the contrary, the electrospun carbon fibers (c, d and e) are very smooth and their diameters are much lower. A hollow structure with a wall thickness of about 0.15 μm could be observed on the cross-section of (a) H1.10 μm, electrospun from a co-axial

Table 1
Processing parameters of oxidation and carbonization.

Processing stage	Temperature (K)	Heating rate (K min^{-1})	Duration (min)	σ (S m^{-1})	Outer diameter (μm)
Oxidation					
Commercial solid fibers	523	1.0	60	–	8.5
Electrospun solid fibers	523	1.5, 1.6, 1.8	40	–	1.65, 1.27, 0.96
Electrospun hollow fibers	523	1.8	30	–	1.30
Hollow-porous fibers	523	1.2	80	–	~250
Carbonization					
Commercial solid fibers	1073	3	120	$\sim 2.0 \times 10^3$	7.4
Electrospun solid fibers	1073	5, 6, 7	60	$\sim 2.1 \times 10^3$	1.40, 1.08, 0.72
Electrospun hollow fibers	1073	7	60	$\sim 2.0 \times 10^3$	1.10
Hollow-porous fibers	1073	4	100	$\sim 2.0 \times 10^3$	~210

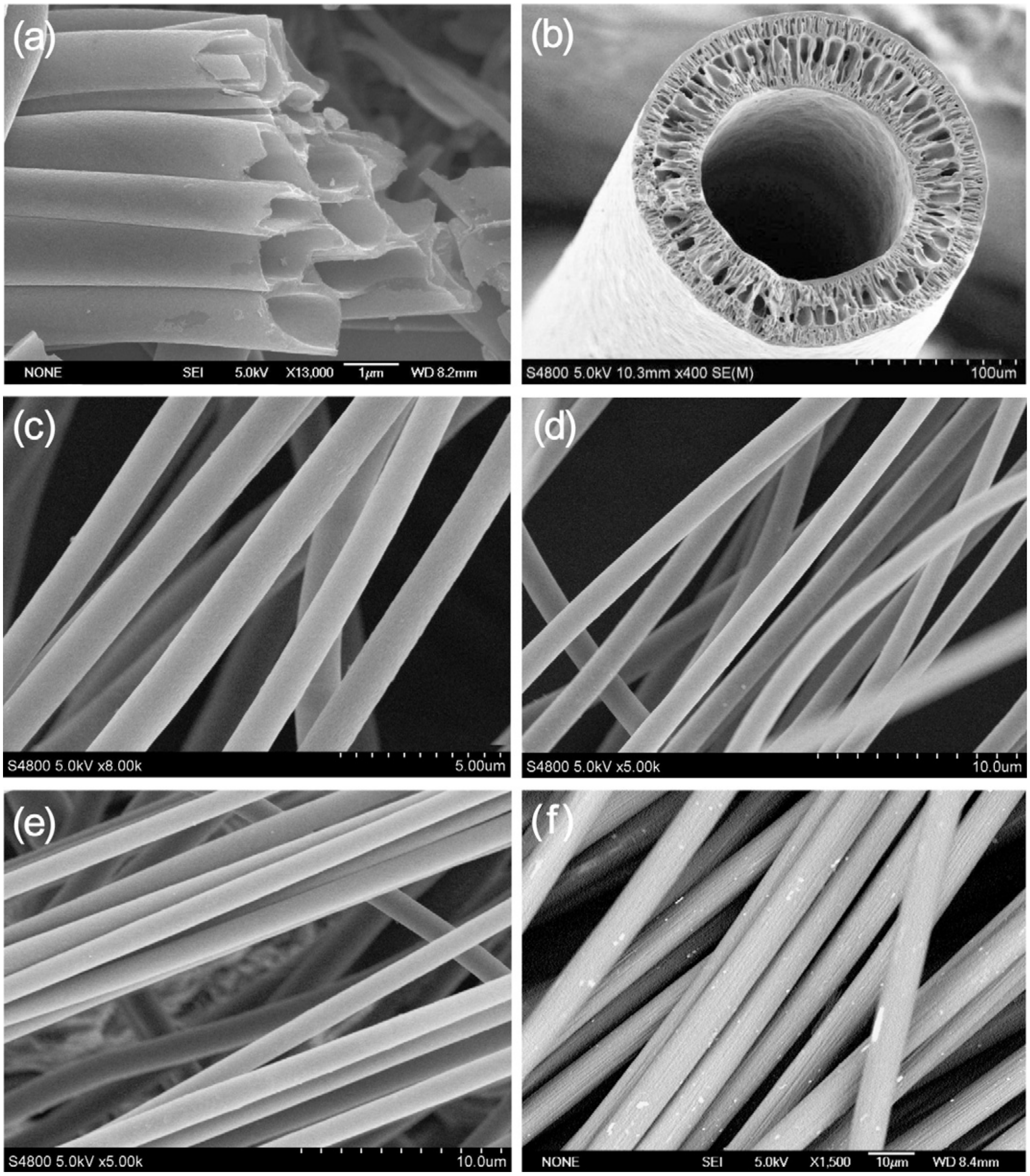

Fig. 1. SEM morphologies of carbon fibers with different outer diameters: (a) H1.10 μm; (b) H210 μm; (c) D0.72 μm; (d) D1.08 μm; (e) D1.40 μm; (f) D7.40 μm.

spinneret. Most impressive are the thick hollow-porous fibers, (b) H210 μm, whose diameter is as high as ∼210 μm. They have a characteristic dual-layer finger-like porous structure with a wall thickness of ∼50 μm. This kind of cross-section was derived from the dry-wet spinning process aided with a coaxial spinneret [18]. It is speculated that the hollow-porous shape will influence the microwave absorption properties [14,15]. In addition, even though their intrinsic conductivity is similar to other carbon fibers in this experiment, their apparent conductivity is nearly three orders lower, 3 S m^{-1}, due to the great porosity incorporated inside the walls [14].

3.2. Complex permittivity

Electromagnetic parameters include the complex permittivity ($\varepsilon = \varepsilon' - j\varepsilon''$) and the complex permeability ($\mu = \mu' - j\mu''$). Since carbon fibers are non-magnetic materials, their complex permeability is normal ($\mu \approx 1 - 0j = 1$). So we only compare the complex permittivity of carbon fibers, including the real part, ε', and the imaginary part, ε'', as shown in Fig. 2.

A general phenomenon could be observed for the solid carbon fibers, that is, the finer the diameter, the higher the permittivity. In addition, it seems that both the real parts and the imaginary parts decrease with increasing frequency. But the hollow carbon fibers show some unique properties, for example, some fluctuations could be observed from those electrospun hollow carbon fibers (H1.10 μm). In comparison of the two kinds of hollow carbon fibers, H1.10 μm and H210 μm, the imaginary parts are very close to each other even though the former have the highest real parts among all the samples. However, the imaginary part of H1.10 μm is lower than that of D0.72 μm, the finest electrospun solid carbon fibers.

Effect of the diameter on the complex permittivity could be more clearly observed when a relationship between ε' (ε'') and

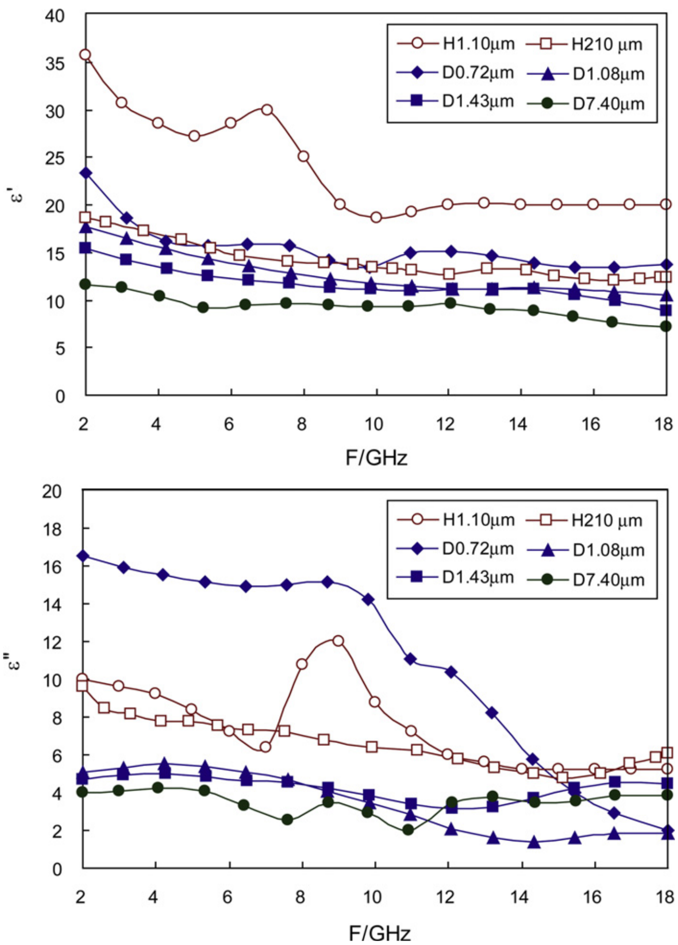

Fig. 2. Real part (ε′) and imaginary part (ε″) of complex permittivity as a function of frequency.

diameter was plotted at a fixed frequency of 2 GHz, as shown in Fig. 3. Both parts increase with decreasing diameter, and a sharp increase could be observed when the diameter decreases below 1.0 μm. Hollow structures give much higher values compared to the solid ones with similar outer diameters.

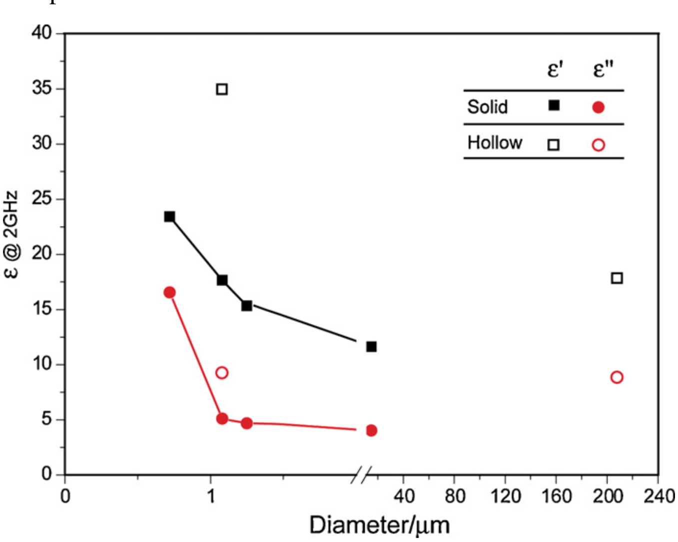

Fig. 3. Effect of diameter on real part (ε′) and imaginary part (ε″) of complex permittivity at 2 GHz.

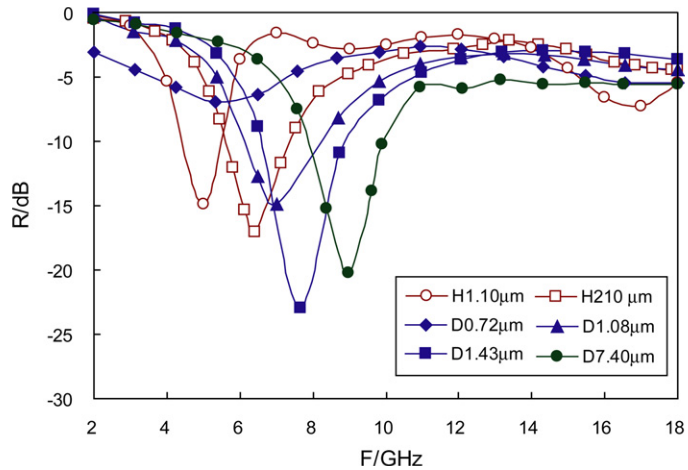

Fig. 4. Calculated reflectivity curves of short carbon fibers.

3.3. Reflectivity

Carbon fibers are conductivity-loss absorbing materials, so the reflectivity of thus obtained single-layer RAM can be calculated according to Eq. (1) [20]:

$$R = 20\log\left|\frac{\tanh(2\pi j fd\sqrt{\varepsilon' - j\varepsilon''}/c) - \sqrt{\varepsilon' - j\varepsilon''}}{\tanh(2\pi j fd\sqrt{\varepsilon' - j\varepsilon''}/c) + \sqrt{\varepsilon' - j\varepsilon''}}\right| \quad (1)$$

where R is the reflectivity, f the frequency, d the thickness of material, j the imaginary unit, and c the vacuum speed of light.

Using a computer aided software, we could obtain reflectivities of carbon fiber absorbers at a fixed thickness, 3 mm, which is commonly considered for dielectric RAMs. The calculated reflectivities are shown in Fig. 4, with their characteristic absorbing parameters extracted and shown in Table 2.

All the reflectivity cures have at least one strong absorption peak in the frequency range of 4–10 GHz. For the solid carbon fibers, the absorption peaks moved to lower frequencies with decreasing diameter, and more specifically for the electrospun solid carbon fibers, the absorption intensity decreased as well. For the hollow carbon fibers, a similar trend was observed, but their peak positions are located at comparatively lower frequencies. For example, as shown in Table 2, the absorption peak of H1.10 μm is located at 5.0 GHz while that of D1.08 μm at 6.9 GHz.

Table 2 also illustrates the bandwidths for $R \leq -10$ dB, which is used to evaluate the absorption bandwidths of RAMs. It indicates that a bandwidth of >2.0 GHz could be obtained for the solid carbon fibers with diameters in the range of 1.08–7.4 μm, as well as a bandwidth of 1.1–1.7 GHz for the two hollow carbon fibers. However, the finest carbon fibers, D0.72 μm, have zero bandwidth due to their weak absorption at the presumed thickness of 3 mm.

3.4. Discussion

To make RAMs, on the one hand, the reflection coefficient is required as low as possible so that the electromagnetic waves

Table 2
Characteristic absorbing parameters of the carbon fibers.

Characteristic absorbing parameters	D7.4 μm	D1.43 μm	D1.08 μm	D0.72 μm	H210 μm	H1.10 μm
Lowest reflectivity	−20.3	−23.0	−15.2	−7.0	−17.1	−15.9
Frequency for the lowest reflectivity	9.0	7.6	6.9	5.4	6.4	5.0
Bandwidth for $R \leq -10$ dB/GHz	2.1	2.3	2.1	0	1.7	1.1

could enter the materials with the maximum intensity, which generally requires a certain amount of permittivity parameters, especially a low imaginary part of permittivity; one the other hand, the electromagnetic wave entered the materials should be absorbed with the maximum intensity, which also requires appropriate permittivity parameters, especially a relatively higher imaginary part of permittivity which enhances absorption in terms of the dielectric loss. The degree of dielectric loss can be evaluated using the dielectric loss tangent according to Eq. (2):

$$tg\,\delta = \frac{\varepsilon''}{\varepsilon'} \quad (2)$$

where δ is the dielectric loss angle.

Therefore, at a proper frequency, f, and a fixed thickness of the material, d, as indicated in Eq. (1), a good combination of real part (ε') and imaginary part (ε'') is needed to obtain the lowest reflection.

But in what a way do the diameter and the hollow structure influence the variation of the real part (ε') and the imaginary part (ε'') of the complex permittivity? Trying to understand that, firstly, we simulated the scattering of electric field on the surfaces of the single short carbon fiber, as shown in Fig. 5.

Single short carbon fibers can be regarded as dipoles, which can consume part of the microwave energy in a way of scattering of the electric field [22]. For the solid fibers in Fig. 5, it can be observed that the scattering tends to become stronger with increasing diameter, from (c) D0.72 μm to (f) D7.40 μm. This is similar to our previous results [21], that both increase of the diameter and conductivity could increase the scattering strength. Also related is the length/diameter ratio, which may lead to a resonance at a proper frequency [9–11]. The exceptional low of the scattering strength in (e) D1.40 μm is probably due to the mismatching of length/diameter ratio, 1 mm/1.40 μm, at the frequency of 10 GHz. However, the scattering strength of hollow fibers is relatively lower than that

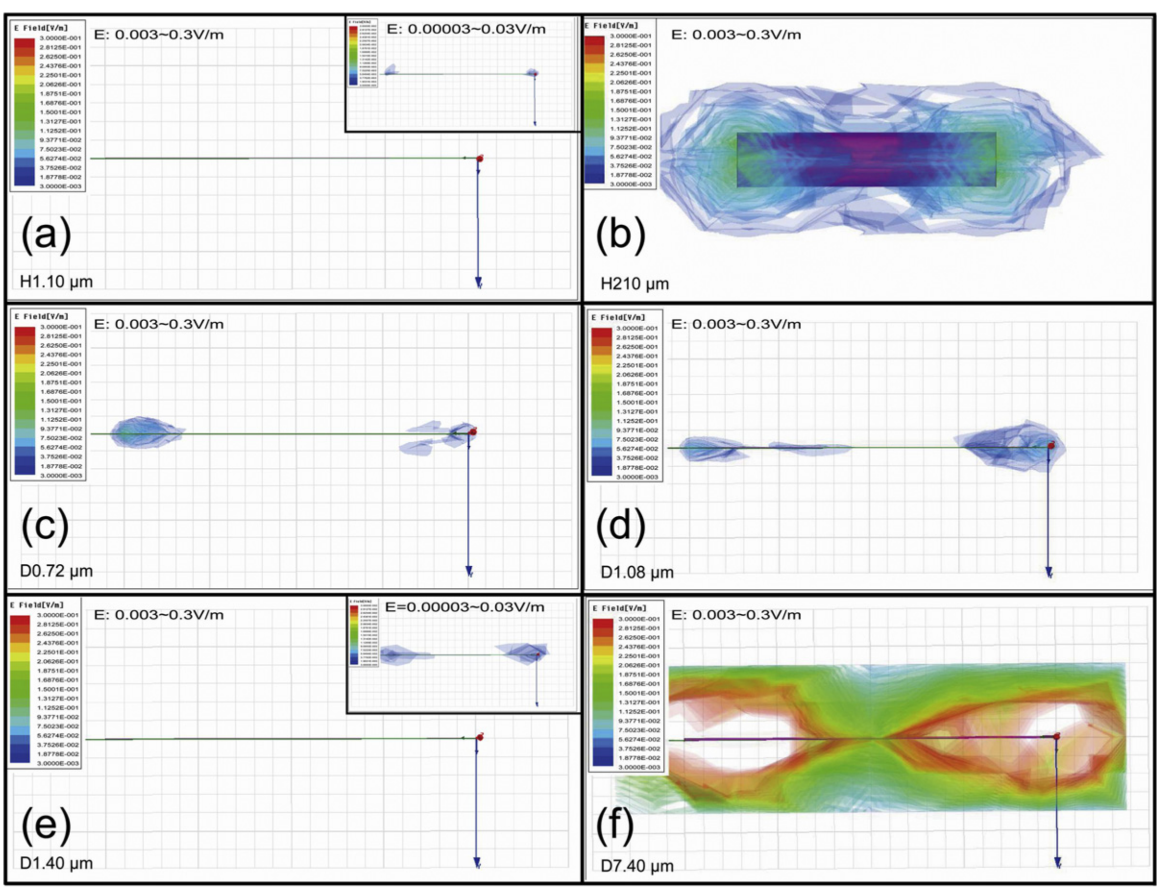

Fig. 5. Scattering of electric field at 10 GHz on the surfaces of the single short carbon fiber: (a) H1.10 μm; (b) H210 μm; (c) D0.72 μm; (d) D1.08 μm; (e) D1.40 μm; (f) D7.40 μm. Inserted in (a) and (e) are observed in a low range of electronic field, 0.00003–0.03 V/m.

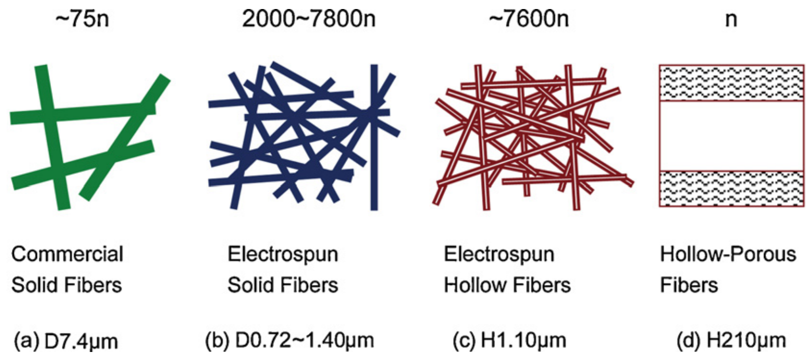

Fig. 6. Schematic illustrations of the network containing randomly arranged short carbon fibers with different outer diameters.

of the solid fibers, as observed from (a) H1.10 μm and (d) D1.08 μm. The peak value of the scattering strength in (b) H210 μm is also much lower than that in (f) D7.40 μm. This is partly due to the hollow structure and a much lower conductivity. So, we may conclude that lowering the diameter and introducing a hollow structure cannot increase the scattering of electric field if only one single short carbon fiber is considered.

Since the mass ratio is the same for all the tests and all the fibers were cut into the same length, a finer diameter means more fibers, especially for the hollow carbon fibers. No doubts that more fibers make the fiber network much more denser. A connected network could be proposed to understand the size-dependent microwave absorption properties of the short carbon fibers, as shown in Fig. 6.

The effect of the outer diameter on the effective length of carbon fibers, or the number of short carbon fibers, can be calculated according to Eq. (3) based on the cross-section areas.

$$L = nL_0 = \frac{4m}{\rho\pi(d_{outer}^2 - d_{in}^2)(1-P)} \quad \text{or}$$
$$\frac{L_1}{L_2} = \frac{n_1}{n_2} = \frac{(d_{outer2}^2 - d_{in2}^2)(1-P_2)}{(d_{outer1}^2 - d_{in1}^2)(1-P_1)} \tag{3}$$

where n is the number of fibers, L_0 short fiber length, m mass ratio, ρ intrinsic density, d_{outer} outer diameters, d_{in} inner diameters for hollow fibers and P is porosity which is only applicable for H210 μm assigned as 0.7.

Fig. 6 shows the schematic illustrations of the randomly arranged carbon fibers with different outer diameters. The numbers of filaments were calculated and are shown above their networks.

Generally speaking, based on the increase of the whole conductivity, more connective a network produces a higher increase of the complex permittivity, especially the imaginary part [14,15]. That is why the increase of complex permittivity with decreasing diameter. In the case of D0.72 μm, the imaginary part increases beyond the proper position leading to a worse impedance match. For the network with similar number of short fibers, take D0.72 μm and H1.10 μm for comparison, the hollow fibers with larger outer diameter have a better impedance match. Their imaginary part of complex permittivity increases more gently and coincides well with the real part. That is, hollow structures could lower the increasing rate of the imaginary part. So, it can be concluded that decreasing diameter and introducing hollow structures are both beneficial to the strong absorption at lower frequencies.

The number of fibers is the lowest in the case of H210 μm, as shown in Fig. 6. Their wall is porous and incorporated with macro-pores and the hollow diameter is as large as 130 μm, both may take effect in leading the attenuated waves to enter inside the fiber and confine them until loosing energy totally. They may consume microwaves as single fibers rather than as networks.

4. Conclusions

(1) Both the real and imaginary parts of the complex permittivity increased with decreasing diameter, especially at around 1.0 μm. Their microwave absorption peaks moved to lower frequencies at the same time. For the solid carbon fibers with an average diameter of 0.72 μm, the imaginary part increased too high making the absorption peak much weak.
(2) For the hollow carbon fibers, the imaginary part of the complex permittivity increase much more gently than the real part. Their real part of the complex permittivity is much higher than that of solid fibers with similar outer diameters and the imaginary part is relatively lower, which gave them a strong absorption peak at the lower frequency.
(3) A connected network was proposed to understand the size-dependent microwave absorption properties of these short carbon fibers. That is, a finer diameter means longer fibers and denser networks, which produces a higher increase of the complex permittivity, especially for the imaginary part. Hollow structures could lower the increasing rate of the imaginary part.

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