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Effect of carbonization temperature on the structure and microwave absorbing properties of hollow carbon fibres

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Abstract

A series of polyacrylonitrile-based hollow carbon fibres (PAN-HCFs) were prepared by carbonizing polyacrylonitrile (PAN) hollow cured fibres at temperature ranging from 550 to 950 °C for 1 h in nitrogen. The effects of carbonization temperature on the structure, elemental compositions, surface electrical conductivity, electromagnetic parameters and reflectivity of PAN-HCFs were investigated. Results indicate that the obtained PAN-HCFs have not been graphitized and the C content and surface electrical conductivity increases as the carbonization temperature increases. The reflectivity of composites of PAN-HCFs and resin is −7.50 dB at 6.06 GHz and the band of the reflectivity under −5 dB is 6 GHz when the carbonization temperature is 750 °C.

Keywords: Carbonization; Polyacrylonitrile; Carbon fibres; Microwave absorbing properties

1. Introduction

With the rapid development of wireless communications, microwave absorbing materials have attracted considerable attention because of the growth of their applications in many electromagnetic facilities such as anechoic rooms, broadcasting, communications, commercial information and radar systems. In view of their applications, excellent microwave absorbing materials should exhibit strong microwave absorption properties over a wide frequency range and need to be low both in thickness and total weight, especially for aircraft [1–4]. Carbon fibre has been widely used in microwave absorbing materials in reducing backscattering from objects or radar targets, electromagnetic interference suppressors and paints [5–9]. In order to improve their microwave absorbing properties, carbon fibres with different cross-sections, such as ribbon carbon fibre and trilobal carbon fibre have attracted worldwide attention due to the facts that they can absorb electromagnetic wave generated from an electric source, and are promising candidates for replacement of circular materials.

Hollow carbon fibres (HCFs) have been investigated over the last few years which are produced by carbonizing raw materials such as polyacrylonitrile (PAN), cellulose, phenolic, or pitch fibres. These fibres are hollow, porous, lightweight, easily handled, and highly conductive. The preparation and characterization of such fibres have been described in Refs. [10–17]. One of the advantages of HCFs, compared to general carbon fibre, is the porous structure of HCFs which can add the reflection and refraction frequency of electromagnetic wave. The PAN-HCFs are proved to be a light conductive radar absorbing materials in view of its hollow-porous structures and microwave absorption properties [18]. In this work, a series of PAN-HCFs were prepared by carbonizing PAN hollow cured fibres at temperatures ranging from 550 to 950 °C for 1 h in nitrogen. The effects of carbonization temperature on their structure and microwave absorbing properties were also examined.

2. Experimental procedure

PAN hollow fibres spun by dry-wet spinning were used as the precursor [19]. Virgin PAN hollow fibres were first dipped in distilled water for 1–2 days. Afterwards, the fibres were oxidized at 250 °C for 1 h in air, carbonized at 550, 650, 750, 850, 950 °C for 1 h in nitrogen with a flow rate of 30 sccm.

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The surface morphologies of PAN-HCFs were characterized by scanning electron microscope (SEM) using JSM-6700F microscope. The crystalline structure of PAN-HCFs was performed by X-ray diffraction (XRD) on a D8ADVANCE type, using CuK_{α} radiation with 2θ from 5° to 90°. Raman spectroscopy was used to study the amorphous structure of the hollow carbon fibres. The Raman spectra were obtained using a laser confocal Raman spectrometer (LABRAM-010) in the range from 400 to 2000 cm^{-1}. The surface electrical conductivity was measured at room temperature by the two probes of the Keithley 2000 digital multimeter. The compression pressures throughout the measurements were maintained both ends of single fibre [20]. The relative complex permittivity $\varepsilon = \varepsilon' - j\varepsilon''$ (ε' and ε'' are the real and imaginary parts of the complex permittivity, respectively) of the HCFs–paraffin composites were measured by Agilent 8720ET vector network analyzer over the frequency range of 2–18 GHz [21,22]. The reflectivity of microwave absorbing materials using the sole absorber was simulated with RAMCAD software [23]. A 180 mm × 180 mm microwave test plate were pressed by hydraulic press and solidified at atmospheric temperature in order to compare the simulated results.

3. Results and discussion

Fig. 1 shows the SEM micrographs of the cross-sections and surface of the PAN-HCFs carbonized from 550 °C to 950 °C. Results indicate that the differences among these SEM images are very small. The di-finger-like porous structure of virgin PAN is preserved after carbonization. It means that carbonization keeps the hollow shape of virgin hollow fibre, and the shape cannot be changed any more when the temperature continues increasing. During the carbonization stage, volatiles evolved and formed the carbon basal planes. The formation of carbon basal planes was due to the crosslinking reaction and the elimination of nitrogen [12]. The bulk density was measured by

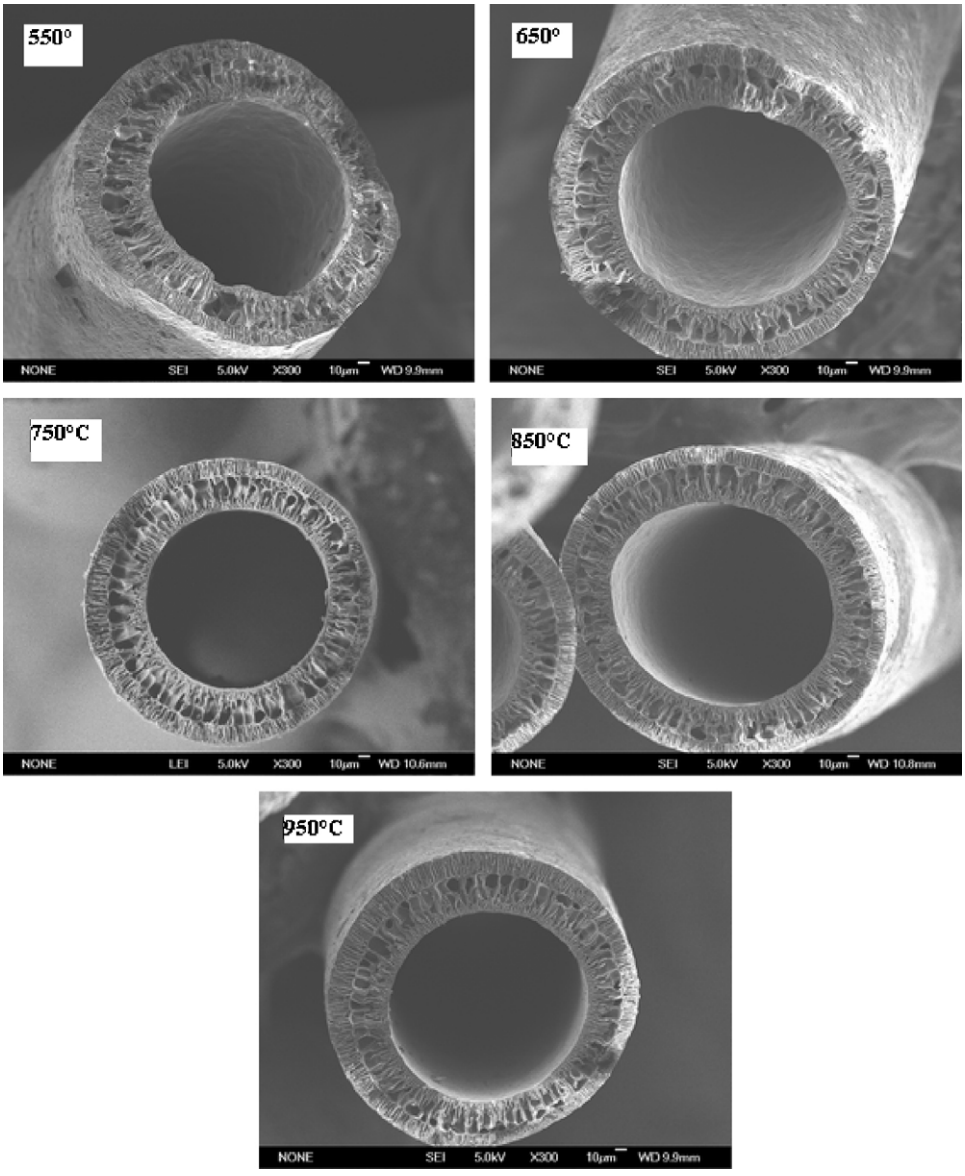

Fig. 1. SEM micrographs of the crossing-sections of PAN-HCFs.

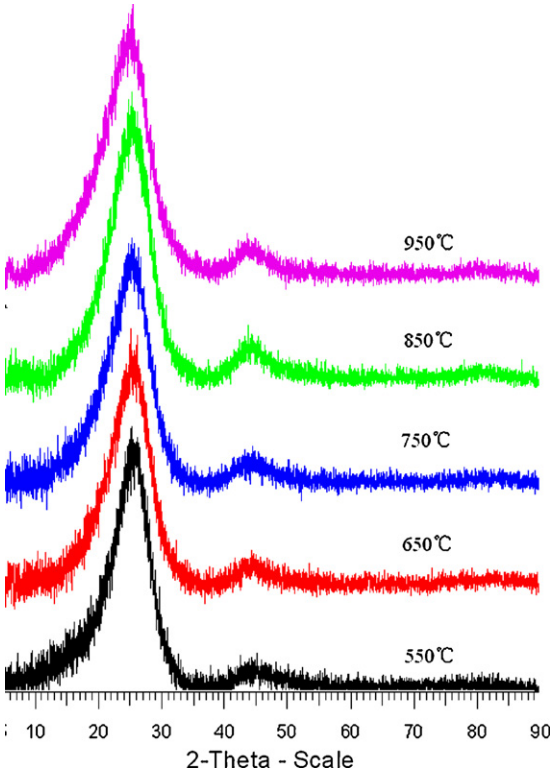

Fig. 2. XRD profiles of PAN-HCFs at various carbonization temperatures.

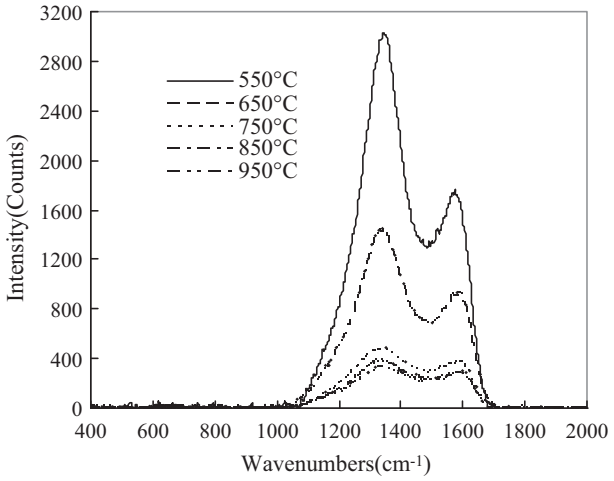

Fig. 3. Raman spectra of PAN-HCFs at various carbonization temperatures.

mercury intrusion pore measurement. As expected, the bulk density, due to its hollow and porous structure, is much less than the general carbon fibre. When intruded at 0.53 psia of pressure, the samples showed a bulk density of 0.5 g mL^{-1}.

In order to explain the effects of different carbonization temperature, XRD was employed to investigate the crystalline structure of the carbonized fibres. As is shown in Fig. 2, there is only one obvious broad band peak at 25° in each spectrum, corresponding to the (0 0 2) diffraction of graphite structure. The absence of the (1 1 0) band (at 44°) even at 950 °C indicates a non-graphitized carbonaceous structure [19,24].

Fig. 2 presents that PAN-HCFs exist disorder and amorphous carbon and carbon compound resulted from the degree of the carbonization. The Raman spectra of PAN hollow cured fibre treated at different temperatures are shown in Fig. 3. It is observed that each spectrum shows two broad peaks centred around 1340 and 1600 cm^{-1}. The normal Raman spectrum for a typical carbonaceous material consists of two peaks, one around 1355 cm^{-1} called D peak (disordered or amorphous), and another around 1600 cm^{-1} called G peak (graphite) [24,25]. The G-peak is the Raman active E_{2g2} mode of graphite involving the in-plane bond-stretching motion of sp^2-hybridized C atoms whilst the D-peak is a breathing mode of A_{1g} symmetry involving phonons near the K zone boundary. The PAN based hollow carbon fibres are amorphous as observed from the Raman spectra patterns which show the presence of the D mode. The D mode is invisible in perfect graphite and only becomes active in the presence of disorder [24,25]. Combined with the analysis of XRD and Raman, it is clearly confirmed that these PAN-HCFs are far from graphitized structure.

The I_D/I_G ratio of Raman spectra is a typical parameter to quantify the degree of disorder in carbon materials, the decrease of the I_D/I_G ratio indicates that the degree of graphitization increases. Table 1 shows the intensity ratio of D-peak to G-peak, the surface electrical conductivity and element compositions for the hollow carbon fibre prepared under different carbonization temperatures. The values of I_D/I_G decrease gradually with increasing carbonization temperature, indicating the structure of the carbon fibres slowly evolved toward ideal graphite whilst the electrical conductivity increases accordingly. As shown in Table 1, the electrical conductivity is 2373.423 Ω^{-1} m^{-1} when carbonization temperature is 950 °C. Table 1 also shows the surface electrical conductivity and element compositions of PAN-HCFs were determined from the degree of carbonization.

Fig. 4 shows the ε' and ε'' of composites of the PAN-HCFs and paraffin in the frequency range of 2–18 GHz. At 2 GHz, the ε' and ε'' of the PAN-HCFs with 550 °C are 2.62 and 0.06. The ε'

Table 1
The relationship of the ratio of D-peak to G-peak and the electrical conductivity and element composition for the prepared hollow carbon fibre.

Temperature (°C)	I_D	I_G	I_D/I_G	Element composition (%)			σ (Ω^{-1} m^{-1})
				N	C	H	
550	3010.8	1493.7	2.02	18.78	69.19	0.757	0.002
650	1425.14	869.489	1.64	18.14	70.91	0.709	2.095
750	474.81	367.445	1.29	16.78	74.05	0.336	78.626
850	375.842	295.939	1.27	15.13	76.54	0.311	772.223
950	329.199	268.593	1.23	10.52	81.26	0.204	2373.423

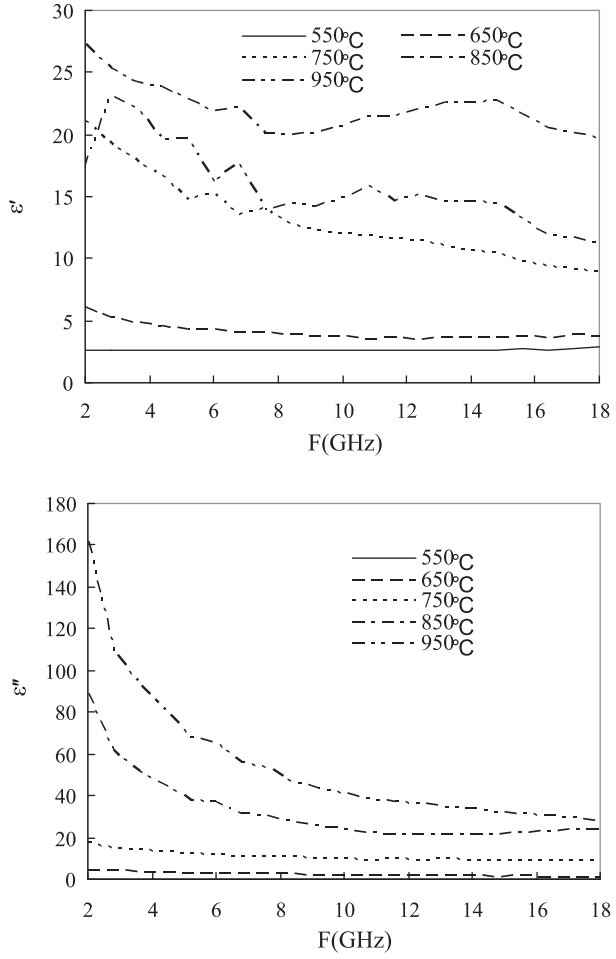

Fig. 4. Electromagnetic parameters of HCF–paraffin composites vs. microwave frequency.

and ε'' of PAN-HCFs gradually increases with the increase of carbonization temperature and reaches 27.29 and 88.89 when carbonization temperature is 850 °C. These characteristic electromagnetic properties, resulting from the surface electrical conductivity, can influence the microwave absorbing properties.

According to transmission line theory, the reflection coefficient of electromagnetic wave, R(dB),under perpendicular wave incidence at the surface of a single-layer material backed by a perfect conductor can be defined by [23]:

$$R = 20\ 1\ g\left|\frac{\sqrt{\mu/\varepsilon}\tanh(j(2\pi f/C)\sqrt{\varepsilon\mu}d) - 1}{\sqrt{\mu/\varepsilon}\tanh(j(2\pi f/C)\sqrt{\varepsilon\mu}d) + 1}\right| \quad (1)$$

$\mu = \mu' - j\mu''$ (μ' and μ'' are the real and imaginary parts of the complex permeability, respectively), for conductive absorbers, $\mu' \approx 1$ and $\mu'' \approx 0$, C is the speed of light, f is the microwave frequency, j is the imaginary unit, and d is the thickness of the coating layer. Fig. 5 shows the calculated reflectance of composites of the PAN-HCFs and paraffin vs. microwave frequency based on given electromagnetic parameters with the thickness of 3 mm. When carbonization temperature is 550 °C, the calculated reflectance exhibits hardly any microwave absorption, due to its lower surface

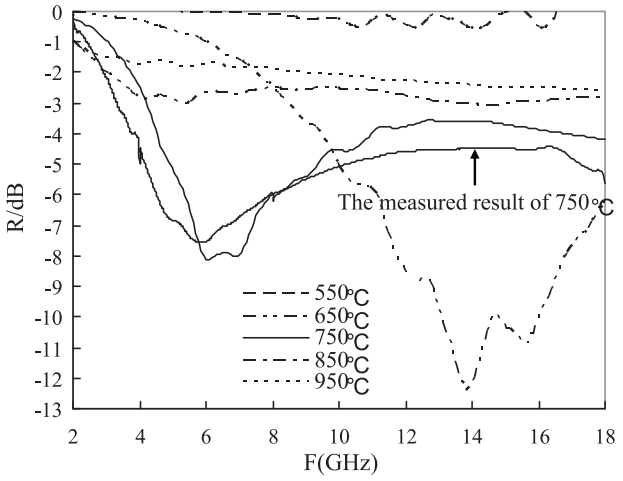

Fig. 5. The reflectivity curves of HCF–paraffin composites vs. microwave frequency.

electrical conductivity. The reflection loss for PAN-HCFs is less than −1 dB for all frequencies between 2 and 18 GHz. When the carbonization temperature is 650 °C, the reflection loss is −12.31 dB at 13.92 GHz and the band of the reflectivity under −5 dB is 8 GHz. When the carbonization temperature is 750 °C, the minimum value is −8.09 at 6.08 GHz, higher than that of −12.31 dB. In addition, Fig. 5 indicates that the location of reflection coefficient apex moved to the lower frequency with the increase of carbonization temperature. In order to compare the simulated results, the measured and calculated results of fibre-filled composites carbonized at 750 °C were also shown in Fig. 5. The reflectivity of composites of PAN-HCFs and resin is −7.50 dB at 6.06 GHz and the band of the reflectivity under −5 dB is 6 GHz when the carbonization temperature is 750 °C. The difference between calculated and measured results may root in the preparation processes and calculated model. However, the calculated results are in good agreement with the experimental results.

The above results indicate that carbonization temperature has great effect on the structure and microwave absorbing properties of hollow carbon fibres. Firstly, the condition of carbonization influence the degree of disorder in carbon materials and the degree of disorder results in different C content in HCFs during the carbonization stage. Secondly, the electrical conductivity leads to the change of complex permittivity and reflectivity. This is mainly due to the suitable impedance matching resulted from an optimal electrical conductivity of HCFs. The electrical conductivity of hollow carbon fibre increases with the increase of C content. Fig. 6 shows the electrical conductivity vs. C content.

According to transmission line theory of the electromagnetic wave, the impedance matching is

$$Z = \sqrt{\frac{\mu\mu_0}{\varepsilon\varepsilon_0}} \approx Z_0\sqrt{j\frac{\mu}{\varepsilon tg\delta_e}} = (1+j)\sqrt{\frac{\omega\mu_0\mu}{2\sigma}} \quad (2)$$

where $tg\delta_e$ is conductive loss tangent, σ is surface electrical conductivity, ω is the angular frequency of the incident plane wave, and μ_0 and ε_0 are the complex permeability and permit-

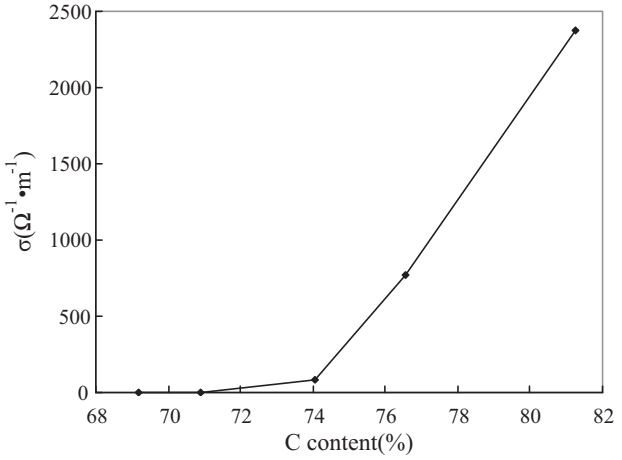

Fig. 6. Electrical conductivity of hollow carbon fibre vs. C content.

tivity of the air, respectively. According to the foregoing Eq. (2), an optimal electrical conductivity facilitates to win suitable microwave absorbing properties. The degree of carbonization can adjust the electrical volume conductivity of PAN-HCFs through selecting a moderate carbonization temperature.

4. Conclusions

A series of PAN-HCFs with di-finger-like porous structure were prepared by carbonized PAN hollow cured fibre at temperature ranging from 550 to 950 °C. The prepared PAN-HCFs have not achieved graphitized structure yet. The surface electrical conductivity of PAN-HCFs increases with increasing carbonization temperature in the range of 550–950 °C. The complex permittivity increases with the increase of carbonization temperature in the range of 550–950 °C. The microwave absorbing properties depend strongly on the carbonization temperature. The reflectivity of composites of PAN-HCFs and resin is −7.50 dB at 6.06 GHz and the band of the reflectivity under −5 dB is 6 GHz when the carbonization temperature is 750 °C. The calculated reflectivity of composites of PAN-HCFs produced by 650 °C and paraffin is −12.31 dB at 13.92 GHz.

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