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Effect of carbonization time on the structure and electromagnetic parameters of porous-hollow carbon fibres

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Abstract

A series of polyacrylonitrile-based porous-hollow carbon fibres (PAN-PHCFs) were prepared by carbonizing PAN porous-hollow cured fibres at 1073 K for different times in nitrogen. The effects of carbonization time on the structure, electrical volume conductivity and electromagnetic parameters were investigated. Results indicate that the degree of graphitization increases as carbonization time increases. The electrical volume conductivity increases as the degree of graphitization and carbonization time increase. The real and imaginary parts of the complex permittivity (ε' and ε'') increase with carbonization time increasing. The values of ε' and ε'' of composites of PAN-PHCFs and paraffin are 13.76 and 10.09 when the carbonization time is 240 min, and the electrical volume conductivity of PAN-PHCFs is 190.47 Ω^{-1} m^{-1}.

Keywords: Carbon fibres; Carbonization; Electromagnetic parameters

1. Introduction

With the progress in the engineering of antennas and electromagnetic interference (EMI) systems, radar absorbing materials (RAMs) are widely used in commercial and military applications. RAMs are made with compounds having a high loss energy which enables them to absorb the incident radiation in synchronized frequencies and dissipate it as heat. In view of their applications, excellent RAMs should have certain properties as follows: (1) exhibit strong radar absorbing properties over a wide frequency range; (2) need to be low both in thickness and total weight, especially for aircraft; (3) have strong mechanical property, etc. [1–4].

Polyacrylonitrile (PAN) copolymers are commercially important, and are used as carbon fibre precursors, as well as for developing porous and activated carbon for a variety of applications, including catalysis, electrochemistry, separation processes, energy storage devices, etc. PAN-based carbon fibre has also been commercially available for over thirty years, and now dominates nearly 90% of all the carbon consumption in the world because of its high tensile strength and low volume fraction of voids. PAN porous-hollow carbon fibres (PAN-PHCFs), with dual-layer di-finger-like porous structure, have attracted considerable attention due to their explosive growth in the utilization of separate and purificatory devices in electronics and pharmaceutical industries [5–9]. Now, PAN-PHCF has also been considered to be a promising candidate in the RAMs field. The main attraction of PAN-PHCFs is their ability to yield significant electrical properties with a suitable electrical conductivity and reduce the weight loading of such fibre-filled composites by virtue of their porous-hollow structures. In addition, it may be speculated that the hollow-porous shape will influence the microwave absorbing properties [10–12].

Carbonization is a very important process for preparing excellent PAN-PHCFs because carbonization largely governs the final structure of the fibre and hence its ultimate properties and a number of excellent papers and reviews have been reported on this subject [13–17]. However, there are few reported experimental results on the electrical properties and electromagnetic parameters. In this work, a series of PAN-PHCFs were prepared by carbonizing PAN porous-hollow cured fibres at 1073 K from 10 min to 240 min in nitrogen. The effects of carbonization time on their structure and electromagnetic parameters were also examined.

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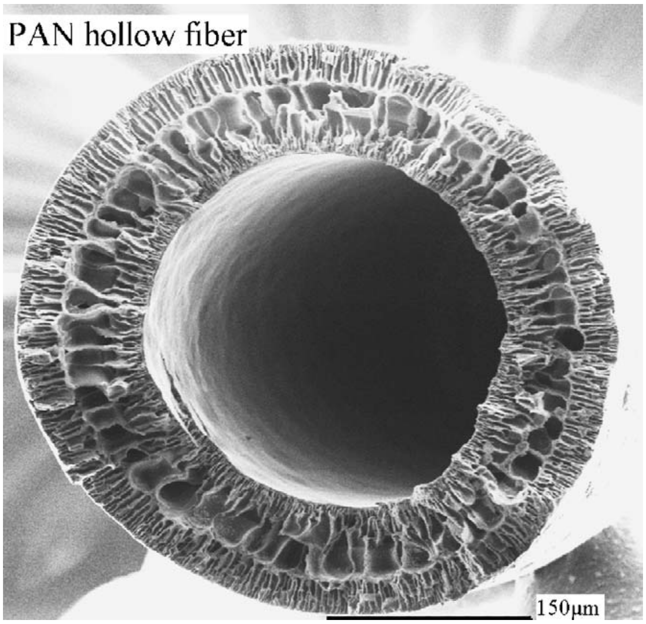

Fig. 1. The cross-section of original PAN porous-hollow fibre.

2. Experimental procedure

PAN porous-hollow fibre spun by dry-wet spinning setup was used as the precursor [18–19]. Fig. 1 shows the porous structure of the PAN hollow fibre. The original PAN hollow fibres were first dipped in distilled water for 2 days. Afterwards, the fibres were oxidized at 523 K for 60 min in air, carbonized at 1073 K from 10 min to 240 min in nitrogen. Fig. 2 shows the flow chart of preparation of PAN-PHCFs.

The cross-section morphologies of PAN-PHCFs were characterized by scanning electron microscope using JSM-6700F microscope. The crystalline structure of PAN-PHCFs was performed by X-ray diffraction (XRD) on a D8ADVANCE type, using CuK$_\alpha$ radiation with 2θ from 5° to 90°. Raman spectroscopy was used to study the amorphous structure of the PHCFs. The Raman spectra were obtained using a laser confocal Raman spectrometer (LABRAM-010) in the range from 400 cm^{-1} to 2000 cm^{-1}. PAN-PHCF was compressed by the two probes of the Keithley 2000 digital multimeter to measure the electrical conductivity of the samples at room temperature by the two-probe method. The compression pressures throughout the measurements were maintained. In order to reduce error, single PAN-PHCF was randomly selected more than 20 and the electrical volume conductivity was measured and the average electrical volume conductivity was calculated according to the collected results [20]. The Transmission/Reflection (T/R) coaxial line was used to determine the electromagnetic parameters of the PAN-PHCFs. 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 $\varepsilon = \varepsilon' - j\varepsilon''$($\varepsilon'$ and ε'' are the real and imaginary part of the complex permittivity, respectively) of the samples was calculated from the measured T/R coefficients over the frequency range of 2–18 GHz [21].

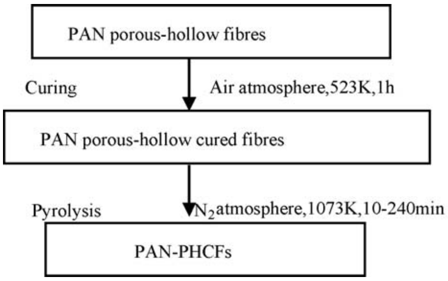

Fig. 2. The flow chart of preparation of PAN-PHCFs.

3. Results and discussion

3.1. Morphology of PAN-PHCFs

Fig. 3 shows the typical SEM micrographs of the cross-section and surface of the PAN-PHCFs carbonized at 1037 K under 240 min because the differences among these SEM images are very small. The cross-sectional shape of PAN in Fig. 1, di-finger-like porous structure, is preserved after carbonization. It means that the hollow shape of virgin hollow fibre is kept with different carbonizing time, and the shape cannot be changed any more when the time 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.

Fig. 4 shows the variation of carbonization yield and shrinkage ratio of PAN-PHCFs with increasing carbonization time. The weight loss and the shrinkage ratio were determined from a change in weight and length before and after carbonization. The carbonization yield and the shrinkage ratio of PAN-PHCFs were calculated as follows:

$$\text{carbonization yield}(\%) = \frac{\text{weight after carbonization}}{\text{weight before carbonization}} \times 100\% \tag{1}$$

$$\text{shrinkage ratio}(\%) = \frac{\text{length before carbonization-length after carbonization}}{\text{length before carbonization}} \times 100\% \tag{2}$$

As shown in Fig. 4, the weight loss and shrinkage ratio of PAN-PHCFs are nearly unaffected with carbonization time, and the values of carbonization yield are about 64% and the values of shrinkage ratio are about 14%. It is suggested that the carbonization yield and shrinkage ratio of PAN-PHCF are not affected by carbonization time. During the carbonization stage, the non-carbon elements are removed as volatiles (i.e., H_2O, HCN, NH_3, CO, CO_2, N_2, and so on) to give carbon fibres with weight loss and shrinkage. The removal of volatiles from fibres becomes subdued with increasing carbonization time so that the weight loss and shrinkage ratio change little.

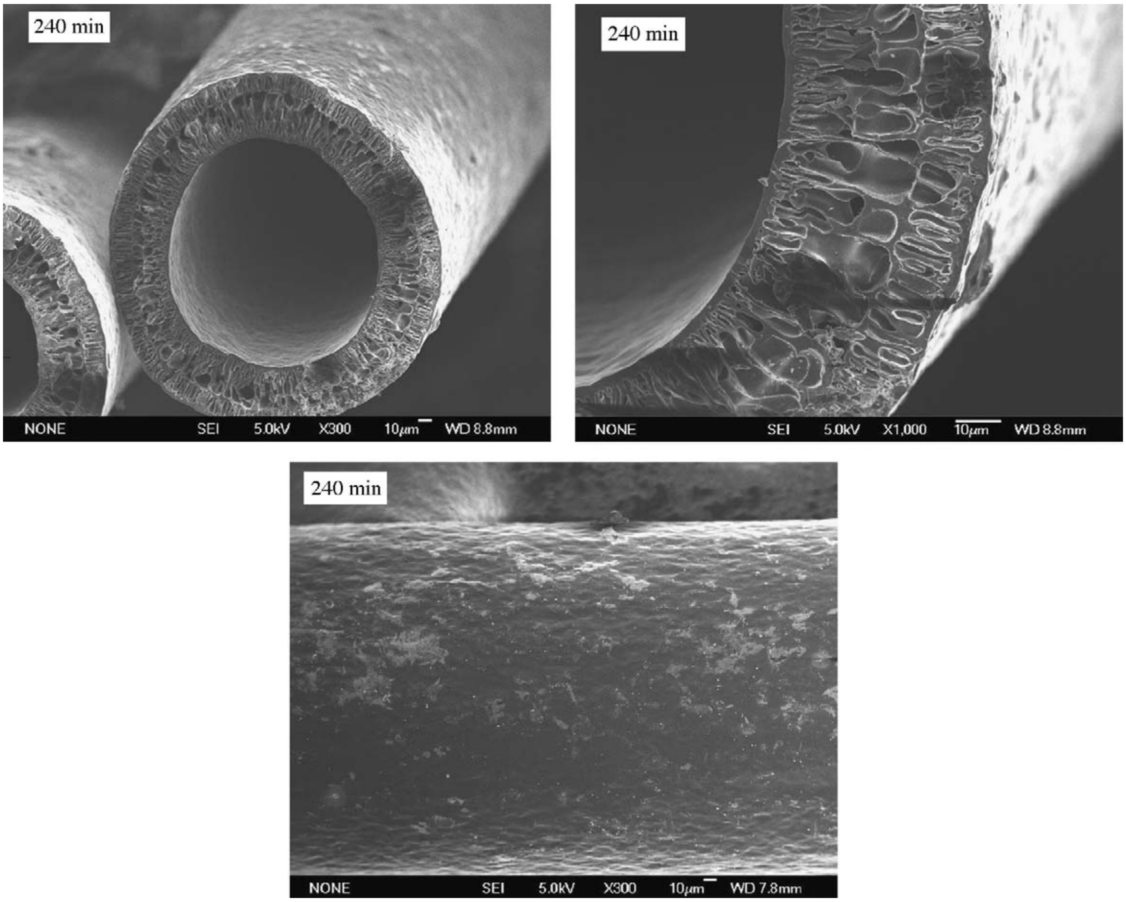

Fig. 3. SEM micrographs of the cross-sections of PAN-PHCFs carbonized at 1073 K for 240 min.

3.2. Structural properties

XRD was employed to investigate the change of crystalline structure of the carbonized fibres to explain the effects of different carbonization times. As is shown in Fig. 5, there are two obvious broad peaks at 25° and 44° in each spectrum, corresponding to the (0 0 2) and (1 1 0) diffraction of graphite structure. The absence of the (1 1 2) peak (at 83°) even after carbonization at 1073 K with 240 min indicates a non-graphitized carbonaceous structure. It may be speculated that the resultant hollow carbon fibre is an intervenient graphite with non-graphite structure [22]. That is, the hollow carbon fibres may partly form crystalline structure. Though the profiles of the PAN-PHCFs carbonized at various times are very similar, some slight differences can be observed. With the increase of carbonization times, the peak representing (1 1 0) diffraction slightly sharpens and upshifts, which indicates a more ordered structure, though the structure of all of the PAN-PHCFs have not been graphitized yet.

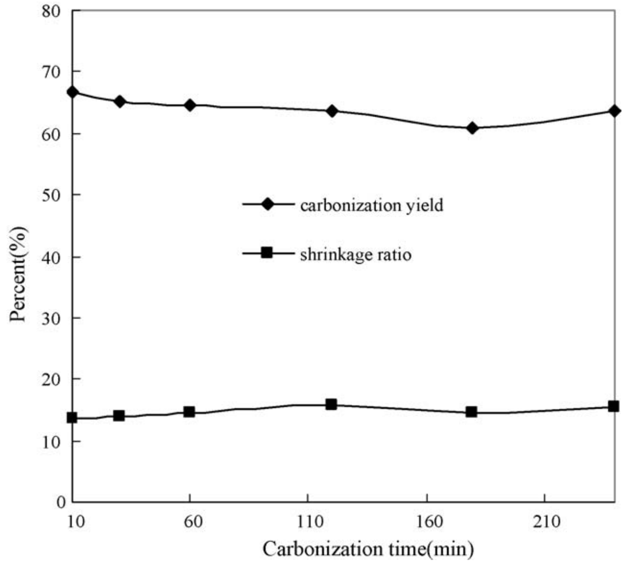

Fig. 4. Carbonization yield and shrinkage ratio of PAN-PHCFs *vs.* carbonization time.

In addition, another factor that affects the electrical performances and electromagnetic parameter is the degree of graphitization during the carbonization process. The effect of carbonization time on the chemical structure of PAN-PHCFs was characterized using Raman technology. The Raman spectra of PAN porous-hollow cured fibre treated at 1073 K for different time are shown in Fig. 6. It can be observed that each spectrum shows two broad peaks centred around 1355 cm^{-1} 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). The G

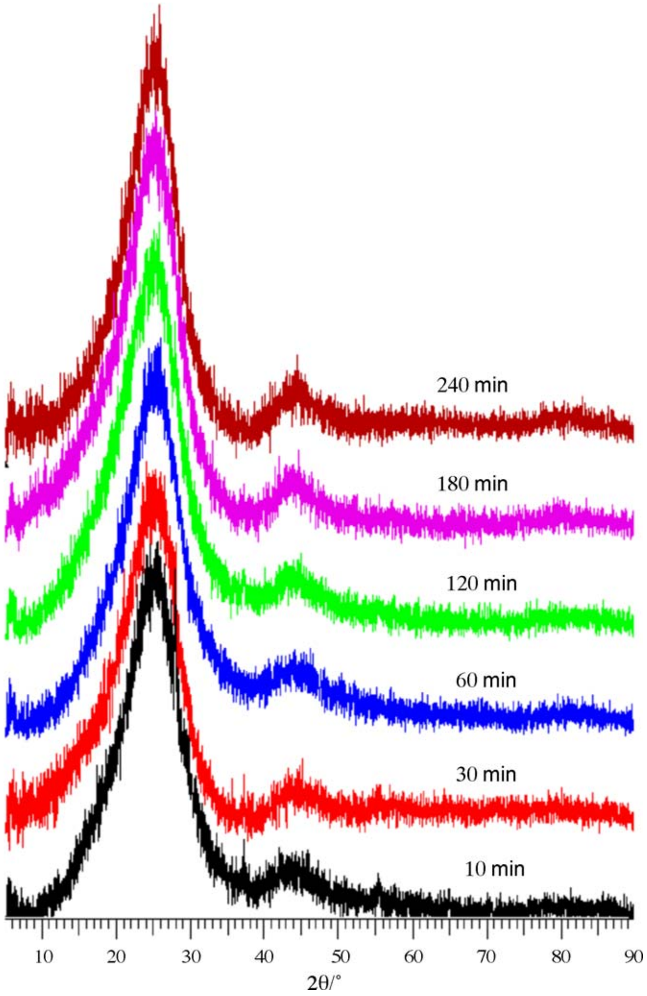

Fig. 5. XRD profiles of PAN-PHCFs at various carbonization time.

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 porous-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 [23–25].

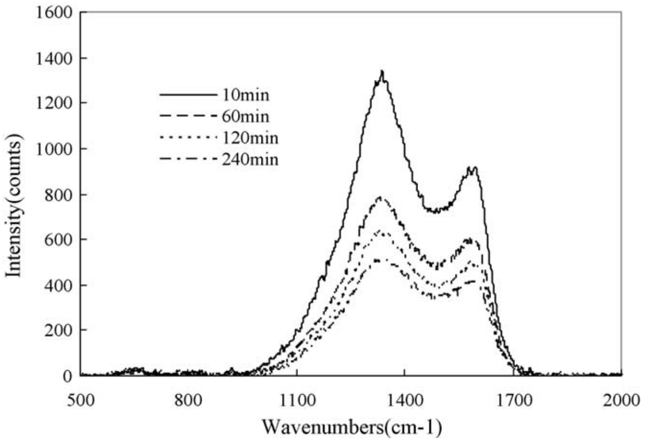

Fig. 6. Raman spectra of PAN-PHCFs at various carbonization time.

Table 1
The intensity ratio of D peak to G peak for the porous-hollow carbon fibre prepared at 1073 K under different time.

Carbonization time(min)	10	60	120	240
I_D/I_G	1.476	1.312	1.283	1.240

The I_D/I_G ratio of Raman spectra is a typical parameter to quantify the degree of disorder in carbon materials, and the decrease of the I_D/I_G ratio indicates that the degree of graphitization increases. Shown in Table 1, the values of I_D/I_G decrease from 1.476 to 1.240 with increasing carbonization time, indicating the structure of the carbon fibres slowly evolved toward ideal graphite. Combined with the analysis of XRD and Raman, it is clearly confirmed that these PAN-PHCFs have a more ordered crystalline structure but far from graphitized structure.

3.3. Electrical volume conductivity

Fig. 7 shows the electrical volume conductivity of PAN-PHCFs with the increase of carbonization time. The electrical volume conductivity of PAN-PHCFs was determined from the degree of carbonization. As shown in Fig. 7, the electrical conductivity of PAN-PHCFs gradually increases with increasing carbonization time before 120 min, then changes indistinctively. The electrical volume conductivity is 190.47 Ω^{-1} m^{-1} when the resultant PAN-PHCFs carbonized at 1073 K for 240 min. It is suggested that the degree of carbonization increases with increasing carbonization time, which influences the crystalline structure of PAN-PHCFs, and a more ordered crystalline structure leads to the change of electrical volume conductivity. However, the extent of the increase of electrical volume conductivity becomes marginal with the increase of carbonization time.

Table 2 shows the relationship between the intensity ratio of D peak to G peak and the electrical volume conductivity for the

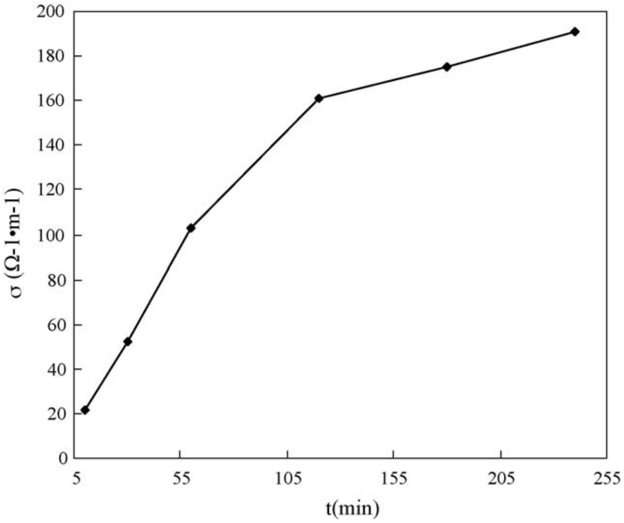

Fig. 7. Electrical volume conductivity of PAN-PHCFs *vs.* carbonization time.

Table 2
The relationship between the intensity ratio of D peak to G peak and the electrical volume conductivity for the porous-hollow carbon fibre.

I_D/I_G	1.476	1.312	1.283	1.240
σ (Ω^{-1} m^{-1})	21.347	103.241	161.009	190.477

PHCF prepared at 1073 K under different time. The values of I_D/I_G decrease gradually with increasing carbonization time, whilst the electrical volume conductivity increases accordingly.

3.4. Electromagnetic parameters

Fig. 8 shows the ε' and ε'' for the PAN-PHCFs in the frequency range of 2–18 GHz. At 2 GHz, the ε' and ε'' of the composites with 10 min are 5.29, 2.04, respectively. The ε' and ε'' of PAN-PHCFs gradually increases with increasing carbonization time and reaches 13.76 and 10.08 when carbonization time is 240 min. In addition, it can be seen that both ε' and ε'' of PAN-HCFs decrease as the microwave frequency increases, that is, the complex permittivity of composite at 2 GHz frequency point is larger than that at 18 GHz. This phenomenon is favorable to the impedance match of microwave absorption properties and increasing the bandwidth. The results show that the complex permittivity of the materials increases with increasing carbonization time. These characteristic electromagnetic properties, resulting from the electrical volume conductivity, can influence the radar absorbing properties.

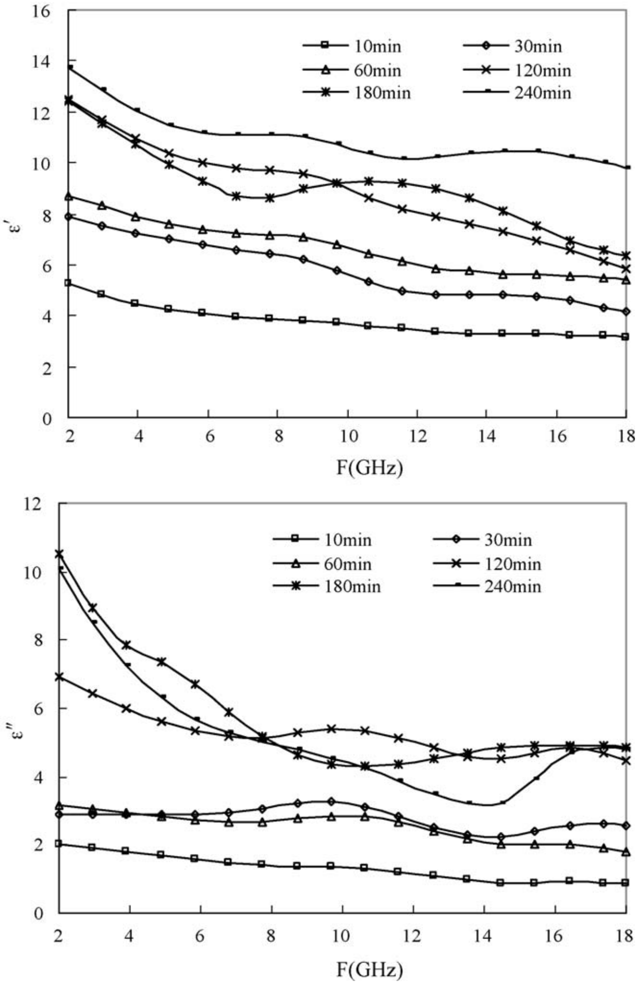

Fig. 8. Electromagnetic parameters of samples *vs.* microwave frequency.

The above results indicate that electrical volume conductivity of PAN-PHCFs resulting from the degree of graphitization plays an important role in the electromagnetic parameters of composites of PAN-PHCFs and paraffin. It is necessary that the excellent PAN-PHCFs should be obtained through adjusting carbonization process.

For conductive absorbers, $\mu \approx 1$ and $\mu'' \approx 0$, and the ε' and ε'' can be defined by [26]

$$\varepsilon' \approx \varepsilon'' = \sqrt{\frac{\omega \mu_0 \mu \sigma}{2}} \tag{3}$$

where $\mu_0 = 4\pi \times 10^{-7}$ H/m, ω is the angular frequency of the incident plane wave and σ is the electrical conductivity. The values of ε' and ε'' increase as σ increases. The degree of carbonization can increase the electrical volume conductivity of PAN-PHCFs through extending carbonization time.

4. Conclusions

A series of PAN-PHCFs with di-finger-like porous structure were prepared by carbonizing PAN hollow cured fibre at 1073 K for different times. The crystalline structure of the prepared PAN-PHCFs is far from graphitized structure. The aliphatic bridges were destroyed and the polyaromatic structure formed after carbonization. The degree of graphitization and the electrical volume conductivity of PAN-PHCFs increase with carbonization time. The electrical volume conductivity increases as the intensity ratio of D peak to G peak in the Raman spectrum decreases. The complex permittivity increased at 1073 K when carbonization time increased from 10 min to 240 min.

References

[1] V.M. Petrov, V.V. Gagulin, Microwave absorbing materials, J. Inorg. Mater. 37 (2) (2001) 93–98.
[2] F. Luo, D.M. Zhu, W.C. Zhou, A two-layer dielectric absorber covering a wide frequency range, Ceram. Int. 33 (2007) 197–200.
[3] H.Y. Lin, H. Zhu, H.F. Guo, et al., Investigation of the microwave-absorbing properties of Fe-filled carbon nanotubes, Mater. Lett. 61 (2007) 3547–3550.
[4] Z.J. Fan, G.H. Luo, Z.F. Zhang, et al., Electromagnetic and microwave absorbing properties of multi-walled carbon nanotubes/polymer composites, Mater. Sci. Eng. B 132 (2006) 85–89.
[5] T.V. Sreekumar, T. Liu, B.G. Min, et al., Polyacrylonitrile single-walled carbon nanotube composite fibers, Adv. Mater. 16 (1) (2004) 58–61.
[6] H.A. Tsai, Y.S. Ciou, C.C. Hu, et al., Heat-treatment effect on the morphology and pervaporation performances of asymmetric PAN hollow fiber membranes, J. Membr. Sci. 255 (2005) 33–47.
[7] L.Y. Jiang, T.S. Chung, R. Rajagopalan, Dual-layer hollow carbon fiber membranes for gas separation consisting of carbon and mixed matrix layers, Carbon 45 (2007) 166–172.
[8] J.F. Sun, G.X. Wu, Q.R. Wang, The effects of carbonization time on the properties and structure of PAN-based activated carbon hollow fiber, J. Mater. Sci. 40 (2005) 663–668.
[9] J.F. Sun, Study on the structure and properties of Polyacrylonitrile-based activated hollow carbon fiber, PhD thesis, Donghua University, Shanghai, 2004.

[10] D.D. Edie, The effect of processing on the structure and properties of carbon fibers, Carbon 36 (1998) 345–362.

[11] W. Xie, H.F. Cheng, Z.Y. Chu, et al., Preparation and microwave absorbing properties of hollow carbon fibers, J. Cent. South. Univ. Technol. 14 (s2) (2007) 112–115.

[12] W. Xie, H.F. Cheng, Z.Y. Chu, et al., Microwave absorbing properties of short hollow carbon fiber composites, J. Inorg. Mater. 23 (3) (2008) 481–485.

[13] G.C. Han, L.M. Marilyn, R. Asif, et al., Stabilization and carbonization of gel spun polyacrylonitrile/single wall carbon nanotube composite fibers, Polymer 48 (2007) 3781–3789.

[14] K. Kokaji, A. Oya, K. Maruyama, et al., Carbonization and graphitization behavior of decacyclene, Carbon 35 (2) (1997) 253–258.

[15] T. Shinn-Shyong, J.H. Pan, Oxidative stabilization of petroleum pitch at high pressure and its effects on the microstructure and carbon yield after carbonization/graphitization, Mater. Chem. Phys. 74 (2002) 214–221.

[16] V. Linda, L. Boris, D. Inbal, et al., Processing and characterization of extruded drawn MWNT-PAN composite filaments, Compos. Part A: Appl. Sci. Manuf. 38 (2007) 1354–1362.

[17] P.S. Tin, Y.C. Xiao, T.S. Chung, Polyimide-carbonized membranes for gas separation: structural, composition and morphological control of precursors, Sep. Purif. Rev. 35 (2006) 285–318.

[18] M.C. Yang, M.T. Chou, Effect of post-drawing on the mechanical and mass transfer properties of polyacrylonitrile hollow fiber membranes, J. Membr. Sci. 116 (1996) 279–291.

[19] D.G. Yu, W.L. Chou, M.C. Yang, Effect of bore liquid temperature and dope concentration on mechanical properties and permeation performance of polyacrylonitrile hollow fibers, Sep. Purif. Tech. 51 (2006) 1–9.

[20] K.L. John, V.J. Judith, G. Sekaran, Electrical conductivity study of porous carbon composite derived from rice husk, Mater. Chem. Phys. 91 (2005) 471–476.

[21] E.J. Vanzura, J.R. Baker-Jarvis, J.H. Grosvenor, et al., Intercomparision of permittivity measurements using the transmission/reflection method in 7-mm coaxial transmission lines, IEEE Trans. Microw. Theory Tech. 42 (11) (1994) 2063–2070.

[22] A.Z. Gerald, S. Bernd, G. Notburga, et al., A reconsideration of the relationship between the crystallite size La of carbons determined by X-ray diffraction and Raman spectroscopy, Carbon 44 (2006) 3239–3246.

[23] C. Pan, L.Q. Ge, Z.Z. Gu, Fabrication of multi-walled carbon nanotube reinforced polyelectrolyte hollow nanofibers by electrospinning, Comp. Sci. Tech. 67 (2007) 3271–3277.

[24] Cla′udio de Almeida Filho, Aldo J.G. Zarbin. Hollow porous carbon microspheres obtained by the pyrolysis of TiO2/poly(furfuryl alcohol) composite precursors, Carbon 44(2006)2869-2876.

[25] J.C. Su, A.C. Lua, Effects of carbonisation atmosphere on the structural characteristics and transport properties of carbon membranes prepared from Kapton® polyimide, J. Membr. Sci. 305 (2007) 263–270.

[26] K.J. Vinoy, R.M. Jha, Radar absorbing materials-from Theory to Design and Characterization, Kluwer Academic Publishers, Boston, 1996, 97-141.