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Influence of heat treatment on physical–chemical properties of PAN-based carbon fiber

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Abstract

The influence of heat treatment at 1400 °C on physical–chemical properties of PAN-based high strength carbon fiber was investigated by means of TG, XRD, XPS as well as the tensile test. The results showed that heat treatment could improve the thermal stability and the degree of graphitization of carbon fiber and decrease the amount of functional groups on the surface. The tensile strength of carbon fiber was not found declined after heat treatment because the change of the microstructure caused by heat treatment was limited.

Keywords: Carbon fiber; Heat treatment; Physical–chemical properties

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1. Introduction

Carbon fibers offer numerous advantages, such as lightweight and excellent mechanical properties at room and elevated temperature. Carbon fiber reinforced composites have been widely used in the fields of aerospace and high technical products. To realize the excellent mechanical properties of carbon fibers in composites, it is necessary to have a desirable fiber/matrix interface to ensure effective load transfer from one fiber to another through the matrix [1,2]. The interfacial properties largely depend on the carbon fiber surface. As a result, many researches focus on the surface treatment of carbon fibers to get a good interface and composites with perfect mechanical properties [3,4]. Surface oxidation of carbon fibers was the dominating surface treatment technique. Surface oxidation can increase the quantity of functional groups on the fiber surface, and then strengthen the interfacial bonding. However, strong interfacial bonding is not always good for mechanical properties of composites, especially for ceramic matrix composites [5,6]. Heat treatment is another treatment technique of carbon fibers and has been applied in the preparation of carbon fiber reinforced ceramic matrix composites [7]. But it is still not well clear which properties of the carbon fiber are affected by heat treatment and how the heat treatment on carbon fiber affected the load transfer mechanism and energy dissipation in ceramic matrix composites.

In this study, the T300 carbon fiber were heat treated at 1400 °C in vacuum, and the physical and chemical properties of as-received and heat treated carbon fibers were examined in order to understand the influence of heat treatment on physical–chemical properties of carbon fiber and gain an insight into how the heat treatment of carbon fibers affected the mechanical properties of carbon fiber reinforced ceramic matrix composites.

2. Experimental

PAN-based high strength carbon fiber with a trade name of T300 was used in this study. The physical properties of the fiber are listed in Table 1. The T300 fiber as received commercially was named as sample T-0. T-4 indicated the

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Table 1
Physical properties of T300 carbon fiber

Species	T300
Filament count	3000
Density (g/cm^3)	1.75
Average diameter (μm)	7
Tensile strength (GPa)	3.45
Young's modulus (GPa)	230
Elongation break (%)	1.5

fibers after heat treating at 400 °C. T-14 was the fiber heat treated at 1400 °C in vacuum for 1 h.

The thermal stability of the samples from 50 °C to 1200 °C was characterized by thermal gravimetric analysis (TGA) at a heating rate of 10 °C/min. A common purity (99%) nitrogen flow 50 cm^3 min^{-1} was used during test. X-ray diffraction (XRD) was used to determine the crystallite characteristics of specimens. XRD patterns of the samples were obtained from a D8ADVANCE diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm) as the source for measuring the interlayer spacing. X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemistry of samples. The data were obtained from an ESCALab220i-XL electron spectrometer using 300 W Al Kα radiation. The base pressure was about 3×10^{-9} mbar. The survey spectrum was collected from 0 eV to 1200 eV, and the binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon. The tensile strength of fiber samples was measured by single fiber strength and bundle strength.

3. Results and discussion

3.1. Thermal stability of carbon fibers

Fig. 1 shows TG curves of carbon fibers under nitrogen from 50 °C to 1200 °C. It is clear that T-0, T-4, and T-14 began to lose weight at 450 °C, 550 °C, and 600 °C and remained 38%, 44%, and 72% of original weight at 1200 °C, respectively, demonstrating that the thermal stability of carbon fibers can be improved by heat treatment. At 450 °C, the weight loss of T-0 was due to the removal of organic sizing on fiber surface. With the increase of temperature, the removal of N, O atoms from the residual nitrogen and oxygen in the precursor fibers was partly responsible for the weight loss. Because sample T-14 suffered weight loss of less than 5 wt.% during heat treatment at 1400 °C, its weight loss under N$_2$ (common purity) from 50 °C to 1200 °C was mainly caused by the attack of impurity in N$_2$ to fibers at elevated temperature, such as O$_2$, CO$_2$, and H$_2$O. TGA suggested that T-14 have a better resistance to the attack of impurity at elevated temperature.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

3.2. Surface chemistry

In Fig. 2, the XPS surveys of T-4 and T-14 exhibited conspicuous features due to carbon and oxygen. Minor peaks due to nitrogen and silicon could also be discerned in T-4's spectrum, while undiscerned in T-14's spectrum. Based on the survey spectrum results, the atom percents of C 1s (≈285 eV), N 1s (≈400 eV), O 1s (≈533 eV) and Si 2p (≈102 eV) in fiber surface were calculated from peaks intensities, which were listed in Table 2. The concentrations of O and N in T-4 were both nearly eight times higher than those in T-14, and the C concentration in T-4 (86.0 at.%) was lower than that in T-14 (98.0 at.%).

The surface activity of carbon fiber is determined by many factors such as the concentration of oxygen atom, the O/C atomic ratio, C 1s binding state and O 1s binding state.

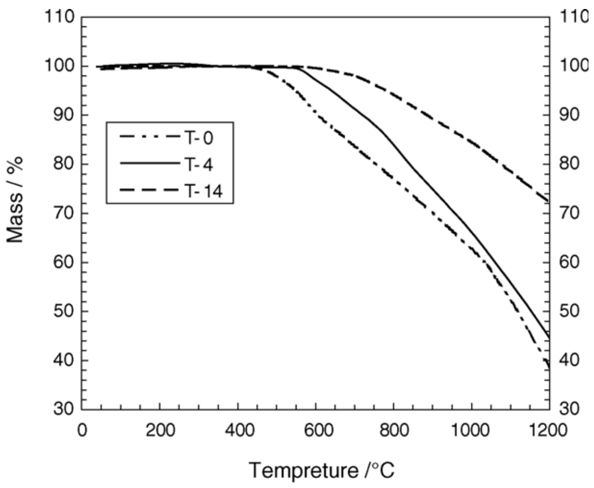

Fig. 1. TG curves of samples.

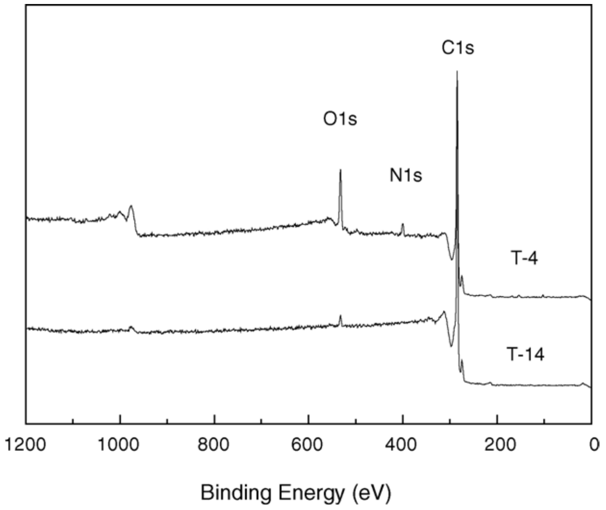

Fig. 2. XPS survey of samples.

Table 2
Fiber surface chemistry of different samples

Samples	O/C	(at.%)			
		C 1s	O 1s	N 1s	Si 2p
T-4	0.114	86.0	9.8	3.3	0.8
T-14	0.013	98.0	1.3	0.4	0.3

The survey spectral features indicated that the O/C atomic ratio of T-14 (0.013) was about 1/10 of that of T-4 (0.11). The C 1s spectrum was indicative of graphitic carbon (284.6 eV), carbon present as phenolic hydroxyl and/or ether groups (≈286.2 eV), carbonyl groups (≈287.6 eV), carboxyl and/or ester functions (≈288.8 eV) and possibly some carbonate species (≈290.6 eV) [8–10]. The O 1s peaks were composed mainly of oxygen bonded in –OH groups (≈533 eV) and in C=O moieties (≈531.5 eV). High relative fraction of carbon and low relative fraction of oxygen with low binding energy implied carbon fiber with low surface activity. Figs. 3 and 4 shows XPS spectra of C 1s and O 1s of T-4 and T-14, respectively. It was found that relative fraction of carbon with low binding energy in T-4 was less than that in T-14 and relative fraction of oxygen with low binding energy in T-4 was more than that in T-14. From the XPS spectra, it maybe concluded that T-4 had high surface activity, whereas T-14 possessed low surface activity. Heat treatment at 1400 °C could decrease carbon fiber surface activity evidently.

3.3. Microstructure study

The average bulk structure of carbon materials can be readily revealed using X-ray diffraction. The XRD patterns of T-0, T-14 and a kind of PAN-based high modulus type carbon fiber M40J (Toray Co. Japan) are shown in Fig. 5. As a result, the diffraction angles 2θ were around 25° and 43°, which were assigned to disordered graphitic 0 0 2 plane and 1 0 1 plane, respectively. The peaks of (0 0 2) reflections and (1 0 1) reflections of T-0 sample were broad, while T-14 had sharp peaks similar to the graphite fiber M40J. The average interlayer spacing d_{002} and the crystallite dimensions $L_{c(002)}$ can be determined by XRD measurements [11–13], by using Bragg and Scherrer formulas, respectively,

$$n\lambda = 2d\sin\theta$$

$$L = \frac{K\lambda}{\beta\cos\theta}$$

where θ is the scattering angle, d is the interlayer spacing, λ is the wavelength of the X-rays, here was 0.154 nm, β is the half-maximum line width in radians. Jeffrey [14] determined that the form factor K is 0.9 for $L_{c(002)}$. The average interlayer spacing d_{002} and the crystallite dimensions $L_{c(002)}$ of samples were calculated from the 0 0 2 diffraction peaks and listed in Table 3. The table showed that sample T-0 had the biggest d_{002} (3.552 Å) and the smallest $L_{c(002)}$ (1.75 nm) of three samples. The data of d_{002} and $L_{c(002)}$ of T-14 were 3.490 Å and 2.48 nm, and graphite fiber M40J had the d_{002} (3.466 Å) and $L_{c(002)}$ (3.00 nm). The results indicated that T-14 had higher graphitization degree than T-0, shortening of interlayer spacing and largening of crystallite dimensions, but lower than M40J. The carbonization temperature of T-0 was about 1400–1500 °C, but the time was very limited. As a result, after T-0 was heat-treated at 1400 °C for 1–2 h, the graphitization degree was improved. However, heating to 1400 °C was not sufficient to obtain similar grophitization form to the graphite fiber, consequently the crystallite characteristics of T-14 were between those of T-0 and M40J, even after extended treating time.

3.4. Tensile strength study

Table 4 shows the tensile strength of three samples measured by single fiber means and fiber bundle mean. Different strength had been obtained by the two testing means. Tensile strength of T-0 tested by single fiber means was lower than that presented by manufacturer and that tested by fiber bundle means, while the data gained by fiber

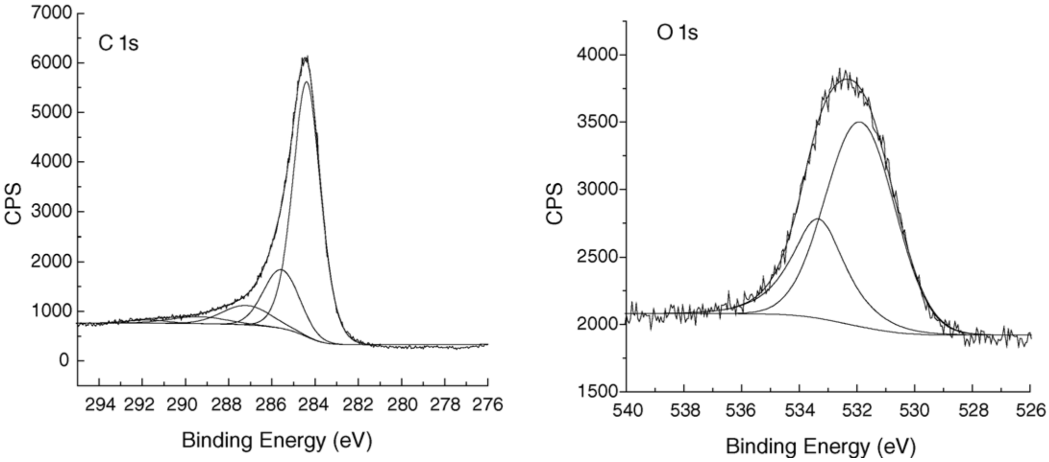

Fig. 3. XPS spectra of C 1s and O 1s of sample T-4.

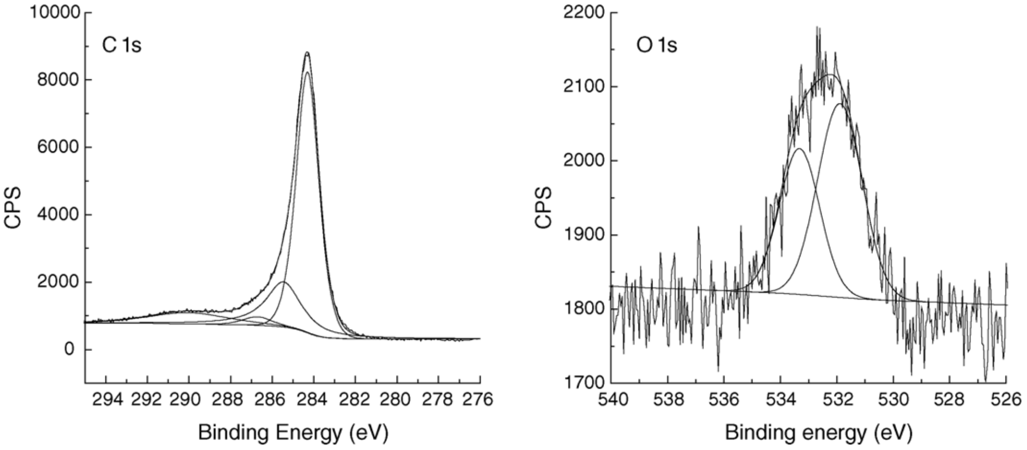

Fig. 4. XPS spectra of C 1s and O 1s of sample T-14.

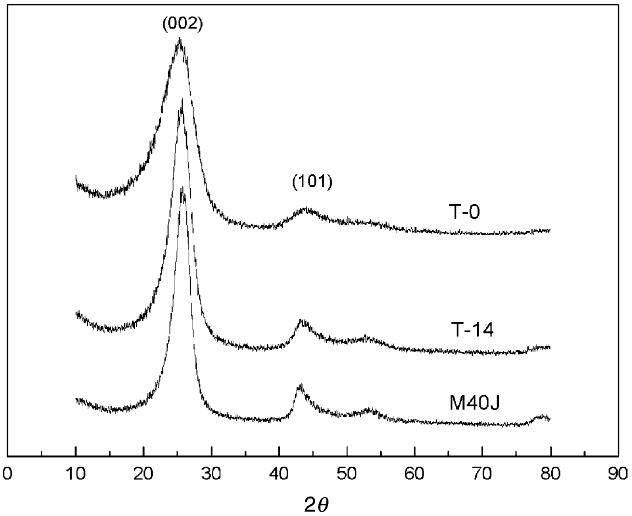

Fig. 5. XRD of samples.

bundle means matched with that presented by manufacturer. The letter presented by manufacturer was obtained by fiber bundle means [15]. The single fiber testing means was insensitive to external factors compared with fiber bundle testing means because the fiber bundle testing means had a relationship with carbon fiber surface state. The carbon fiber bundle should be resin-impregnated and cured before testing. If carbon fiber had low surface activity, resin could not solidify fibers well and fibers would slip in resin under stress. As a result, monofilament could not rupture simultaneously and the ultimate destructive load can but be attributed to part monofilament. Therefore, the tested strength by fiber bundle means was lower than actual datum. The strength of T-0 tested by fiber bundle means was credible because the fiber had sufficient surface activity and could be well solidified by resin. The surface activity of T-4 without surface sizing and T-14 heat treated at 1400 °C both was weakened, so the strength data gained by fiber bundle means was incredible. The tensile strength of samples by single fiber means could be thought credible. There were not obvious changes in the tensile strength of T-0, T-4, and T-14. It could be concluded that heat treatment at 1400 °C did not affect the strength of carbon fiber because the influence of heat treatment at 1400 °C on the crystallite structure was limited.

Table 3
Crystallite characteristic of samples

Samples	$\Delta\theta_{1/2}$ (°)	2θ (°)	d_{002} (Å)	L_c (nm)
T-0	4.65	25.04	3.552	1.75
T-14	3.28	25.49	3.490	2.48
M40J	2.72	25.67	3.466	3.00

Table 4
Tensile strength of samples by two testing ways

Samples	By single fiber means		By fiber bundle means	
	σ_1 (GPa)	σ_1/σ_0^* (%)	σ_2 (GPa)	σ_2/σ_0^* (%)
T-0	3.25	94.2	3.49	101.2
T-4	3.20	92.8	2.85	82.6
T-14	3.36	97.4	1.98	57.4

σ_0^* was the tensile strength of T300 carbon fiber presented by manufacturer (3.45 GPa).

4. Conclusions

The characterization of heat-treated carbon fiber has demonstrated that physical and chemical the characteristics of the carbon fiber have changed. Heat treatment can improve the thermal stability of carbon fiber and decrease the surface activity due to the decrease of the amount of oxygen and nitrogen atoms and an increasing carbon fraction. Heat treatment can also improve the graphitization degree of carbon fiber, by decreasing the interlayer spacing and largening of crystallite dimensions. Heat treatment at 1400 °C does not damage the fiber' single tensile strength.

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