



Graphitization of polyacrylonitrile carbon fibers and graphite irradiated by γ rays

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ABSTRACT

To investigate the effect of γ -ray radiation on the microstructure of carbon fibers (CF) and graphite, the carbon fibers and graphite were irradiated by ^{60}Co source at room temperature. X-ray diffraction results indicate that the interlayer spacing d_{002} of CF and graphite decreased after irradiation. The intensity of (002) peak in CF decreased while the peak of the (002) plane in graphite becomes sharper after irradiation. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy determines that γ -ray irradiation slightly improves the carbon content of CF surface layer. Compton scattering effect and heating caused by γ -ray are proposed to be responsible for the graphitization of CF and graphite.

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1. Introduction

Carbon fibers (CF) have superior properties in strength, modulus, stiffness and lightness and thus are widely used as reinforcement in carbon fiber reinforced plastics, metals, ceramics and C–C composites [1,2]. These applications may be sensitive to the environment, particularly to the influence of high-energy radiation. The latter can affect the structural properties of CF, thus limiting the range of their applicability. Additionally, the other carbon-based material, graphite, is also important in nuclear power technology. Irradiation of graphite especially with neutrons and other particles has been of great interest since the development of the atomic pile, where it was used as moderator of the nuclear fission reaction [3].

As the electromagnetic radiation of shortest wavelength and highest energy, gamma ray irradiation can induce chemical reactions at any temperature in the solid, liquid and gas phases without any catalyst [4,5]. The application of irradiation to CF as the method modifying the CF surface inertness has been studied [6] and the formation of domains of hexagonal diamond was found via gamma irradiation of graphite [7]. Limited attention has been devoted to the radiation effect of CF and graphite graphitization caused by high energy electromagnetic radiation like γ -ray.

In this study, polyacrylonitrile(PAN)-based CF and graphite were irradiated by γ -ray. X-ray diffraction analysis of fibers and graphite was conducted and the effect of γ -ray irradiation on the elemental composition of CF surface layer was also investigated.

2. Experimental

2.1. Materials and irradiation

The CF investigated was the same as the previous literature [6]. The graphite powder (LG-150-90) was supplied by Qingdao Tianhe Graphite Company of China. Several bundles of CF were wound up on a frame about 30 cm and the graphite powder and CF were placed in a glass container. The air was extracted and N_2 was filled up to one normal atmospheric pressure in the glass container. It was then sealed tight. The samples were irradiated at room temperature. The irradiation field was provided by Harbin Ruipu Irradiation Technology Company of China. The intensity of ^{60}Co γ -ray source was 1.5×10^4 Ci.

2.2. Measurements

X-ray diffraction traces were obtained from bundles of parallel fibers and graphite powder. The X-ray diffraction traces obtained with the bundles in the plane were used to calculate the d_{002} spacing using the Bragg equation [8]. The fibers were characterized by scanning electron microscopy equipped with energy dispersive spectrometer (SEM-EDS) and X-ray photoelectron spectroscopy (XPS). The as-received and irradiated fiber samples were extracted in acetone before measurements.

3. Results and discussion

3.1. X-ray diffraction characterization

Fig. 1 shows X-ray diffraction intensity distribution in the vertical direction, measured for untreated and irradiated fibers. The diffraction

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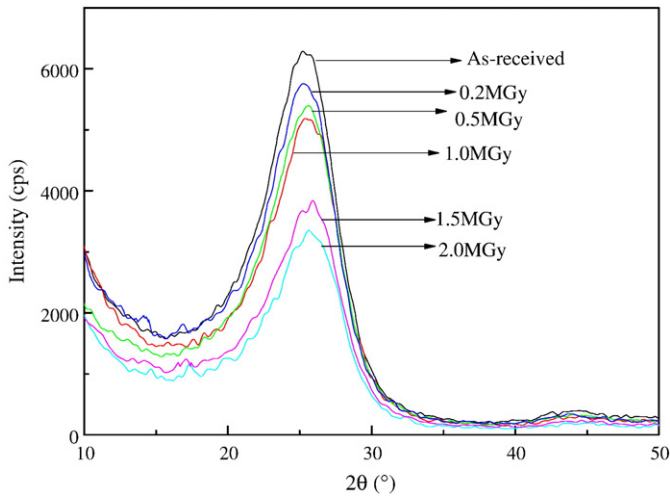


Fig. 1. X-ray diffraction intensity distribution for the CF irradiated at different doses.

patterns of each irradiation-treated counterpart were almost identical. The main peak can be seen to occur at approximately 25.5° 2θ , corresponding to the (002) reflections of the pseudo-graphite structure [9]. There also appears a much weaker band at $\sim 44^\circ$ 2θ , which is usually assigned to the (10) turbostratic band of disordered carbon materials. The weakest band at $\sim 53^\circ$ 2θ corresponds to the (004) reflections of the pseudo-graphite structure. The intensity of (002) peak decreased and the diffraction angle of (002) peak increased as the absorbed dose of irradiated fibers increased. The former may be owing to the formation of glassy carbon domains [7]. The d_{002} spacing of all the treated and untreated CF is collected in Table 1. It can be seen from the table that the average d_{002} interlayer spacing, indicative of the degree of graphitization, decreases gradually from 0.352 nm for the untreated fibers to the 0.345 nm for the fibers irradiated at the dose of 2.0 MGy. Compared to that of untreated fibers, the value of treated fibers is closer to the ideal value of the spacing of graphite layers in a perfect graphite crystal (0.335 nm), therefore indicating the improvement of average graphitization of the treated fibers.

The CF showed a kind of skin/core structure where the thick and long domains in skin run parallel to the core [10]. The behavior in the skin and core is considerably different and the crystallite in the skin is significantly bigger and higher oriented, compared to the core with turbostratic layer structure. XRD analysis of CF summarizes the overall structural changes including the skin and core structure. To investigate the graphite structure in the skin of CF, the graphite powder was irradiated as the model of the fiber skin.

Fig. 2 shows X-ray diffraction intensity distribution of graphite powder untreated and irradiated at dose of 2.0 MGy. After irradiation, no new peak from graphite powder appeared. The main peak can be seen to occur at approximately 26.2° 2θ , corresponding to the (002) reflection of graphite structure. On the other hand, the peak of the (002) plane becomes sharper after irradiation. It can be calculated from the Bragg

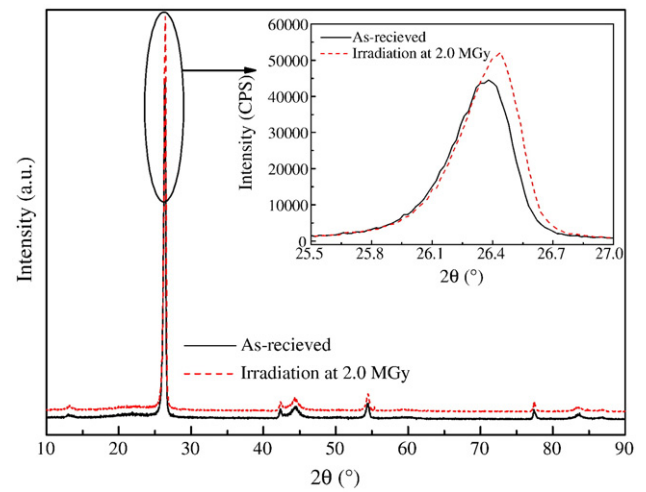
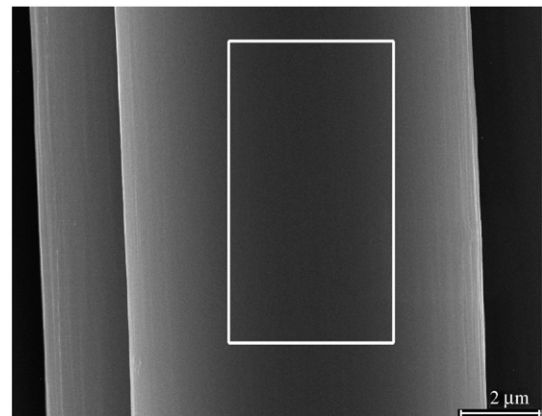
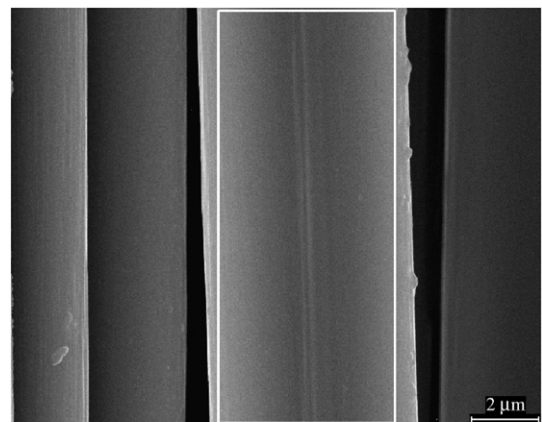


Fig. 2. X-ray diffraction intensity distribution for graphite powder.

equation that the d_{002} interlayer spacing, indicative of the degree of graphitization, decreases from 0.33756 nm for untreated graphite powder to the 0.33706 nm for the irradiated graphite powder, therefore indicating the high level of graphitization of graphite powder irradiated at 2.0 MGy. According to the equation in literature [11], the degree of graphitization was increased from 75% for untreated graphite to 81% for irradiated graphite. As a result, it is presumed that the graphitization of pseudo-graphite structure of CF skin is improved by γ -ray irradiation.



(a) as-received



(b) irradiated

Fig. 3. SEM micrographs of as-received and irradiated CF for EDS analysis.

Table 1
X-ray diffraction structural parameters of CF.

	$2\theta[002]$ ($^\circ$)	d_{002} (nm)
As-received	25.30	0.3520
0.2 MGy	25.32	0.3517
0.5 MGy	25.44	0.3501
1.0 MGy	25.62	0.3477
1.5 MGy	25.74	0.3460
2.0 MGy	25.79	0.3454

3.2. SEM-EDS analysis

The SEM images of as-received and irradiated CF were shown in Fig. 3. The selected area for EDS mapping was shown by rectangle in Fig. 3. More than ten specimens were tested for both of as-received and treated CF and the average value was taken in the present. No remarkable differences in micrographs can be observed on untreated and irradiated CF. Compared with the original CF, the treated CF surface was marginally rougher. It could be interpreted by γ photons etching process on CF surface. According to SEM-EDS analysis (more than 500 nm in depth), the percentage of carbon was increased and ranged from 95.24 wt.% for as-received CF to 96.22 wt.% for irradiated CF, while the XPS spectra (~ 6 nm in depth) showed that the amount of surface carbon reduced from 87.4 wt.% to 78.2 wt.% after irradiation at 2 MGy. It was indicated that the carbon amount of CF bulk was increased and the carbon amount of CF surface was decreased remarkably after irradiation. It is possible that radiolysis of CF causes the emission of H_2 , hydrocarbons and also CO/CO_2 [12,13] from fiber bulk and the carbon radicals of fiber surface react with O_2 when the irradiated CF meets with air.

The Compton scattering effect is mostly responsible for the interaction of gamma ray with CF and graphite. The predominant interaction mechanism is ionization [7]. The electron and scattered photon are produced after the incident photon interacts with carbon atom of CF and graphite. Then the carbon free radical is created by anion or cation radical mechanisms [14]. The amount of first class flaws is decreased and the graphitization of CF is improved. In addition, it is highly likely that gamma irradiation causes the significant heating in CF and graphite.

4. Conclusions

Large decrease in the d_{002} interlayer spacing of CF and graphite has been achieved by γ -ray irradiation and an approximately linear

dependence on absorbed dose has been suggested. The intensity of (002) peak in CF decreased while the peak of the (002) plane in graphite becomes sharper after irradiation. The carbon content of CF surface layer was improved by irradiation. The γ -ray irradiation was an effective method for improving the graphitization degree of PAN-based CF and graphite.

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