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Microstructure evolution in γ-irradiated carbon fibers revealed by a hierarchical model and Raman spectra from fiber section

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ABSTRACT

The surface activity and mechanical properties of carbon fibers (CFs) were improved simultaneously by magical γ-irradiation. However, microstructure evolution rules of γ-irradiated CFs were still ambiguous. As a representative, T1000 CFs were irradiated by γ-rays and then observed by X-ray diffraction, X-ray photoelectron spectroscopy and Raman spectroscopy from fiber surface, deducing the paradoxical results in terms of fiber structural transformation due to the different penetration depth of above measurements. Therefore, a hierarchical model composed of outer-surface, sub-surface and core parts had been proposed, which allowed us to understand the microstructure evolution of irradiated CFs profoundly. Subsequently, Raman spectra from fiber cross-section were performed to further confirm the accuracy of new model. The results demonstrated that oxygen-containing functional groups were significantly introduced into the outer-surface by the combined effect of γ-rays and reactive media, which increased the surface activity and disordered the structure of outer-surface part. Meanwhile, γ-irradiation improved the graphitic order and atomic rearrangement of sub-surface and core parts regardless of medium effect. Furthermore, the graphitization of sub-surface part showed more notable increase than that of core part under γ-irradiation. This paper would offer the key to reveal the relationship among microstructure, surface activities and mechanical properties of γ-irradiated CFs.

1. Introduction

Carbon fibers (CFs) are used increasingly in a wide variety of applications because of their high tensile strength and modulus combined with light weight [1,2]. It is widely accepted that the application of CFs is mainly dependent on the surface activities and mechanical properties [3,4]. In order to improve the surface properties, various surface treatments have been carried out such as electrochemical processing [5], wet chemical oxidation [6,7], gas phase oxidation in ozone [8], high-energy beams [9], plasma treatment [10], electrostatic spray painting [11] and so on. The conventional surface modification methods improve the surface activity of CFs but sacrifice their mechanical performance due to the increase of grooves and defects of fiber surface. Meanwhile, extensive studies have been performed to improve mechanical properties of CFs. Sung et al. [12,13] have reported that the application of magnetic field on CFs in carbonization process can improve the tensile strength of CFs due to the suppression of surface defects. Jones and Thrower [14] have improved the tensile strength of CFs via boron-doping owing to the decrease of internal defects. However, these methods have not changed the surface activities or sacrificed the surface properties of CFs. As a result, it is still a huge challenge for improving the surface activities and mechanical properties simultaneously.

In recent years, it has been shown that γ-irradiation is an effective method for altering the surface activities and improving the mechanical properties of CFs [15–25]. In the predecessors' works and our previous articles [16,17,20–22,24,25], modifications of polyacrylonitrile (PAN)-based CFs surface induced by γ-irradiation were investigated exhaustively. It was found that the surface energy and amount of containing-oxygen functional groups were increased significantly after irradiation. Xu et al. [25] have improved the surface energy of CFs from 42.2 mJ/m^2 to 50.5 mJ/m^2 after irradiation in acrylic acid. Li et al. [21] have modified the surface roughness of CFs by γ-irradiation in air, and found that the oxygen/carbon ratio of CFs increased rapidly after irradiation.

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Meanwhile, there are a number of recent studies on the improvements of mechanical properties of CFs by γ-irradiation [17,18,20,22,26]. Researchers agreed that the tensile strength of irradiated CFs increased firstly, and then decreased with the increase of irradiation dose. However, there are still large differences in the inflection point of radiation dose. For the Young's modulus of γ-irradiated CFs, Xiao et al. [17] believed that the Young's modulus of T700 CFs would no longer increase when the radiation dose was higher than 30 kGy, and then remained almost constant with further irradiation. Li [18] and Xu et al. [20,22] believed that the Young's modulus of γ-irradiated CFs increased with the increasing irradiation dose (less than 2 MGy). However, the microstructure evolution rules of irradiated CFs are still ambiguous. As a result, it is difficult to understand the relationship among microstructure, surface activities and mechanical properties of γ-irradiated CFs. Unfortunately, systematic study on the microstructure evolution of γ-irradiated CFs has not been reported in the previous literature.

In this paper, T1000 CFs were selected due to the superhigh mechanical properties compared with other CFs, and irradiated in media with different activity. Then the structures of CFs were characterized by X-ray diffraction (XRD), Raman spectroscopy from fiber surface, X-ray photoelectron spectroscopy (XPS) and dynamic contact angle. The structural transformation of CFs was discussed by hierarchical model composed of outer-surface, sub-surface and core parts, which allowed us to understand the microstructure evolution rules of CFs profoundly [15,17,27,28]. Meanwhile, Raman spectra from fiber cross-section were performed to confirm the accuracy of new model, which could help to understand exactly the microstructure evolution of the sub-surface and core parts. Finally, the microstructure evolution rules of the outer-surface, sub-surface and core parts were discussed in detail on the basis of hierarchical model.

2. Experimental

2.1. γ-Irradiation experiments

The CFs were placed in glass containers and irradiated in argon (Ar), air and epoxy chloropropane (ECP) at room temperature. Irradiation with ^{60}Co point-source irradiator was carried out at Tianjin Institute of Technical Physics. The absorbed dose was accumulated to 100 kGy with dose rate of 0.3 kGy/h, which was based on consulting previous literature [17,18,20–23].

2.2. Characterizations

The mechanical tests of fibers were performed in a universal testing machine with a load cell of 10 N. Measurements were made by attaching a filament to a gauge paper case with 20 mm distance, as reported elsewhere [29]. The specimen was set up to test, by cutting the paper case and using a crosshead speed of 5 mm/min to break. Not less than 20 filaments for each specimen were tested. The Young's modulus was extracted from the slope of stress-strain curve [30].

The crystal structure of CFs was characterized by XRD with Cu Kα radiation, operated at 40 kV and 150 mA. The interval resolution of 2θ was 0.02°, X-ray wavelength was 0.15418 nm, and the value of dwell time was 10 min. The X-ray diffraction traces obtained with the bundles in the plane were used to calculate the d_{002} spacing. The d_{002} spacing of CFs was estimated directly using the Bragg equation [31]. Raman spectroscopy was performed on a LABRAM-HR confocal laser micro-Raman spectrometer using an Ar^+ laser with 532 nm to determine the quality and graphitization degree of CFs from fiber surface and cross-section, respectively. The diameter of laser spot on the sample was about 0.5 μm. Raman spectra from fiber cross-section were obtained by first embedding the single filaments in thermoplastic matrix, then by cutting the cross-section in the plane normal to fiber axis with diamond knife. The Raman spectra were curvefitted to a Lorentzian function using a nonlinear least-squares routine. XPS investigations were carried out with a PHI 5700 ESCA system with Al Ka (1486.6 eV) radiation to characterize changes of chemical components of different CFs. Thermogravimetric analysis (TGA) was conducted with a Netzsch TG 209F1 under N_2 atmosphere with a heating rate of 10 °C/min. The contact angles of various CFs were measured using the measurement instrument of dynamic contact angle (Dataphysics Co. Ltd.).

3. Results and discussion

3.1. Survey of γ-irradiated CFs based on the traditional methods

Fig. 1 showed the XRD patterns of CFs irradiated in different media. The main peak could be seen to occur at approximately $2\theta = 25.5°$ corresponding to the (002) reflections of the pseudo-graphite structure [16]. It could be seen from Fig. 1 and Table 1 that the d_{002} interlayer spacing, indicative of the degree of graphitization, decreased gradually from 0.3471 nm for the pristine fibers to 0.3403 nm (Ar), 0.3421 nm (air) and 0.3447 nm (ECP) for the irradiated CFs, which was more closer to the 0.3354 nm for hexagonal graphite, indicating the improvement of the graphitization degree of irradiated CFs [32]. The similar changes in graphitization degree of γ-irradiated CFs could be seen in previous reports [17,18].

Fig. 2 showed representative Raman spectra for surface scan of the pristine and irradiated CFs. The intensity ratio of D band and G band (I_D/I_G) decreased from 0.9338 for the pristine fibers to 0.8926 (Ar), 0.9013 (air), but increased to 0.9539 (ECP). The decrease of I_D/I_G indicated higher percentage of sp^2 hybridization carbon atoms in irradiated CFs, which was the evidence of the improvement of graphitization degree on the CFs irradiated in Ar and air [33]. However, the opposite results occurred in ECP, which was consistent with Liu et al. [15].

The composition of pristine and irradiated CFs was determined by XPS and the results were given in Table 2. Carbon and oxygen were the major surface elements and chlorine element was found on the surface of CFs irradiated in ECP. As shown in Table 2, the ratio of O/C increased distinctly when the CFs were irradiated in air and ECP, and especially in ECP, the ratio of O/C increased from 0.1056 for the pristine fibers to 0.2728 (ECP). It might be attributed to the

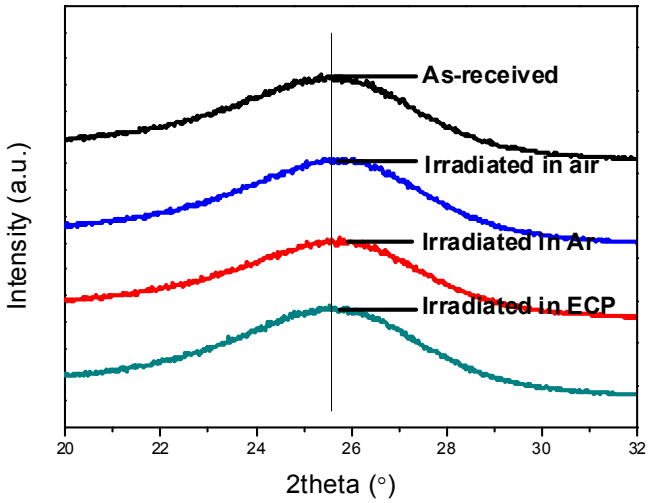

Fig. 1. X-ray diffraction profiles of pristine and irradiated CFs.