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The effect of gamma ray irradiation on PAN-based intermediate modulus carbon fibers

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ABSTRACT

Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) were conducted on PAN-based intermediate modulus carbon fibers to investigate the structure and surface hydrophilicity of the carbon fibers before and after gamma irradiation. Two methods were used to determine Young's modulus of the carbon fibers. The results show that gamma ray irradiation improved the degree of graphitization and introduced compressive stress into carbon fiber surface. Gamma ray also improved the carbon fiber surface hydrophilicity through increasing the value of O/C and enhancing the quantity of oxygen functional groups on carbon fibers. No distinct morphology change was observed after gamma ray irradiation. The Young's modulus of the fibers increased with increasing irradiation dose.

1. Introduction

Carbon-based materials are widely used in many fusion plasma devices [1], spacecrafts, rockets [2] and civil industry. Carbon fibers possess outstanding mechanical, physical and chemical properties such as low density, low coefficient of thermal expansion, superior tensile strength, high modulus, good chemical inertness and resistance to elevated temperature [3–5], for which, carbon fibers were widely used as reinforcing materials [6,7]. Carbon fiber composites (CFCs) consisting of reinforcing carbon fibers embedded in a carbon or graphite matrix are widely used in aerospace industry due to their strength, heat shielding properties, and a number of other specific characteristics [8]. CFCs are also currently used in fusion research devices as plasma facing components (PFCs) and they are intended to be used as PFC in ITER [1] for the reason that the erosion owing to hydrocarbon formation and hydrogen retention in redeposited carbon are concerned for tritium safety and maintenances of fusion devices [9]. Therefore, the structural stability of such materials under heavy irradiation is crucial for the safety of nuclear facilities. Ion irradiation had been carried out on carbon fibers or CFCs to investigate their surface erosion [8] and deuterium trapping conditions [10]. Neutron irradiation was used to study the performance of a high-quality balanced weave composite at doses sufficient to cause swelling and disintegration of nuclear graphite [11]. Less attention has been paid to carbon fibers irradiated by high-energy electromagnetic radiation. Xu et al. [12] improved the graphitization degree of polyacrylonitrile (PAN)-based carbon fibers and graphite by gamma ray irradiation up to 2MGy dose. They also improved the tensile strength of the fibers and the interlaminar shear strengths (ILSS) values of epoxy-carbon fiber composite significantly through introducing carbonyl and carboxyl or ester functional groups onto carbon fiber surface after gamma ray irradiation of 300 kGy dose [13]. Kim et al. [14] used electron beam to bombard the carbon fiber and successfully enhanced wettability with polymer matrix on carbon fibers without sacrificing their intrinsic mechanical properties. Li et al. [15] applied gamma ray irradiation graft technology to enhance the surface oxygen content of carbon fibers and improved the ILSS of carbon fiber reinforced composites (CFRC) in suitable treatment conditions. Tiwari et al. [16] also improved the ILSS of polyetherimide-carbon fiber composites (to the maximum of almost 60% increase) and raised the wear performance such as lower friction coefficient in adhesive wear mode by gamma irradiation treatment. In addition, PAN-based intermediate modulus carbon fibers can be applied in civil industrial fields such as sports products because of their appropriate properties and cheapness.

In this work, in order to examine the reliability of PAN-based intermediate modulus carbon fibers in irradiation environment, the high-energy gamma ray irradiation was applied onto these carbon fibers. The primary purpose of the experiment was to determine the high-energy gamma ray irradiation-induced changes of the structure, surface hydrophilicity and mechanical properties of the carbon fibers after gamma ray irradiation. Structure change, surface hydrophilicity and Young's modulus of the carbon fibers after gamma irradiation were analyzed and discussed in this paper.

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2. Experimental

PAN-based intermediate modulus carbon fibers in the current study were supplied by Jilin Carbon Factory of China. The detailed information is presented in Table 1. The samples were placed in glass containers and irradiated in atmosphere at room temperature. Irradiation was carried out at Institute for Agricultural Application of Atomic Energy, An-hui Academy of Agricultural Science. The gamma ray was generated by ^{60}Co and the average photon energy is 1.25 MeV. The irradiation dose was accumulated to 200 kGy and 2 MGy with dose rate of 2.08 kGy/h by adjusting the distance between the samples and the ^{60}Co irradiator.

Raman spectroscopy was performed on a LABRAM-HR Confocal Laser Micro-Raman spectrometer using an Ar^+ laser with 514.5 nm to determine the quality and graphitization of carbon fibers before and after irradiation. XRD were made on D/MAX2500VL/PC to measure the structure parameter d_{002} of all samples. The chemical state of the surface was examined by X-ray photoelectron spectroscopy (XPS) on ESCALAB250. The microstructure and morphology of the carbon fibers was observed by field emission scanning electron microscopy (SEM, Sirion 200). Young's modulus was measured by two methods. One was tested on a self designed nano-micro scale internal friction apparatus through forced resonant peak method at Solid State Physics Institute, Chinese Academy of Sciences. Another was measured using single fiber drawing on a dynamic mechanical thermal analyzer (TA DMTAQ 800) and the modulus was determined by the stress–strain curve.

3. Results and discussion

3.1. Structure change

Raman spectroscopy is often used to evaluate the degree of structural perturbation and stress/strain distribution [14,17,18]. Fig. 1 shows the Raman spectroscopy on the surface of the PAN-based intermediate modulus carbon fibers before and after irradiation. Note that the penetration depth of Raman measurements from the surface of carbon fibers was estimated to be a few hundred angstroms [19–21] or 0.1–0.2 μm [22]. So Raman results only reflect the surface information of carbon fibers. There are three different bands of D (1300–1400 cm^{-1}), G (1500–1600 cm^{-1}) and 2D ($\sim$2700 cm^{-1}) in Fig. 1. D band is due to breathing mode of A_{1g} symmetry of in-plane substitutional heteroatoms, vacancies, grain boundaries or other defects, G band is assigned to in-plane symmetry allowed E_{2g2} mode of highly oriented graphite related to the vibration of sp^2 hybridization carbon atoms and the second order 2D band is an intrinsic property of well-ordered sp^2 carbons in two-dimensional grapheme lattice without any kind of disorder [23,24]. Table 2 summarizes the specific information of the Raman spectroscopy. As displayed in Fig. 1 and Table 2, we can obtain four interesting informations as follow.

Firstly, it is clear that the D and G bands become simultaneously sharper while the value of I_D/I_G (defined as R) and full width at half maximum of G band ($FWHM_G$) decreases from 0.976 and 66.35 cm^{-1} to 0.957 and 61.53 cm^{-1}. The decrease of R indicated higher percentage of sp^2 hybridization carbon atoms and less disorder and defects in treated fibers with increasing the gamma irradiation dose, which is the evidence of the improvement of graphitization of the irradiated fibers. $FWHM_G$ probes those sp^2 clusters resonant at a particular excitation. It would be small if the cluster were defect-free. So it is related to the graphitization extent [25]. Lower bond length and bond angle disorder are responsible for the decrease of $FWHM_G$ at a given excitation according to Ref. [23]. Vázquez-Santos et al. [22] reported the improving graphitization of carbon fibers through heating in which they also found the decrease of $FWHM_G$.

Secondly, the position of the G band shifts from 1601.90 to 1585.22 cm^{-1} with increasing gamma dose to 2MGy. The position of D and G bands could qualitatively reflect the structural change of carbon fibers. The down shifting of G band by non-negligible $\sim$17 cm^{-1} toward graphite value (1580 cm^{-1}) manifests an increase in the degree of graphitization which should be attributed to the defects decrease and graphitic order improvement induced by irradiation [22,26].

Thirdly, we can barely see the peak of the untreated fiber at around 2700 cm^{-1} defined as 2D band in Fig. 1 showing amorphous nature in pristine fibers. The bulge tends to be higher when increasing gamma dose, although the highest 2D band of the fabrics by 2 MGy dose irradiation is not apparent because of its large, quite broad and very low peak. As mentioned above, 2D band is an intrinsic property of well-ordered sp^2 carbons, so larger peak height of 2D band after gamma irradiation demonstrates that gamma irradiation up to 2 MGy dose can reduce amorphous carbon and defects in the carbon fibers, also indicating the improvement of the degree of graphitization of irradiated fibers.

Finally, the gamma radiation brought about a shift to high frequency in the 2D band varying from 2709.70 to 2722.80 cm^{-1} after irradiation of 2 MGy dose. As frequencies of Raman bands are directly related to the interatomic force constants, these shifts provide a clear measure of the way in which the stress is distributed within the molecular structure of the carbon fibers [19]. The sensitivity of the 2D band towards fiber deformation is double that of first-order bands, for which, for a given strain, the displacement of 2D band is larger than that of G and D bands. So laser Raman spectroscopy can be applied to follow the deformation of carbon fibers as a function of applied strain through 2D band analysis [27–29]. Upshifts of 2D band are used as a calibrating agent to calculate microscopic stress/strain. An upshift implies stiffening or shortening of C—C bond length (d_{C-C}) in accordance with $FWHM_G$ results discussed above, which is a consequence of compressive stress/strain. As we know, PAN-based carbon fibers show a kind of skin/core structure where the skin is significantly higher oriented and the core has turbostratic structure [21,30]. Most of the intensity of the Raman spectroscopy originates from that thin skin structure of the carbon fibers. Since much of their strength is determined by the nature of the bonding between the matrix and the surface of the fiber, Raman spectroscopy is able to fully describe the behavior of the interface of several carbon fiber-polymer composites [29]. The compressive stress and strain was calculated by the following formulas [17,18]:

$$\sigma_{comp}(\mathrm{GPa}) = -0.1 \times \Delta\omega\ (\mathrm{cm}^{-1}) \tag{1}$$

$$\varepsilon_{comp} = -\Delta L/L = \Delta\omega/\omega \tag{2}$$

where σ_{comp} is the microscopic compressive stress, ω is the peak position of the 2D band, ε_{comp} is the microscopic strain and L is the bond length. On the basis of Eqs. (1) and (2), the approximate compressive pressure and strain exerted on the surface of the treated carbon fiber under 200 kGy and 2 MGy dose were 1.17 GPa, 1.32 GPa and 4.30×10^{-3}, 4.83×10^{-3}, respectively. The compressive stress and strain introduced in the surface of the carbon fibers may due to the reduction of defects in carbon fibers. According to Ref. [31], there were a lot of dangling bonds and vacancies in the carbon atom network before irradiation. The repulsive force between sigma bonding electrons at a graphite carbon atom with a dangling bond should generate the stress relaxation so that the fiber before irradiation was almost stress-free. After gamma irradiation, gamma irradiation-induced defect annealing, which will be discussed below, annihilated the vacancies and decreased the density of the dangling bonds. In other words, gamma irradiation shortened and strengthened C—C bonds which increased bond energy and