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Effect of γ-ray radiation on the polyacrylonitrile based carbon fibers

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ABSTRACT

To investigate the effect of γ-ray radiation on the microstructural and mechanical properties of carbon fibers, carbon fibers were irradiated by ^{60}Co source. The interlayer spacing d_{002} of carbon fibers decreased after irradiation. The Young's modulus and density of the fibers increased with increasing dose. The tensile strength of fibers was found to increase at low dose and decrease at high dose. Additionally, Compton scattering effect caused by γ-ray is proposed to be responsible for the structural and mechanical changes of fibers. The results indicated that γ-ray irradiation was an effective method for improving the mechanical properties and graphitization degree of polyacrylonitrile based carbon fibers.

1. Introduction

In comparison with conventional engineering materials such as metals and ceramics, carbon fibers have superior properties in strength, modulus, stiffness and lightness. They are widely used as reinforcement in carbon fiber reinforced plastics, metals, ceramics and C–C composites, which principally depend on the strength and modulus of carbon fibers (Coqueret et al., 2009; Lee et al., 2007; Sung et al., 2002; Xu et al., 2007a). Recent developments have provided the rapid growth in mechanical properties of carbon fibers. General concern exists about their relatively poor tensile strength and modulus along the fiber axis, since the practical strength and modulus of carbon fibers are far lower than the theoretical strength and modulus of carbon fibers. Poor longitudinal tensile mechanical properties in carbon fibers are most probably attributed to their unique microstructure which consists of carbon crystallite layers, crystallite disorder regions and needle-like pores oriented along the fiber axis (Oya and Johnson, 2001). The degree of preferential orientation along the fiber axis of the layer planes is mainly responsible for the Young's modulus of the fibers. Perfectly graphitic fibers theoretically have the highest Young's modulus of about 1000 GPa due to the high degree of alignment of the grapheme planes along the fiber axis (Loidl et al., 2003).

Extensive studies have been devoted to the treatment of carbon fiber bulk in order to improve their mechanical properties, including imposing a magnetic field on the polyacrylonitrile (PAN) based carbon fibers in the carbonization process(Sung et al., 2002), application of tension during the initial oxidation step at 220 °C (Watt and Johnson, 1969), modifying the precursors prior to stabilization (Willkinson, 2000), boron-doping (Allen et al., 1971) and fast neutron irradiation (Wicks, 1975). Although the mechanical properties of the final fibers have been improved via these methods, there are some drawbacks, such as their high facilities, high energy consumption, high maintenance cost and poor effect.

In recent years, γ-ray irradiation is being extensively investigated as means of altering properties of polymeric materials, such as films, fibers, powders and molded objects (Hiroki et al., 2009; Jipa et al., 2008; Li et al., 2007). Gamma ray irradiation can induce chemical reactions at any temperature in the solid, liquid and gas phase without any catalyst(Clough, 2001; Salah et al., 2009). The large and thick three-dimensional fabrics could also be treated by irradiation without consideration of the shape of the samples, which is convenient for industrialization (Akhavan et al., 2004; Machi, 1996). The radiochemical effect of γ-ray on PAN has been investigated (Hill et al., 1992; Tarakanov, 1995; Zhao et al., 1999) for several decades when PAN was used as a precursor to produce high-quality carbon fibers. Some gases (H_2, HCN, NH_3 and N_2) were produced when PAN samples were irradiated at room temperature using ^{60}Co γ-radiation. The high energy radiolysis of PAN has been observed to produce at least two radicals; one resulting from H abstraction from the methylene group, to form a chain radical, and the other from radical addition to the nitrile group, to form a polyimine radical. These radicals were consistent with a dominant cross-linking reaction. The γ-irradiation of PAN reduced the reaction temperature in thermal treatment, and accelerated the formation of conjugation structures via the cyclization of the nitrile groups. The duration of oxidation of irradiated PAN was reduced significantly. The application of

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irradiation to carbon fibers as the method modifying the carbon fiber surface inertness has been also studied (Xu et al., 2007b) and γ-ray surface treatment for commercial carbon fibers has been employed. Limited attention has been devoted to the radiation effect of carbon fiber structure caused by high energy radiation like γ-ray.

In this study, PAN-based carbon fibers were irradiated by γ-ray. X-ray diffraction analysis of fibers was conducted and then the densities of irradiated fibers were determined to study the structure change of fibers. The effects of γ-ray irradiation on the tensile strength and Young's modulus of carbon fibers were also investigated.

2. Experimental

2.1. Materials

The PAN-based carbon fibers investigated in current studies were manufactured by Jilin Carbon Factory of China (average diameter was 7 μm, 3×10^3 single filaments per tow, linear mass was 0.161 g m^{-1}). The precursor of fiber was oxidized at 280 °C and carbonized at 1400 °C. The irradiation field (^{60}Co γ-ray source) was provided by Harbin RuiPu Irradiation New Technology Company of China. The irradiation dose rate was 6.0 kGy h^{-1}.

2.2. Irradiation of carbon fibers

Several bundles of carbon fibers were wound up on a frame about 30 cm and the carbon fibers 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 deposited into the ^{60}Co point-source irradiator and irradiated at room temperature.

2.3. Measurements

X-ray diffraction traces were obtained from bundles of parallel fibers using nickel-filtered Cu Kα radiation, with a wavelength of 0.15418 nm, from a Rigaku D/man-rBX generator. 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 the carbon fibers was estimated directly using the Bragg equation (Cuesta et al., 1998).

The as-received and irradiated fiber samples were extracted in acetone before the density measurement, to remove the impurities and resin with which fibers had been coated during manufacture. Two types of liquid, tetrabromoethane ($Br_2CHCHBr_2$) and carbon tetrachloride (CCl_4), with dissimilar densities 2950–2965 and 1594 kg m^{-3} at 20 °C, respectively, were mixed in the proportion required to ensure that the fiber sample floated in the middle of the mixture. The density of the mixture, and hence the sample density, was calculated from knowledge of the proportions of each component. For each processing condition, the densities of at least five small bundles were measured and the average value and measurement errors were determined.

The tensile strength and Young's modulus of the fibers were determined from the stress-elongation curves. The measurements were carried out according to ASTMD3379M standards (single-fiber method). The curves were obtained in a universal test machine. Individual filaments were glued to a cardboard tab using an epoxy material. The gauge length was 20 mm and the crosshead speed was 1 mm/min. The test was repeated with 40–45 single filaments to make it possible to obtain an average value. The diameters of the fibers were visually observed using SEM and the sectional area was then calculated.

3. Results and discussion

3.1. X-ray diffraction characterization

X-ray diffraction has been shown to provide a sensitive method for characterizing the structural perfection in carbon fibers (Kaburagi et al., 2003). Fig.1 shows X-ray diffraction intensity distribution in the vertical direction, measured for untreated and irradiated fibers. The main peak can be seen to occur at approximately 25.5° 2θ, corresponding to the (0 0 2) reflections of the pseudo-graphite structure (Endo, 1988; Huang and Young, 1995). There also appears a much weaker band at ~44° 2θ, which is usually assigned to the (10) turbostratic band of disordered carbon materials. The weakest band at ~53° 2θ corresponds to the (0 0 4) reflections of the pseudo-graphite structure.

The diffraction patterns of each irradiation-treated counterpart were almost identical. Some differences can be pointed out from the different X-ray diffractometer traces. The intensity of (0 0 2) peak decreased and the diffraction angle of (0 0 2) peak increased as the absorbed dose of irradiated fibers increased. The d_{002} spacing of all the treated and untreated carbon fibers 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.

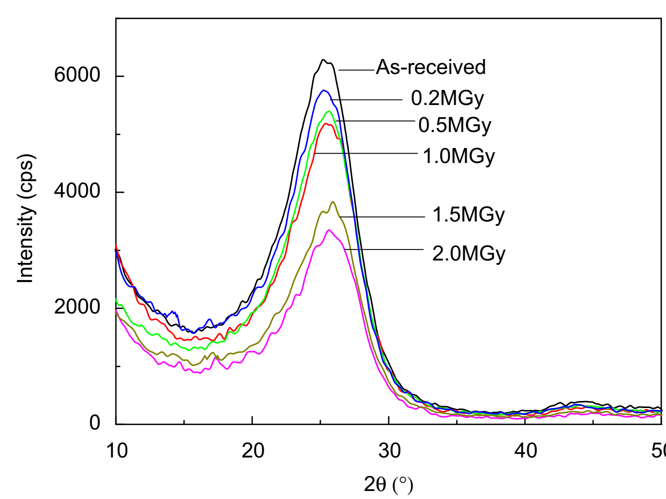

Fig.1. X-ray diffraction intensity distribution for the carbon fibers irradiated at different doses.

Table 1
X-ray diffraction structural parameters of carbon fibers.

	2θ[0 0 2] (°)	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. Influence of irradiation on density

The influence of absorbed dose on the fiber density is evident from Fig.2. The data were taken from the first series of experiments at ten absorbed doses (0–2.0 MGy). The curve shows that the density increased with the absorbed dose. It may be seen that the main density increased occurs in the first 0–0.5 MGy dose and there was an approximately linear relationship between density and absorbed dose (0–0.5 MGy). Then this density increase was less pronounced above 0.5 MGy. It was found that the deviation increased slowly as the irradiation dose increased. However, the density of irradiated fibers was much far away from the density of perfect graphite (2266 kg m^{-3}) though the packing fraction of fibers was increased from 77.4% for the as-received fiber to 79.5% for the fiber irradiated at 2 MGy dose.

It is indicated that the difference in the density changes is caused by the highly porous nature of the PAN-based fibers, as reported by Bacon (Bacon and Schalamon, 1968). It is expected that γ-ray irradiation, like hot stretching and temperature (Ozbek and Isaac, 2000), affects the porosity (and hence the density) of PAN-based carbon fibers. The reduction of point-defect and interlayer spacing may be responsible for this result during γ-ray irradiation.

3.3. Change in tensile strength

The effect of irradiation dose on tensile strength of carbon fibers is presented in Fig.3. From Fig. 3, which shows the tensile strength of carbon fibers as a function of absorbed dose, we can see that during the dose region (0–0.2 MGy), the tensile strength of carbon fibers was increased remarkably. The carbon fibers irradiated at a dose of 0.2 MGy outperformed the original fibers by a significant margin of 10%. Prolonged irradiation degraded the tensile strength of carbon fibers. Above 1 MGy dose the tensile strength decreased below the untreated value.

Unlike most reactor graphite, which consists of well-crystallized, relatively randomly oriented polycrystalline aggregates, carbon fibers derive their inherently high mechanical properties from a highly oriented, relatively poorly graphitized, layer structure. The susceptibility of tensile strength to irradiation strongly depends on the perfection of the internal structure formed during heat-treatment (Wicks, 1975).

The failure in fibrous materials is induced by flaws, and it is suggested that there is the existence of two classes of fiber defects: the first class would correspond to minor defects which are inherent to the process and the precursor. These defects include pores and structure imperfections. Being more numerous, they would be uniformly distributed along all filaments. The other class of defects would correspond to major ones, which are attributed to the formation of cracks in the fibers due to excessive weight loss during the stabilization and carbonization steps. Being present in a smaller number, they would be less uniformly distributed (Prauchner et al., 2005).

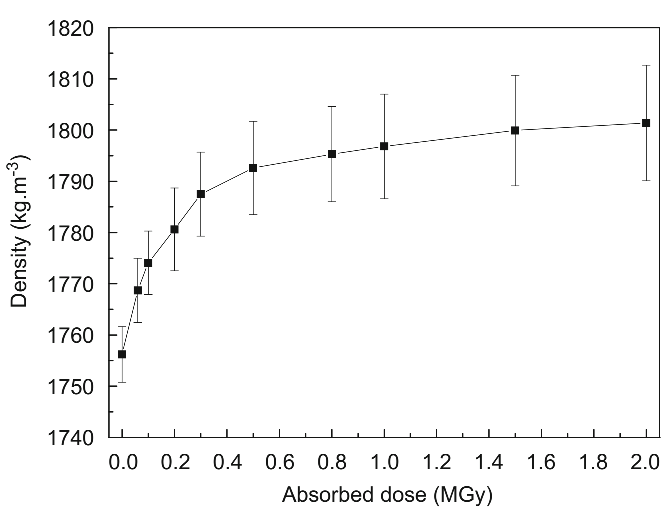

Fig.2. Effect of γ-ray irradiation on the density of carbon fibers.

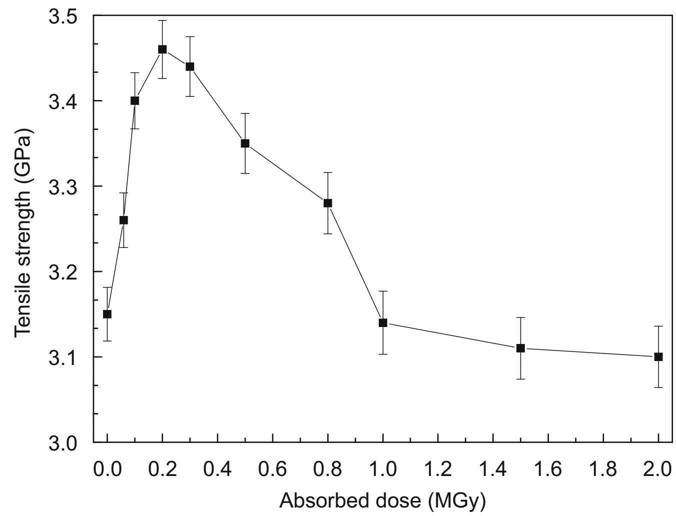

Fig.3. Effect of γ-ray irradiation on the tensile strength of carbon fibers.

In graphite plane of carbon fibers, there are some carbon double and treble bonds around flaws. The carbon free radicals are easily produced from carbon double and treble bonds by γ-ray irradiation (Khan et al., 2006). Then the carbon free radicals form the new ring structure and the amount of first class flaws is decreased (Cataldo et al., 2004). As a result, radiation may improve the strength of fibers, which is the predominant effect at low dose. In addition, the tensile strength of carbon fibers is also governed, in part, by the crystallite size, fibers having larger crystallites being weaker. The prolonged irradiation may improve the graphitization (Hulman et al., 2005) and grow the crystal size, and hence does harm to the tensile strength of carbon fibers. Therefore, the phenomenon that the absorbed dose affects the strength is interpreted as being the result of two conflicting effects that the weakness induced by an improvement of graphitization is offset by the decreasing defects of irradiated carbon fibers in low dose (Willkinson, 2000). In other words, the effect of graphitization improvement and increase in crystallite size is weaker than that of decreasing flaws on fiber strength at low dose, and the reverse thing occurs at high dose.

3.4. Change in Young's modulus

Fig. 4 shows the change of Young's modulus of carbon fibers with the increase of absorbed dose. It is indicated that there is an approximately linear relationship between the modulus of fibers and the absorbed dose. The carbon fibers irradiated at highest dose of 2.0 MGy showed a 13.8% higher average tensile modulus, compared with the as-received. However, there is no simple formula that can be used to relate the process parameter to the physical and mechanical properties simultaneously, and further investigation is required to give any mathematical expression of these relationships.

The changes in Young's modulus caused by γ-ray irradiation are of the same character as those obtained by heat-treatment of

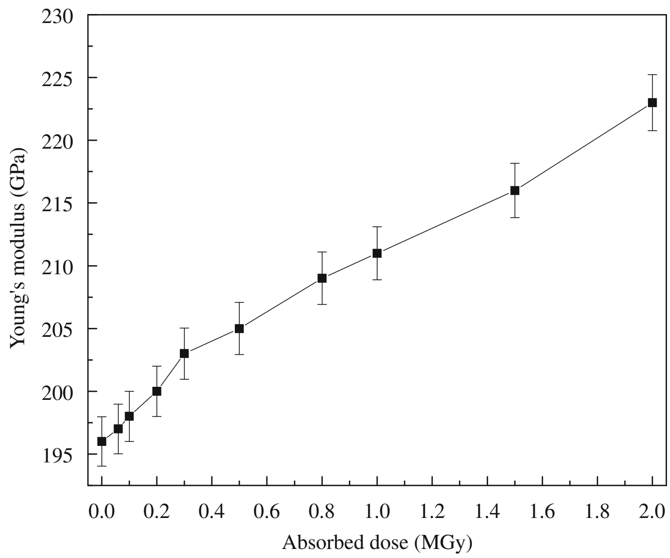

Fig.4. Effect of γ-ray irradiation on the Young's modulus of carbon fibers.

fibers, except that the changes are much more pronounced in the latter case. This is due to the fact that turbostratic materials (i.e. $d_{002} > 0.335$ nm) are, in essence, defect structures. As these defect regions are reduced by γ-ray irradiation and the interlayer spacing approaches that of single crystal graphite, the material is able to take advantage of the mechanical properties displayed by the graphite crystal (Krasheninnikov and Banhart, 2007). The improvement of graphitization and growth of crystal size lead to the increase of Young's modulus (Sammalkorpi et al., 2005). Further investigations about mechanical properties of irradiated carbon fibers will be made.

4. γ-ray interaction with carbon fibers

Gamma rays interact with matter in three different ways: photoelectric effect, Compton scattering and pair production. The photoelectric effect is dominant at lower energies and pair production happens at higher energies (energies several times the threshold for this: 1.022 MeV). The Compton effect is the dominant process of gamma ray absorption for photons of intermediate energy (around 1.0 MeV quantum energy). ^{60}Co emits two gamma rays, one at 1.173 MeV and the other at 1.332 MeV. Carbon is the dominant element in carbon fiber and has a low atomic number. Therefore, it is concluded that the Compton scattering effect is mostly responsible for the interaction of gamma ray with carbon fibers (Campbell and Mainwood, 2000).

In Compton scattering, charged particles such as electrons and protons interact with atoms primarily by Rutherford scattering (Coulomb scattering) and cause ionization and atomic displacements. But the predominant interaction mechanism is ionization which is the process of removing orbital electrons from atoms and producing positive ions and free, or unbound electrons. The electrons ejected from the atoms by γ-photons, have high kinetic energy and are the direct cause of the formation and disappearance of interstitial atoms and other kinds of transformation in a solid (Cataldo, 2000). The electron and scattered photon are produced after the incident photon interacts with carbon atom of carbon fiber in Compton scattering. Then the carbon free radical is created by anion or cation radical mechanisms (Crivello et al., 1997; Ercin et al., 2005; Ichikawa and Ota, 1987; Khan et al., 2006; Panda et al., 2001; Shukla et al., 2005). The amount of first class flaws is decreased and the graphitization of carbon fiber is improved.

5. Conclusions

The effect of γ-ray irradiation on the structure and mechanical properties of polyacrylonitrile based carbon fibers has been determined. Large decrease in the d_{002} interlayer spacing has been achieved by γ-ray irradiation and an approximately linear dependence on absorbed dose has been suggested. Carbon fibers initially increase in strength, at low dose, but reduction in strength occurs at high dose. Young's modulus and the density are substantially increased with the increase in absorbed dose. The decrease of flaws and microstructural parameters such as d_{002} interlayer spacing can be closely related to the variations of density, tensile strength and Young's modulus.

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