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

Zhiwei Xu a, *, Yudong Huang b, Chunying Min c, Lei Chen a, Li Chen a

a Key Laboratory of Advanced Braided Composites, Ministry of Education, Composite Research Institute, Chenglin Road, Tianjin Polytechnic University, Tianjin 300160, China
b School of Chemical Engineering & Technology, Harbin Institute of Technology, P.O. Box 410, Harbin 150001, China
c School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

ARTICLE INFO

Article history:
Received 11 December 2009
Accepted 2 March 2010

Keywords:
Carbon fiber
γ-ray radiation
Microstructure
Mechanical properties

ABSTRACT

To investigate the effect of γ-ray radiation on the microstructural and mechanical properties of carbon fibers, carbon fibers were irradiated by 60Co source. The interlayer spacing d002 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.

© 2010 Elsevier Ltd. All rights reserved.

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 poor longitudinal tensile mechanical properties along the fiber axis (Lee et al., 2007; Sung et al., 2002; Xu et al., 2007a). 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 (H2, HCN, NH3 and N2) were produced when PAN samples were irradiated at room temperature using 60Co γ-rays. 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 

* Corresponding author. Tel.: +86 022 24528089; fax: +86 022 24528052
E-mail address: xuchwei@tjpu.edu.cn (Z. Xu).
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 (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 N2 was filled up to one normal atmospheric pressure in the glass container. It was then sealed tight. The samples were deposited into the 60Co 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 from bundles in the plane were 0.15418 nm, from a Rigaku D/mana-rBX generator. 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.

![Graph showing X-ray diffraction intensity distribution for carbon fibers](image)

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

Table 1

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>2θ(0 0 2) (°)</th>
<th>d_{002} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>25.30</td>
<td>0.3520</td>
</tr>
<tr>
<td>0.2 kGy</td>
<td>25.32</td>
<td>0.3517</td>
</tr>
<tr>
<td>0.5 kGy</td>
<td>25.44</td>
<td>0.3501</td>
</tr>
<tr>
<td>1.0 kGy</td>
<td>25.62</td>
<td>0.3477</td>
</tr>
<tr>
<td>1.5 kGy</td>
<td>25.74</td>
<td>0.3460</td>
</tr>
<tr>
<td>2.0 kGy</td>
<td>25.79</td>
<td>0.3454</td>
</tr>
</tbody>
</table>

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 diffractometry 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.
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 $\gamma$-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 $\gamma$-ray irradiation.

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 (Practical, 2005).

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 $\gamma$-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.

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 $\gamma$-ray irradiation are of the same character as those obtained by heat-treatment of
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; Erkin 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.

Acknowledgments

We acknowledge the Tianjin Natural Science Foundation (08JCZDJC24400) and Natural Science Foundation of the Jiangsu Higher Education Institutions of China (09KJB430002) for financial support.

References


