Radiation Physics and Chemistry 81 (2012) 622–627

Contents lists available at SciVerse ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Radiation-induced crosslinking of polyacrylonitrile fibers and the subsequent regulative effect on the preoxidation process

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ARTICLE INFO

Article history:
Received 17 November 2011
Accepted 20 February 2012
Available online 3 March 2012

Keywords:
Polyacrylonitrile
Fiber
Irradiation
Crosslinking
Thermal property
Preoxidation

ABSTRACT

To investigate the radiation effect on polyacrylonitrile (PAN) fibers as well as on the preoxidation process, PAN fibers were irradiated by γ-rays at room temperature at 50–500 kGy in vacuum and then were thermally oxidized in air. Gel fraction determination indicated that γ irradiation led to the predominant crosslinking of PAN fibers, with G values (the number of event per 100 eV absorbed) of $G(X)=0.28$ and $G(S)=0.16$ for chain crosslinking and scission, respectively. It was found that irradiation caused a slight change in the crystal structure and tensile strength at low dose. Radiation led to a reduction of the onset temperature of cyclization reaction and moderated the exothermic behavior. The density of the PAN fibers after thermal oxidation was used to evaluate the preoxidation extent. It was proven that radiation could significantly accelerate the preoxidation process and consequently shortened the preoxidation time. Radiation crosslinking may have potential application in the production of PAN-based carbon fibers.

1. Introduction

Polyacrylonitrile (PAN) fibers are one of the most important precursors for the production of high-performance carbon fibers (Bashir, 1991; Cato and Edie, 2003). The manufacturing of carbon fibers from the PAN precursor usually involves three processes, namely, preoxidation, carbonization, and graphitization. The preoxidation process is essential, time-consuming (Beltz and Gustafson, 1996), and intensely exothermic (Donnet et al., 1984). Various reactions are involved in this process and are classified as oxidative and cyclization reactions (Gupta et al., 1995). The cyclization, i.e., oligomerization of the nitrile groups, forms a ladder chain structure and consequently improves the thermal stability of the fibers. Researchers have paid much attention to optimizing the preoxidation process during the last decades. Pretreatment with chemical agents such as $KMnO_4$ (Mathur et al., 1994), $CoCl_2$ (Ko and Chen, 1999), CuCl (Li et al., 2006), $CoSO_4$ (Zhang and Wang, 2002) on PAN copolymers has been proven to promote the preoxidation process of the PAN fibers. This pretreatment resulted in an enhanced rate of the cyclization reaction, a decreased temperature of cyclization, and a shortened preoxidation time. However, boric acid (Qin et al., 2007b) (H_3BO_3) had a retardant effect on cyclization.

The major objective of this work was focused on the modification of PAN fibers by radiation in an attempt to replace the pretreatment with an oxidizing agent such as $KMnO_4$. The radiation technique has two advantages over the conventional method. One is that the possible crosslinking of PAN fibers results in a better thermal stability. The other advantage is that the modified polymer is homogeneous and free from any impurities. It has been previously found that irradiation induces PAN to produce a predominant crosslinking structure (Hill et al., 1992). The effect of radiation on PAN via electron beam (Dietrich et al., 1996; Miao et al., 2010; Yuan et al., 2010), γ-ray (Tarakanov, 1995; Mascia and Paxton, 1991; Zhao et al., 1999), UV (Aggour and Aziz, 2000; Yuan et al., 2011), and X-ray irradiation (Dossantos and Kawano, 1994; Murthy and Radhakrishna, 1983) has been investigated. Because fibers have much higher degrees of crystallization and orientation than the bulk material, the effects of γ irradiation on the structural and thermal properties of PAN fibers should be specially studied in detail to evaluate the potential application of radiation technology in producing carbon fibers.

In this work, PAN fibers composed of a poly(acrylonitrile-co-methylacrylate) copolymer were subjected to γ irradiation, and the subsequent variations in the structure and properties of the fibers were investigated. The radiation effect on the preoxidation process was investigated by measuring the density of the preoxidized PAN fibers.

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doi:10.1016/j.radphyschem.2012.02.029

2. Experimental

2.1. Materials

Wet-spun PAN fibers containing 1.1% (mol/mol) methylacrylate as a co-monomer were used in this work. The polymer composition was determined by NMR and FT-IR. The number-average molecular weight (M_n) of the PAN fibers was 1.2×10^5 g/mol, as measured by gel permeation chromatography (GPC). The original PAN fibers with a linear density of 1.20 dtex had a tensile strength of 6 cN/dtex and an elongation of 12%. A single tow contained 3000 filaments.

2.2. Irradiation and preoxidation

The PAN fibers were packed into the glass tubes (diameter: 5 cm, 30 cm in length) and then the tubes were sealed off after evacuation up to 10^{-2} Pa. The tubes were irradiated by ^{60}Co γ-rays at room temperature with a dose rate of 4.3 kGy/h. The variation of dose was 50–500 kGy by changing irradiation time. The irradiated samples were then exposed to air for characterization and preoxidation. Preoxidation of the PAN fibers was performed using an isothermal heating progress at 220 °C or 250 °C in clean air. The PAN fibers with different preoxidation extents were obtained by holding the samples for different times at the given temperature.

2.3. Measurements

In the gel measurement, dimethylsulfoxide (DMSO) was used as the solvent to remove the soluble fraction of PAN fibers. A dried and weighed PAN fiber sample was placed in a 150-mesh stainless basket and then immersed in DMSO for 24 h at 80 °C. Then, the basket was extracted with methanol for 12 h to eliminate the solvent swelled in the sample, and the residual component was dried at 80 °C in vacuum for 24 h. The G values of crosslinking ($G(X)$) and scission ($G(S)$), which represent the number of crosslinking or scission per 100 eV absorbed, were calculated using the Charlesby–Pinner equation (Charlesby and Pinner, 1959).

Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC-822^e differential scanning calorimeter at a heating rate of 10 °C/min under N_2 or air atmospheres. Thermogravimetric analysis (TGA) was carried out in a Netzsch TG-F3209 thermal analyzer. The TGA scan was carried out at a heating rate of 10 °C/min from 100 °C to 900 °C in N_2 gas flow.

The tensile strength was measured using an electronic single filament strength tester (LLY-06E) at a constant speed of 20 mm/min. The filament gauss length was 20 mm. The average of the data for 50 filaments was reported for each sample.

X-ray diffraction spectra of the samples were recorded within the angle range $2\theta=5$–50° on a D/max-pc XRD-2550 diffractometer using CuK_α ($\lambda=1.54056$ Å) at 40 kV and 200 mA. The data were collected at a scan speed of 10°/min with a scanning step of 0.02°. The crystallinity was calculated from the areas of the crystalline diffraction peaks and the amorphous zone using Hinrichen's method (Hinrichsen, 1972). The orientation index was calculated using the following equation:

$$\pi=\frac{180-H}{180}\times100\%$$

where π is the orientation index and H is the width at the half-maximum intensity.

The densities of the PAN fibers with various preoxidation extents were measured by sink-float method using a gradient mixture of n-heptane and carbon tetrachloride at 28 °C.

3. Results and discussion

3.1. Radiation crosslinking of PAN fibers

The PAN fibers changed from white to pale yellow after γ-ray irradiation at dose higher than 50 kGy and a gel was formed. The PAN fibers irradiated to 200 kGy were compared with the original fibers with respect to the solubility in DMSO, as shown in Fig. 1(a). It can be seen that a yellow gel formed for the irradiated sample, while the original fibers dissolved completely in 4 h. Shrinkage was clearly observed for the irradiated sample due to the disorientation of the PAN fibers after swelling by the solvent.

Fig. 1(b) shows the gel fraction as a function of absorbed dose over the dose range of 50–500 kGy in vacuum. The gel fraction was approximately 60% at a dose of 50 kGy and then increased gradually with increasing dose. A gel fraction of 90% was achieved at 500 kGy. PAN is a predominantly crosslinking type of polymer upon irradiation (Murthy and Radhakrishna, 1983). The crosslinking may result from the recombination of the backbone radicals or addition of backbone radicals to the nitrile groups on the adjacent chains. Because the crosslinking predominantly occurs in the amorphous region and preferentially near the surface of crystalline regions (Charlesby, 1977), it may result in structural changes in the fibers.

Fig. 2 shows the Charlesby–Pinner plot of PAN fibers irradiated to various doses. The G values of croslinking and scission were calculated to be $G(X)=0.28$ and $G(S)=0.16$ $(100\,\text{eV})^{-1}$, respectively. Therefore, radiation crosslinking predominantly occurs in the PAN fibers, though chain scission occurs to some extent. Our results are different from the values of $G(X)=0.59$ and $G(S)=0.0$ reported by Hill

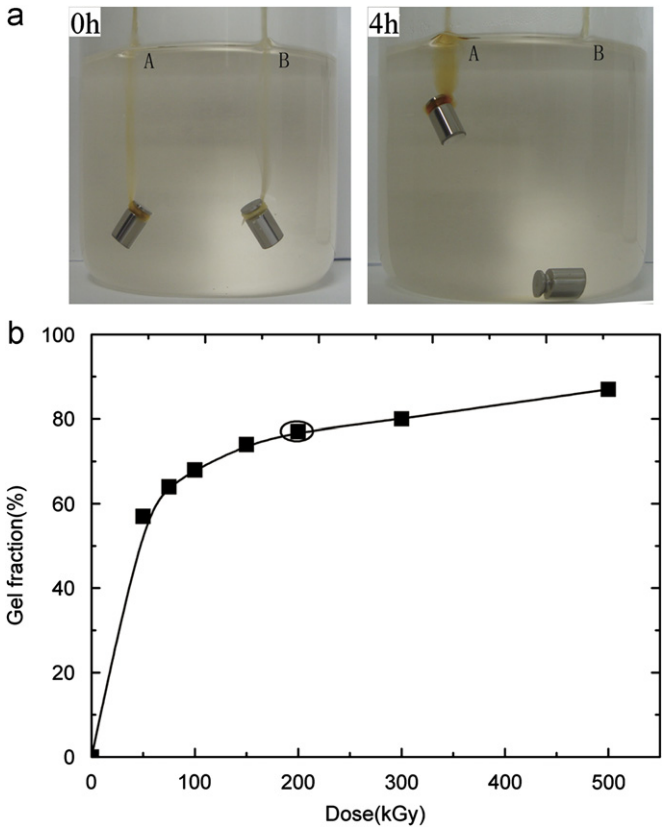


Fig. 1. (a) Photos of PAN fibers before and after immersed in DMSO. (b) Gel fraction of PAN fibers irradiated at various doses in vacuum. A and B correspond to the sample irradiated to 200 kGy and the original fiber, respectively.

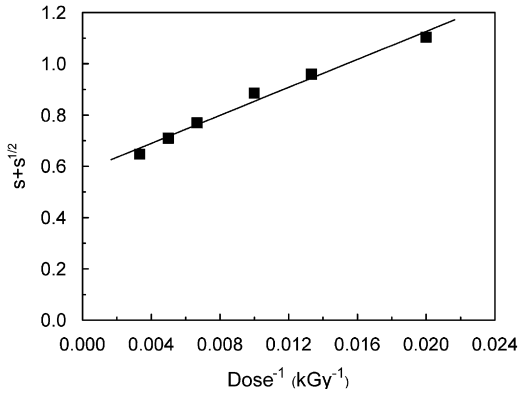


Fig. 2. Charlesby–Pinner plot for PAN fibers irradiated in vacuum at room temperature (s=soluble fraction).

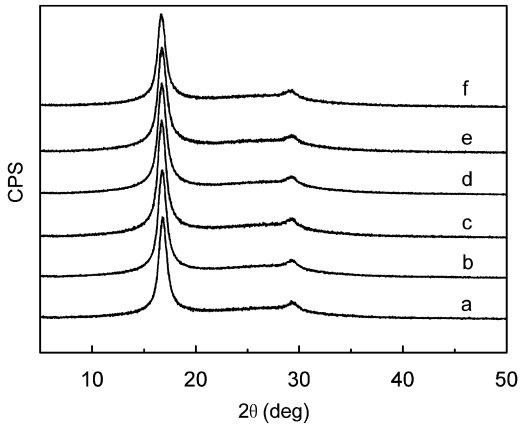


Fig. 3. XRD patterns of PAN fibers irradiated at doses of (a) 0, (b) 50, (c) 100, (d) 200, (e) 300 and (f) 500 kGy.

et al. (Hill et al., 1992) for PAN powder with a weight-average molecular weight (M_w) of 1×10^5 g/mol. In their work, the soluble fraction was determined by measuring the concentration of PAN completely dissolved in DMSO using GPC. The high degrees of crystallinity and orientation of PAN fibers led to the trapping of the backbone radicals in the crystalline regions and severely restricted their mobility at room temperature. After exposure to air, the trapped radicals induced oxidative degradation of PAN fibers via the reactions with oxygen. Therefore, a lower $G(X)$ value was obtained in our work.

Fig. 3 shows the XRD patterns of the irradiated PAN fibers at various doses. The intense peak at $2\theta=17^\circ$ and the weak peak at $2\theta=29^\circ$ are the characteristic diffraction peaks of PAN crystallites (Gupta and Maiti, 1982). It was obvious that the original crystal structure was not destroyed by irradiation. The crystallinity slightly decreased from 62.3% to 59.7% over the investigated dose range. The orientation index marginally decreased from 86.8% to 85.9% when the dose was increased to 2 MGy, indicating that the highly oriented structure was maintained even at much higher absorbed dose. It implies that crosslinking dominantly occurs in the amorphous region. The entropic force of aligned PAN chains in amorphous region normally causes shrinkage and decrease in orientation during thermal treatment. However, when the PAN fiber chains are crosslinked by γ irradiation before thermal treatment, the orientation of oxidative stabilized fibers is expected to be much higher than that for the non-irradiated PAN fibers, and the resultant carbon fibers may have higher modulus. The investigation of carbon fibers made from radiation crosslinked PAN fibers is still in progress.

3.2. Thermal behavior of radiation-crosslinked PAN fibers

The preoxidation process is involved with heat evolution and mass change. Therefore, DSC and TG are usually used to analyze the oxidative stabilization process by previous workers (Cui et al., 2010; Han et al., 2010; Qin et al., 2007a; Sun et al., 2010; Wang et al., 2007; Xu et al., 2008). Figs. 4 and 5 exhibit the DSC curves and TG curves of the original and irradiated PAN fiber samples, respectively. Only one characteristic exothermic peak was observed at approximately 280 °C in N_2, corresponding to the

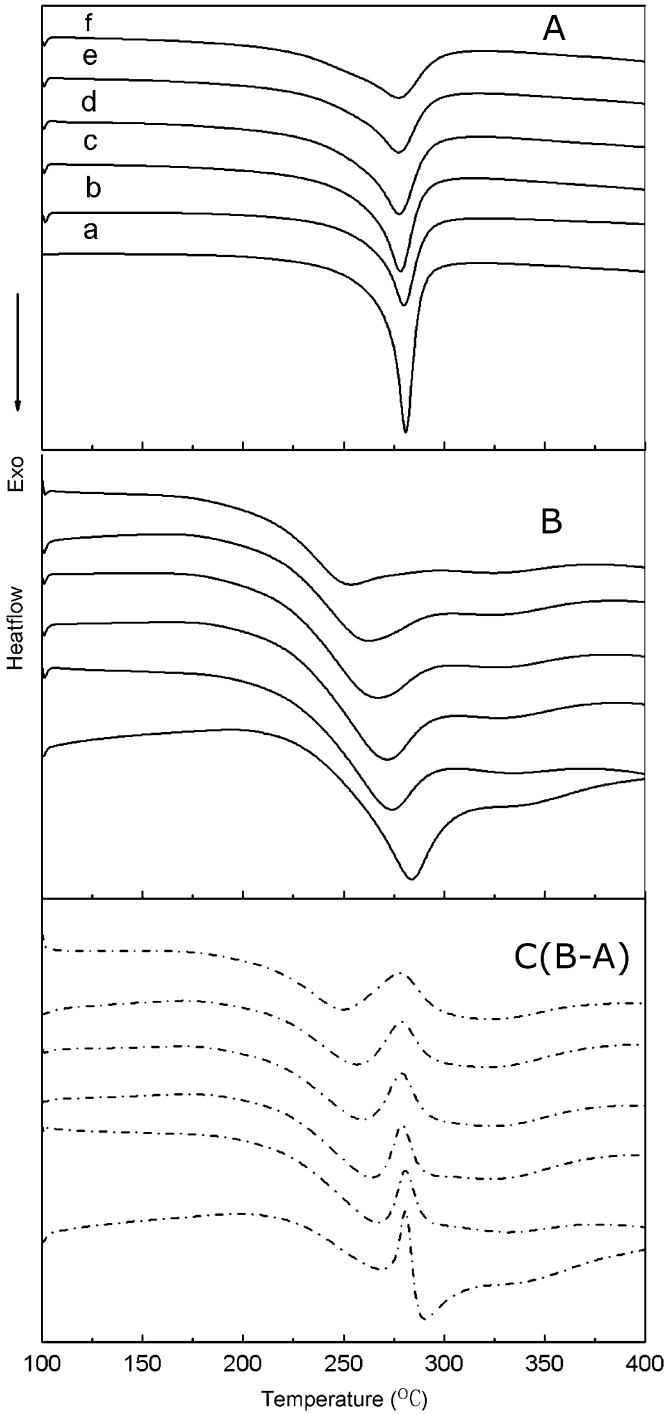


Fig. 4. DSC curves of PAN fiber samples irradiated with various doses. (A) Under nitrogen atmosphere. (B) Under air atmosphere. (C) Difference between B and A. (a) Original fiber, (b) 50 kGy, (c) 100 kGy, (d) 200 kGy, (e) 300 kGy, and (f) 500 kGy.

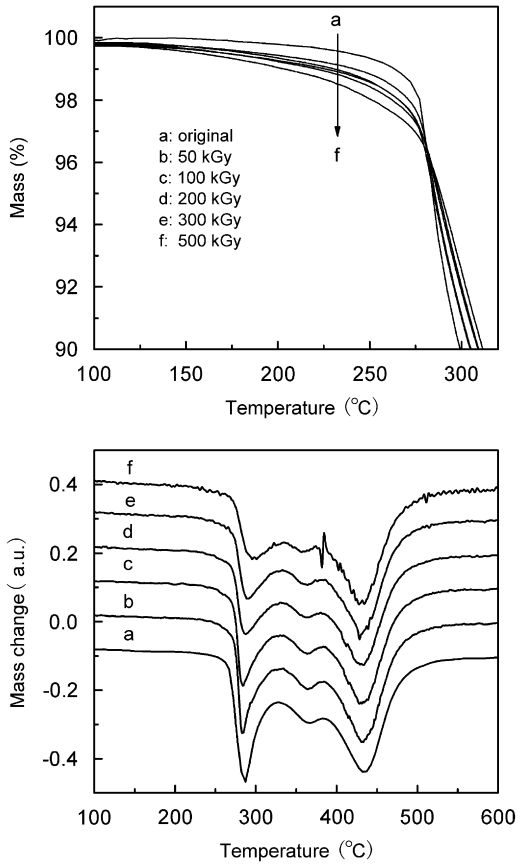


Fig. 5. TG and DTG curves of PAN fibers irradiated at various doses. (a) Original fiber, (b) 50 kGy, (c) 100 kGy, (d) 200 kGy, (e) 300 kGy, and (f) 500 kGy.

cyclization of nitrile groups (Turner and Johnson, 1969; Yu et al., 2010). The peak temperatures remained almost unchanged after irradiation, but the exotherm was spreading over a broader temperature range for the irradiated samples. This spreading trend becomes more obvious with increasing absorbed dose. It can be concluded that irradiation led to a decrease in the onset temperature of cyclization reaction, alleviated the exothermic behavior and this effect could be regulated by dose. The crosslinked structure and the trapped radicals induced by irradiation should be responsible for the alleviating effect. It is reasonable to assume that the crosslinking site is correlated with nitrile groups of PAN.

As shown in Fig. 4(B), the DSC curves of the PAN fibers measured in air exhibited double exothermic peaks. The peak at the lower temperature was due to the cyclization reaction, in accordance with the DSC measurements in N_2. The peak at the higher temperature followed by a downward trend was due to the oxidation reaction. Interestingly, the peak temperature of oxidation reaction remained almost unchanged after irradiation. This result indicates that irradiation has a significant effect on cyclization but little effect on oxidation, further confirming the assumption of crosslinking via nitrile groups.

Owing to the occurrence of various reactions, i.e., cyclization and oxidation, when PAN fibers are thermally treated in the presence of oxygen, the exothermic peaks due to these reactions may overlap. By subtracting the curves in Fig. 4(A) from those in Fig. 4(B), two exothermic peaks were obtained, as shown in Fig. 4(C), in which the contribution of the cyclization reactions was removed. Oxygen is not involved in the reaction mechanism of cyclization (Rahaman et al., 2007), so these two peaks in Fig. 4(C) can be attributed to the reactions between oxygen and PAN molecules. These two peaks are assigned to the primary and the secondary oxidations, respectively, according to the work by Gupta et al. (Gupta et al., 1995; Gupta et al., 1996). As a result, the DSC curves obtained in an air atmosphere have a triplet character, which could facilitate the understanding of the various reactions during the preoxidation process. In addition, it has also been found that the primary oxidation occurs prior to cyclization.

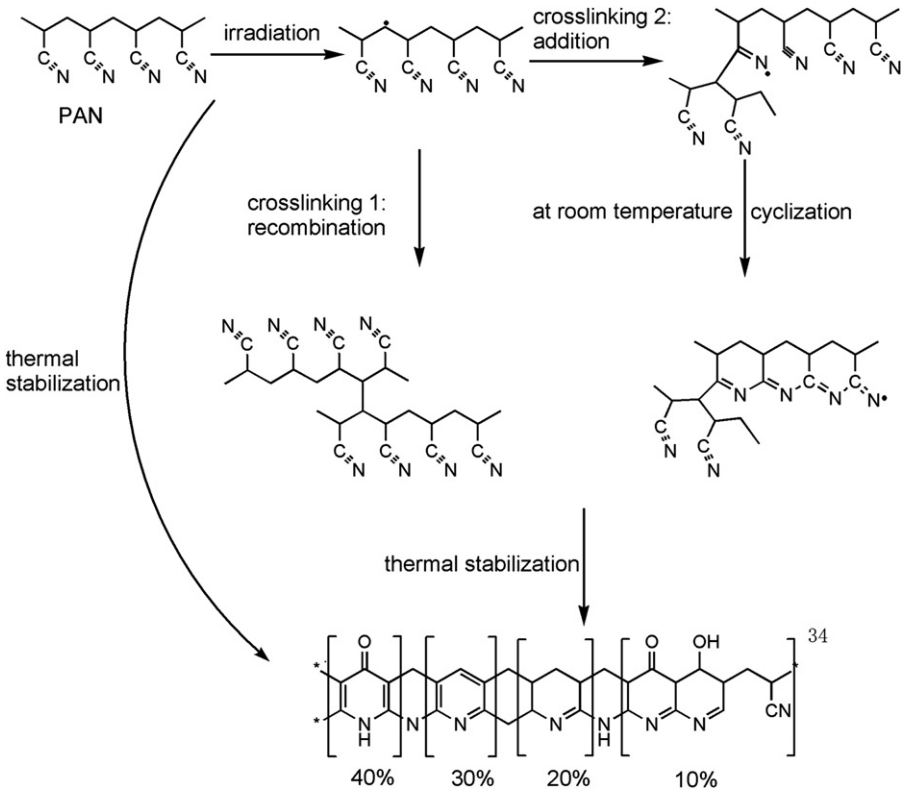
As indicated in Fig. 4, it can be concluded that irradiation has a significant effect on the cyclization of PAN fibers by broadening and reducing the intensity of the exothermic peak, but little effect on primary and secondary oxidations. Fig. 5 further shows the TG and DTG (differential thermogravimetric) curves of PAN fibers with and without irradiation. It was obvious that decomposition (weight loss) of all the irradiated samples began at lower temperature and the weight loss at temperature below 400 °C was less than that of the original fibers. Therefore, irradiation crosslinking may improve the carbon yield. This trend became more obvious at higher dose. The weight loss of irradiated PAN fibers at lower temperature is believed to be mainly due to the cyclization and dehydrogenation reactions in N_2 (Sun et al., 2009), not to decomposition via C–C bond scission. These results indicated that the cyclization reaction of the irradiated PAN fibers was initiated at a lower temperature and proceeded slowly. This finding is consistent with the DSC analysis.

Based on the above results, a mechanism for the radiation induced crosslinking is proposed and presented in Scheme 1. The backbone radicals induced by γ-ray irradiation may recombine to form crosslinking structure or add to the nitrile groups of the adjacent chains to crosslink (Hill et al., 1992) and form new macromolecular radicals. The radicals located at =N may initiate cyclization at room temperature. The crosslinked and partially cyclized structure in PAN fibers may be responsible for the reduction of the onset temperature of cyclization and the alleviation of the exothermic process. The preoxidized PAN fibers (Takahagi et al., 1986) could be obtained from both the original and radiation crosslinked PAN fibers by thermal treatment in air.

3.3. Radiation effect on the mechanical properties and the preoxidation process

The tensile strength decreased slightly at low doses and then remained almost unchanged at higher doses, as shown in Fig. 6. A slight decrease in tensile strength was caused by the cyclization, and low levels of degradation. However, due to the formation of a crosslinked structure in the amorphous region and the high orientation index, the decrease in strength was very limited even at a dose of 500 kGy.

The preoxidation step is essential for producing carbon fibers and has a great impact on the performance of the resulting carbon fibers. Therefore, it is important to evaluate the effect of radiation treatment on the preoxidation process, though the DSC measurements revealed a significant effect of radiation on the cyclization reactions. The PAN fibers with various preoxidation extents were obtained by thermally treating the PAN fibers in air at 220 °C or 250 °C for various times. The density of the preoxidized PAN fibers, which increases as the volume contracts due to cyclization and oxygen uptake during heat treatment of the fibers in air, is an important indicator of the preoxidation extent (Turner and Johnson, 1969; Thorne and Marjoram, 1972; Zhang et al., 2004). Fig. 7 shows the density of fibers as a function of the preoxidation time for irradiated (200 kGy) and original PAN fibers thermally treated at 220 °C or 250 °C in air. It can be seen that the density increases with the preoxidation time for both samples. Compared with the original fibers, the irradiated fibers exhibited a higher preoxidation extent, as indicated by the higher density under the same preoxidation conditions. It should also be noted that the



Scheme 1. The hypothesized mechanism of irradiation induced crosslinking of PAN fibers.

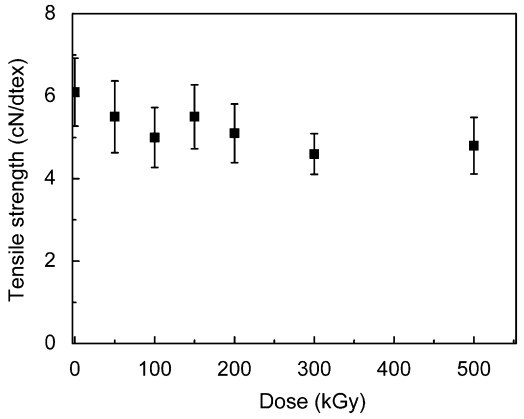


Fig. 6. Tensile strength of PAN fibers irradiated at various doses.

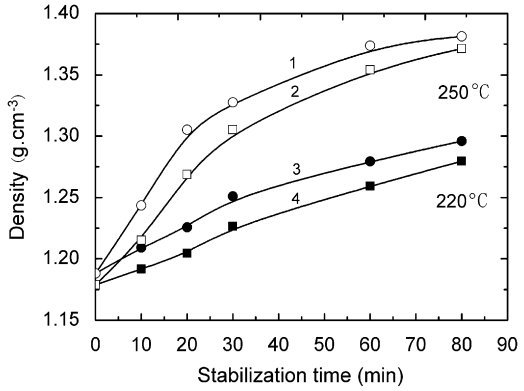


Fig. 7. The density of preoxidized PAN fibers as a function of preoxidation time. Curves 1 and 3: fibers irradiated at 200 kGy; Curves 2 and 4: original fiber. -■- and -●-: thermally oxidized at 220 °C; -○- and -□-: thermally oxidized at 250 °C.

density (1.1881 g/cm^3) of the PAN fibers irradiated at a dose of 200 kGy was higher than that of the original fibers (1.1789 g/cm^3) because of the denser crosslinked structure produced by irradiation. The higher preoxidation extent of irradiated samples implies that radiation treatment has accelerated the preoxidation process. Shorter preoxidation time or a lower temperature is required for the irradiated samples to achieve the same preoxidation extent. Combined with the DSC analysis, the advantages of radiation crosslinking can be concluded as following: lowering the onset temperature of the cyclization reactions, alleviating the exothermic behavior, and accelerating the preoxidation process. In addition, the broader exothermic range for the radiation crosslinked PAN samples is essential to protect the macromolecular backbone from decomposition during the cyclization reaction, as already reported by Zhao et al. (1999).

4. Conclusions

Irradiation resulted in the crosslinking of PAN fibers at a relative low dose, and the crosslinked fibers retained the highly oriented structure and had a slight decrease in the tensile strength. However, the exothermic behavior of the cyclization reactions of radiation crosslinked PAN fibers was significantly moderated and the effect could be regulated by varying the absorbed doses. It was speculated that the crosslinking resulted mainly from the addition of backbone radicals to nitrile groups. The crosslinked PAN chains in the amorphous region were expected to keep the orientation of the preoxidized PAN fibers. We conclude that the most important contribution of radiation crosslinking to preoxidation process is a reduction of the onset temperature and a significant shortening of the preoxidation time. Our results indicate that the radiation technology has potential applications in the production of carbon fibers.

Acknowledgments

The project was supported by the National Natural Science Foundation of China (Grant No. 10905088) and the Key Program of Knowledge Innovation Project of the Chinese Academy of Sciences (Grant No. KJCX2-YW-N33).

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