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

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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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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

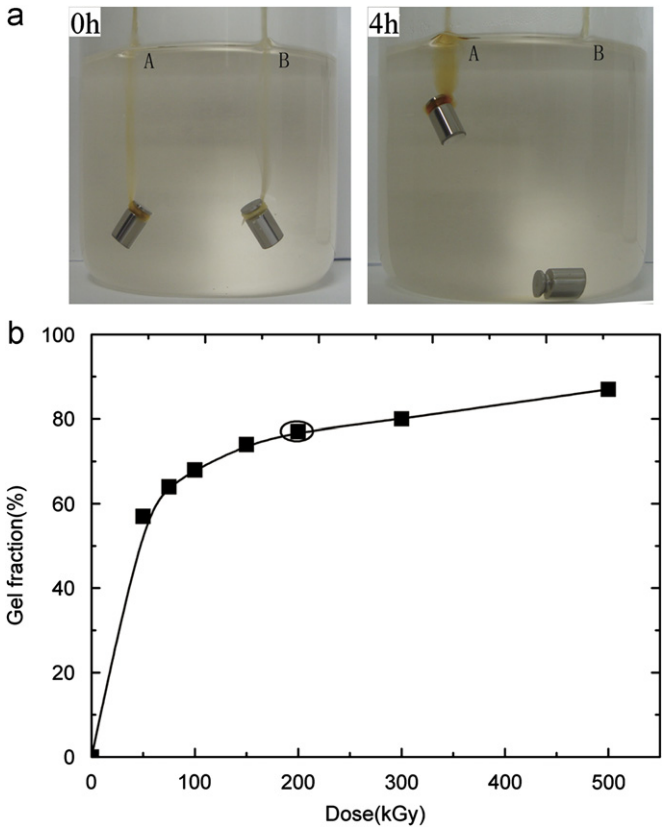

Fig. 1. (a) Photos of PAN fibers before and after immersed in DMSO. (b) Gel fraction of PAN fibers irradiated at various doses in vacuum. A and B correspond to the sample irradiated to 200 kGy and the original fiber, respectively.