Radiation Physics and Chemistry 94 (2014) 9–13

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

Radiation oxidation and subsequent thermal curing of polyacrylonitrile fiber

Weihua Liu [a], Mouhua Wang [a], Zhe Xing [a,b], Guozhong Wu [a,*]

[a] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
[b] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- PAN fiber was irradiated in the presence of oxygen to induce oxidation at room temperature.
- Oxidation degradation occurred at the fiber surface.
- Oxidation thickness increased with oxygen pressure.
- The oxidized region can be converted to a gel by the thermal treatment.

ARTICLE INFO

Article history:
Received 12 December 2012
Accepted 19 June 2013
Available online 27 June 2013

Keywords:
Polyacrylonitrile fiber
Radiation oxidation
Thermal curing

ABSTRACT

Polyacrylonitrile (PAN) fibers were exposed to gamma-ray irradiation at room temperature under vacuum, air and oxygen to investigate the radiation oxidation effects on PAN fibers. Radiation-induced oxidation degradation and crosslinking was evaluated by measuring the gel fraction. It was found that radiation oxidation took place mainly on the fiber surface due to the limited penetration of oxygen into PAN fibers from the surface, and the oxidation thickness increased with the oxygen pressure. Chain scission was dominant in the oxidized area, and crosslinking occurred in the inner part of the fibers. However, the oxidized regions of the fibers can be converted to gel via crosslinking by thermal curing at 160 °C in a N_2 atmosphere. Higher extents of radiation oxidation degradation led to a greater increase in the gel fraction. These results suggest that the radiation treatment of PAN fibers prior to thermal oxidation may be useful for manufacturing carbon fibers.

1. Introduction

Radiation technology has been used widely in the modification of polymeric materials for many years. Ionizing radiation can induce various phenomena in polymers, such as promoting chain branching to crosslinking and chain scission to degradation. Crosslinking and degradation processes occur simultaneously, and the dominating process is determined by the treatment conditions and the intrinsic polymer properties (Spinks and Woods, 1990; Singh and Silverman, 1992). Crosslinking improves materials properties, such as thermal stability, and strength (Bhardwaj and Bhardwaj, 1994; Hanna et al., 2012; Huaiyu et al., 2011; Sánchez-Soto et al., 2001; Sharma et al., 1995; Szabo et al., 1996), while chain scission induces damage. In the presence of oxygen, radiation oxidation occurs in any polymer, and leads to chain scission, which is associated with remarkable changes in the mechanical properties of the starting materials (Costa et al., 2008; Dannoux et al., 2008; Dole, 1991). The extent of radiation oxidation in a polymer material is dependent on the radiation conditions, such as dose, dose rate, oxygen pressure, and irradiation temperature, as well as the structure of the polymer. Polyacrylonitrile (PAN) has been found to be crosslinkable by gamma radiation (Hill et al., 1992) in vacuum, but chain scission is the main reaction in the presence of oxygen.

PAN fiber is known to be the main precursor of carbon fiber; therefore, the curing (crosslinking) of PAN fiber has been extensively studied by thermal oxidation (Fitzer and Muller, 1975; Gupta and Harrison, 1996, 1997). Many researchers have focused on optimizing the thermal oxidation process. Chemical reagents (Ko and Chen, 1999; Mathur et al., 1994; Zhang and Wang, 2002) and ionizing radiation (Tarakanov, 1995; Jipa et al., 2008; Miao et al., 2010; Yuan et al., 2011; Zhao et al., 1999) have been used for the curing of PAN fiber precursor for the fabrication of high-performance carbon fiber. The radiation curing of PAN fibers has been reported to be an effective method to improve thermal oxidation by regulating exothermic behaviors, improving the properties of the resulting

* Corresponding author. Tel./fax: +86 21 39194526/+86 21 5955 8905.
E-mail address: wuguozhong@sinap.ac.cn (G. Wu).

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.06.015

carbon fibers, and also increasing the yield of carbon fibers. In previous reports, PAN fibers were irradiated mainly in the absence of oxygen to avoid oxidation degradation. There is almost no report focusing on the radiation oxidation of PAN fibers. Because the radiation oxidation can be induced at room temperature, the oxygen introduced into PAN molecular chains may facilitate the thermal oxidation curing of PAN fibers to produce carbon fibers. In this work, the radiation oxidation and subsequent thermal curing of PAN fibers were carefully investigated to elucidate the radiation effects on PAN fibers.

2. Experimental

2.1. Materials

Wet-spun PAN fiber containing 1.1% (mol/mol) methylacrylate as co-monomer was used. The number-average molecular weight (M_n) was 1.2×10^5 g/mol, as measured by gel permeation chromatography (GPC). PAN fibers with a linear density of 1.20 dtex showed a tensile strength of 6 cN/dtex and an elongation at break of 12%.

2.2. Irradiation and thermal curing process

The weighted PAN fibers were packed into glass tubes (3 cm in diameter and 30 cm in length), which were evacuated to a pressure of 10^{-2} Pa and were sealed off for irradiation in vacuum or filled with oxygen at a pressure of 0.3 MPa for irradiation in oxygen. The samples were wrapped with aluminum foil, exposed to gamma-ray irradiation in air, and were irradiated up to 500 kGy at a dose rate of 4.3 kGy/h. Radiation was performed at room temperature in a ^{60}Co source at the Shanghai Institute of Applied Physics.

Thermal curing was carried out in a blast oven. The irradiated samples were placed into a stainless steel tube, which was subsequently evacuated, and filled with N_2. The samples were put in the oven, which had been heated to 160, and stored for 1 h.

2.3. Gel-fraction determination

Dimethylsulfoxide (DMSO) was used to measure the gel fraction of the samples. The weighted PAN fiber was placed in a 150-mesh stainless basket and immersed in DMSO at 80 °C for 24 h. The sample was then washed with methanol, and dried in vacuum. This procedure was repeated until a constant weight was obtained.

3. Results and discussion

3.1. Effects of radiation oxidation on gel fraction of PAN fiber

Fig. 1 shows the relationship between the dose and gel fraction of PAN fibers irradiated in three different atmospheres. In vacuum, the critical dose at the gel point is approximately 15 kGy. The gel fraction increases sharply with dose until 50 kGy; then the gel fraction increases gradually up to 100%. This behavior is typical for radiation-induced crosslinkable polymers. In air and oxygen, the shape of the dose–gel fraction curves is similar, but the gel point dose shifts to a higher dose; moreover, the saturated gel fraction decreases with the increase in oxygen pressure. The estimated gel point dose and the saturated gel fraction are presented in Table 1. Because the oxygen content in PAN fiber is proportional to the oxygen partial pressure, the relative initial oxygen concentrations (before irradiation) in atmosphere are estimated to follow the ratio of 0:1:15 for PAN fibers irradiated in vacuum, air, and oxygen

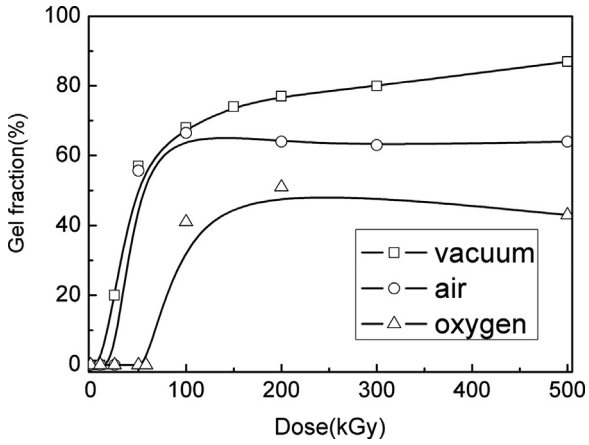

Fig. 1. Dose dependence on gel fraction for PAN fibers irradiated under three different atmospheres; vacuum (□), air (○), oxygen 0.3 MPa (△).

Table 1
Estimated dose at gel point, saturated gel fraction, and initial oxygen concentration in PAN fiber under three different irradiation conditions.

Irradiation environment	Gel point dose (kGy)	Gel fraction (%) at saturation	Initial oxygen conc. in PAN fiber (relative)
Vacuum (O_2: 0 MPa)	15 ± 3	95	0
Air (O_2: 0.021 MPa)	18 ± 3	65	1
Oxygen (O_2: 0.30 MPa)	60 ± 10	50	15

(0.3 MPa), respectively (as seen in Table 1). The shift in the critical dose seems to be proportional to the ratio of the initial oxygen concentration in PAN fibers.

In the presence of oxygen, radiation oxidation in PAN fiber takes place in a manner similar to that observed for other polymers, and chain scission is the main chemical reaction (Arakawa et al., 1982; Dannoux et al., 2008; Longieras et al., 2007; Luisetto et al., 2003). Generally, the primary radicals produced by radiation react with oxygen to form secondary radicals that amplify the propagation process and lead to new oxidation products. In PAN fiber, oxidation reactions should be limited to the skin area because it is difficult for oxygen to penetrate into the fiber. The increase in the gel point dose for irradiation in air and oxygen atmospheres reflects the greater oxygen uptake by the PAN fiber during irradiation.

3.2. Gel-fraction change due to thermal treatment after irradiation

Fig. 2 shows the changes in the gel fraction by thermal treatment at 160 °C in N_2 for PAN fibers irradiated at various doses at room temperature. At a low dose of 50 kGy, oxidation degradation occurs predominantly in oxygen and the gel fraction is very low. At 100 kGy, the gel fraction increased twice as high (87% from 41%) as that for PAN irradiated in oxygen, while the increase was only a few percent for irradiation in vacuum. For PAN fiber irradiated in air, the increase in the gel fraction after thermal treatment is intermediate to the increases observed following the irradiation in vacuum and oxygen. For PAN fiber irradiated to 200 kGy, the change is similar to that observed for a dose of 100 kGy. However, at a higher dose (e.g., 500 kGy) in oxygen, thermal treatment is much less effective in increasing the gel fraction due to severe oxidation degradation.

Fig. 2 shows that the gel fraction induced by radiation crosslinking is not greatly affected after thermal treatment. Therefore, it