Applied Surface Science 265 (2013) 519–526

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

The influence of the short-term ultraviolet radiation on the structure and properties of poly(*p*-phenylene terephthalaramide) fibers

Shineng Li, Aijuan Gu, Jie Xue, Guozheng Liang*, Li Yuan

Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Materials Science & Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

ARTICLE INFO

Article history:
Received 12 July 2012
Accepted 14 November 2012
Available online 23 November 2012

Keywords:
Short-term ultraviolet radiation
Poly(*p*-phenylene terephthalaramide) fibers
Surface
Structure
Property

ABSTRACT

The influence of the short-term (<20 h) ultraviolet (UV) radiation (at 60 ± 3 °C with a relative humidity of 50 ± 1 RH%) on the integrated performance of poly(*p*-phenylene terephthalaramide) fibers was comprehensively studied, and the mechanism behind the influence was intensively discussed by detecting the overall changes in both chemical and morphological structures. Results demonstrate that the short-term UV radiation has different effect on the core part from the surface part of PPTA fibers. Specifically, the short-term UV radiation slightly decreases the crystalline index without changing the chemical structure of the core part of PPTA fibers; while that introduces a large amount of oxygen atoms on the surfaces of UV-KF fibers, and induces a distinctive increase in the surface roughness of fibers even the irradiation time is only 1 h. These structural changes make UV-KF fibers show decreased contact angle and improved wettability while remaining the outstanding glass transition temperature. All parameters of tensile properties including tenacity, break extension, energy to break and modulus almost linearly decrease as the irradiation time extends; however, these parameters almost level off when the irradiation time is longer than 3 h. After irradiated for 18 h, the tenacity, break extension, energy to break of UV-KF fiber is 88%, 90%, and 86% of the corresponding value of original fiber, respectively.

1. Introduction

As one of the most important kind of high performance organic fibers, poly(*p*-phenylene terephthalaramide) (PPTA) fiber, or named as aramide fiber, has attracted increasing attentions of both scientists and engineers worldwide owing to its attractive integrated performances such as outstanding mechanical properties and excellent thermal stability [1–3], and thus make PPTA fiber become the most suitable material for preparing some special products such as high performance boats, airplanes and space crafts, bulletproof materials, etc. [4–6]. These products are mainly serviced out of door, so they should have a very good weathering resistance [7,8].

Some researchers found that PPTA fibers can absorb UV light [9], and their tensile properties would decrease after a long time UV radiation [10–14]. However, unfortunately, only about a dozen of articles were focused on this subject since the birth of PPTA fibers, and different researchers attributed different factors to the deterioration [15–19], so the true nature behind the aging mechanism is far from enough.

As we have known that besides high mechanical property, outstanding thermal resistance is another attractive merit of PPTA fibers, while the poor surface wettability is the biggest shortcoming of the fibers [20], so it is necessary to investigate the influence of UV radiation on the thermal resistance and surface wettability of PPTA fibers. However, no literature reported an overall study on the effect of UV radiation on the integrated performance including mechanical property and thermal resistance as well as surface properties. Obviously, this phenomenon is not beneficial to outline the structure-property relationship of PPTA fibers, and thus limiting the development and applications of PPTA fibers. Therefore it is of great interest to systematically research the influence of UV radiation on the integrated performance of PPTA fibers, and reveal the nature behind.

On the other hand, it is worthy to note that previous works focused on studying the tensile property of PPTA fibers after irradiated for a long time (at least 24 h). This situation neglected the initial change of the structure of the fibers after the UV radiation, and thus it is not possible to get a comprehensive knowledge on the nature behind the change in the integrated performance of the fibers induced by the UV irradiation. There is only one article reported the short-term UV-radiation on PPTA fibers, it stated that a 6 h-UV radiation would decrease the tensile properties and change the surface morphology of Kevlar fiber [21], but no extensive investigation was conducted on revealing the mechanism

* Corresponding author. Tel.: +86 512 61875156; fax: +86 512 65880089.
E-mail address: lgzheng@suda.edu.cn (G. Liang).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.11.038

of the change in the macro-properties from the view of microstructure.

Based on above introduction, we believe it is of great importance and interest to intensively study the effect of the short-term (shorter than 24 h) UV radiation on the structure and integrated properties of PPTA fibers, and thus gets a clear irradiation mechanism.

2. Experimental

2.1. Raw materials

PPTA fibers (Kevlar-49) were made in DuPont Company, USA. Acetone and petroleum were all commercial reagents with analysis grades, and used as received. Distilled water was produced in our lab.

PPTA fibers were boiled in acetone, petroleum and distilled water for 3 h, successively, to remove the surface finishes during the filament spinning, and then the fibers were dried at 80 °C in a vacuum oven for 12 h. The resultant fibers were coded as KF, and regarded as the original (or control) fibers for this investigation.

2.2. The UV radiation of KF fibers

KF fibers were put into an UV-aging instrument and irradiated for x h. The carbon arc lamp of the instrument emits UV beam of wavelength ranging from 295 to 360 nm. The temperature and relative humidity in the radiation chamber were (60 ± 3) °C and (50 ± 1) RH%, respectively. Then the fibers were dried under vacuum. The resultant fibers were designed as UV-KF(x h), which x takes the values of 1, 2, 3, 12 and 18.

2.3. Measurements and characterizations

Attenuated Total Reflection Infrared (ATR-IR) Spectrometry was recorded using a Nicolet 5700 FT-IR spectrometer (USA) attached to an attenuated total reflection (ATR) apparatus, the resolution of wave number was 4 cm^{-1}, and the average result of 60 automatic scans from 650 to 4000 cm^{-1} was output as the test result.

Thermogravimetric (TG) analyses were carried out on a TA Instruments (SDT 2910, USA) in the range from 25 to 800 °C under a nitrogen atmosphere with a flow rate of 50 mL/min and a heating rate of 10 °C/min. The initial degradation temperature (T_{di}) is the temperature at which the weight loss of the sample reaches 5 wt%.

Dynamic Mechanical Analysis (DMA) scans were performed with a fiber-tension mode using a Dynamic Mechanical Analyzer TA Q800 (USA) from −150 to 350 °C at a heating rate of 5 °C/min and a frequency of 3.5 Hz.

X-ray Photoelectron Spectroscopy (XPS) was recorded employing an AXIS-ULTRA DLD X-ray Photoelectron Spectroscope (England) with monochromatised Al Kα radiation from a 250 W X-ray source ($h\nu$ = 1486.6 eV) having a pressure in the analysis chamber of 10^{-9} Torr.

A Scanning Electron Microscope (SEM, Hitachi S-4700, Japan) coupled with Energy Dispersive Spectrometer (EDS) was employed to observe the morphologies of fibers. Five measurements were conducted for each sample, and the average value was taken as the final result.

The surface topography of fibers was observed employing an Atomic Force Microscopy (Multimode V, USA) in an air atmosphere using a tapping mode. A single fiber was fastened on a steel sample-mount by twin adhesive. The scanning rate was 1 μm/s and the scanning scope was 3 μm × 3 μm. The typical surface roughness of fibers can be calculated using the software of the instrument.

The surface free energy and contact angle of a bundle of fibers were measured using a dynamic contact angle analysis system (OCAT 21, Germany). A bundle of fibers was cut into 1.5 cm in length, and fixed indirectly to a wire hook suspended from the microbalance of the system. The fibers were immersed into the testing liquid by raising the elevating stage at a constant speed of 1 mm/min, and then the dynamic contact angles (θ') were obtained schematically by the measurement. In our experiment, water (a strong polar solvent with a surface tension of 72.8 mN/m) and ethylene glycol (a weak polar solvent with a surface tension of 48.3 mN/m) were chosen as testing liquids. Tensile properties of a single fiber were measured by an Electronic Single Fiber Tensile Strength Tester (YG004N, Nantong Hongda Experiment Instruments. Co. Ltd., China) according to the Chinese Standard GB/T14337-2008, at least fifty samples for each kind of fibers were tested. All tests were carried out in the environment with a temperature of (20 ± 1) °C and a relative humidity of (65 ± 1) RH%. The typical tensile values of fibers can be calculated using the software of the instrument.

Wide Angle X-ray Diffraction (WAXD) curves were measured on a Rigaku D/Max (Rigaku Co. Ltd., Tokyo, Japan) diffractometer with a Bragg-Brentano geometry using Cu Kα radiation (λ = 1.5405 Å), and analyzed with Jade-5.0 software program. The data were collected over the 2θ ranged from 5° to 80°. The separation of overlapping reflections was performed with a fitting peak program after various intensity corrections which assume that every crystalline peak belongs to the Gaussian type, and the amorphous halo is centered at 21°.

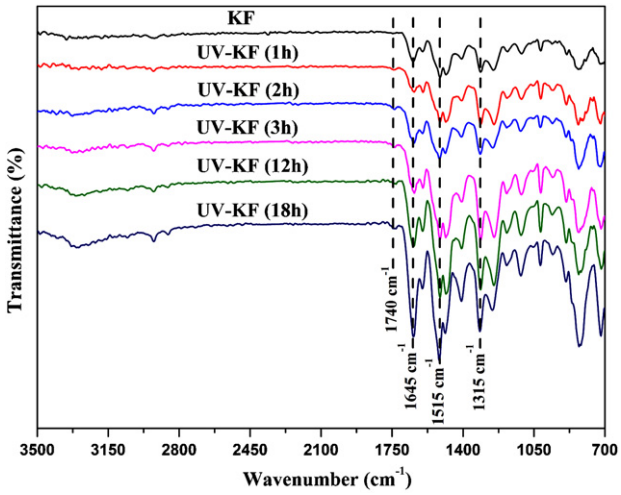

Fig. 1. ATR-IR differential spectra of KF and UV-KF fibers.

3. Results and discussion

3.1. Influence of the UV radiation on the structures of PPTA fibers

3.1.1. Chemical structure

Fig. 1 depicts the ATR-IR spectra of KF and UV-KF fibers with different irradiation time. All spectra have many similar peaks, but they also show big differences, suggesting that UV radiation changes the chemistry of original fibers. First, compared with the spectrum of KF fibers, that of each kind of UV-KF fibers shows an additional peak (at 1740 cm^{-1}), reflecting the formation of carboxylic acids and scission of amide groups. Second, the intensities of some peaks increase after UV-radiation, indicating the variety of the amounts of some bonds. In detail, as the irradiation time enlarges, the peak (at 1645 cm^{-1}) attributing to the stretching peak of —C=O peak becomes stronger, suggesting that the hydrogen bonds between adjacent C=O and N—H groups have been disconnected, this may be attributed to the rupture of the molecular chains