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Structure and performances changes during tensile of aromatic copolysulfonamide fibers under different thermal temperatures via in-situ synchrotron SAXS/WAXS

Xiaoyun Li[a,1], Jinchao Yu[b,1], Jianning Wang[b], Kang Chen[b], Xiuhong Li[a], Yumei Zhang[b,*], Fenggang Bian[a,*], Jie Wang[a]

[a] Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China
[b] State Key Laboratory for Modication of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, China

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ABSTRACT

In *situ* studies of structure and performance changes in aromatic copolysulfonamide (*co*-PSA) fibers during stretching at different thermal exposure temperature range from room temperature to 300 °C were carried out using synchrotron small angle X-ray scattering and wide angle X-ray scattering techniques. Results showed that the optimum microstructure and mechanical property of *co*-PSA fibers were achieved when stretched at 200 °C, the fibril length, fibril misorientation, crystal sizes L_{002} reached minimum, the long period became maximum at the same strain indicating that lamella and fibrils aligned perfectly, fiber structure compactness at 200 °C. During stretching at RT to 200 °C, at low strain, fibril length, crystal size L_{002} increased, fibrils oriented along stretching direction, the long period was enlarged; the opposite trend evolution of structure appeared under high strain. But stretching at 300 °C, L_{002} increased, fibril orientation became poor, the lamellae destroyed easily resulting in the decreasing strength. It can be concluded that *co*-PSA fibers remain good property under thermal at 200 °C, external force use environment.

1. Introduction

Aromatic Polysulfonamide (PSA) fibers can be potentially utilized in the field of high-temperature filtration, protective textiles, flame retardancy and insulation materials [1]. So, the fibers will be exposed to light, thermal and others environment intentionally or accidentally. And the excellent mechanical properties, light and thermal stabilities are the basis for its application of harsh environment [1–3]. Therefore, a great effort has been dedicated to improving the performance of PSA fibers [4–11]. But for fibers, it was inevitable that the fiber was damaged when exposed to light, thermal or external force environments while in use [12–17]. It would be caused the mechanical, physical and chemical property degradation. So, it is necessary to investigate that the degradation of microstructure and properties under thermal, light, external force, and combined effect occasions.

The degradation on structure, properties and aging mechanism of fiber under thermal, light exposure have been gained extensive studies by researchers. Researches showed that the strength retention of *co*-PSA fiber at 250 °C, 300 °C can attain up to 70% and 50% respectively [11]. Ren et al. [18] pointed out that the strength of *co*-PSA fiber increased with increasing the thermal temperature until 250 °C. The effect of thermal exposure on property and structure of Kevlar fibers when exposed to nitrogen atmosphere at different temperatures was for a duration of 15 min by Hineleh, Abdo and Brown [14–16]. From the data of differential thermal analysis and thermodynamic analysis, the result showed that the Kevlar 49 became thermal degradation at 550 °C, the crystallinity and microparacrystallite reached the maximum values at 400 °C. Yue et al. [14] studied the thermal degradation performance of Kevlar 29 under both atmosphere and vacuum environments at temperatures of 100–300 °C, it was found that the tensile strength and the tensile strain decreased with increase in treatment temperature. Similar phenomenon also can be observed in the lycocell fiber, and the number of intermolecular hydrogen bond was found to decrease when the temperature above at 70 °C [16].

Generally, the multilayer structure such as morphology (e.g. fibrils, porous) and crystal of fiber was changed by thermal exposure. In addition, the thermal exposure at the selected temperatures is a very important factor which can alter the multilayer structure of fibers from

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[*] Corresponding authors.
E-mail addresses: zhangym@dhu.edu.cn (Y. Zhang), bianfenggang@sinap.ac.cn (F. Bian).
[1] These authors have contributed equally to this work.

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chemical structure to macrostructure, and then changed interstructure which can induce the evolution of properties. For Kevlar 29, it was found that the fiber degrade under thermal use environment, and free-radical was formed, inducing to interchain crosslinks formation in the fiber, which can be improved the compressive properties [19]. The change of *co*-PSA fiber in performance under thermal exposure at 250–320 °C have been investigated by Yu et al. [17]. The result showed that the tensile strength and initial modulus reduced, and with increase of temperature and time duration, the cross-linking density increases which induced the fibrils length decreased.

Although the degradation of thermal exposure duration on structure and properties for fibers have been investigated, there were few studies for fiber on structural, morphological evolution, and evaluated the mechanical property of the PSA fibers when used under thermal, light, external force combined effect occasions. Therefore, in our present study, an experiment corresponding to thermal exposure and external force for the *co*-PSA fibers was designed to investigate the evolution in microstructure and properties. Small angle X-ray scattering (SAXS) and wide-angle angle X-ray scattering (WAXS) technique combined with an in-situ uniaxial stretching apparatus were carried out to study the evolution of microstructure and properties of *co*-PSA fibers during stretching at different thermal exposure temperature. This study provided some information about structural evolution and mechanical property evaluation during degradation under thermal at the different selected temperatures, external force combined effect occasions, which is useful to select the right fiber according to the use environment.

2. Experimental

2.1. Materials and sample preparation

The aromatic *co*-polysulfonamide (*co*-PSA) fibers were made commercially available by Shanghai Tanlon Fiber Co., Ltd, China. The chemical structure of co-PSA has been shown by the common formula in Scheme 1. The intrinsic viscosity η of co-PSA was 0.7 dL g^{-1}, measured in dimethylsulfoxide (DMSO) at 25 °C. The fibers were prepared by using wet-spinning technology and subjected to coagulation, plastic stretching, washing, drying, heat stretching, and heat setting.

2.2. In-situ synchrotron X-ray measurements

In-situ X-ray measurements were carried out at the beamline BL16B1 in the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the radiation source was $\lambda = 0.124$ nm. The bundles of co-PSA fibers were held for 600 s at selected temperatures to reach a thermal equilibrium. The bundle of *co*-PSA fibers were stretched at a crosshead speed of 10 μm s^{-1} for SAXS and 1 μm s^{-1} for WAXS on a uniaxial Linkam TST 350. And the chosen temperature were room temperature, 50 °C, 100 °C, 150 °C, 200 °C and 300 °C respectively. The scattering patterns were collected by Mar165 CCD with pixel size of 79 μm × 79 μm. Image collection time was 5 s and 60 s for SAXS and WAXS measurement, respectively. The sample to detector distance was 1820 mm for SAXS and 135 mm for WAXS. All X-ray scattering data were corrected for background scattering and X-ray absorption. Xpolar (Precision Works Inc., NY, USA) and Fit2D software was used to analyze WAXS, SAXS patterns and thus obtained the one-dimensional integrated intensity profiles.

3. Results and discussion

3.1. Mechanical properties of co-PSA fibers during stretching at various thermal exposure temperatures

The typical stress-strain curves of all the *co*-PSA fiber samples at different temperature are shown in Fig. 1(a). The mechanical property including tenacity, initial modulus and elongation at break of different temperature during stretching is plotted in Fig. 1(b). The tenacity and initial modulus of *co*-PSA fiber increased but did not increase monotonously with the stretch at higher temperature (Fig. 1(b)). From Fig. 1(b), it was clearly seen that the tenacity, initial modulus and elongation of *co*-PSA fiber increased with temperature below 200 °C. And a maximum tenacity and elongation were achieved during stretching at 200 °C, then the tenacity and elongation decreased with increasing temperature. Compared with the tenacity stretching at room temperature, the tenacity of *co*-PSA fiber stretching at 100 °C, 150 °C, 200 °C were increased by about 4%, 22% and 31%, while the tenacity of *co*-PSA fiber stretching at 300 °C were decreased by 13%. Ren et al. [18] pointed out that the strength of *co*-PSA fiber increased with increasing the heating temperature until 250 °C. Such a marked change in mechanical property of *co*-PSA fibers may be due to the evolution of internal structure. So the following section, morphological and structural explanation for mechanical property change during stretching will be discussed.

3.2. Uniaxial stretching of co-PSA fibers at room temperature

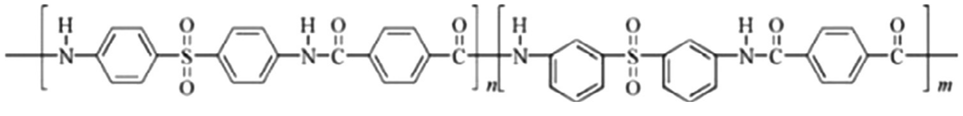
Fig. 2 illustrates the selected 2D WAXS and SAXS patterns collected at different applied strains during tensile stretching at room temperature (25 °C) for *co*-PSA fibers, along with the engineering stress-strain curves. It was seen that the scattering from the crystal for *co*-PSA fibers was weak at 0% strain. In the initial 2D WAXS pattern, only the diffraction arcs locating on the equator and meridian which can be indexed (0 0 2) and (1 0 0) respectively appeared. After stretching, the reflection plane (0 0 2), (1 0 0) became more obvious. The azimuthal spreads of all diffraction spots first narrowed (before 10% strain) then wider. The azimuthal spreads of the (0 0 2) reflection peak at different strains are shown in Fig. 3(a). And the liner intensity profiles from WAXS of (0 0 2) and (1 0 0) reflection at different strains at room temperature is shown in Fig. 4(a) and (c). From Figs. 3 and 4, it is easily found that scattering of the (0 0 2) and (1 0 0) reflection showed rapid and complex changes during stretching. The azimuthal intensity of peak became narrowed with increasing strain below 10% in Fig. 3, which was due to the changed of crystal orientation. In *co*-PSA fibers, the (0 0 2) plane is often used for evaluated crystal orientation [7,11]. The chain orientation factor (*f*) in the crystal structure was estimated by Hermans' factor:

$$f_c = \frac{3\langle \cos^2 \phi_{c,z} \rangle - 1}{2} \tag{1}$$

where ϕ is the angle between the chain axis and the reference axis (stretching axis). $\langle \cos^2 \phi_{002} \rangle$ is defined as [7]:

$$\langle \cos^2 \phi_{c,z} \rangle = \langle \cos^2 \phi_{002} \rangle = \frac{\int_0^{\pi/2} I(\beta_{002}) \sin^2 \beta_{002} \cos^2 \theta_{002} \cos\beta_{002}\, d\beta_{002}}{\int_0^{\pi/2} I(\beta_{002}) \cos\beta_{002}\, d\beta_{002}} \tag{2}$$

where β_{002} is the azimuthal angle of the (0 0 2) plane, $I(\beta_{002})$ is intensity variation of the azimuthal angle of the (0 0 2) reflection, as shown in Fig. 3, and is the Bragg angle of (0 0 2). The crystal orientation factors



Scheme 1. Chemical structure of co-PSA fibers (n:m = 3:1).