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Lamellar and fibrillar structure evolution of poly(ethylene terephthalate) fiber in thermal annealing

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ABSTRACT

The evolutions in lamellar and fibrillar structures of poly(ethylene terephthalate) (PET) industrial fiber during taut-ends thermal annealing were investigated mainly using synchrotron radiation small-angle X-ray scattering (SAXS). Wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) results indicated that high modulus and low shrinkage PET fiber (HMLS) had high crystallinity and perfect crystals, whereas high modulus and low elongation fiber (HMLE) possessed relatively low crystallinity and defective crystals. As annealing temperature raised, the original four-spot SAXS pattern gradually turned into the coexistence of two- and four-spot pattern, together with the enhanced scattering intensity. The analysis of the lamellar peaks showed that the annealing process had a significant influence on the thickness of crystalline and amorphous region, as well as the long period at 125, 200 and 240 °C. At the same time, the lateral size of the lamellae raised, whereas the lamellar surface inclination declined. In addition, the streak scattering across the beam stop was attributed to the fibrils. Results suggested that fibrils subjected to thermal effect tended to grow in longitudinal direction and became more oriented along the fiber axis. This study might help to predict structure and property changes at high temperatures for PET fiber and any other well oriented fiber that has a lamellar and fibrillar structure.

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most versatile thermoplastic polymers with widespread applications in plastic, film and fiber due to its high melting point, good mechanical properties, and chemical resistance [1]. The features of high glass transition temperature and slow crystallization rate offer various methods of controlling its morphology to obtain desired properties [2]. Over the past decades, structure formation of PET under different conditions have attracted much attention.

Heat setting is an important industrial process to set up molecular configurations by supplying thermal energy to the molecular chains, and thus rids them of instabilities. A large number of studies have reported the effect of heat setting on structures and properties of PET fiber and film. Some researchers focused on the thermal effect on the commercial PET fiber. For example, Gupta et al. [3–9] conducted a systematic research on the structure-property relationship in heat-set PET fibers in the early 1980s. In these papers, they mainly studied the structure changes, elastic modulus, anelastic behavior, thermal properties and physical characteristics. Later, Rodriguez-Cabello et al. [10] studied the behavior of PET fiber in free-ends annealing for 1 h. It was found that the conformational transition from trans to gauche caused amorphous chain coiling and loss of orientation. Instead of annealing the PET fiber for a long time, Cho et al. [2] treated the PET fiber to an extremely short heat treatment at 190 °C for 1.2 s, and found the relaxed amorphous chains promoted the formation of micro-crystals in the amorphous region, which can further increase the initial modulus. In these days, some researchers tend to pay more attention to the structural formation of glassy PET during thermal annealing. For instance, Asano et al. [11] studied the crystallization of oriented amorphous PET film at different temperatures for different annealing times. Radhakrishnan [12] found

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that the structural organization of PET chains during isothermal crystallization consisted of three stages, i.e. thermodynamic relaxation, self-organization and crystallization. Uchiyama et al. [13] studied the structure formation of oriented PET film crystallized at 100 °C, 150 °C, 200 °C and 250 °C. Typical four- and two-spot SAXS patterns appeared in the cold- and hot-drawn PET, respectively. In addition, the density difference between the crystalline and amorphous phase related to the *c*-axis tilting and the lamellar inclinations. Lately, Keum et al. [14,15] reported that a transient mesophase appears before the actual crystallization process begins in a study on PET fibers in annealing.

These investigations mentioned above were conducted on a static state, and the time-resolved SAXS and WAXD measurements have been performed recently to further study the structure formation in annealing during uniaxial drawing. Abou-Kandil et al. [16] studied the structure formation of oriented PET film during annealing and found the existence of a liquid crystalline transient mesophase prior to crystallization, which is consistent with Keum et al.'s results [14,15]. Kawakami et al. [17–21] took great efforts to investigate the strain-induced superstructure of glassy PET above glass transition temperature. They found an equatorial streak scattering in SAXS patterns at the later stages of plastic deformation zone, indicating formation of a microfibrillar structure. Okada et al. [22] conducted a similar work as Kawakami and he considered the X-shaped and four-spot patterns to be due to isolated single lamellae and stacked lamellae, respectively.

These previous studies have provided valuable information on structure formation in thermal annealing and drawing, including mesophase, crystallinity, orientation, conformational transition, crystalline layer and lamellar inclination. Mechanical properties, thermal shrinkage, microindenter hardness were also involved. However, there are few detailed SAXS investigations on commercial PET industrial yarn in a lamellar and fibrillar scale. PET industrial yarn is widely used as reinforcement in passenger radial tires. In the rubber dip process for the yarns, PET fibers undergo heat treatment for several minutes at around 100–240 °C, which may deteriorate the fiber structures and properties. In this study, two kinds of PET industrial fibers were annealed at various temperatures to simulate the above process or other applications at high temperatures above T_g. The design of present study is inspired by the quest for PET fiber that can readily keep its original structures and properties when subjected to high temperatures. The developments of crystalline thickness, amorphous thickness, lamellar inclination, lamellar lateral size, as well as the fibril length and misorientation were discussed in detail. Furthermore, such an exhaustive investigation of the hierarchical structure of the various structural elements that make up the fiber is essential for further study and application of PET fibers.

2. Experimental section

2.1. Materials

The experimental PET industrial fibers were produced under different conditions by Jiangsu Hengli Chemical Fibre Co., Ltd., and were designated as HMLS and HMLE, respectively. HMLS is a dimensional stable fiber used in applications that demand high modulus and low shrinkage, while HMLE is a conventional high modulus fiber with low elongation. Intrinsic viscosities of the two fibers fall within the range of 1.0–1.1 dL/g. The more relevant physical characteristics before annealing are shown in Table S1. The biggest difference between the two fibers is the shrinkage property. Note that both HMLS and HMLE have low elongation compared with other types of traditional PET industrial fibers, such as high tenacity (HT), and low shrinkage (LS) fibers. The mechanical properties of different types of PET fiber are available in our previous work [23].

2.2. WAXD measurement

WAXD was carried out at BL15U1 beamline in Shanghai Synchrotron Radiation Facility (SSRF). The energy and wavelength of the X-ray radiation were 20 keV and 0.6199 Å, respectively. The fiber samples prepared in a bundle type (~1000 deniers) were horizontally mounted in a custom-built sample holder and the acquisition time for WAXD measurement was 5 s. The WAXD patterns were recorded with a MarCCD detector (Rayonix SX-165). The sample-to-detector distance and the size of the beamspot were 191 mm and 3 μm × 2 μm, respectively. The diffraction angle was calibrated using CeO_2 from SSRF. All data were corrected for background scattering before analysis and treated with a software of Fit2D (http://www.esrf.eu/computing/scientific/FIT2D/).

Crystallite size was calculated according to the Scherrer equation [24] and the meridian crystallite size was estimated from the nearly meridian plane ($\bar{1}05$). The crystal volume (V_c) was calculated using Kiang's method [25]. The number of crystal grains per cubic centimeter was calculated from the crystallinity and crystal volume [23]. Hermans crystallite orientation factor (f_c) was calculated from the azimuthal scan of three equatorial planes viz. (010), ($\bar{1}10$) and (100) [26,27]. More information about the analysis is available in Supporting Information (WAXD Analysis).

2.3. SAXS measurement

SAXS was carried out at BL16B1 beamline in SSRF. The fiber bundle (~4000 deniers) was horizontally mounted in a custom-built instrument, whose chamber can be heated to specific temperatures by hot air. The fibers were kept in a taut state at constant length and equilibrated in the heated chamber for 2 min at the desired temperature (i.e., 20 °C, 95 °C, 125 °C, 200 °C, 240 °C) before the engagement of the SAXS measurement. Note that the sample were still kept at annealing temperatures rather than cooled to ambient temperature during the SAXS measurement. The energy of the X-ray radiation was 10 keV, resulting in a wavelength of 1.2398 Å. The acquisition time for SAXS measurement was 10 s and the SAXS patterns were recorded with a MarCCD (Rayonix SX-165). The sample-to-detector distance was 2080 mm and the size of the beamspot was 1 mm × 1 mm. The effective scattering vector q ($q = 4\pi\sin\theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of X-ray) lies in the range 0.079–2.1 nm^{-1}. The scattering angle was calibrated using chicken collagen standard from SSRF. All data were corrected for background scattering before analysis and treated with the software Fit 2D.

2.4. DSC measurement

A TA instrument MDSC 2910 was used for calorimetric analysis of a small quantity (4–6 mg) of finely chopped PET fibers (length less than 2 mm). Thermograms were collected under a constant flux of nitrogen with a heating rate of 10 °C/min in the temperature range of 20–310 °C. Crystallinity was calculated, assuming the enthalpy of melting of crystals, ΔH_m^*, to be 117.6 J/g. The crystalline mass fraction is then calculated by the following equation [10,28]

$$X_{c,m} = \frac{\Delta H_{m,x}}{\Delta H_m^*} \quad (1)$$

where $\Delta H_{m,x}$ is the enthalpy of the melting of the PET fiber.