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Effect of melt spinning conditions on the fiber structure development of polyethylene terephthalate

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ABSTRACT

The effects of spinning conditions on fiber properties are not well explained by the fiber structures because the birefringence, crystallinity, and SAXS patterns are often similar. In this study, the effects on the fiber structure development of polyethylene terephthalate after necking was analyzed by simultaneous WAXD/SAXS measurements. An X-shaped SAXS pattern was observed for all fibers drawn at the minimum draw ratio. In contrast, by drawing under a drawing stress of 100 MPa, the strong diffraction of the smectic phase and an obviously larger long period less than 1 ms after necking were observed for fibers spun at 500–1500 m/min, while almost no smectic phase was observed for fibers spun at 2000 m/min. A higher crystallization rate and clear draw ratio dependence of crystallization rate were also observed for the fiber spun at 2000 m/min. The clear differences in structure development can explain their differences in tensile strength and thermal shrinkage.

1. Introduction

Polyethylene terephthalate (PET) fibers are widely used synthetic fibers. There are a multitude of studies on the structure and physical properties of PET fibers. The mechanical and thermomechanical properties of highly drawn fibers strongly depend on melt spinning conditions. However, the effect of melt spinning conditions on structural parameters such as birefringence, crystallinity, and crystal orientation factor is too small to explain the observed differences in the properties of PET fibers. In this study, we try to explain the effect of melt spinning conditions on the above-mentioned physical properties of resultant fibers focusing on the fiber structure development process.

The structure of a PET fiber is mostly determined by the drawing process. However, the properties of the obtained fiber are also influenced by the spinning conditions because they determine the maximum draw ratio. Indeed, the spinning conditions are selected to fit the application of the fibers being produced. For example, a partially oriented yarn (POY) is obtained at a spinning speed of 2000–4000 m/min under a high spin-line tension. POYs are suitable to produce fibers with a high modulus and low shrinkage, and are used in products requiring dimensional stability at high temperature, like tire cords. Meanwhile, high-tenacity fibers can be prepared by spinning at low speed and then drawing to a high draw ratio. High-tenacity fibers are used in products requiring high tensile strength, like seat belts [1]. In recent years, a new spinning procedure called laser spinning has been proposed [2,3]. In this procedure, rapid fiber heating by a laser beam irradiated onto molten fibers lowers the spin-line stress with minimal thermal decomposition. The resulting fibers possess a uniform network structure, which leads to the improved tensile strength of the maximally drawn fibers [2]. There have been similar trials for producing high-strength fibers, collectively referred to as “melt structure control”, which formed uniform molecular network structures by controlling the melt spinning process [2–9].

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Fiber structure development after neck drawing has been observed for PET [10–13,18], polyethylene naphthalate (PEN) [14], polypropylene [15], polyphenylene sulfide [16], and polybutylene terephthalate (PBT) [17] in wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) images captured with synchrotron X-rays at SPring-8. In particular, we previously analyzed the effect of the draw ratio on the fiber structure development of PET [10]. We found that the amount of smectic phase increased with draw ratio until a certain point, and then the d-spacing of the smectic phase enlarged as draw ratio further increased. These results could explain the change of mechanical and thermomechanical properties of drawn fibers, which means the analysis of fiber structure development can be considered as a new valuable structure evaluation procedure to design the physical properties of drawn fibers. We use the same procedure to investigate the effects of spinning conditions on fiber structure development in this study. That is, here we analyze the effects of a spinning speed of 500–2000 m/min and laser spinning on the development of PET fiber structure. The fiber structure development is analyzed by measuring the time dependence of structural parameters including the amount of smectic phase, d-spacing of smectic phase, degree of crystallinity, and long period.

2. Experimental

2.1. Samples

The fibers used for drawing in this study were prepared by melt spinning PET (IV = 1.3 dL/g) provided by Toray Co. The polymer was heated 310 °C, extruded from a nozzle with a single hole at a mass flow rate of 4.8 g/min, and taken up at 500–2000 m/min. The nozzle diameter (D) was 1.0 mm, and L/D = 3. In addition, CO_2 laser irradiation from three directions was focused onto the fibers at a position just under 2.5 mm from the nozzle, and taken up at 500 m/min. This process is hereafter referred to as laser spinning. The random polarized laser beam, whose wavelength and diameter were 10.6 μm and 4.5 mm, respectively, was generated by a PIN-60R laser (Onizuka Glass Co., Ltd.). The emitted laser beam was branched into four by a beam splitter. One branch was used to monitoring the beam power, while the other three were irradiated onto the fiber from three directions at an angle of 120° from each other in a horizontal plane. The laser power per branch was 10 W.

2.2. Drawing

The drawing system was the same as reported elsewhere [11]. A fiber was fed continuously from a feed roller, heated by the CO_2 laser beam, and drawn by the speed difference between the feed and take-up rollers. The fiber running speed after necking was fixed at 110 m/min, and the draw ratio was changed by modulating the fiber feeding speed. A random polarized laser beam with a wavelength and diameter of 10.6 μm and 6 mm, respectively, was generated by a PIN-30R laser (Onizuka Glass Co., Ltd.). The beam was irradiated onto the running fiber from three different directions. The drawing tension was measured by a tension meter (HS-1500S, Eiko Sokki Co., Ltd.). A 100-gf pickup was installed between the neck-drawing point and take-up roller. The drawing stress was calculated from the drawing tension and diameter of the drawn fiber.

2.3. Online measurement

The principle of the online measurement system was reported previously [11]. WAXD/SAXS patterns were obtained by irradiation of an X-ray beam onto the running fiber. The X-ray beam was 40 μm in the vertical direction and 50 μm in the horizontal direction. By moving the laser irradiation position, the distance from the necking point to the X-ray irradiation position was changed. The elapsed time after necking was calculated by dividing the distance by the running speed of the fiber.

The synchrotron X-ray beam used in this study was from SPring-8 BL03XU (FSBL), and an undulator was used to obtain an ultrahigh-intensity X-ray beam. The wavelength of the X-ray beam was 0.10 nm. For WAXD and SAXS measurements, the camera length was 78.7 and 1788 mm, respectively, exposure time for each measurement was 1 and 50 s, respectively, and the detector was a 1032 × 1032 pixel flat panel detector (50 μm/pixel) and 672 × 512 pixel CCD (126 μm/pixel), respectively. After the subtraction of air scattering, the obtained image was normalized by the total integrated intensity to compensate for the fluctuation of X-ray irradiation volume.

The average position of the necking point and its fluctuation width were determined by analysis of still images taken from the video movie recorded during each measurement. The resolution time was calculated by a reported method [18] by the position resolution, which was calculated from the fluctuation width of the necking point (0.09–0.20 mm), length of the necking point (0.12–0.31 mm), and width of the X-ray beam (0.05 mm). The obtained time resolution was 0.09–0.18 ms.

2.4. Birefringence

The birefringence for each fiber was measured by a polarized microscope (BX51-33POC, Olympus Co., Ltd.) with a monochromic filter of 546 nm. Tricresyl phosphate was used as an immersion oil. The average and standard deviation of birefringence were calculated for 10 samples.

2.5. Thermomechanical tests

Thermal and mechanical properties of drawn fibers were analyzed by tensile tests, thermomechanical analysis (TMA), and differential scanning calorimetry (DSC). The strength, elongation, Young's modulus, and natural draw ratio (NDR) were measured by a universal testing machine (Autograph AGS-X, Shimadzu Co. Ltd.) equipped with a 50-N load cell and air chuck. The sample length and elongation rate were 40 mm and 100%/min, respectively, and the average and standard deviation of the strength, elongation, and Young's modulus were calculated for every ten samples. The NDR was defined as the draw ratio at which the tensile stress began to rise again with the dissipation of necking point.

A thermomechanical analyzer (TMA/SS6100, SII Nanotechnology Inc.) was used to measure thermal shrinkage factor and shrinkage stress at heating rates of 5 and 10 K/min, respectively. The sample length was 10 mm for both measurements. DSC was conducted using a calorimeter (Thermoplus DSC8230, Rigaku Co. Ltd.) with a heating rate of 10 K/min. A powdered cut fiber sample was used for DSC measurements.

3. Results and discussion

3.1. As-spun fibers

The formation conditions, structure, and physical properties of as-spun fibers are listed in Tables 1 and 2. Crystallinity and birefringence increased while NDR and elongation decreased as spinning speed increased. In particular, because of its higher crystallinity and lower cold crystallization temperature than those of the other samples, the fiber taken up at 2000 m/min can be regarded as a POY. In contrast, the laser-spun fiber possesses lower

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