Effects of spinning speed and draw ratio on the fibril structure development of poly(ethylene terephthalate) fiber after neck-drawing

The properties of polymeric materials are strongly related to their higher-order structure. However, the higher-order structure is very complicated, that is, the molecular chains are considerably entangled with each other, part of them are oriented along certain axes, and part of them are crystallized. Thus, it is difficult to predict the properties of polymeric products quantitatively from the limited information of the higher-order structure. The mechanical and thermal properties, namely tensile strength and thermal shrinkage are particularly important properties of synthetic fibers and films, but they cannot be designed accurately from the ordinary higher-order structure parameters, such as the molecular orientation, crystallinity, crystal and amorphous orientations, crystallite size, and disorder parameters. For example, the tensile strength of industrial-grade poly(ethylene terephthalate) (PET) fibers is far below the theoretical value, less than 5% in general, despite the high crystal orientation and high crystallinity. This is due to the lack of information on the fibril structure, which is thought to be a bundle of highly oriented molecular chains and thought to bear the external force applied on the fibers and films. The bundle structure is formed by the orientation-induced crystallization during the melt-spinning and/or drawing processes with the extension of entangled molecular chain networks. Kikutani *et al.* [1] suggested that the uniformity of molecular chain networks determines the fibril structure and influences the tensile strength of the obtained PET fibers. It is difficult to observe the fibril structure directly by SAXS measurements of the obtained fibers because there is no obvious density difference between the fibrils and the surrounding matrix. However, we found a fibrillar-shaped smectic phase of nm-order width and 10-nm-order length during the development of the fiber structure less than 1 ms after necking [2]. This should be the embryo of the microfibrils and should influence the tensile strength of the resulting fiber [3]. Thus, in this study, we focused on the fibril structure development after necking and also on the effects of the processing conditions of the spinning speed of the fiber before the drawing and the draw ratio or drawing stress.

By obtaining WAXD and SAXS patterns during a continuous neck-drawing process, we analyzed the fibril structure development after the necking, i.e., the rapid extension of a fiber or film with a rapid change in diameter. The running fiber was drawn continuously by the speed difference between the fiber-feeding and take-up rollers while heating by CO_2 laser irradiation [4]. Owing to the rapid and homogeneous heating by laser irradiation, the location of the necking point hardly changed during the on-line measurement. Also, by moving the laser-irradiation point, we were able to change the distance between the necking point and the X-ray beam irradiation point, and analyze the fiber structure at a certain elapsed time after the necking. The ultrahigh intensity X-ray beam of SPring-8 **BL03XU** used in this study enable high-precision measurements not only with an improved S/N ratio but also with a 0.1 ms time resolution. The high time resolution allowed us to analyze the effects of processing conditions on the fibril structure development.

SAXS patterns obtained during drawing under the same drawing stress of about 100 MPa are shown in Fig. 1. The figure indicates the development of a long-period structure, involving phase separation from the fibrillar-shaped smectic phase to a series of crystallites and amorphous phases connecting them, that is, so-called microfibril. It is interesting that the structure development clearly depends on the spinning speed and laser irradiation on the spin-line, but the SAXS pattern of the drawn fiber does not change significantly among the samples. This reveals that the *in situ* measurement of fibril structure development

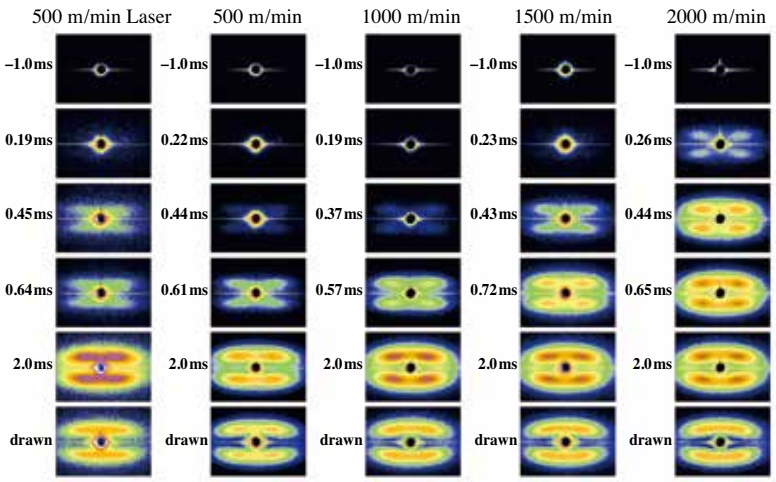

Fig. 1. SAXS patterns for certain elapsed times after necking. The drawing stress was about 100 MPa for all samples.

can provide more information about the fibril structure than structure analyses of the obtained products. This is because the effect of metastable fibrillar-shaped structure can be observed during the structure development, but it is obscured by the development of a density difference between the crystallites and the surrounding amorphous phase. For example, the long period obtained from the SAXS pattern is plotted against the elapsed time after necking in Fig. 2. Although the long period becomes almost the same for each drawn fiber regardless of the spinning speed, the development profiles are clearly different between the fibers taken-up at 500 m/min and 1000–2000 m/min. The fiber taken-up at 500 m/min required a longer time for the formation of long period structure, and showed a clear decrease in the long period with elapsed time. The delay of phase separation, or crystallization, can be explained by the effect of the smectic phase on inhibiting crystallization because more amount and a longer fibril length of the fibrillar-shaped smectic phase for the taken-up at 500 m/min than those at 1000–2000 m/min were observed by the WAXD measurement.

The model of fibril structure development based on the *in situ* WAXD and SAXS measurements is shown in Fig. 3. At the minimum drawing stress for stable drawing of about 30 MPa, at which the draw ratio is almost the same as the natural draw ratio, no smectic phase was formed, a clear X-shaped pattern was observed for the SAXS pattern about 0.3 ms after necking, and the X-shaped pattern was transformed into a four-point pattern within 1 ms after necking. This indicates that crystallites were formed along the shear-band-like structure formed by the necking. With increasing drawing stress for a low-speed spun fiber, so-called undrawn yarn (UDY), the fibrillar-shaped smectic phase tended to develop along the fiber axis, inhibiting the direct crystallization from the oriented amorphous phase. The fibrillar-shaped smectic phase was transformed into microfibrils composed of series of crystallite/amorphous structure until 2 ms after necking. In contrast, for the higher-speed spun fiber, so-called partially oriented yarn (POY), the oriented nuclei that formed in the spinning process are thought to inhibit the development of the smectic phase. As a result, POY is suitable for producing low shrinkage fibers because lamella crystals that mutually interlock with each other tend to be formed. In contrast, UDY is suitable for producing high-strength fibers because uniformly ordered fibrils tend to be formed.

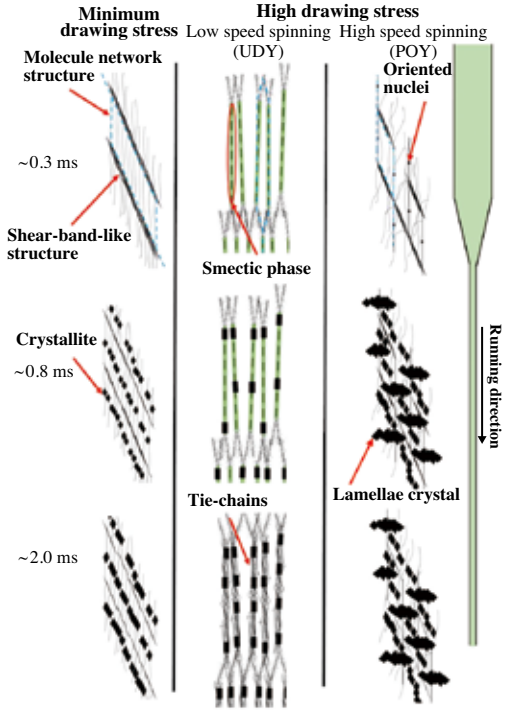

Fig. 3. Schematic diagrams of fiber structure development. The structures of the molecular network in the fibers are shown as blue lines.

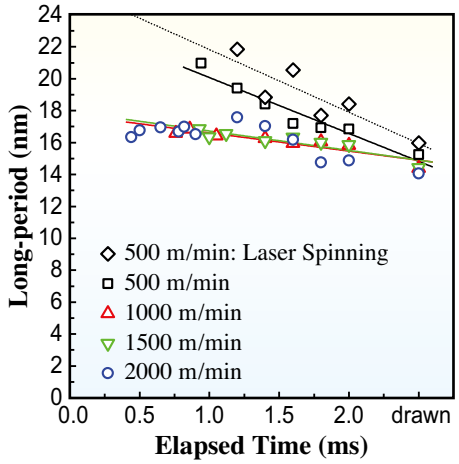

Fig. 2. Long periods obtained from SAXS patterns plotted against the elapsed time after necking.

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