

Quantitative design of fiber strength by structural development analysis of PET

The improvement of mechanical properties has always been a major research theme for synthetic fibers because they are their most important characteristics. In particular, the strength of synthetic fibers is far lower than their theoretical values. For example, the 1.1 GPa strength of industrial-grade poly-(ethylene terephthalate) (PET) fiber corresponds to only 4% of the theoretical value. The causes were explained to be the molecular weight limitations, incomplete molecular orientation and crystallinity, and, in particular, the inhomogeneity in the molecular orientation. The external force is mainly born by the micro-fibril, which consists of highly oriented molecule chains. For ductile materials such as a PET fiber, the strength is decided mainly by the “taut tie-chains” in the amorphous phase, that connect the crystallites in the micro-fibril. Therefore, to produce high-strength synthetic fibers, one should generally aim for a high molecular weight and a high molecular orientation. However, because a high molecular weight causes poor spinnability and drawability, it is difficult to form fibers with highly oriented molecular chains. Thus, the concept of “melt structure control” was proposed to obtain high-strength fibers, whereby a homogeneous chain network structure is formed by melt spinning, followed by the-high-draw ratio drawing of the network [1,2]. Conjugated melt spinning, in which two types of polymers are simultaneously extruded from a spinneret, has been investigated as one technique of melt structure control. For example, as shown in Fig. 1, by the conjugated spinning of PET with a thermotropic liquid-crystalline polymer (TLCP), PET fibers that have obviously higher strength than the single-component-spun and drawn fibers were obtained by high-draw-ratio drawing [2]. The polystyrene (PS) selected as the coupling polymer with PET in this study, identically to the TLCP shown above, has a higher activation energy of extensional viscosity and a higher glass transition temperature (T_g) than PET, so the stress applied in the spin-line was mostly loaded onto the PS component and the PET component was relaxed after the solidification of the PS component. Therefore, the PET fiber could be drawn to a higher draw ratio, resulting in a high strength PET fiber. In addition, it is noteworthy in Fig. 1 that the molecular orientation was almost saturated at about 0.8 for both conjugated and single-component spun fibers, although the fiber strength largely differed. This indicates that the information on the fiber structure, such as molecular orientation, crystallinity, and crystallite size, is

insufficient for estimating fiber strength quantitatively. Therefore, we attempted to establish a new category of structural information for estimating the strength of resulting fiber, that is, the process of fiber structure development.

A schematic diagram of the *in situ* measurement system is shown in Fig. 2. By laser irradiation, the running fiber can be heated almost instantaneously as well as homogeneously [3]. It has the merit of accurate on-line measurement of fiber structure development, because the necking location during the continuous fiber drawing process is almost stationary. By taking the WAXD and SAXS images at a certain distance D , one can analyze the fiber structure at a certain elapsed time after necking. The ultrahigh-intensity X-ray beam of BL03XU used in this study yielded high-precision measurements not only with an improved S/N ratio but also with a 0.1 ms time resolution. The high time resolution permits us to analyze the effects of process conditions on fiber structure development. More concretely, the effects of conjugated spinning with a PS component, the molecular weight of the PET, and the draw ratio were analyzed in this study [4].

A part of the results is shown in Fig. 3: the normalized integrated intensities of both smectic (001') and crystal equatorial diffractions. The smectic

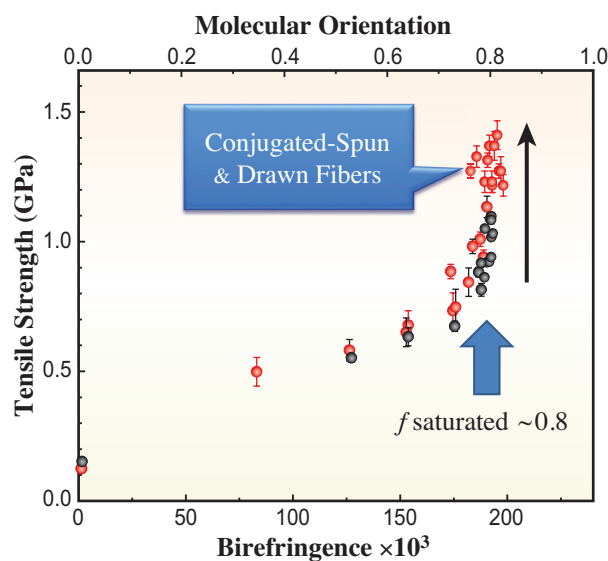


Fig. 1. Strength of drawn PET fibers plotted against their birefringence. Although the molecular orientation was almost saturated for the maximally drawn fibers, the strength of conjugated-spun and drawn was clearly higher than that of single-component spun and drawn fibers.

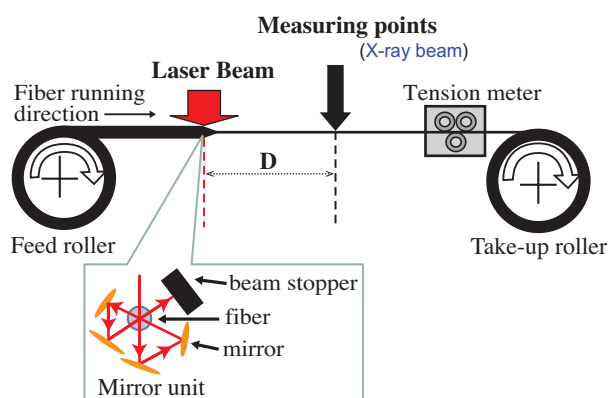


Fig. 2. Schematic diagram of *in situ* measurement system.

phase is the fibrillar-shaped mesophase regarded as the embryo of the microfibril that bears most of the external force [5]. By drawing the higher molecular weight PET to a higher draw ratio, a larger amount of the fibrillar smectic mesophase was formed after necking, and a more highly oriented crystal was formed after the extinction of the smectic mesophase. Accordingly, fibers with higher strength and higher thermal shrinkage stress were obtained. On the other hand, by conjugated spinning with a PS component, the amount of the smectic mesophase formed by

the conjugated spinning process was drastically decreased. No crystallization induction time was observed, and the crystallization, particularly the growth of a lamellar crystal, was promoted by the conjugated spinning. Therefore, it was revealed that the fibrillar smectic mesophase seems to inhibit the development of the lamellar crystal at the initial stage of fiber structure development, and the resultant fibrillar structure tends to result in a higher strength, but a relatively lower modulus and yield strength of the fiber.

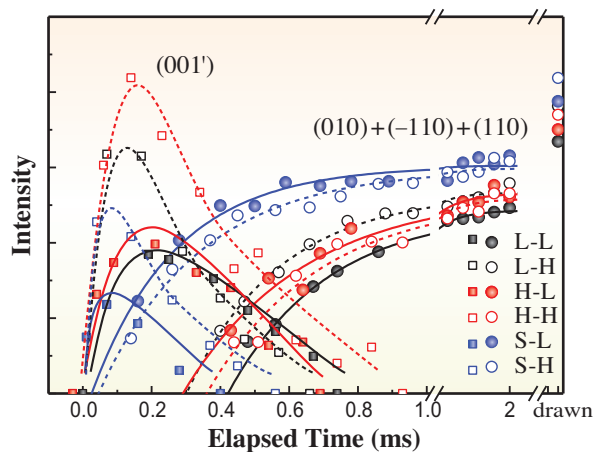


Fig. 3. Integrated intensity of (010), (-110), and (100) diffractions of PET crystal, along with the intensity of smectic (001') diffraction are plotted against the elapsed time after necking. The first and second letters of the sample name indicate the materials and draw ratios. L: low IV PET, H: high IV PET, S: low IV PET conjugated spun with PS, and almost the minimum (L), and maximum (H) draw ratios for stable drawing.

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References

- [1] T. Kikutani: "Fundamental and Practical Technologies for Nano-structured Polymeric Materials", CMC Press, (2008) 56.
- [2] K. Nakata *et al.*: Int. Polym. Proc. **27** (2012) 386.
- [3] W. Okumura *et al.*: Int. Polym. Proc. **17** (2002) 24.
- [4] K. Sugawara, T. Ikaga, K. H. Kim, Y. Ohkoshi, K. Okada, H. Masunaga, T. Kanaya, M. Masuda and Y. Maeda: Polym. **79** (2015) 37.
- [5] T. Yamaguchi *et al.*: J. Polym. Sci.: Part B: Polym. Phys. **46** (2008) 2126.