Microanalysis for Polymer Materials by X-ray Microscopes

Polymer fibers have excellent mechanical properties and are light in spite of their flexibility, so they are widely used as clothing, nonwoven fabric, reinforced fiber for advanced composite materials and so on. Generally, polymer fibers are obtained from a polymer solution or a molten polymer by the spinning method at above the melting point of the polymer. This process would form a gradual structure in the radial direction of a polymer fiber, because solidification occurs from the outer region of the polymer fiber during coagulation in poor solvents or during the cooling process. Therefore, a polymer fiber has different microstructures between the outer region and the inner region. The unique microstructure of a polymer fiber is called the skin/core structure.

Recently, with the development of microscopic processing techniques, precise measurement for the structural analysis of very small areas has become increasingly important. The X-ray diffraction method has been widely used for the structural analysis of polymer materials. The transmission electron diffraction method requires a thin sample and a high-vacuum condition. However, no special pretreatment of samples is required for the X-ray diffraction method.

An X-ray microbeam of 10 keV was obtained using a phase zone plate, which was made of tantalum at beamline **BL24XU** [1]. A rhodium-coated plane mirror was introduced in the upstream of the experimental hutch in order to eliminate higher order Bragg reflections properly for different photon energies. The focused beam size at the sample position was evaluated to be 1.1 μm (vertical) × 1.3 μm (horizontal) by the knife-edge method.

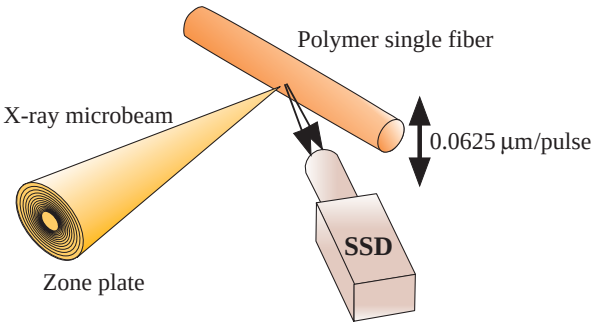

Fig. 1. Schematic representation of the X-ray microdiffraction method for the polymer single fiber. The sample holder was fixed on the high-precision sample stage and the fiber axis was aligned in the horizontal direction.

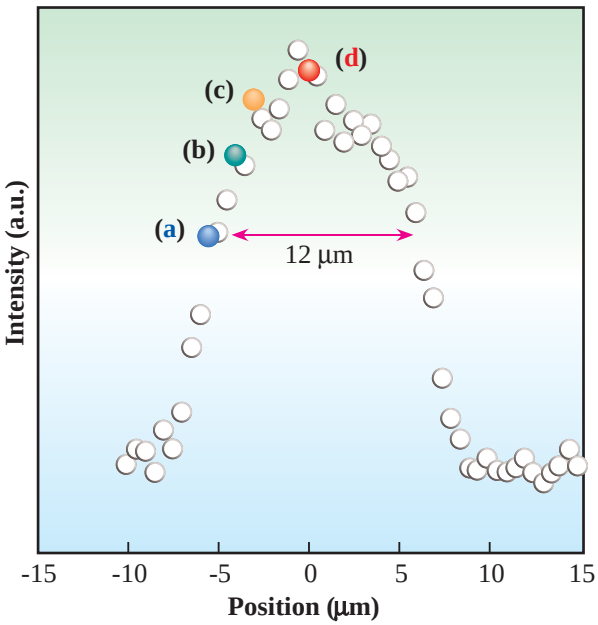

Fig. 2. Intensity profile of Thomson scattering from Kevlar[29] single fiber. Sampling steps of 0.5 μm/point were employed.

As the beam size is small, it is very important to confirm the irradiated area of the X-ray microbeam on samples. An optical microscope, which was set on the X-ray beam path, was used to align the sample position roughly. However, more precise alignment of the X-ray microbeam is very difficult using optical microscope for smaller samples such as a polymer single fiber. In this study, we proposed a novel technique by the Thomson scattering method for the precise alignment of the X-ray microbeam position as shown in Fig. 1.

Figure 2 shows the intensity profile of Thomson scattering from a Kevlar[29] single fiber (fiber diameter *ca.* 12 μm). One-dimensional scans were performed perpendicular to the fiber axis. The intensity of the Thomson scattering is proportional to the number of electrons at the regions where the X-ray penetrated the sample. With changing sample position ((a)-(d)), X-ray diffraction patterns were detected using an imaging plate as shown in Fig. 3. The X-ray exposure time was 600 s per pattern. Judging from the spot-like equatorial reflections (110 and 200 reflections), the degree of the molecular orientation of the skin region (Fig. 3(a)) is higher than that of the core region (Fig. 3(d)).

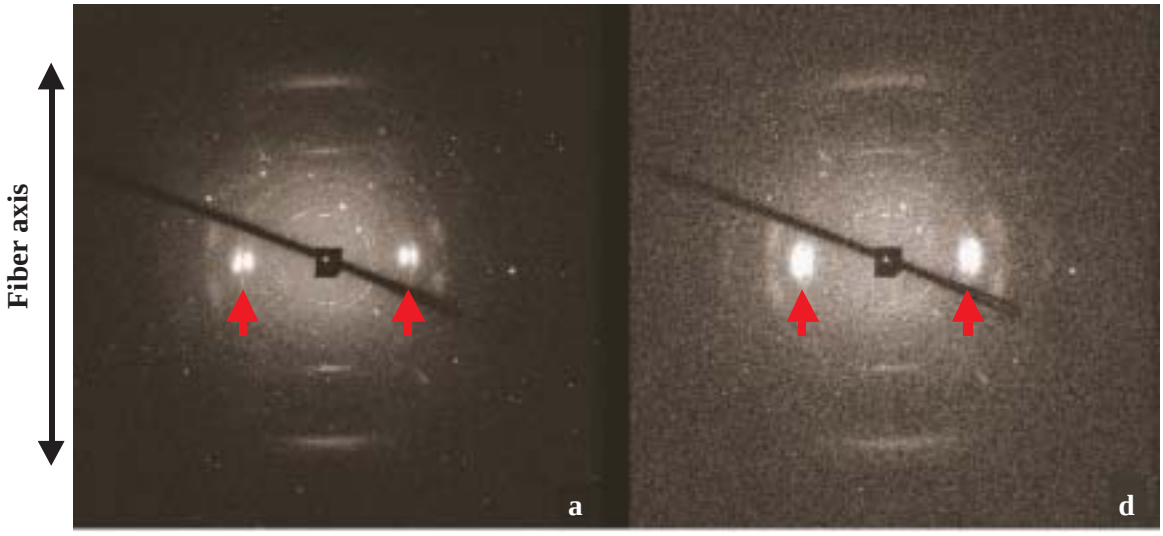

Fig. 3. X-ray fiber pattern of Kevlar[29] single fiber. **(a)** skin region and **(d)** core region.

Figure 4 shows the equatorial diffraction profiles of the Kevlar[29] single fiber at different points ((a)-(d) in Fig. 1) along the fiber axis. In the core region (d) of the single fiber, the peak intensity is $I_{110} < I_{200}$. However, they are reversed when approaching the skin region (a), that is, the peak intensity of 110 reflection gradually increased as the measurement position approached the skin layer. This implies that the b-axis of the Kevlar crystal, which is the direction of a hydrogen bond, is oriented in the radial direction of the fiber [2,3].

According to these results, the X-ray microdiffraction method demonstrated to be a powerful tool for the structural analysis of small areas for polymer materials.

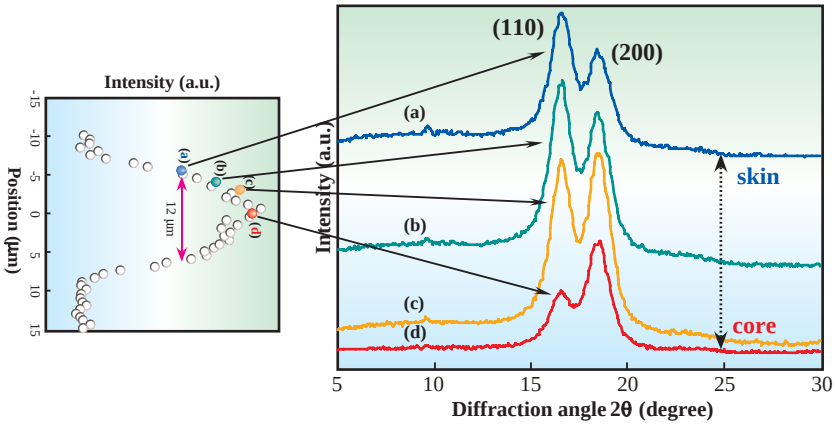

Fig. 4. Equatorial diffraction profiles of Kevlar[29] single fiber at different measurement points along the fiber axis.

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References

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