

## Effect of submicron structures on the mechanical behavior of polyethylene

Polyethylene (PE) is one of the most widely used polymers in daily life owing to its excellent mechanical properties and processability, and is used for products such as plastic bags, plastic wrap, stretch wrap, pipes, and covering of cables. High-density polyethylene (HDPE) is a PE produced by the polymerization of ethylene. Linear low-density polyethylene (LLDPE) is a PE commonly made by the copolymerization of ethylene with  $\alpha$ -olefins such as butene, hexene, or octene to reduce crystallinity. The type and quantity of the  $\alpha$ -olefins have significant effects on the physical properties of LLDPE. In this study, we first observed changes in the structures of LLDPE that are on the order of 100 nm to 1 µm (submicron scale) by timeresolved ultra small-angle X-ray scattering (USAXS), then showed that the changes on the submicron scale dominate the mechanical behavior of LLDPE and HDPE under uniaxial stretching.

The crystals in PE form hierarchical structures, as shown in Fig. 1 [1]. The structures include crystalline lattice structures, where molecular chains are systematically folded and packed; lamellar structures, where crystalline and amorphous parts are alternately stacked; branch structures consisting of the lower crystalline region (LCR) and higher crystalline region (HCR); and spherulitic structures filled with the branch structure. The changes in the hierarchical structures under deformation induce a yield point in stress-strain (S-S) curves during the uniaxial stretching of PE at room temperature (cold drawing) as shown in Fig. 2. The yield point is a measure of the tenacity of PE and the control of the yield point is important in PE material design. One yield point is observed in the S-S curve of HDPE during cold drawing. However, some LLDPEs exhibit two yield points in the S-S curve [2], and the presence of these two yield points gives them characteristic mechanical behaviors.

In previous studies, the yielding behaviors of LLDPE and HDPE have been discussed in terms of the changes in crystalline lattice and lamellar structures, which are investigated by small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS), during cold drawing. However, researchers have not investigated the effects of the changes in the submicron structures on the yielding behaviors, though it is expected that the structures on the submicron scale themselves would also affect the yielding behaviors [2]. The USAXS technique that uses synchrotron radiation enables us to perform in situ observations on the submicron scale [3]. We thus investigated the changes in the LCR and HCR of the submicron branch structures in LLDPE and HDPE during uniaxial stretching by time-resolved USAXS, as well as the changes in the lamellar and lattice structures by time-resolved SAXS and WAXS. We, then, clarified how the changes in the submicron structures affect the yielding behaviors.

The USAXS, SAXS, and WAXS measurements during drawing were performed with an incident wavelength of 0.2 nm in the second hutch of beamline at SPring-8 **BL03XU** [4]. The drawing speed was 1 mm/min. The details of the experiments are shown elsewhere[1].

Figure 2 shows S–S curves for LLDPE and HDPE. Here,  $\lambda$  is an extension ratio defined as  $\lambda = L/L_0$ , where  $L_0$  and L are the sample lengths before and after applying strain, respectively. Two yield points, one at  $\lambda = 1.07$  or the 1st yield point (1YP) and the other at 1.17 or the 2nd yield point (2YP), were observed for LLDPE, while one yield point (YP) at  $\lambda = 1.05$  was observed for HDPE.

As shown in Fig. 3, the USAXS patterns of LLDPE show the characteristic changes at each yield point. After 1YP, the so-called butterfly pattern associated



Fig. 1. Schematic illustration of the hierarchical structure of polyethylene spherulites.

with the enhancement of the density fluctuations on the sub-microscopic scale appears. The decrease in stress is caused by the reduction in the density of LCR. In HCR, the fragmentation of lamellar structures occurs, leading to the development of the chevrontype morphology, consequently. The mechanical melting of lamellar structures also occurs in HCR. After 2YP, the streak-like scattering perpendicular to the drawing direction appears in the USAXS patterns, reflecting the formation of string-like voids or necking. The formation of voids originates from further reduction in the density of LCR and enhances the reduction rate of the stress. In the HCR region, recrystallization occurs from the stretched polymer chains, and fibrillar structures are developed. The recrystallization causes the stress to rise gradually.

Figure 3 also shows the USAXS patterns of HDPE. After the YP, a strong inhomogeneity characterized by butterfly patterns is observed, and a strong streak develops, reflecting the immediate state of the generation and elongation of voids. The formation of chevron-type morphology and the mechanical melting occur in the same way as in LLDPE, but on the sub-microscopic scale, a strong enhancement of density fluctuations and void formation occur almost simultaneously, resulting in a single yield point.

The void formation does not occur at the 1YP but at the 2YP for LLDPE, while voids are formed at the YP in HDPE. This difference is caused by the fact that the lamellar structures in LLDPE are less stable than those in HDPE. The modulus of the lamellar structure in LLDPE is lower than that in HDPE, so the enhancement of density fluctuation with strain in HDPE is greater than that in LLDPE. The stability of



Fig. 2. S–S curves of LLDPE and HDPE. The arrows indicate the yield points.

the crystals in LLDPE depends on the comonomer species and their quantity in LLDPE so the yield behaviors may be strongly affected by these factors.



Fig. 3. Schematic illustrations of the changes in the hierarchical structures in (a) LLDPE and (b) HDPE.

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## References

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