Annealing Effect on Surface Crystal Structure of Polyethylene Thin Films

The molecular aggregation structure at the surface of polymeric materials is strongly related to their physical properties such as friction and adhesion. However, the intrinsic features of the molecular aggregation structure at the surface of crystalline polymers have not yet been clarified on the molecular scale. We have been investigating the crystal structure at the solid surface of polyethylene (PE), a typical example of crystalline polymers, by grazing incidence X-ray diffraction (GIXD) measurements. In the case of melt-crystallized PE thin films, it was revealed that the lattice dimension in the in-plane direction was smaller in the near-surface region than in the bulk region. Moreover, we found for the first time that the paracrystalline lattice distortion in the in-plane direction was larger in the near-surface region than in the bulk region but the crystallite size was almost the same between these two regions [1]. On the other hand, Burell and Wehrum *et al.* reported the local alignment of polymer chains at the surface of spin-cast poly(ethylene telepthalate) thin films during annealing [2]. In order to control the surface structural and physical properties of polymeric materials, it is important to clarify the chain packing structure at the surface of crystalline polymers under various conditions. In this study, the annealing effect on crystal structure at the surface was investigated for PE thin films by synchrotron-source GIXD measurements.

High-density polyethylene without additives (HDPE; Hizex 1300J, MI = 14, Mitsui Chemicals, Inc.) was used as a sample. Thin films with a thickness of *ca.* 400 nm were prepared onto silicon substrates from a *p*-xylene solution of HDPE by a dip-coating method. Thus, the obtained films were annealed at various temperatures (T_a) for 24 hours under nitrogen atmosphere. Figure 1 shows the schematic geometry of the in-plane GIXD measurement. In order to measure reflections from crystallographic planes perpendicular to the sample surface, in-plane GIXD measurements were carried out for the films at beamline **BL13XU** [3] using incident X-rays with a wavelength of 0.1280 nm. When the incident angle (α_i) of X-rays to the sample surface is smaller than the critical angle (α_c), the X-rays undergo total external reflection and penetrate into the sample as evanescent waves. Around α_c, the penetration depth changes drastically from several micrometers to several nanometers. Therefore, surface-sensitive and bulk-sensitive profiles were obtained by in-plane GIXD measurements at α_i = 0.11˚ ($< \alpha_c$) and 0.20˚ ($> \alpha_c$), respectively.

Figure 2 shows the annealing temperature dependence of the lattice constants *a*, *b* and *c* of the orthorhombic unit cell in the near-surface and bulk regions of HDPE thin films calculated on the basis of in-plane GIXD profiles. The *a* and *b* in the near-surface region of the as-prepared films were smaller than those in the bulk region. This tendency was also observed for the films annealed at high T_a which would be released from residual stress induced by dip-coating. Therefore, in-plane GIXD analysis implied that the crystal density in the near-surface region would be essentially higher than that in the bulk region. In the near-surface region, PE chains were considered to be packed closely together to minimize the surface free energy of the films.

Paracrystalline lattice distortion in the in-plane direction was evaluated with the (110) reflection and its higher-order reflections on the basis of the paracrystalline lattice analysis proposed by Hosemann [4]. In the paracrystalline lattice model, the lattice vectors of adjacent unit cells vary in magnitude and direction due to the large displacement of lattice points from their ideal positions, which results in a loss of the long-range crystallographic order. The integral width $\delta\beta$ of a
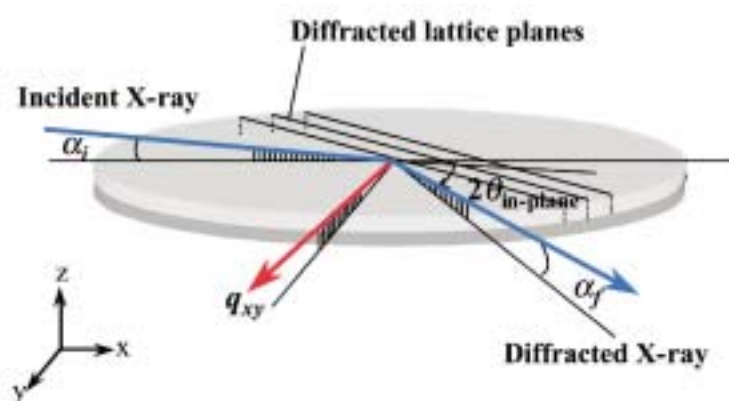

Fig. 1. Schematic geometry of the in-plane GIXD measurement. α_i: incident angle, α_f: take-off angle, q_{xy}: scattering vector.

reflection is expressed by $(\delta\beta)^2 = (1/\bar{a}^2)[(1/N^2) + \pi^4 g^4 h^4]$. Here, g is the standard deviation of the Gaussian distribution divided by the average lattice vector $\bar{a}$, h is the scattering order and N is the number of scattering units. In other words, g is a parameter used to evaluate the degree of paracrystalline disorder and N corresponds to crystal size. Figures 3(a) and 3(b) show the annealing temperature dependences of $g_{(110)}$ and $N_{(110)}$ in the in-plane [110] direction in the near-surface and bulk regions of the HDPE thin films, respectively. In the case of the as-prepared films, the (220) reflection from the near-surface region was not clearly detected. This indicated extremely large lattice distortion. Also, the $g_{(110)}$ in the near-surface region of the annealed films was larger than that in the bulk region. Therefore, paracrystalline lattice distortion in the in-plane direction would be essentially larger in the near-surface region than in the bulk region. On the other hand, the $N_{(110)}$ in the near-surface region was smaller than or the same as that in the bulk region. The decrease in $g_{(110)}$ and the increase in $N_{(110)}$ from $T_a = 343$ K to 393 K were large in the near-surface region. These results suggest that structural reorganization accompanying partial-melting and recrystallization drastically occurred in the near-surface region of the films.
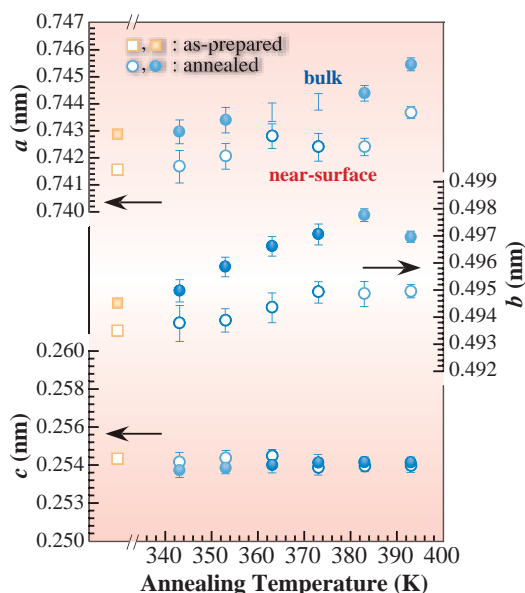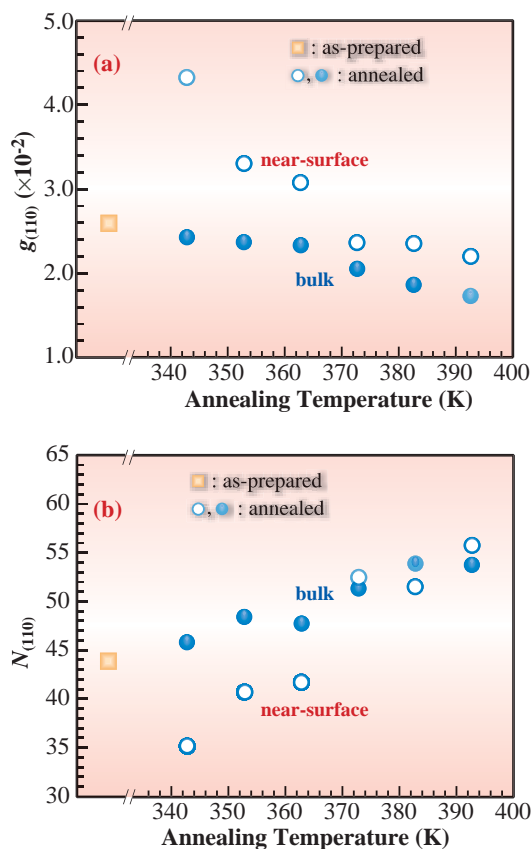

Fig. 3. Annealing temperature dependence of $g_{(110)}$ (a) and $N_{(110)}$ (b) for dip-coated HDPE thin films. Open circles: near-surface region, filled circles: bulk region.

Fig. 2. Annealing temperature dependence of the lattice constants a, b and c of the orthorhombic unit cell in the near-surface and the bulk regions measured for dip-coated HDPE thin films. Open circles: near-surface region, filled circles : bulk region.

Sono Sasaki[a,*], Atsushi Takahara[b] and Tisato Kajiyama[c]

(a) Graduate School of Engineering, Kyushu University
(b) Institute for Materials Chemistry and Engineering, Kyushu University
(c) Kyushu University

Present address : SPring-8 / JASRI

E-mail: sono@spring8.or.jp

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