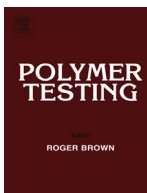




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Material behaviour

Rheo-optical Raman study of microscopic deformation in high-density polyethylene under hot drawing

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ABSTRACT

In situ observation of the microscopic structural changes in high-density polyethylene during hot drawing was performed by incorporating a temperature-controlled tensile machine into a Raman spectroscopy apparatus. It was found that the load sharing and molecular orientation during elongation drastically changed at 50°C. The microscopic stress of the crystalline chains decreased with increasing temperature and diminished around 50°C. Moreover, the orientation of the crystalline chains was greatly promoted above 50°C. These microscopic structural changes were caused by the thermal activation of the molecular motion within lamellar crystalline chains owing to the onset of relaxation of the crystalline phase.

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1. Introduction

The mechanical properties of semicrystalline polymers, such as polyethylene (PE), drastically change with temperature, which are accompanied by at least three relaxations: including α , β , and γ relaxations [1]. The α relaxation of high-density polyethylene (HDPE) occurs in a wide range of temperature from 30 to 120°C, and the activation energy varies from 90 to 300 kJ/mol [1–3]. Nakayasu *et al.* reported that the α relaxation in HDPE can be divided into two relaxations: α_1 and α_2 at low and high temperatures, respectively [4]. They reported the activation energies as ~117 kJ/mol for the α_1 relaxation and ~210 kJ/mol for the α_2 relaxation. The α_1 and α_2 relaxations were assigned as relaxation in the grain boundaries and thermal activation of the intrachain motion, respectively. These assignments were confirmed by dynamic mechanical analysis (DMA) of PE single-crystal mats [5] and PE with different molecular weight distributions and branch structures [6]. Because molecular motion is activated in the

α relaxation region, the drawability of polymeric materials is highly enhanced. Thus, most films and fibers are commonly produced at high temperatures.

The effect of α relaxation on the deformation of semi-crystalline polymeric materials has been investigated by various methods, such as DMA, nuclear magnetic resonance and X-ray diffraction, mainly using highly drawn specimens [5,7,8]. Jiang *et al.* [9] conducted *in situ* small- and wide-angle X-ray measurements of PE under hot drawing. They found that the long period drastically decreases with strain in the neck-formation region below 100°C, while the long period remains unchanged with elongation above 120°C. However, investigations by *in situ* measurements, which can directly observe the deformation mechanism, are very limited.

Because α relaxation is due to inter- or intracrystalline relaxation, drastic changes in molecular mobility occur under hot drawing. Rheo-optical techniques, such as infrared (IR) absorption and Raman scattering, are suitable to elucidate the microscopic mechanism of deformation [10–14]. Although IR spectroscopy has been applied to hot drawing of thin films [15,16], this method has several intrinsic disadvantages, such as most IR active modes being mainly ascribed to vibrations of side chains, and only the

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orientation parameter $\langle P_2 \rangle$, which is a measure of the average orientation degree, can be determined. However, Raman spectroscopy has several advantages over IR spectroscopy, such as the skeletal C–C stretching vibration being strongly Raman active, load sharing on the polymer chains can be directly observed [17] and the higher-order orientation parameter $\langle P_4 \rangle$ can be estimated. Then, by using Raman spectroscopy, we can discuss the molecular orientation more precisely [18–21]. In this work, Raman spectra of HDPE were monitored under tensile stretching at high temperatures in a range of the α -relaxation processes. To accomplish this, we mounted a small tensile machine with a heat chamber on a Raman spectroscopic system.

2. Experimental

In this study, we used Ziegler–Natta-catalyzed HDPE ($M_w = 10 \times 10^4$, $M_n = 1.7 \times 10^4$) supplied by Tosoh Corporation. A sheet of HDPE about 1 mm thick was prepared by a hot-press method, where the pellets were melt and compressed at 210°C for 5 min at 20 MPa followed by quenching in iced water. The sample sheet was annealed at 110°C for 5 h. The test specimens for the measurements were cut from the annealed film with a double-edge-notched die (2-mm gauge length and 4-mm width). The density of the sample was determined to be 953 kg/m³ by the Archimedes method. The volumetric crystallinity was determined to be 68% by assuming that the density of the amorphous and the crystalline phases were 855 and 1000 kg/m³ [22], respectively. The lamellar thickness of the sample was determined to be about 17 nm by SAXS measurements.

Dynamic mechanical spectra were measured from –50°C to 140°C at a constant frequency of 10 Hz and a heating rate of 2 °C/min using a UBM DVE-V4 dynamic mechanical analyzer (UBM, Kyoto, Japan). As shown in Fig. 1, one broad relaxation peak was observed, which was identified conventionally as α (overlapping α_1 and α_2). The α_1 and α_2 processes were observed at 62 and 121°C, respectively.

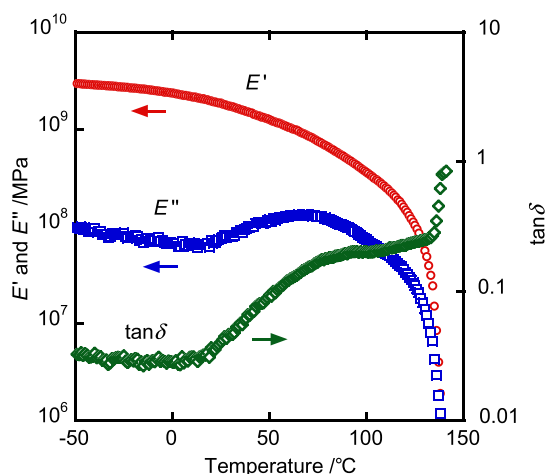


Fig. 1. Dynamic mechanical spectra of HDPE at a constant frequency of 10 Hz.

A schematic representation of the apparatus for the *in situ* Raman spectroscopic measurements for hot drawing is shown in Fig. 2. A temperature-controlled tensile machine for microscopy (10073B, Japan High Tech Co. Ltd.) was installed in the *in situ* Raman spectroscopy apparatus that we recently developed [23]. The laser light from a He–Ne laser (LASOS) was monochromated with a laser line filter, and irradiated onto the notched portion of the specimen with a spot size of 1 mm in diameter. The elongation speed was set to 1 mm/min and the drawing temperature was tuned from 20°C to 80°C. The scattered light was collected with a concave mirror and collimated with a convex lens into an optical fiber, and the excitation light was removed with a Raman long-pass filter. An intensified charge-coupled device camera equipped with a monochromator (PIXIS100 and SpectraPro 2300i, Princeton Instruments) was used as the detector. For polarized Raman spectroscopy, a pair of wire-grid polarizers was inserted as the polarizer and the analyzer. The non-polarized spectra were accumulated 10 times with an exposure time of 1 or 2 s. The polarized spectra were collected in *zz*, *yz*, and *yy* geometries and accumulated 10 times with an exposure time of 2 s.

The C–C stretching modes of PE are strongly Raman active [24–27]. The anti-symmetric (1063 cm^{–1}) and symmetric (1130 cm^{–1}) stretching modes correspond to vibrations of carbon atoms along and perpendicular to the molecular chain, respectively. The experimental Raman spectra in the C–C stretching region (1050–1150 cm^{–1}) were successfully fitted with a sum of two Voigt functions using the nonlinear Levenberg–Marquardt method, and the peak positions and peak areas for the two peaks were determined [23]. The uncertainties in determining the peak shifts and the peak areas were less than ± 0.22 cm^{–1} and $\pm 5\%$ (except at 80°C, less than $\pm 10\%$), respectively.

The peak shifts of the symmetric and anti-symmetric vibrations were defined as the deviation of the Raman shifts from that of the undrawn specimens:

$$\Delta\nu_s = \nu_s - \nu_s^0, \quad (1)$$

$$\Delta\nu_{as} = \nu_{as} - \nu_{as}^0, \quad (2)$$

where the superscript 0 denotes the undrawn specimens. From the direction of the symmetric and anti-symmetric vibrations, $\Delta\nu_s$ and $\Delta\nu_{as}$ were interpreted as the microscopic stresses perpendicular and parallel to the polymer chain, respectively.

The orientational behavior of the polymer chain was evaluated with the orientation parameters obtained by polarized Raman spectroscopy [18–21,28]. The orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are defined as a function of the chain orientation angle θ with respect to the draw axis as

$$\langle P_2 \rangle = \frac{3\langle \cos^2 \theta \rangle - 1}{2}, \quad (3)$$

$$\langle P_4 \rangle = \frac{35\langle \cos^4 \theta \rangle - 30\langle \cos^2 \theta \rangle + 3}{8}. \quad (4)$$

The values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ were evaluated from the integrated intensities of the 1130 cm^{–1} band in the

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