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Temperature Dependence of the Crystal Lattice Modulus and the Young's Modulus of Polyethylene

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ABSTRACT: The temperature dependence of the crystal lattice modulus of polyethylene was measured by X-ray diffraction with use of ultradrawn films produced by gelation/crystallization from dilute solution. Measurements were carried out in the temperature range 20–150 °C for specimens with draw ratios >300. The measured crystal lattice modulus was in the range 211–222 GPa, and the values were independent of temperature. In contrast, the storage modulus of an ultradrawn film with a draw ratio of 400, 216 GPa at 20 °C, decreased to 130 GPa at 140 °C. This discrepancy was related to an increase in the amorphous content and a decrease of the amorphous modulus with increasing temperature.

Introduction

In crystalline polymers, the crystal lattice modulus in the molecular chain axis direction is equivalent to the theoretical value of Young's modulus. Extensive work has been reported by X-ray diffraction,[1-4] Raman spectroscopy,[5] and inelastic neutron scattering.[6] The Raman and neutron-scattering methods, however, involve an unfavorable assumption[5,6] concerning the frequency of the absorption bands in a polymeric system, in addition to the difficulty in estimating the lamellar thickness parameter by small-angle X-ray scattering. In contrast, X-ray diffraction measurements have the advantage of estimating the crystal lattice modulus directly from the stress–strain relationship. This method was used by Sakurada et al.[1,2] for many polymers, and a detailed analysis for polyethylene was reported by using oriented specimens with different molecular weights and crystallinities. It was concluded that the values of the crystal lattice modulus are independent of the above factors.

Recently, Matsuo et al. have studied the crystal lattice modulus of polyethylene to determine whether the stress within a specimen is the same as the external applied stress.[3] The measurements were carried out at 20 °C with ultradrawn films produced by gelation/crystallization from dilute solutions according to the method of Smith and Lemstra.[7,8] The measured crystal lattice modulus was in the range 213–229 GPa, which is lower than the value reported by Sakurada et al.[1,2] The observed values were independent of the elongation ratios from 50 to 300 within experimental error.[3] This independence supports the assumption that the homogeneous stress hypothesis is valid, and the concept of independence was confirmed by a linear elastic theory[9] using a composite model of crystalline and amorphous phases.

However, there has been no report concerning a change in the crystal lattice modulus at elevated temperatures.

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This article deals with the temperature dependence of the crystal lattice modulus in the molecular chain direction as well as that of the Young's modulus. Measurements were carried out with ultradrawn polyethylene films with draw ratios >300. In the following article,[10] the temperature dependence is represented by a linear elastic theory based on a model in which anisotropic amorphous layers lie adjacent to oriented composite layers with the interface perpendicular to the stretching direction.

Experimental Section

The sample was linear polyethylene (Hercules 1900/90189) with an intrinsic viscosity of 30 dL/g, corresponding to a molecular weight of 6×10^6. Gel films were prepared by crystallization from Decalin solution. The gel films were cut into strips, which were elongated to the desired draw ratio at 135 °C.[11,12] For all specimens, the draw ratios were in the range 300–400.

The density of the films was measured by pycnometry in chlorobenzene–toluene. Since the density was very dependent on the presence of residual antioxidant in the film, great care was taken to remove it. Thus the drawn specimen was cut into fragments and immersed in ethanol for 30 days and subsequently vacuum-dried for 1 day prior to measuring the density. The removal of the antioxidant was confirmed by infrared absorption measurements. The fragments were put in chlorobenzene–toluene in an ultrasonic washing instrument to ensure that the solvent penetrated into the specimen, and the density was measured by pycnometry. The crystallinities of specimens with draw ratios >300 was greater than 95%.

Crystal strain was provided by a constant stretching apparatus that has been described elsewhere.[3] The specimen was mounted horizontally in the stretching clamps and examined by X-ray diffraction using Cu Kα radiation from a rotating anode X-ray tube (Rigaku RDA-rA operated at 200 mA and 40 kV). The intensity distribution from the crystal (002) plane was measured with point focusing by using a system in which the incident beam was collimated by a circular collimater 2 mm in diameter, and the diffraction beam was detected by a square slit with dimensions 0.9 mm × 0.9 mm. The incident beam was monochromatized by a curved graphite monochromator. The intensity distribution was measured at a step interval of 0.1° with a time of 10 s in the range 71–79° (twice the Bragg angle). When the measurement of the crystal lattice modulus was carried out at elevated temperatures, the test specimen was sometimes torn at the position where it was irradiated by the X-ray beam. Accordingly, the fixed time interval chosen (10 s) was only one-tenth the interval measured at 20 °C previously.[3] The change of the peak position at a reference temperature T_0 as a result of the applied stress was estimated from the deviation of the center of gravity of the intensity distribution function as follows:

$$2\Delta\theta(\sigma,T_0) = 2\theta_{max}(0,T_0) - 2\theta'_{max}(\sigma,T_0) \quad (1)$$

where

$$2\theta_{max}(0,T_0) = \frac{\int_{2\theta_1}^{2\theta_2} 2\theta_B I(\theta_B,T_0)\, d\theta_B}{\int_{2\theta_1}^{2\theta_2} I(\theta_B,T_0)\, d\theta_B} \quad (2)$$

$$2\theta'_{max}(\sigma,T_0) = \frac{\int_{2\theta'_1}^{2\theta'_2} 2\theta_B I'(\theta_B,T_0)\, d\theta_B}{\int_{2\theta'_1}^{2\theta'_2} I'(\theta_B,T_0)\, d\theta_B} \quad (3)$$

where $I(\theta_B,T_0)$ and $I'(\theta_B,t_0)$ are the intensity distribution functions in the undeformed and deformed states, respectively, and $2\theta_{max}(0,T_0)$ and $2\theta'_{max}(\sigma,T_0)$ are the corresponding average maxima of the diffraction peak position.

The crystal lattice strain ϵ_c is related to $\Delta\theta(\sigma,T_0)$ in eq 1 as follows:

$$\epsilon_c(T_0) = -\cot[\theta_{max}(0,T_0)]\Delta\theta(\sigma,T_0) \quad (4)$$

Thus, the crystal lattice modulus $E_c(T_0)$ is

$$E_c(T_0) = \sigma/\epsilon_c(T_0) \quad (5)$$

where σ is the external applied stress due to the constant load.

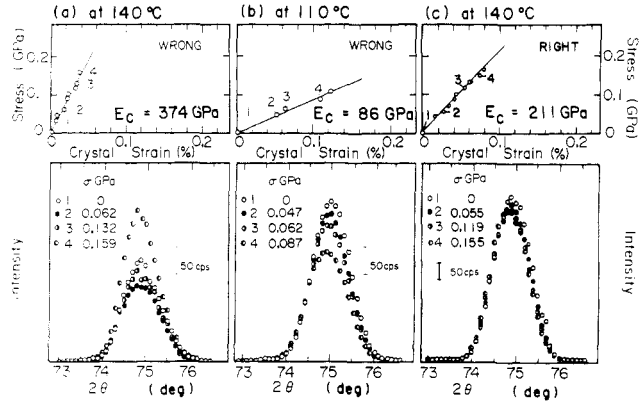

Figure 1. Relationship between X-ray diffraction intensity distribution and the crystal lattice modulus: (a) wrong result; (b) wrong result; (c) good result.

When the crystal lattice modulus is measured at an arbitrary temperature T, the same method can be used as follows:

$$\epsilon_c(T) = -\cot[\theta_{max}(0,T)]\Delta\theta(\sigma,T) \quad (6)$$

$$E_c(T) = \sigma/\epsilon_c(T) \quad (7)$$

where

$$2\Delta\theta(\sigma,T) = 2\theta_{max}(0,T) - 2\theta_{max}(\sigma,T) \quad (8)$$

From eq 4 and 6, the linear thermal expansion coefficient α of the c axis is given by

$$\alpha = \partial(\Delta\epsilon)/\partial T \quad (9)$$

where

$$\Delta\epsilon = \epsilon_c(T) - \epsilon_c(T_0) \quad (10)$$

The mechanical properties of the bulk specimens were estimated from measurements of the complex dynamic tensile modulus. The measurements were carried out over the range −150 to 150 °C at a fixed frequency of 10 Hz by using a Viscoelastic spectrometer (VES-F, Iwamoto Co. Ltd). The gage length of the specimen was 40 mm, and the width was about 1.5 mm. In the measurement, the drawn film was subjected to a static strain corresponding to an initial stress of about 0.15 GPa in order to superpose a dynamic strain of 0.025%.

Birefringence measurements were made with a optical microscope (crossed polarizing lenses) with use of a Berek compensator for measuring the retardations.

Results and Discussion

To measure the crystal lattice modulus exactly, we took great care to avoid further elongation of the drawn test specimen under the external applied stress at temperatures above 100 °C. Further elongation under a constant stress, termed creep, is associated with viscoelastic properties and invalidates the homogeneous stress hypothesis. This creep phenomenon can be negligible if the molecular chains are fully aligned and extended and if the test specimen is almost completely crystalline.

Figure 1 shows examples of the change in the X-ray intensity distribution with increasing external applied stress at the indicated temperatures above 110 °C. These profiles serve to determine whether the test specimens are suitable for measuring the crystal lattice modulus as a function of temperature. It is obvious that the change in the profile of the diffraction intensity is extremely sensitive to creep, and the resultant data become wrong. A correct result is obtained when the intensity distribution remains constant under different external applied stresses. For retention of a sample strain less than 10% even at 145 °C (close to the theoretical melting point of 145.5 °C),[13] all specimens drawn beyond $\lambda = 300$ were annealed for 2 h at 140 °C and cooled slowly to room temperature at a constant stress of 0.1 GPA prior to measurement of the

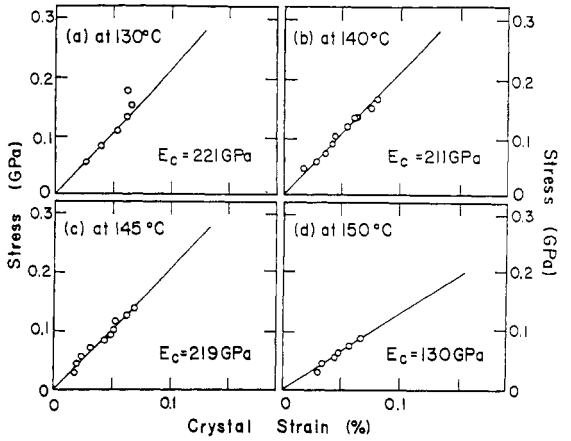

Figure 2. Temperature dependence of the crystal lattice modulus up to 120 °C.

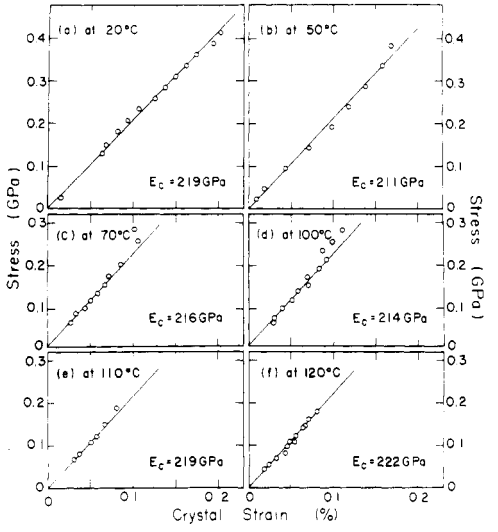

Figure 3. Temperature dependence of the crystal lattice modulus up to 150 °C.

crystal lattice strain. Through this process, the sample strain under an applied constant stress of 0.15 GPa was confirmed to be less than 10% at 145 °C. Therefore it would be expected that this procedure causes further increases of molecular orientation and crystallinity and plays an important role in avoiding creep and thus assuring a good result, as shown in Figure 1c.

Figures 2 and 3 show the temperature dependence of the crystal lattice modulus. It is evident that within the experimental error, the measured values are independent of temperature below the melting point (145.5 °C).[13] The sample remains intact above the melting point because of superheating effects. In contrast, the crystal lattice modulus decreases considerably beyond the melting point. Such a temperature dependence of the crystal lattice modulus is quite different from the generally observed for the Young's modulus.

Figures 4 and 5 show the crystal strain of the c axes against temperature in the free state with no applied stress and at various indicated stresses. In eq 10, the crystal strain $\epsilon_c(T_0) = T_0 = 20$ °C was set to be 0. The linear thermal expansion coefficient of the c axis was estimated to be -2.27×10^{-5}/°C. This value is independent of the applied stress, which satisfies the relationship of eq 9 and supports the validity of the resultant value.

Figure 6 shows the temperature dependence of the complex dynamic tensile modulus of an ultradrawn film with a draw ratio of 400. This specimen has a modulus of 216 GPa at 20 °C, corresponding to the crystal lattice

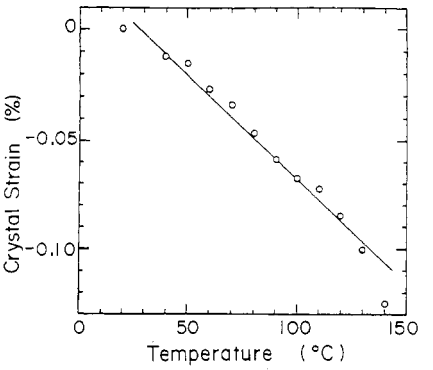

Figure 4. Crystal lattice strain of the crystal (002) plane versus temperature at a fixed state without stress.

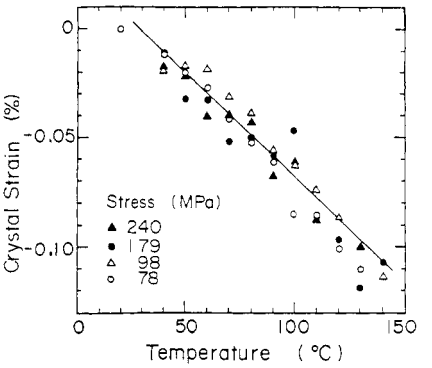

Figure 5. Crystal lattice strain of the crystal (002) plane versus temperature at the indicated stresses.

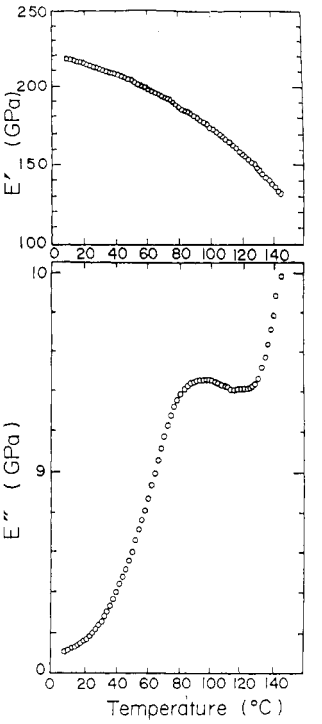

Figure 6. Temperature dependence of the complex dynamic tensile modulus for an ultradrawn film with a draw ratio of 400.

modulus, as described in a previous article.[9] The dynamic modulus was measured for various temperatures from 10 to 140 °C at 10 Hz. The storage modulus E' decreases with increasing temperature. This tendency is similar to the results that have been observed generally for semicrystalline polymers. Even at 140 °C, E' is >130 GPa and corresponds to about 60% of the crystal lattice modulus. Such an exceptional mechanical property can only be realized by ultradrawing. Usually, E' of commercial poly-

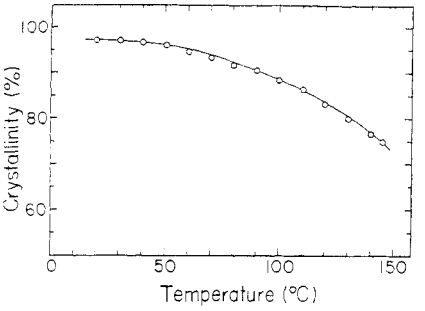

Figure 7. Temperature dependence of crystallinity with a fixed dimension in the stretching direction for the ultradrawn film with a draw ratio of 400.

ethylene fibers (films) decreases drastically at temperatures above 100 °C. This means that the temperature dependence of the Young's modulus becomes less as the molecular orientation and crystallinity increase. The loss modulus E' facilitates understanding of the mechanical dispersion. According to the reports,[14-17] the dispersion peak corresponds to the α mechanism associated with crystal dispersion, and the dispersion can be separated into two components. The α_1 mechanism in single-crystal and spherulitic systems is associated with grain boundary phenomena of deformation and/or rotation of crystallites (crystal mosaic block) within a viscous medium. The α_2 mechanism involves the crystal disordering transition due to the onset of torsional oscillation of polymer chains within the crystal lattice. The detailed analysis for ultradrawn films will be discussed elsewhere in terms of a different aspect.[18]

The crystal lattice modulus is independent of temperature, while the storage modulus decreases with increasing temperature. This difference suggests that the temperature dependence of the Young's modulus is strongly affected by an increase in amorphous content with increasing temperature. The temperature dependence of crystallinity must be determined to check this concept.

Figure 7 shows the change in crystallinity for the ultradrawn specimens (λ = 400) with increasing temperature and a fixed dimension in the stretching direction. The crystallinity was estimated from the intensity distribution of the (002) crystal plane as follows:

$$X_c(T) = 97.2\frac{A(T)}{A(T_0)} \tag{11}$$

where 97.2 is the percentage of crystallinity measured by pycnometry at 20 °C, and $A(T)$ and $A(T_0)$ are the areas under the X-ray intensity distribution curves at T and T_0 (20 °C), respectively. The X-ray diffraction intensity distribution curves were observed at a step interval of 0.1° with a time of 10 s in the range 71–79° (twice the Bragg angle). $A(T)$ and $A(T_0)$ are given by[19]

$$A(T) = \frac{\int_0^{\pi} W(\theta_j,T)\, I(\theta_j,T)\, d\theta_j}{\int_0^{\pi} W(\theta_j,T)\, d\theta_j} \tag{12}$$

$$A(T_0) = \frac{\int_0^{\pi} W(\theta_j,T_0)\, I(\theta_j,T_0)\, d\theta_j}{\int_0^{\pi} W(\theta_j,T_0)\, d\theta_j} \tag{13}$$

where $I(\theta_j,T)$ at T and $I(\theta_j,T_0)$ at T_0 (20 °C) are the areas of the X-ray diffraction intensity distribution curves measured at θ_j, which denotes the polar angle between the stretching direction and the reciprocal lattice vector of the (002) plane. $W(\theta_j,T_0)$ and $W(\theta_j,T)$ are the weighting factors, which are assumed to be equivalent to the orientation distribution functions of the reciprocal lattice vector of the (002) plane at T_0 and T, respectively, and are represented by $I(\theta_j,T_0)$ and $I(\theta_j,T)$.

$$W(\theta_j,T_0) = \frac{I(\theta_j,T_0)}{\int_0^{\pi} I(\theta_j,T_0) \sin\theta_j\, d\theta_j} \tag{14a}$$

$$W(\theta_j,T) = \frac{I(\theta_j,T)}{\int_0^{\pi} I(\theta_j,T) \sin\theta_j\, d\theta_j} \tag{14b}$$

As can be seen in Figure 7, the crystallinity decreases with increasing temperature. The crystallinity remained about 74% even at 145 °C, which is close to the equilibrium melting point of 145.5 °C estimated by Flory and Vrij.[13] This behavior may be explained by assuming that the polymer chains in the melt retain the extended chain arrangement and therefore that the entropy of fusion is smaller than the value calculated from random coils in the molten state. Actually, the apparent melting point was 155 °C by differential scanning calorimetry (DSC) measurement at a heating rate of 10 °C/min.[17] This effect is thought to ensure the retention of the high modulus characteristics of ultradrawn films at temperatures near the theoretical melting point.

The decrease in the area of the X-ray diffraction intensity distribution curve from the (002) plane with increasing temperature is attributed to a decrease in crystallinity and an increase in thermal fluctuation arising from lattice distortion. The two contributions can be separated by using the methods proposed by Ruland[20,21] and Kilian[22,23] for undrawn films. However, we could not apply their methods to the present ultradrawn polyethylene films with sample thicknesses less than 4 μm because the specimens were torn at the position where they were irradiated by the X-ray beam for 3 h at temperatures above 80 °C. In spite of the difficulty in measuring the lattice distortion, it seems that the present treatment is reasonable for estimating the temperature dependence of crystallinity, since the crystal lattice modulus is independent of temperatures up to 145 °C as shown in Figure 2 and 3. It would be expected that if the lattice distortion causes a significant decrease in the area of the X-ray diffraction curve, the crystal lattice modulus should decrease with increasing temperature.

On the basis of the homogeneous stress hypothesis by Takayanagi's model,[24] the Young's modulus may be written approximately by using the crystal lattice modulus E_c, the amorphous modulus E_a, and the crystallinity X_c as follows:

$$\frac{1}{E} = \frac{X_c}{E_c} + \frac{1 - X_c}{E_a} \tag{15a}$$

Equation 15a can be rewritten as follows:

$$\frac{E}{E_c} = \frac{E_a/E_c}{1 - [1 - (E_a/E_c)]X_c} \tag{15b}$$

If E_a is assumed to be independent of temperature, E_a/E_c can be estimated to be about 0.5 by substituting X_c = 0.97 and E/E_c = 0.97 at 20 °C into eq 15b. Thus we have

$$\frac{E}{E_c} = \frac{1}{2 - X_c} \tag{15c}$$

The Young's modulus E is approximately equal to the storage modulus E'.

Figure 8 shows the temperature dependence of E'/E_c for the experimental data (open circles) and the results (closed

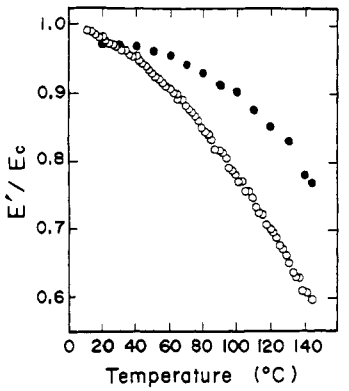

Figure 8. Temperature dependence of E'/E_c for experimental data (open circles) and the results (closed circles) calculated from eq 15c.

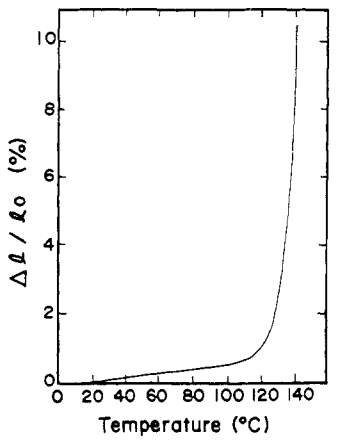

Figure 9. Temperature dependence of bulk strain ($\Delta l/l_0$) in the stretching direction for an ultradrawn film with a draw ratio of 400 from the measurement of the complex dynamic tensile modulus of Figure 6.

circles) calculated from eq 15c, when E_c is fixed at 222 GPa. The calculated plot is in poor agreement with the experimental results. This discrepancy indicates that the amorphous modulus E_a tends to decrease with increasing temperature although the crystal lattice modulus is independent of temperature below 145 °C as shown in Figures 2 and 3.

Figure 9 shows the thermal expansion behavior of the specimen in the stretching direction as measured by a Viscoelastic spectrometer (VES-F). The strain increases as the temperature increases. This tendency becomes considerable above 120 °C and is associated with the peak position of the α mechanism shown in Figure 6. This result is quite different from the behavior of the crystal lattice strain shown in Figure 4. Therefore, it is evident that the creep of the bulk specimen is strongly affected by the characteristics of the amorphous phase but is independent of those of the crystal phase.

Figure 10 shows the orientation function $2\pi q_j(\cos\theta_j)$ of the reciprocal lattice vector of the (002) plane for the specimen with $\lambda = 400$. The data show an extremely sharp profile with a maximum value at $\theta_j = 0°$, indicating that the c axes have a preferred orientation in the stretching direction. The orientation factors of crystallites, F_{200} and F_{400}, which are discussed later, 0.999 99 and 0.999 98, respectively. Furthermore, the other orientation factors F_{202}, F_{402}, and F_{404}, were obtained from the functions $2\pi_j$ (cos θ_j), which represent the reciprocal lattice vectors of the (110), (200), and (020) planes. They were equal to 0 within experimental error. This characterizes the random orientation of the a and b axes around the c axis. The profiles

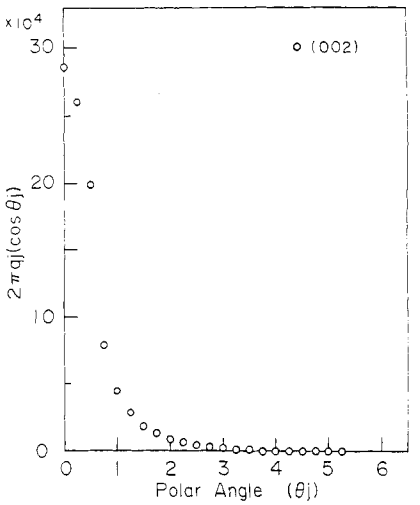

Figure 10. Orientation distribution function of $2\pi q_j(\cos\theta_j)$ of the reciprocal lattice vector of the crystal (002) plane in the temperature range 20–140 °C.

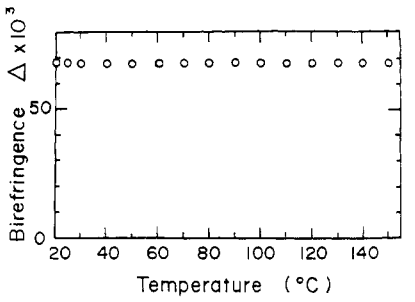

Figure 11. Temperature dependence of birefringence for an ultradrawn film with a draw ratio of 400.

of the orientation distribution functions $2\pi q_j(\cos\theta_j)$ of the four crystal planes were confirmed to be independent of temperature up to 140 °C. This indicates that the orientation distribution of crystallites is hardly affected by temperature in specimens with such an extremely high degree of crystallite orientation.

The orientation of amorphous chain segments was determined from birefringence data as estimated by subtraction of the crystalline contribution from the total birefringence, assuming simple additively as indicated in the following equation:[25]

$$\Delta_{total} = X_c\Delta_c + (1 - X_c)\Delta_a + \Delta_f \qquad (16)$$

where Δ_{total} is the total birefringence of the bulk specimen, Δ_c is the crystalline birefringence, Δ_a is the amorphous birefringence, and Δ_f is the form birefringence. In eq 16, Δ_c and Δ_a are given by

$$\Delta_c = \Delta_c^\circ F_{200} \qquad \Delta_a = \Delta_a^\circ F_{200}^{am} \qquad (17)$$

where Δ_c° and Δ_a° are the intrinsic birefringences of the crystalline and amorphous phases, respectively, in the stretching direction.

Figure 11 shows the changes in birefringence with increasing temperature. The total birefringence 67.6×10^{-3} is independent of temperature; this value is much higher than the intrinsic crystal birefringence Δ_c°, 58.5×10^{-3}, which is the reverse of what is normally observed. The discrepancy is probably due to the fact that the value of Δ_c° may be incorrect and that Δ_f, which has been neglected, may be significant. The intrinsic birefringence of the crystalline phase is calculated from the three principal refractive indices of crystal of the n-paraffin ($C_{36}H_{74}$) reported by Bunn and de Daubeny.[26] This calculation is based on the assumption that the principal refractive

indices can be estimated by assuming the atomic arrangements within the crystal unit cell and neglecting the uncertain effects of the internal field. Furthermore, the form birefringence cannot be neglected because a number of voids were observed within the drawn specimens under scanning electron microscopy.[27] Unfortunately, there is no way at present to estimate the form birefringence in our laboratory. The result in Figure 11 indicates that as a crude approximation, the temperature dependence of the molecular orientation cannot be observed from birefringence data in spite of a significant transition from crystalline to amorphous as shown in Figure 7. This means that birefringence is not sensitive enough to detect small changes in the molecular orientation due to the transition because of the small difference in the values of Δ_c° (58.5×10^{-3}) and Δ_a° (52×10^{-3}). Accordingly, an experimental method for this purpose is needed. It is evident that since the crystal lattice modulus is independent of temperature, the temperature dependence of the Young's modulus is due to an increase in amorphous content and a decrease in the amorphous modulus with increasing temperature.

Conclusion

The temperature dependence of the crystal lattice modulus was measured by X-ray diffraction with use of ultradrawn films with elongation ratios >300. The modulus is in the range 211–222 GPa and is independent of temperature up to 145 °C, which is close to the equilibrium melting point. This behavior is quite different from that of bulk specimens. Measurement of the complex dynamic tensile modulus indicates that the storage modulus E' decreases with increasing temperature, even for ultradrawn films ($\lambda = 400$) whose E' at 20 °C is 216 GPa. The thermal expansion coefficient of the crystal c axis was -2.27×10^{-5}/°C. In contrast, the thermal expansion coefficient of bulk polymer in the stretching direction was positive.

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Mathematical Treatment of the Temperature Dependence of the Crystal Lattice Modulus and the Young's Modulus of Polyethylene

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ABSTRACT: A mathematical representation based on linear elastic theory is proposed for investigating the temperature dependence of the crystal lattice modulus in the chain direction and the Young's modulus. Mathematical formulation was carried out for a composite model of crystalline and amorphous phases. This description indicates that the crystal lattice modulus and the linear thermal coefficient as measured by X-ray diffraction are different from the intrinsic crystal lattice modulus and the coefficient. The calculated results are in good agreement with the experimental results for an ultradrawn polyethylene film with a draw ratio of 400, showing that the crystal lattice modulus is independent of temperature while the Young's modulus decreases with increasing temperatures.

Introduction

In the preceding article,[1] the temperature dependence of the crystal lattice modulus was measured by X-ray diffraction with use of ultradrawn films with elongation ratios in excess of 300. The modulus is in the range 211–222 GPa and is independent of temperature up to 145 °C, which is close to the equilibrium point. In contrast, measurement of the complex dynamic tensile modulus indicated that the storage modulus E' decreases with increasing temperature, even for an ultradrawn film ($\lambda = 400$) whose E' at 20 °C is 216 GPa. This discrepancy was related to an increase in the amorphous content with increasing temperature. Furthermore, the thermal expansion coefficient of the crystal c axis was -2.27×10^{-5}/°C, while the thermal expansion coefficient of bulk polymer in the stretching direction was positive. This contradictory be-

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