

Temperature Dependence of the Young's Modulus of Oriented Polyethylene

Leon Govaert,^{*,†} Brian Brown, and Paul Smith[‡]

Materials Department, University of California at Santa Barbara,
Santa Barbara, California 93106

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ABSTRACT: The negative dependence on temperature of the Young's modulus of solution-spun/drawn ultrahigh molecular weight polyethylene (UHMW-PE) was examined in the range between 25 and 125 °C. The data were analyzed employing a previously published model, wherein the oriented fiber is regarded to be comprised only of two components, i.e., perfectly oriented and unoriented segments, denoted helical and coil, respectively. The modulus of the helical elements, which is equivalent to the theoretical axial modulus, has been reported to be constant in the temperature range of interest. Consequently, the decrease in Young's modulus is discussed in terms of a decrease of the modulus of the "coil" segments (E_c) with increasing temperature. The observed variation of E_c correlated surprisingly well with the calculated change in the crystalline shear modulus resulting from the increase with temperature of the a -axis of the orthorhombic unit cell of polyethylene.

Introduction

This study addresses some aspects of the well-known strong negative temperature dependence of the mechanical properties, both long and short term (creep, and modulus and strength, respectively) of melt-^{1,2} and gel-spun³ high-modulus polyethylene fibers. The documented reduction of Young's modulus with increasing temperature seemingly is contradictory to important results obtained in X-ray studies^{4,5} which showed that the axial, crystalline modulus is, in fact, within experimental error, independent of the temperature in the range of 20–125 °C. On the basis of a homogeneous stress hypothesis, Matsuo et al. rationalized the observed temperature dependence of the Young's modulus of oriented polyethylene in terms of both an increase of the fraction of "amorphous" material and a decrease of the modulus of the amorphous phase with temperature.⁵ However, recent calorimetric studies revealed that in the temperature range of interest there is no detectable decrease in crystallinity.^{6–8} Moreover, dilatometric experiments^{9,10} indicated that volume expansion with temperature of drawn polyethylene is completely reversible, which excludes partial melting at elevated temperatures below the melting point.

In this paper we analyze the observed temperature dependence of the Young's modulus of oriented polyethylene with a previously presented model for the development of the stiffness with draw ratio of flexible-chain molecules.^{11,12} It is concluded that the decrease of the stiffness of oriented polyethylene in the relevant temperature range can be adequately described with a constant axial chain modulus and a temperature-dependent crystal shear modulus. The latter could be derived quantitatively from thermal expansion of the unit cell of polyethylene, which was previously determined by wide-angle X-ray scattering.^{9,10}

Experimental Section

Samples used in this study were gel-spun fibers of ultrahigh molecular weight polyethylene ($M_w = 2\,000\,000$) which were prepared according to standard methods (cf. ref 3). The dried UHMW-PE fibers were drawn at 110 °C using an Instron tensile tester (Model 1122) equipped with a thermostatically controlled

oven. Fibers of draw ratios of 5, 10, 15, and 20 were produced in a single drawing step. Higher draw ratios were achieved in a two-stage drawing process: initially, the fibers were drawn five times at 110 °C, and subsequent drawing to the final ratio was carried out at 120 °C. These relatively low deformation temperatures were selected in order to prevent nonaffine deformation, which would obscure subsequent theoretical analysis of the data. The cross-head speed typically was 50–100%/min, based on the original fiber length. The draw ratios were calculated from linear density measurements before and after drawing and from thermal shrinkage measurements carried out at 160 °C.

The Young's moduli of the drawn fibers were measured using the tensile tester described above at temperatures of 25, 50, 75, 100, and 125 °C. The initial gauge length was 20 mm, and the rate of elongation was 100%/min. Cross-sectional areas were calculated from linear density measurements assuming a density of 0.96 g/cm³ for the PE fibers.

Results and Discussion

Figure 1 shows the familiar plot of Young's modulus versus the draw ratio at various temperatures. In accord with previous reports,^{5,10} at a constant draw ratio the modulus decreased drastically with increasing temperature.

In order to elucidate the origin of this strong, negative temperature dependence of the modulus, the data in Figure 1 will be analyzed employing a previously presented model for the development of the axial Young's modulus with the draw ratio of flexible, linear polymers.^{11,12} In this theory, a partially oriented fiber is considered to be comprised of only two types of elastic elements, i.e., "helix" elements that are perfectly oriented about the draw axis (denoted by the suffix "h") and "coil" elements that are unoriented (denoted by "c"). The latter elements include those segments that traditionally are labeled as amorphous, as well as off-axis, crystalline units (see ref 12). The fraction of helix elements (f_h) is obtained as a function of the draw ratio from classical rubber elasticity:

$$f_h = \frac{3\lambda^3}{2(\lambda^3 - 1)} [1 - (\lambda^3 - 1)^{-1/2} \tan^{-1} \{(\lambda^3 - 1)^{1/2}\}] - \frac{1}{2} \quad (1)$$

Following Ward and co-workers,¹³ the model assumes a uniform stress distribution in the helix and coil elements, which are characterized by their respective moduli E_h and

[†] Centre for Polymers and Composites, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

[‡] Department of Chemical and Nuclear Engineering, University of California at Santa Barbara.

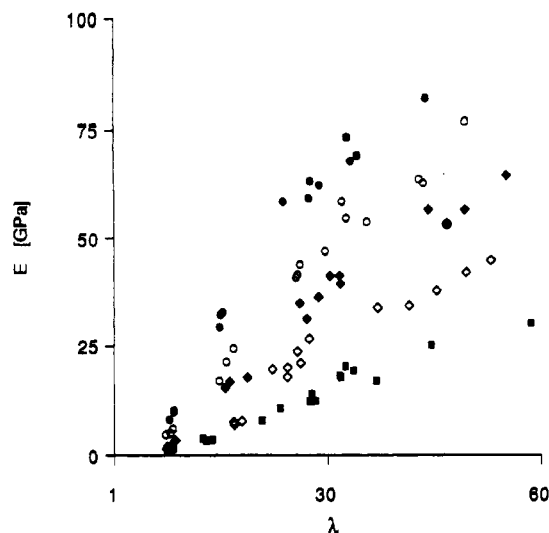


Figure 1. Young's modulus of polyethylene as a function of the draw ratio at temperatures of 25 (●), 50 (○), 75 (◆), 100 (◇), and 125 °C (■).

E_c ; thus

$$E = [f_h E_h^{-1} + (1 - f_h) E_c^{-1}]^{-1} \quad (2)$$

Here E_h is equivalent to the theoretical axial chain modulus. E_c , strictly speaking, is the Young's modulus associated with the variety of coil segments present in the oriented polymer. However, it was previously reasoned that E_c is strongly correlated, if not equal, to the lowest crystal shear modulus (see discussion in ref 12 and below). From eqs 1 and 2 the functionality between the modulus (E) and the draw ratio (λ) for oriented flexible, linear polymers becomes

$$E = \left[E_c^{-1} - \left[\frac{3\lambda^3}{2(\lambda^3 - 1)} [1 - (\lambda^3 - 1)^{-1/2} \tan^{-1} \{ (\lambda^3 - 1)^{1/2} \}] - \frac{1}{2} \right] (E_c^{-1} - E_h^{-1}) \right]^{-1} \quad (3)$$

which, for $\lambda > 5$, to a good approximation reduces to

$$E = [E_h^{-1} + (E_c^{-1} - E_h^{-1})(3\pi/4)\lambda^{-3/2}]^{-1} \quad (4)$$

Note that a plot of E^{-1} against $\lambda^{-3/2}$ is predicted to yield a straight line with an intercept at $1/E_h$; the value of E_c may be derived from its slope.

Within the simple mathematical framework of the above theory, one may attempt to describe the observed reduction with temperature of the Young's modulus of the oriented polyethylene fibers, in principle, by variation of the values of E_h , E_c , or both. However, as was already pointed out in the Introduction, recent X-ray studies unambiguously showed that in the temperature range of interest, i.e., 25–125 °C, the axial chain modulus (often referred to as the crystal or theoretical modulus) of polyethylene is virtually independent of the temperature.^{4,5} Thus, in the following analysis, E_h was taken to be constant and equal to the previously^{11,12} established value of 300 GPa, which is within the range of 290–320 GPa published by other authors.^{14–16}

The (temperature-dependent) values of E_c were derived from plots of E^{-1} vs $\lambda^{-3/2}$, shown in Figure 2; the results are shown in Figure 3. A systematic decrease of this modulus was seen with temperature, gratifyingly reaching a value of essentially zero around the equilibrium melting temperature of polyethylene.

In a previous paper the argument was presented that E_c is closely related, if not equal, to the lowest shear modulus of the crystalline phase.¹² A rationale was

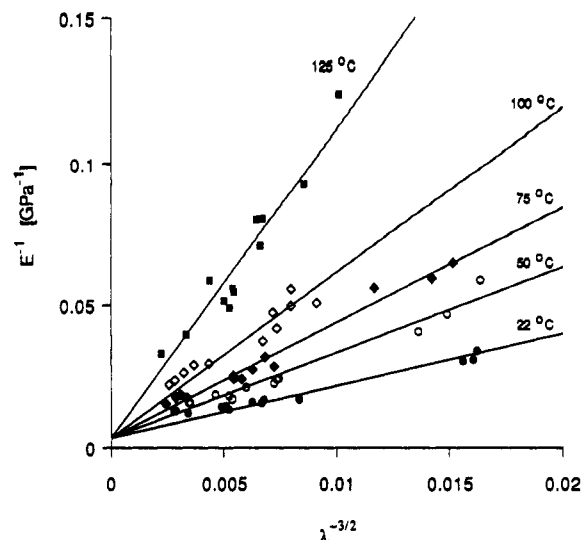


Figure 2. E^{-1} versus $\lambda^{-3/2}$ plot of the data in Figure 1.

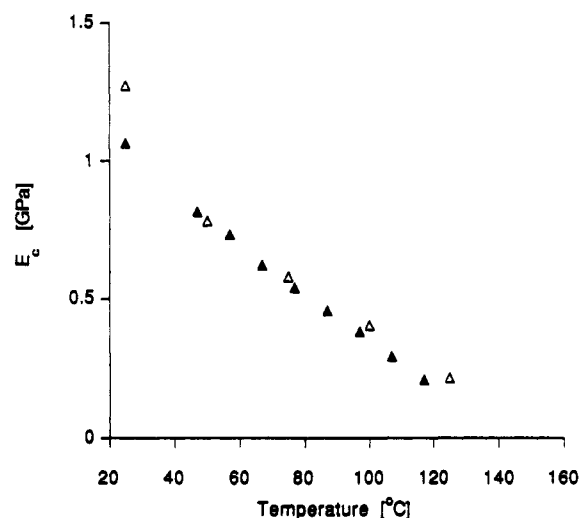


Figure 3. Temperature dependence of the modulus E_c (open symbols) and the crystalline shear modulus (closed symbols) (see text).

developed based on the assertion that even in modestly oriented polyethylene the so-called amorphous, or non-crystalline, phase, which in its relaxed state typically has a modulus on the order of megapascals, has been extensively stretched, ultimately causing a yield in the adjacent crystalline phase. Thus, it would appear that the stiffness of these extended amorphous segments, at this point in the deformation process, exceeds the lowest crystal shear modulus and no longer is the limiting contribution to the modulus of the moderately oriented polymer. This view was corroborated by the fact that values of E_c derived for a variety of polymers coincided with the respective shear moduli of the different materials for which data were available.¹²

Thus, an (indirect) attempt was made to calculate the temperature dependence of the shear modulus based on dimensional changes in the crystalline (orthorhombic) unit cell of polyethylene. These dimensions were recently determined by wide-angle X-ray diffraction as a function of temperature employing a well-characterized, highly oriented sample.^{9,10} The results of these measurements are summarized in Figure 4. This figure reveals that the c -axis displayed a very small, linear decrease with temperature ($\alpha = -12.6 \times 10^{-6} \text{ K}^{-1}$); the b -axis remained essentially constant, whereas the a -axis expanded significantly with increasing temperature. An exaggerated schematic representation of the thermal lattice expansion

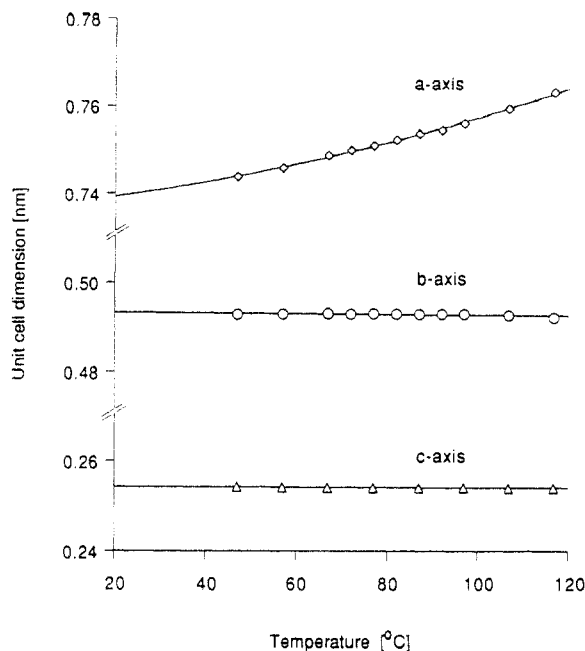


Figure 4. Temperature dependence of the unit cell dimensions of orthorhombic polyethylene.¹⁰

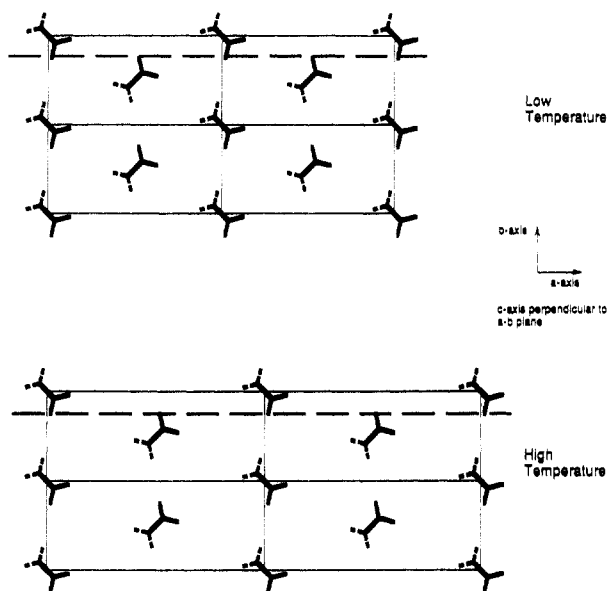


Figure 5. Exaggerated representation of the effect of temperature on the dimensions in the *a-b* plane of the polyethylene orthorhombic unit cell. The broken line represents the plane of the lowest shear modulus.

in the *a-b* plane is depicted in Figure 5.

The small expansion of the cross-sectional area of the *a-b* plane ($\sim 3\%$ over 100°C) could, in principle, cause a small decrease of the axial crystalline modulus derived from X-ray measurements. Due to experimental errors in this technique this decrease is, however, generally not observed,^{4,5} and the possible effect on E_h is neglected in this work.

By contrast, larger temperature-dependent effects are anticipated for the off-axis crystalline moduli. Since these properties are dominated by the weak van der Waals interactions between the present polyethylene chains, they are bound to be sensitive to small changes in the interchain dimensions.

The crystallographic data of Figure 4 were used as a basis for a numerical evaluation of the effect of temperature on the crystalline shear modulus. In the present study, only the crystalline shear modulus in the *a-c* plane

(shear direction = *c*-axis; see Figure 5) is considered, since this shear mode, as shown by Tashiro et al.,¹⁶ is of the lowest modulus. For the intermolecular H-H and C-H interactions a Lennard-Jones potential was employed:

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \quad (5)$$

where ϵ is the minimum potential energy and σ is the interatomic distance where the potential energy equals zero.

From the basic unit cell dimensions in Figure 4 the positions of the hydrogen atoms were determined under the assumptions that the angles $\angle\text{HCH} = 109.5^\circ$ and $\angle\text{CCC} = 112^\circ$, the distance $\text{H-C} = 1.09 \text{ \AA}$, and the setting angle equals 45° .¹⁶

In the calculation, the covalent bonds were regarded to be rigid. The secondary C-H and H-H interactions were approximated by nonlinear springs, the force constant being defined as the second derivative of the potential functions (eq 5). Subsequently, the shear modulus in the *a-c* plane was calculated from the 3-dimensional arrangement of springs, the latter, off course, being specific for each temperature. Initially, the parameters for the Lennard-Jones type potentials were taken from Scott et al.¹⁷ Using their parameter values, the shear modulus in the *a-c* plane (see Figure 5) was evaluated. From these calculations it was concluded that the contribution of the C-H atomic pairs was negligible. Therefore, only the H-H atomic interactions with $r < 3 \text{ \AA}$ were taken into account. The values of the parameters σ and ϵ were subsequently varied to yield the best fit of the calculated shear modulus to the experimentally observed temperature dependence of E_c . As shown in Figure 3, excellent agreement between E_c and the calculated *a-c* shear modulus was obtained with $\epsilon = 0.5 \text{ kcal/mol}$ and $\sigma = 2.43 \text{ \AA}$.

Although the above analysis was carried out in a somewhat unorthodox and empirical manner, the values of the parameters ϵ and σ , remarkably, are within range of the corresponding values found in the literature. For the minimum potential energy ϵ of an intermolecular van der Waals interaction, values are reported that range from 0.1 to 5 kcal/mol.^{17,18} The present value of 0.5 kcal/mol obtained for the H-H interaction is of the same order of magnitude as the bond strength between two methane molecules (0.3 kcal/mol).¹⁹ The value of 2.43 Å for the distance parameter σ yields an interatomic distance of 2.7 Å for the minimum potential energy. This leads to a value of the van der Waals radius of 1.35 Å, which is only slightly higher than reported values for hydrogen (1.2 Å).^{17,19} Considering the multiple interactions within the crystal, this deviation also seems to be acceptable.

The results presented in Figure 3 strongly suggest that there is a direct, and surprisingly simple, correlation between the temperature dependence of the Young's modulus of oriented polyethylene and the calculated variation with temperature of the crystalline shear modulus. This finding, once more, points to the importance of interchain interactions as a principal factor determining the mechanical properties of oriented polymers.

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Registry No. (CH₂=CH₂)_x (homopolymer), 9002-88-4.