3500 *Macromolecules* **1992,** *25,* 3500–3502

Thermal Conductivity in Ultraoriented Polyethylene

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Received November 13, 1991; Revised Manuscript Received March 4, 1992

ABSTRACT: On a set of strips of ultraoriented polyethylene of ultrahigh molecular weight the thermal diffusivity has been measured at room temperature. The draw ratio λ was between 12 and 250. The diffusivity increases with draw ratio and begins to level off at about $\lambda = 50$. The maximum diffusivity $\alpha \sim 1.9 \times 10^{-5}$ m^2/s corresponding to a thermal conductivity of $k = 37.5$ W/mK obtained in the stretching direction is 4 times that of steel. In the perpendicular direction the diffusivity decreased to $\alpha = 10^{-7}$ m^2/s (i.e., half its initial value). The plot of conductivity versus modulus enables an extrapolation to the ultimate modulus (300 GPa), yielding $k^{\parallel} \leq 80$ W/mK. This value being higher than that of many metals corresponds to a crystal in the impurity-governed range, i.e., the lower limit of crystal thermal conductivity.

Introduction

The properties of oriented polymers are fascinating subjects of research since the anisotropy ratio of the direction-dependent properties may be quite large. The theoretical elastic moduli of the polyethylene (PE) crystal illustrate this fact: in the chain direction $c_{33} = 257$–320 GPa is calculated, while in the perpendicular direction $c_{11} = 6.3$–13.8 GPa and $c_{22} = 9.3$–12.5 GPa are predicted.[1] Brillouin scattering experiments on one sample of ultraoriented PE[2] gave the elastic constants $c_{33} = 115.6$ GPa and $(c_{11} + c_{22})/2 = 7.3$ GPa. Since chain orientation is almost perfect at higher draw ratios,[3,4] the increase in the modulus is a result of structural perfection. One property that is very sensitive to orientation, crystallinity, and crystal perfection is the thermal conductivity. A review for polymers is given in ref 5. We have shown that the dependence on the orientation of samples with different crystallinities could be described by an aggregate model.[6] Other approaches have been used to calculate the contributions of amorphous and crystalline phases and their orientation separately,[7] although these approaches involved unmeasurable parameters. But already the results of ref 8 showed that an aggregate model becomes inappropriate for highly drawn samples. In a recent paper Issi and co-workers[9] published quite spectacularly high values of the thermal conductivity of PE fibers up to 30 W/mK parallel to the fiber direction.

We have measured the thermal diffusivity both in the orientation direction and in the perpendicular direction of two sets of samples, low-density PE (LDPE) stretched up to $\lambda = 7$ and a linear low-density PE (LLDPE), by drawing samples prepared by gelation/crystallization from solution. The draw ratios were $\lambda = 12$–250. Other investigations of the latter samples are published in ref 3. For the former set the direction-dependent sound velocities at gigahertz frequencies have been measured[10] by Brillouin scattering. This enables us to discuss the thermal conductivity results in terms of the simple equation

$$k = \frac{1}{3}\rho c_p v l \tag{1}$$

where ρ = density, c_p = specific heat per mass at constant pressure, v = sound velocity, and l = mean-free path of energy-propagating phonons. While very often used, this equation is oversimplified for a real understanding of the underlying processes. This may be demonstrated using the data in ref 11.

The drawing process changes the density and the specific heat only slightly. The isotropic longitudinal sound velocity of low-density PE is $v = 2433$ m/s and that of high-density PE $v = 2400$ m/s.[12] [There is obviously a remarkable dispersion between the hypersonic and the ultrasonic range. In the latter the velocity of sound is only 1970 m/s at 30 °C (Arnold, N. D.; Guenther, H. H. *J. Appl. Polym. Sci.* **1966,** *10,* 731).] In LDPE samples drawn to $\lambda = 7$ it is $v^{\parallel} = 5500$ m/s and $v^{\perp} = 2300$ m/s parallel and perpendicular to the stretching direction, respectively.[10] Thus $v^{\parallel}/v^{\perp}$ contributes only by a factor of 2.4 to the heat conduction ratio. The experimental value on the same sample, however, is $k^{\parallel}/k^{\perp} = 16$. $k^{\perp}$ itself decreases to about $k_0/2$. The corresponding drop in the velocity of sound $v^{\perp}$ amounts only to 2.5%. Obviously other effects are even more prominent than just the velocity of sound. One is the direction-dependent phonon density distribution in anisotropic solids which strongly enhances the conductivity by focusing the group velocity into the parallel direction. This effect of an anisotropic sound velocity has been stressed in ref 11 where details may be found. Considering this effect properly, we arrive at 6.4 as the total factor of the elastic contribution. The excess is due to the mean-free path, which is extremely sensitive to structural perfection.

Experimental Section

The sample preparation of the low-density PE is described in detail in ref 11. The preparation of the ultraoriented samples is described in ref 3.

The direction-dependent diffusivity measurements were performed by a modified De Senarmont method: Point heating with a laser beam causes elliptical heat flow within a thin slab or foil. The temperature $T(t,x)$ of a spot at a certain distance x in the direction parallel or perpendicular to the draw direction was monitored as a function of time t by infrared radiation using an In–Sb detector. The result was fitted to the (3-dimensional) solution of the heat conduction equation incorporating the actual boundary conditions. During the measurements the samples are held under high vacuum. The heat losses by infrared radiation from the surfaces are experimentally minimized by reflecting shields close to the samples. The method has been compared to measurements of the PTB (Physikalisch Technische Bundesanstalt, Braunschweig, Germany) using a sample of reactor steel in the temperature range 100–300 °C and a PTFE (polytetrafluoroethylene) sample in the temperature range 60–200 °C. The agreement is within 5%. Details may be found in ref 13. For sample widths $w < 5$ mm the conditions for an accurate measurement are no longer met. We then used an experimental

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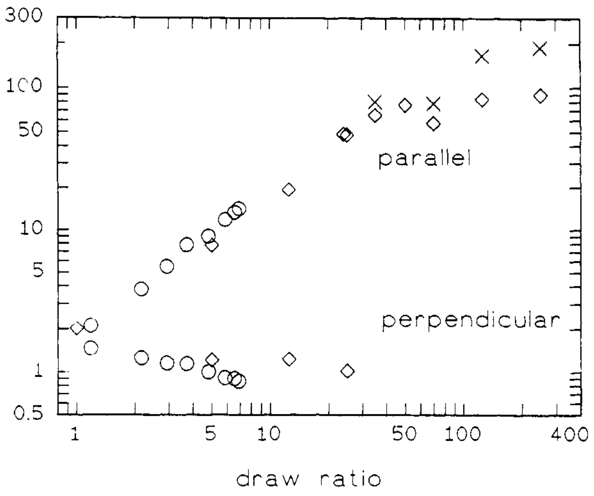

Figure 1. Thermal diffusivity of oriented polyethylene as a function of draw ratio λ at $T = 300$ K: (◇) measurements on ultraoriented LLDPE, (×) dto corrected to a sample width of $w = 5$ mm, (○) measurements on LDPE under stress.

relation $k(w)$ in order to correct to a width of $w = 5$ mm. This relation has been determined using an oriented sample and splitting it into a sequence of smaller ones. Since the relation found is linear, the corrections are well-defined.

Results and Discussion

The results of our measurements are seen in Figure 1. The diffusivity in the chain direction increases with the draw ratio. The slope is the same for LDPE and ultrahigh molecular weight PE (UHMW-PE). This is not unexpected since orientation of the crystals must proceed[14] very similarly upon stretching in both polymers. The shift of UHMW-PE on the λ-scale is due to the difference in the structure of the isotropic material. It is disentangled in the case of UHMW-PE. Thus the first stages of deformation may be different. In the perpendicular direction the diffusivity decreases to about half of its initial value. The absolute thermal conductivity in the chain direction can be calculated by $k = \alpha\rho c_p$. Using $\rho = 987$ kg/m^3 (for the sample with the highest draw ratio[3]) and $c_p = 2$ J/(g K) we arrive at a factor of 2×10^6 N/(m^2 K) for the conversion. For the other samples the relative accuracy may be 5%. The overall accuracy should be better than 20%.

We can compare our results to that of Issi and coworkers.[9] Their "Pennings-fiber" with $M_w \sim 1.5 \times 10^6$ and $E'' \sim 100$ GPa is similar in its properties to our material with $M_w = 6 \times 10^6$ and $E'' \sim 130$ GPa (5 kHz) and $E'' \sim 90$ GPa (0.11 kHz) for $\lambda \sim 250$. Our uncorrected value (we present the uncorrected value as well because, without considering any correction procedure, it poses a lower bound of the true value) of 17 W/mK is somewhat lower than the 30 W/mK of ref 9. However, the corrected value of 37.5 W/mK fits well. To judge the agreement, one should have the following in mind:

The temperature in ref 9 was 200 K, and in this work it was 300 K. In this temperature range, the thermal conductivity is about constant (increasing in the amorphous regions and decreasing in the crystalline regions).

In conclusion we state that the above-mentioned facts count for an excellent agreement. It further means that both very different measuring methods yield consistent values. The high unidirectional conductivity in ultraoriented PE can be taken as a fact. This is additionally corroborated by our measurements perpendicular to the chain direction. The anisotropy ratio $A = k^{\parallel}/k^{\perp}$ finally amounts to $A \sim 180$ for the corrected values (uncorrected 90) and is comparable to that of pyrolytic graphite[17] with $A \sim 220$ and boron nitrite with $A \sim 80$–90.[18] $A \sim 90$–100 of a polydiacetylene single crystal has been published in ref 16. But for this polymer the parallel conductivity amounts only to 1 W/mK corresponding to the relatively small modulus $c_{\text{chain}} \sim 45$ GPa.[19]

While for draw ratios $\lambda \leq 4$ the behavior may well be described by an aggregate model using the X-ray orientation parameter of the crystal c-axis,[6] this is not possible for the higher draw ratios. This statement may be understood by considering the principal bounds for a system of differently oriented units whose properties are considered invariant under deformation. One is the direct (parallel) averaging and the other the inverse (series) averaging. For both, the isotropic value, i.e., the orientationally averaged conductivity tensor, represents an invariant:

$$k^{\circ} = \frac{1}{3}\,\text{trace}\,\mathbf{k} = \frac{1}{3}(k^{\parallel} + 2k^{\perp}) \tag{2}$$

$$\frac{1}{k^{\circ}} = \frac{1}{3}\,\text{trace}\,\mathbf{k}^{-1} = \frac{1}{3}\left(\frac{1}{k^{\parallel}} + \frac{2}{k^{\perp}}\right) \tag{3}$$

Equation 2 is for the parallel averaging and eq 3 for the series averaging. It immediately follows that for the perpendicular conductivities the relations in eq 4 (parallel) and eq 5 (series) must hold.

$$k^{\perp} = \frac{3k^{\circ} - k^{\parallel}}{2} \tag{4}$$

$$k^{\perp} = 2\frac{k^{\circ}}{3 - k^{\circ}/k^{\parallel}} \geq \frac{2}{3}k^{\circ} \tag{5}$$

Using the experimental values, eq 4 clearly would give negative results and the measured $k^{\perp}$ eventually falls short of the lower limit of eq 5. Thus the aggregate model will not be applicable in the case of highly oriented polymers. This is also obvious by the fact that the thermal conductivity and the modulus still increase in the range of complete chain orientation (e.g., constant birefringence). In contrast to these mixing rules the thermal conductivity of this material can alternatively be considered as that of a macroscopic single crystal with more or less severe distortions. A first step in this direction was given in ref 8. These authors found a relation between Young's modulus at 200 K and the thermal conductivity in the stretching direction at 100 K. At these temperatures the amorphous phase is already in the glassy state, i.e., solidlike. We have taken this view in a recent paper.[11] We have shown that the mean-free path is the quantity which finally determines the magnitude of the thermal conductivity in an oriented polymer system. The velocity of sound varies with $v \propto c_{33}^{1/2}$ to its limiting value and so does the phonon focusing effect. The specific heat contribution is even counterbalancing to a small amount. The reason is that a higher sound velocity corresponds to a higher Debye temperature for the phonons in the stretching direction

$$\theta_D^{\parallel}/\theta_D^{\circ} = v^{\parallel}/v^{\circ} \tag{6}$$

where v° is the average sound velocity for comparison. Hence, at constant temperature, the argument T/θ_D in the Debye function becomes smaller, giving a lower specific heat.

In a nearly perfect structure, the mean-free path and in turn the thermal conductivity in the range of the conductivity maximum depends primarily on the remaining imperfections. A very crude estimation plotting the tem-

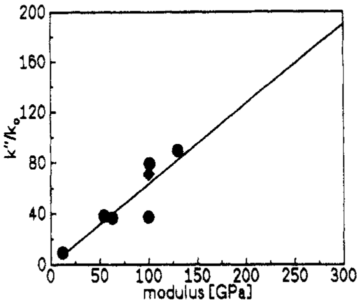

Figure 2. Conductivity–modulus relation of oriented polyethylene. k_0 is the isotropic value (0.41 W/mK). The modulus is measured at 110 Hz.[3] Only the corrected values are depicted. The ♦ is from ref 9. The solid line corresponds to eq 7.

peratures of the conductivity maximum versus the Debye temperature using data of diamond and graphite yields $T(k_{\max}) \sim 40$ K for the parallel direction of a PE crystal. If such a maximum could be observed, we would be dealing with "perfectly oriented crystallike" material.

The conductivity range accessible in principle for these structures may be more than 1 decade higher. This estimate is based upon the theoretical conductivity in the impurity-free Umklapp regime of a single crystal calculated by ref 15.

The present type of material includes a lot of typical defects. Its conductivity must be defect controlled. We can try to establish a relation to Young's modulus like in refs 8 and 20. The idea behind this is the following: In eq 1 the velocity of sound gives $k \sim E^{1/2}$. If structure scattering is dependent on the wavelength of the phonons, another exponent enters, which in a special model is just 2. As is seen in Figure 2 the corrected values follow a linear relationship in concordance with the cited literature.[8] Including all our experimental points we arrive at

$$k''/k_0 = -0.216 + 0.634E'' \text{ (GPa)} \qquad (7)$$

At $T = 300$ K, $k_0 = 0.41$ W/mK, giving a limiting value of ~80 W/mK at $E'' = 300$ GPa. If we consider one of the two points at ~100 GPa as an outlier, this value will be increased to ~84 W/mK, but this is more or less marginal. We believe the extrapolated value to be a reliable estimate of a material produced by stretching already existing molecules. It appears to be unrealistic in this case to obtain a structure so devoid of entanglements, folds, and kinks that its conductivity will be governed by Umklapp processes.

Conclusions

The effect of the ultraorientation process on the thermal conductivity of PE is as significant as that on Young's modulus. Whereas the modulus may further increase only by a factor of 1.5–2, the heat conduction could increase theoretically by a factor of ~15. For the present procedures of producing high-strength material, an upper limit of $k^{\parallel} \sim 80$ W/mK is estimated corresponding to a factor of ~4. Thus thermal conductivity measurements may provide a valuable tool for monitoring the development of structural perfection. Moreover, it is a challenge to produce an insulating material with such high unidirectional thermal conductivity in excess of that of many metals.

Acknowledgment. We gratefully acknowledge the help of W. Hurler for providing the width correction curve. This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the SFB 239.

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Registry No. PE (homopolymer), 9002-88-4.