on the theoretical estimates of various properties is displayed in Table III. One sees that the solubility parameter and the elastic constants change relatively little but that the ratio α_P/κ_T (hence, our estimate of the thermal expansion coefficient) exhibits a very strong dependence on the atomic radii, jumping from its original negative value to a positive one (which actually is close to the experimental ratio α_P/κ_T for glassy atactic polypropylene under the appropriate conditions).

Thus, small uncertainties in the potential parameters can well be tolerated in predicting the solubility and the elastic constants with our approach but appear to render our estimate of the thermal expansion coefficient unreliable.

Registry No. Polypropylene (homopolymer), 9003-07-0.

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Theoretical Study of the Influence of Strain Rate and Temperature on the Maximum Strength of Perfectly Ordered and Oriented Polyethylene

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ABSTRACT: The stochastic model for failure of perfectly ordered and oriented polymer filaments, previously introduced, is used for a theoretical study of the influence of strain rate and temperature on the maximum tensile strength of polyethylene of two (monodisperse) molecular weights (2.2×10^4, 3.3×10^5). The model predicts polyethylene to display a strong strain rate and temperature dependence of the maximum strength; higher strength is predicted at low temperatures and at high strain rates. At strain rates exceeding 10^4 min^{-1} the theoretical ultimate strength ($\sim$24 GPa) is recovered for both molecular weights studied. At high strain rates and at low temperatures, polyethylene of both high and low molecular weight fails in a brittle mode and fracture is accompanied by a substantial amount of C–C bond cleavage. Failure at low strain rates and/or high temperatures is found to be creep-like and is dominated by secondary bond breakage. The effects of the strain rate and, to a lesser extent, of the temperature are more pronounced for low than for high molecular weight polyethylene. Good qualitative agreement is found between the present theoretical work and related experimental data.

1. Introduction

In a previous theoretical study,[1] we developed a stochastic model based on the kinetic theory of fracture,[2,3] to describe failure of perfectly oriented and ordered polymer filaments. The model was applied to polyethylene, and it was used to investigate the effect of the molecular weight on the maximum tensile strength at constant (room) temperature and at a fixed strain rate (1 min^{-1}).

It is well-known that the test temperature and strain rate, among other testing conditions, have a major effect on the measured fiber properties.[4,5] Employing the previously introduced model,[1] we explore here the influence of both the strain rate and the temperature on the tenacity

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of perfectly oriented and ordered polyethylene fibers of finite (monodisperse) molecular weight. The present study deals exclusively with the effect of temperature on fracture phenomena that are initiated by the external stress. Temperature effects on internal degrees of freedom, such as rotation and translation modes, are not considered; therefore, the present approach is incapable of describing the polymer melting transition and the temperature dependence of the moduli.[6] The present explorative study is nevertheless an instructive exercise that allows us to investigate the influence of temperature on the bond breakage process itself and its limiting effect on the maximum tensile strength.

2. Stochastic Model

The essential features of the model are briefly reviewed. The filament is represented by a 3-dimensional (x, z, y) simple cubic array of up to $6 \times 6 \times 1000$ nodes, each node representing a group of m methyl units. Neighboring nodes are joined in the x and z directions by m secondary bonds of the van der Waals type, each single bond having an elastic constant K_2. Only nearest-neighbor interactions are considered. In the y direction, stronger forces with elastic constant K_1 account for the primary (C–C) bonds. For simplicity, we assume that the displacements of the network nodes along the coordinate axes are mutually independent, and we focus on the displacements along the y axis, along which the fiber is strained.

The simulation is started from an unstrained array in which all the bonds are unbroken, except for a few randomly distributed broken C–C bonds, which account for the finite molecular weight of the polymer chains. The fiber is then strained at a constant rate, and the bonds are broken at a rate

$$v = \tau \exp[(-U + \beta\sigma)/kT] \qquad (1)$$

where U is the activation energy, τ is the thermal vibration frequency, T is the (absolute) temperature, β is an activation volume, and σ is the local stress

$$\sigma = K\epsilon \qquad (2)$$

Here, K and ϵ are the elastic constant and the local strain, respectively. Local temperature rises due to high rates of deformation are neglected. This assumption seems reasonable in view of the exceedingly small dimensions of the "test sample" (~36 polymer chains per cross section).

The model is executed with the help of a Monte Carlo lottery, which visits the bonds at random and breaks a bond according to a probability

$$p = v/v_{\max} \qquad (3)$$

Here, $v_{\max}$ is the rate of breakage of the most highly strained bond in the array. After each visit of a bond, the "time" t is incremented by $1/[v_{\max}n(t)]$, where $n(t)$ is the total number of unbroken bonds at time t. After a small time interval δt has elapsed, the bond-breaking process is stopped. The "sample" is then strained along the y axis by a small amount, given by the strain rate $\dot{\epsilon}$, and the network is relaxed to its minimum energy configuration, using the method described in ref 1. After that step, secondary bonds are allowed to reform between nodes coming in perfect regard to each other, to within a small error δy.[1] The system is then relaxed again, and the axial stress at one end of the "fiber" is calculated. The Monte Carlo process of bond visiting is then restarted for another time interval δt. And so on, and so forth, until the sample breaks. This procedure, performed at a constant strain rate and temperature, yields a stress–strain curve, the maximum of which is referred to as the maximum tensile strength of the fiber for a given molecular weight under specified "test conditions".

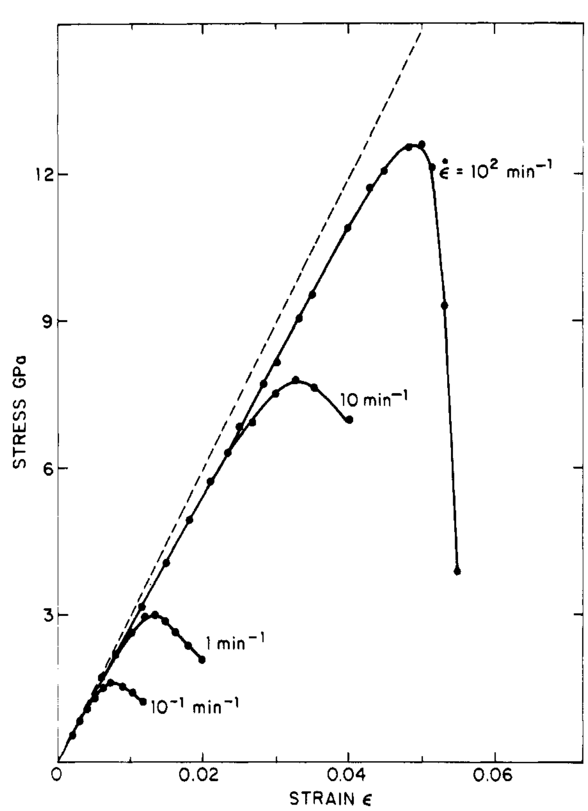

Figure 1. Stress–strain curves calculated for a monodisperse polyethylene fiber with $M = 2.2 \times 10^4$ at different strain rates $\dot{\epsilon}$. Three-dimensional simple cubic arrays of up to $6 \times 6 \times 1000$ nodes (with $m = 100$ methyl groups per node) were used in the simulations. van der Waals forces were broken (or reformed) in groups of 25 units.[1] Cylindrical boundary conditions along the x axis were imposed. Curves for $\dot{\epsilon} = 1$ min^{-1} and $\dot{\epsilon} = 10$ min^{-1} have not been calculated in their entirety, due to a lack of computer time. The dashed line indicates a slope equal to the theoretical modulus (=300 GPa). The values of δt used in the simulations range from 0.02 s (at $\dot{\epsilon} = 10^{-1}$) to 0.000 01 s (at $\dot{\epsilon} = 10^4$). As far as we could determine, our results are insensitive to these values provided that δt is chosen much smaller than the total time for breaking.

3. Results

Approximate values of the parameters in eq 1 and 2 for polyethylene have been reported and discussed in ref 1. For secondary bonds the shear modulus $K_2 = 3$ GPa and $U = 0.65$ kcal/mol, with $\beta = (2.5\ \text{Å})^3$. For primary bonds the axial modulus $K_1 = 300$ GPa and $U = 25$ kcal/mol, with $\beta = (1.54\ \text{Å})^3$. The atomic vibration frequency $\tau = 10^{11}\ \text{s}^{-1}$. As mentioned in the introduction, the present work does not consider the temperature dependence of the atomic vibration frequency and the elastic moduli. Such a study would be a formidable task, well beyond the scope and intent of this paper.

3.1. Effect of Strain Rate at Room Temperature. Figure 1 shows the strain rate dependence of the stress–strain curves for low molecular weight monodisperse polyethylene ($M = 2.2 \times 10^4$). The figure shows that the strain rate has no effect on the modulus (=300 GPa, dashed line). The maximum strength and the mode of failure, by contrast, display a marked dependence on the strain rate $\dot{\epsilon}$. At low rates ($\dot{\epsilon} = 10^{-1}$–1 min^{-1}), intermolecular slippage, involving rupture of secondary bonds, occurs in preference to primary bond breakage. Under such circumstances, plastic deformation by flow is observed and the curves exhibit a bell shape with a slow decrease of the stress toward the breaking point. At higher rates ($\dot{\epsilon} > 10$

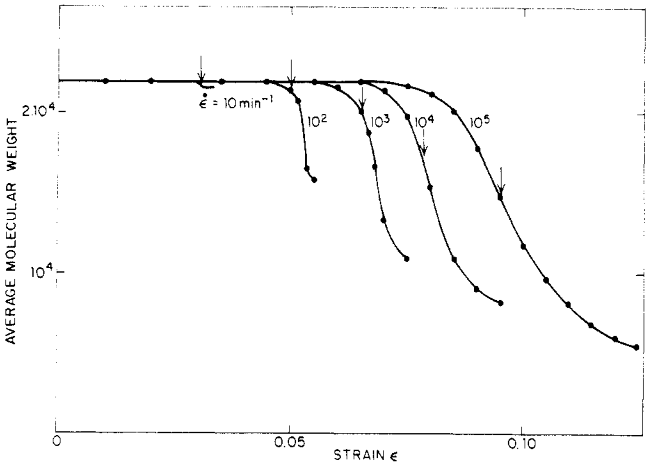

Figure 2. Dependence of the average molecular weight on the strain for monodisperse polyethylene with initial $M = 2.2 \times 10^4$ at different strain rates $\dot{\epsilon}$. The arrow indicates the maximum in the corresponding stress–strain curve (see Figure 1).

min^{-1}), both primary and secondary bonds are found to rupture and, as a result, fracture of the sample appears to proceed in a brittle manner (see Figure 1, $\dot{\epsilon} = 10^2$ min^{-1}).

This observation is further illustrated in Figure 2, which displays the changes of the average polymer molecular weight, monitored during the various strain "experiments". This figure reveals an important decrease in the molecular weight at high strain rates. Note also that an increase in the strain rate by a factor of 10 shifts these decay curves to higher strain values by ~1%, in agreement with other theoretical work.[4] Further investigation shows that an increase in the strain rate also decreases the total (i.e., van der Waals and primary) fraction of broken bonds at the maximum strength. Indeed, the higher the rate, the shorter the time interval a stressed bond spends at a certain stress level and the smaller the probability for bond breaking at that level. That result, together with the observed increase with $\dot{\epsilon}$ of the number of broken C–C bonds at maximum strength (arrow in Figure 2), clearly indicates that low molecular weight samples, although commonly characterized by creep-like behavior, exhibit brittle fracture when strained at very high rates.

For high molecular weight samples ($M = 3.3 \times 10^5$), the calculations indicate that fracture is always of a brittle nature, even at a rate as low as 0.01 min^{-1}. Results (not reproduced) also show that the total fraction of broken bonds in a sample with $M = 3.3 \times 10^5$ is about 10 times smaller than that observed for $M = 2.2 \times 10^4$, at constant $\dot{\epsilon}$. This is primarily due to the much smaller number of broken van der Waals bonds in the former case.

The rate dependence of the maximum strength of perfectly oriented and ordered polyethylene of the two molecular weights studied is plotted in Figure 3. For the low molecular weight sample a very strong dependence is found. For example, the maximum tensile strength increases from ~1.5 to 7 GPa upon increasing the strain rate from 10^{-1} to 10 min^{-1}. These observations are in qualitative agreement with recent experimental results of Cansfield et al.[7] for low molecular weight polyethylenes ($\bar{M}_n = 2 \times 10^4$, $\bar{M}_w = 6 \times 10^4$–$10^5$). These authors reported that the tensile strength increased from 0.65 to 1.2 GPa upon increasing the strain rate from 10^{-3} to 10^{-1} s^{-1} (~10^{-1} to 10 min^{-1}). The experimentally observed strain rate dependence is weaker than in the present calculations. This is to be expected, however, since the theoretical predictions are for monodisperse polyethylene of $M = 2.2 \times 10^4$; the experimental observations are for specimens having a significant fraction of higher molecular weight material for which the $\dot{\epsilon}$ dependence of the strength is less pronounced (see Figure 3 and ref 8 and 9). Figure 3 also indicates that even low molecular weight specimens ($M = 2.2 \times 10^4$), in principle, can reach the ultimate strength (~24 GPa) provided that they are strained at sufficiently high rates ($\dot{\epsilon}$ ~ 10^4 min^{-1}) and temperature raises can be neglected. Note that our results do not predict the decrease with rate of the strain at maximum stress, observed experimentally.[7] However, these effects are also associated with a strong rate dependence of the Young's modulus, which is due to a nonperfectly ordered and oriented structure, in contrast to that assumed in the present work (see Concluding Remarks).

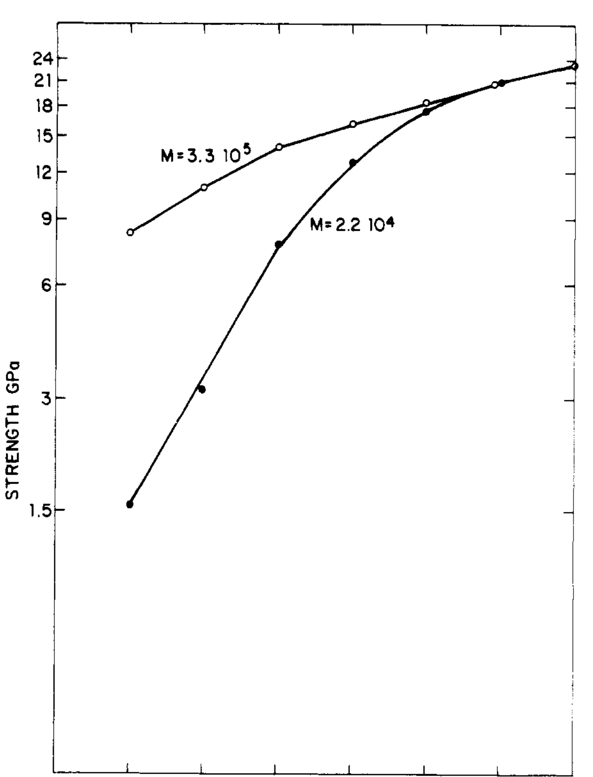

Figure 3. Dependence of the maximum strength on the strain rate for two different molecular weights.

Table I
Dependence of the Time at Maximum Strength on the Strain Rate $\dot{\epsilon}$ for Two Different Molecular Weights

	time at maximum strength, s	
$\dot{\epsilon}$, min^{-1}	$M = 2.2 \times 10^4$	$M = 3.3 \times 10^5$
10^{-1}	2.88	18.6
1	0.73	2.24
10	0.16	0.32
10^2	0.028	0.036
10^3	0.0039	0.0042
10^4	0.00046	0.00046

Of course, as the strain rate is increased, the time to failure of a specimen decreases. Values for the time at the maximum stress are given in Table I. The data presented in the table also reveal that, for a given $\dot{\epsilon}$, the time for fracture increases with the molecular weight since the stress that is reached is higher. At very high rates ($\dot{\epsilon} > 10$ min^{-1}), these times become independent of M, since the corresponding values for the maximum stress are comparable and close to the ultimate tensile strength (see Figure 3).

It is important to note that the strain rate dependences of the strength and of the mode of failure itself are very sensitive to the temperature (see also ref 6).

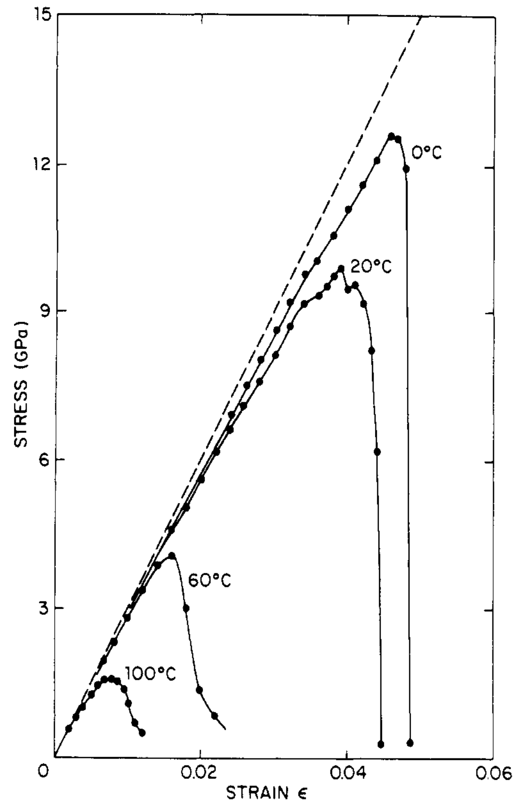

Figure 4. Stress–strain curves calculated for polyethylene with $M = 3.3 \times 10^5$ at different temperatures. The figure is for a strain rate $\dot{\epsilon} = 1$ min^{-1} and $\delta t = 0.02$ s. The dashed line indicates a slope equal to the theoretical modulus (=300 GPa).

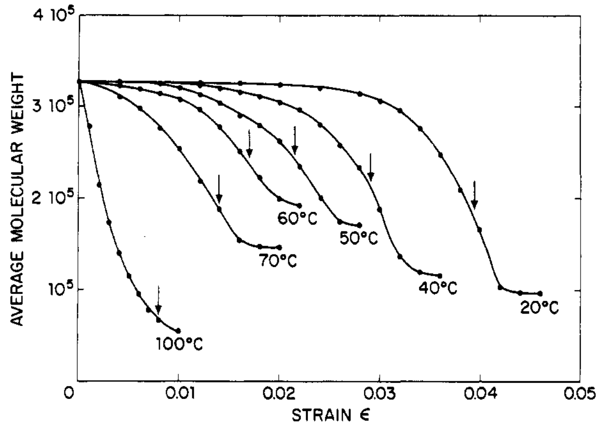

Figure 5. Dependence of the average molecular weight on the strain for monodisperse polyethylene with initial $M = 3.3 \times 10^5$ at different temperatures. The arrow indicates the maximum in the corresponding stress–strain curve (see Figure 4).

3.2. Effect of Temperature at Constant Strain Rate (1 min^{-1}). Figure 4 shows the dependence of the stress–strain curves on the temperature for the high molecular weight polyethylene ($M = 3.3 \times 10^5$). The theoretical tensile modulus (=300 GPa) is naturally recovered in all the stress–strain curves, irrespective of the temperature (see section 4). Below room temperature, a brittle mode of fracture is observed, accompanied with molecular fracture. However, if the temperature is increased (20 °C $< T <$ 60 °C), creep-like behavior occurs, as is inferred from an increase in the fraction of broken secondary bonds (from ~6% to ~55%) and a reduction in the fraction of broken C–C bonds. This results in a less important decrease in the average molecular weight at a test temperature of 60 °C in comparison with that occurring at 20 °C, see Figure 5. Above 60 °C, the simulations show an important increase in the thermal activation of the primary bonds, which start to break already at low strain values. This is a consequence of the relatively low effective activation energy (25 kcal/mol) of those bonds.[10] That low value is also supported by the good agreement between our model and experiment for creep rupture data.[11] Accordingly, a significant decrease in the average molecular weight is observed (Figure 5). This phenomena is further illustrated in Figure 6, which shows the molecular weight distribution at the maximum stress at two different temperatures. At 60 °C (and below) about 50% of the macromolecules still are of the initial molecular weight. By contrast, at 100 °C, none of the initial macromolecules is intact.

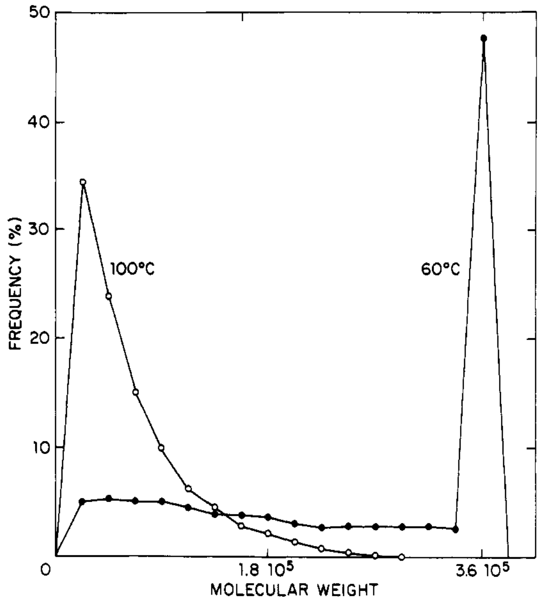

Figure 6. Molecular weight distribution at maximum stress for monodisperse polyethylene with $M = 3.3 \times 10^5$ at two different temperatures.

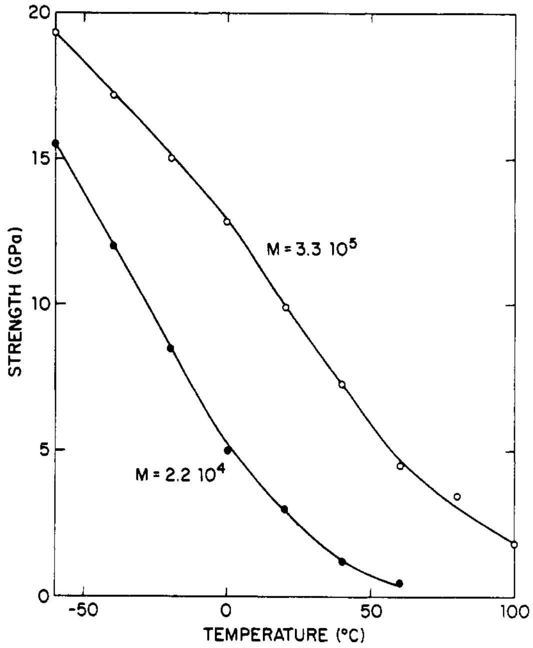

Figure 7. Dependence of the maximum strength on the temperature for the two different molecular weights studied.

The results of the temperature dependence of the maximum strength for the two molecular weights studied are summarized in Figure 7. At low temperatures ($T <$ −50 °C), the curves for both a low and a high molecular weight converge toward approximately the same value of

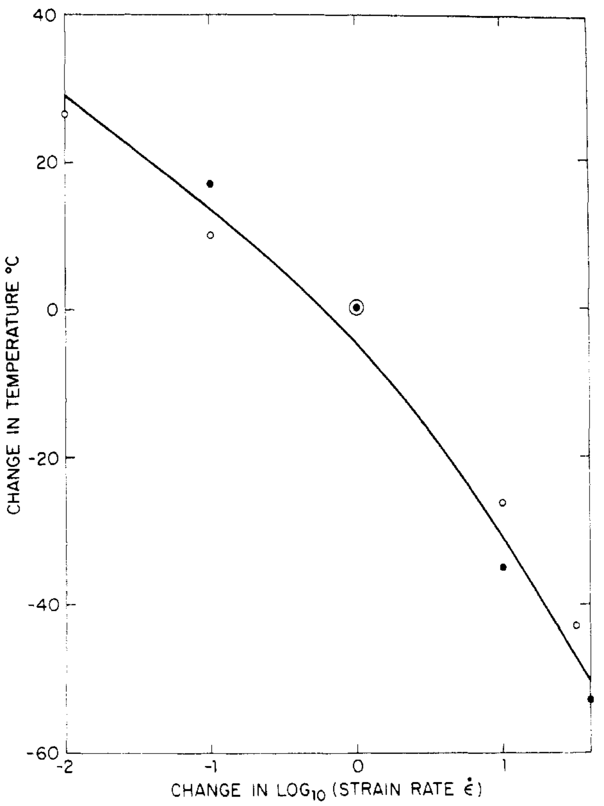

Figure 8. Change in temperature plotted against the change in the logarithm of the strain rate needed to produce the same change in strength. The symbols are as follows: (●) $M = 2.2 \times 10^4$; (○) $M = 3.3 \times 10^5$.

the strength. As the temperature is increased, the strength rapidly decreases. Extrapolation with temperature of the tenacity of the high molecular weight sample leads to a zero strength value at about 130 °C, which is in the range of the experimental melting point of polyethylene. Although our approach is incapable of predicting that transition, the above result indirectly lends support to the choice of parameter values used in our thermal description of the bond fracture process.

The calculations presented in sections 3.1 and 3.2 gratifyingly indicate, in agreement with a bulk of experimental and theoretical work notably for elastomers, that the effect of decreasing temperature on the strength is quite similar to that of increasing rate of deformation; see e.g., ref 12–14. It is tempting to inquire whether these effects can be unified in any way. Figure 8 compares the change in temperature to the change in the logarithm of the rate of strain needed to produce the same changes in strength for two different molecular weights. Although the rate and temperature dependence of the maximum strength are strongly dependent on the molecular weight (see sections 3.1 and 3.2), the sets of data for the two molecular weights appear to be well represented by one "master curve". This finding is in good agreement with experimental results on the yield stress of many different polymers.[15] However, the slope of the curve in Figure 8 is about twice that reported in ref 15. That discrepancy can be partly accounted for, at high temperatures, by the dependence of the modulus itself on T and, at high strain rates, by local temperature raises. Both effects would lead to a decrease of the slope in Figure 8.

4. Concluding Remarks

The present study is certainly not an exhaustive investigation of the effect of temperature and strain rate on the maximum strength of perfectly ordered and oriented polyethylene fibers. In its current form, the stochastic model employed in this work is incapable of accounting for the temperature and/or strain rate dependence of the relaxation rates, the atomic vibration frequency, the activation energies and volumes, or even the crystalline unit cell dimensions of the polymer. As a result, the calculated Young's modulus appears independent of the testing conditions (sections 3.1 and 3.2). This result is in flat contradiction with experimental data obtained in studies on the mechanical properties of oriented polyethylene fibers; it is well-documented that Young's modulus, as well as the dynamic modulus, increases with strain rate, or frequency, and decreases with increasing temperature.[16–17] It could be argued that those reported experimental results were obtained with moderately oriented fibers (modulus 10–100 GPa), in which a significant fraction of amorphous material was present. And it could be suggested that the experimentally observed temperature and rate dependence of the modulus is primarily caused by the (dynamic) mechanical properties of the amorphous phase. (Indeed, it has been reported that the temperature dependence[17] of the modulus of oriented polyethylene decreased with higher values of the modulus, i.e., with a reduced fraction of amorphous and misaligned material.) We do not wish however to address this issue, simply because the model, in its present state, does not allow us to do so.

It is the purpose of the present study to investigate the effects of temperature and strain rate on the primary and secondary bond-breakage process and to explore their limiting contributions to the maximum strength of perfectly ordered and oriented polyethylene. The presented calculations indicate that the maximum strength is markedly dependent on both the temperature and the strain rate. This strong influence of temperature and strain rate is observed without invoking the effect of these two experimental variables on the modulus, which would enhance such dependence even more. These findings are in general agreement with experimental results.

A final word of caution should be mentioned with regard to the quantitative results obtained in the present study, such as the slopes of the tenacity/temperature and tenacity/strain rate curves, the amount of C–C bond cleavage, and the resulting changes in molecular weight. These results are critically dependent on exact knowledge of the values of the parameters in the failure model, such as the effective activation energies and volumes. Particularly in light of the uncertainties in the values of these parameters (see discussions in ref 1), it is evident that the quantitative results presented in this study should not be taken too literally and should be regarded merely as expected trends.

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(10) Indeed, taking $U = 45$ kcal/mol leads to no observation of this effect at temperatures below 300 °C. Our choice of $U = 25$

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kcal/mol is supported by thermal degradation experiments, which are found to proceed in two stages: an initial stage characterized by low U ($\sim$25 kcal/mol) and accounting for 1-10% weight loss, and a second stage for the remaining part which degrades with higher U ($\sim$55 kcal/mol) (see: Regel, V. R.; Amelin, A. V.; Pozdnyakov, O. F.; Sanfirova, T. P.; Ioffe, A. F. *Int. Symp. Macromol. 1972*, Helsinki, Finland, July 2-7, 1972, *5*, 163). That initial stage of the degradation process has been explained by the existence of weak links in the polymer, which, in turn, determine its mechanical properties.

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Comparison of Experiment and the Proposed General Linear Viscoelastic Theory. 2. Stress Relaxation Line Shape Analysis

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ABSTRACT: For testing the proposed general linear viscoelastic theory, the molecular weight (MW) range of the studied samples is extended to as low as $1.24M_e$, overlapping the previous MW range from $13M_e$ to $31M_e$. It is found that the proposed general theory describes quantitatively the linear viscoelastic relaxation spectra over the entire MW range that has been studied. The conclusions about the $\mu_X(t)$, $\mu_B(t)$, and $\mu_C(t)$ processes made in paper 1 are further confirmed. Especially, the theory explains why and how the modulus plateau gradually disappears with decreasing MW. From the spectrum line shape analysis in the $\mu_A(t)$ region, a very significant phenomenon is discovered: With decreasing MW, the friction coefficient for the polymer chain segment to move in the direction perpendicular to the chain contour decreases and converges to the friction coefficient value along the chain contour, which is independent of MW. The effect is attributed to the anisotropic distribution of free volume on the polymer chain—i.e., more free volume at the polymer chain ends than in the interior portion of the chain.

I. Introduction

The effect of chain entanglement on polymer viscoelastic behavior has been an important research subject of polymer physics.[1,2] The concept of chain entanglement started more than half a century ago. Not until the introduction of the idea of reptation by de Gennes[3] to account for the constraint effect of entanglement was it possible to describe the dynamics of long polymer chains in concentrated systems in a meaningful way. In 1978, Doi and Edwards[4-7] recognized the important relation of the reptation motion and the mechanical properties of a concentrated system and derived a rheological constitutive equation. Their theory has successfully explained many characteristic features of viscoelasticity of concentrated polymer systems.

The Doi-Edwards theory mainly dealt with the polymer dynamics and viscoelastic behavior in the terminal region. In the previous report (referred to as paper 1 below),[8] it was theoretically shown how four modes of polymer molecular dynamics affected the linear viscoelasticity of flexible linear polymers. The four dynamic modes $\mu_A(t)$, $\mu_X(t)$, $\mu_B(t)$, and $\mu_C(t)$ are respectively the Rouse chain motion between two adjacent cross-linked points (assuming entanglement points fixed), the chain slippage through entanglement links, the primitive chain-length fluctuation, and the reptational motion corrected for the chain-length fluctuation effect. A general stress relaxation function containing all these dynamic modes was obtained. It was shown that the theory is universal as we normalize molecular weight (MW) with respect to the entanglement MW, M_e, which can be determined from the plateau modulus.

The theory was used to analyze the stress relaxation line shapes of three polystyrene samples of very narrow MWD and of MW's ranging from 186 000 to 775 000. Consistent good agreements between theory and experimental results were obtained. The theory also explained the MW dependence of the zero-shear viscosity ($\eta_0 \propto M^{3.4}$ for $M > M_c$ and $\eta_0 \propto M$ for $M < M_c$) and the steady-state compliance J_e.

Experimentally, the stress relaxation modulus does not show a clear plateau region in the medium and low-MW range ($<8M_e$). Analyzing the stress relaxation line shape in this MW region is a very critical and important test of the theory, even though the theory has predicted the MW dependence of the first and second moments of the relaxation time spectrum (i.e., η_0 and J_e).

Here, a series of polystyrene samples of very narrow MWD and of MW's ranging from 422 000 to 16 700 ($31M_e$-$1.24M_e$) have been studied. The measured stress relaxation line shapes are uniquely quantitatively described by the proposed general linear viscoelastic theory. The conclusions about the $\mu_X(t)$, $\mu_B(t)$, and $\mu_C(t)$ processes made in paper 1 are further confirmed. The prominent role played by the $\mu_B(t)$ mode of motion in the medium and low-MW region is clearly demonstrated. The theoretical analysis of the experimental results shows why and how the modulus plateau gradually disappears with decreasing MW.

About the $\mu_A(t)$ process, a very significant phenomenon is discovered in this study: The friction coefficient for a polymer chain segment to move in the direction perpendicular to the chain contour (extracted from the line shape analysis of the $\mu_A(t)$ process) decreases with decreasing MW in the MW region MW $< 10M_e$. The ratio of K'/K (i.e., the ratio of the friction coefficients for the polymer chain segment to move perpendicular to vs. along the chain contour) decreases from a plateau value of 3.3 at high MW to a limiting value of 1 at low MW ($M_c >$ MW $> M_e$), while K is independent of MW. The physical meaning of this phenomenon is explained in terms of the free volume associated with the polymer chain ends.

II. Theory

Following a step-shear deformation and before the

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