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Yielding of polyethylene through propagation of chain twist defects: Temperature, stem length and strain-rate dependence

S. Nikolov *, D. Raabe

Department of Microstructure Studies and Metal Forming, Max-Planck-Institut für Eisenforschung, Max-Planck-Street 1, 40237 Düsseldorf, Germany

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Abstract

The temperature, the stem length and the strain-rate dependence of the yield stress of polyethylene (PE) is investigated via a modified crystal plasticity approach. Yielding is considered in terms of nucleation and propagation of [001] screw dislocations with Burgers vector $c/2$ due to migration of 180° chain twist defects. The stress-induced twist motion within the dislocation cores is modeled as an Eyring activated rate process. This gives an inelastic contribution to the dislocation core energy depending on the stem length and the strain rate and results in improved predictions of the crystal plasticity approach. The model is compared to available experimental data as well as to the predictions of the modified crystal plasticity approach proposed by Brooks and Mukhtar.

Keywords: Polyethylene; Yield stress; Crystal thickness

1. Introduction

Despite the considerable theoretical and experimental efforts since the early 1970s, the molecular mechanisms behind yielding of semi-crystalline polymers in general, and polyethylene crystals in particular, are still a matter of controversy. The main difficulties in the investigation of these materials are caused by their very complex morphology and the impossibility to isolate and study separately the amorphous and the crystalline phases. Most often, yielding of polymer crystals is attributed either to the generation and propagation of screw dislocations [1–7], or to partial melting-recrystallization under adiabatic conditions [8–10]. Peterson [1] and Young [2] have shown that thermal fluctuations, coupled with local shear stress, may generate screw dislocations from the edges of the crystalline lamellae. Flory and Yoon [8] proposed an alternative concept, namely, that the applied stress and the adiabatic heating during deformation cause a partial melting-recrystallization process. In general, it is believed that crystal plasticity could not explain the observed dependence of the intercrystalline long period on the temperature of deformation, while the melting-recrystallization concept is unable to explain the development of preferred crystallographic orientation during deformation and phenomena like crystal phase change and twinning, which have been reported to occur in polymer crystals [5].

On the other hand, the strain-rate and the pressure dependence of the yield stress of polyethylene have been studied using the Eyring transition state theory [11,12]. Despite the ability of the Eyring approach to reproduce the experimental data for semi-crystalline polymers with good accuracy, there are some conceptual difficulties to interpret its main fitting parameter, the so-called activation volume, in terms of the crystalline properties and geometry. Actually, a consistent, physically-based integration of the strain-rate dependence into a crystal plasticity approach for semi-crystalline polymers still remains an open issue. Another difficulty is the inability of the classical crystal plasticity to predict both the temperature and stem length dependence of the yield stress of polyethylene in its original formulation [3]. Recent improvements in this direction have been proposed by Brooks and Mukhtar [6] and Argon et al. [13] and are commented further.

In the present work, we propose a modified crystal plasticity approach, which is capable to reproduce the experimentally observed temperature, stem length and strain-rate dependence of the yield stress of polyethylene. First, we show that the approach of Brooks and Mukhtar predicts a negative core

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* Corresponding author. Tel.: +49 211 6792 653; fax: +49 211 6792 333.
E-mail address: nikolov@mpie.de (S. Nikolov).

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energy for higher temperatures due to the overestimated temperature dependence of the core energy. In order to solve this problem, we consider [001] screw dislocations in PE crystals as resulting from nucleation and propagation of 180° chain twist defects with associated Burgers vector *c*/2. The stress-induced twist motion within the dislocation cores is proposed to be an Eyring activated rate process, which allows us to incorporate the strain-rate dependence in the crystal plasticity approach and to obtain more realistic predictions for the stem length dependence of the yield stress. The activation barrier for twist motion is modeled according to the work of Tuijnman [14] on α-relaxation in polyethylene crystals. The predictions of the proposed model are compared to available experimental data for different polyethylene grades as well as to the predictions of the crystal plasticity approach developed by Brooks and Mukhtar.

2. Modified crystal plasticity approach

2.1. The model of Brooks and Mukhtar

According to the model developed by Brooks and Mukhtar [6] (hereafter referred to as the BM model), the macroscopic yield stress of semi-crystalline polymers subjected to uniaxial tension or compression reads:

$$\sigma_y = \frac{K}{\pi}\alpha(T)\exp\left(-\frac{2\pi\Delta G_c}{Kb^2 l} - 1\right) \qquad (1)$$

where K is the crystalline shear modulus related to ($hk0$)[001] slip; ΔG_c is the activation energy necessary for nucleation of [001] screw dislocations; b is the corresponding magnitude of the Burgers vector; l represents the stem length along the c lattice direction in the crystalline lamella, usually tilted at a certain angle to the lamella normal. The function $\alpha(T)$ is given by:

$$\alpha(T) = \frac{b}{r_0}\exp\left(\frac{2\pi E_0}{Kb^2 l}\right) \qquad (2)$$

where E_0 and r_0 are the dislocation core energy and radius, respectively. In addition, $\alpha(T)$ is empirically fitted so that Eq. (1) can reproduce the yield stress at different temperatures:

$$\alpha(T) = 0.4992 - 0.00119T \qquad (3)$$

Combining Eqs. (2) and (3), we can express the core energy per unit length E_0/l in the BM model as:

$$\frac{E_0}{l} = \frac{Kb^2}{2\pi}\ln\left[\frac{r_0}{b}(0.4992 - 0.00119T)\right] \qquad (4)$$

As in [6], we take the magnitude of the Burgers vector to be equal to the c lattice parameter, i.e. $b = 0.254$ nm. The dislocation core radius obtained by computer simulations is $r_0 = 1$ nm [15]. The expression for the shear modulus K (MPa) as a function of temperature is taken from Brooks et al. [16]:

$$K = 3740.806 - 8.106T + 0.0189T^2 - 0.000025T^3 \qquad (5)$$

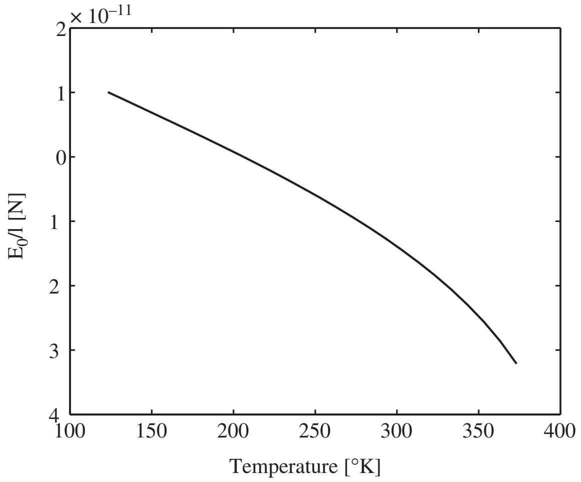

Fig. 1. Dislocation core energy per unit length vs. temperature obtained with the BM model.

The core energy per unit length as a function of the temperature obtained with Eq. (4) is plotted in Fig. 1. It is seen that the core energy predicted by the BM model is positive only at very low temperatures and becomes increasingly negative for temperatures $T > 200$ °K, which has no physical sense. The change of the Burgers vector to $b = c/2$ proposed by some authors [5,7] encounters the same problem but at higher temperatures. Moreover, the temperature dependence of the core radius and the Burgers vector in Eq. (4) have only a marginal effect on the estimated core energy because, within the temperature window $0 < T < 400$ °K, the lattice parameters a and b of the PE unit cell increase with temperature by about 7 and 2%, respectively, while the c lattice dimension remains virtually unchanged [17]. In conclusion, the assumption about the temperature dependence of the core energy in the BM model, Eqs. (3) and (4), seems to be not justified.

2.2. Dislocations due to chain twist defects

The results obtained with the BM model suggest that the the direct application of the crystal plasticity for small-molecules crystals to yielding of polymer crystals may not give a physically consistent explanation of the experimental evidence. In order to solve this problem, here we reconsider the underlying microscopic deformation mechanisms taking into account the long-chain nature of the polymer molecules. In the following, we consider yielding of PE crystals as the result of stress-induced generation and propagation of chain twist defects within the crystal, as previously suggested in [5,7]. This molecular mechanism (Fig. 2) has been proposed long ago by Fröhlich [18] for relaxation in paraffins. Later, Mansfield and Boyd [19] developed a more refined model for the dielectric and the viscoelastic relaxation processes in PE crystals postulating the existence of smooth 180° twists. More recently, molecular dynamics studies confirmed that 180° twist defects in the crystals can propagate smoothly along the chains like solitary waves (solitons) and are stable against thermal fluctuations [21,22]. On the other hand, Crist et al. [4] and

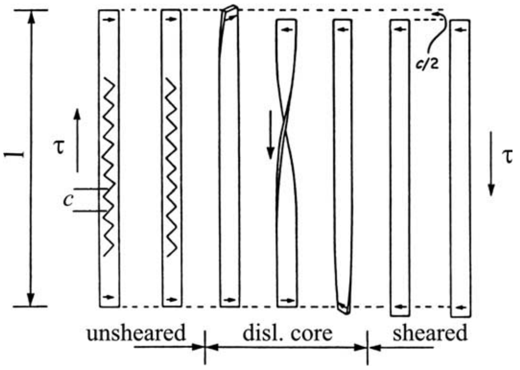

Fig. 2. Screw dislocations with Burgers vector $b=c/2$ due to propagation of 180° chain twist defects (after Boyd [20]); τ is the applied shear stress, the zig-zag lines within the stems represent the conformation of the PE molecules.

Séguéla et al. [5] used the chain twist concept to interpret the temperature dependence of the yield stress of polyethylene in the context of dislocation generation and propagation.

In order to analyze dislocations obtained through the propagation of chain twist defects, it is necessary to better understand the processes and the energetics in the dislocation cores containing the twists (Fig. 2). It is noted that the structure of such cores and the associated core energy are profoundly different from that observed in small-molecules crystals. In the latter, the dislocation cores are line defects and the strain in the core region is very large—atoms are displaced by about one lattice constant over the entire length of the dislocation. In contrast, the twists are localized in relatively narrow zones along the chains and the strain in the misfit region caused by the twist is only a few per cent [21]. Away from the twist, the distortion rapidly decreases to zero because the forces exerted by the surrounding chains bring the distorted chain back into the crystallographic register [20].

From the above considerations, we expect the core energy of a screw dislocation related to the propagation of a smooth twist to be much smaller than the corresponding core energy of a small-molecules crystal. The total core energy related to a moving twist defect can be divided into two parts: (i) elastic energy from distortion within the misfit zone and (ii) free energy change due to the stress-induced twist motion. Then, the change in free energy ΔG associated with the formation of a nucleus of a pair of pure screw dislocations under a shear stress τ can be written similarly to the expression given by Brooks and Mukhtar [6] as:

$$\Delta G = \frac{Kb^2 l}{2\pi} \ln\left(\frac{r}{r_0}\right) + 2(E_0 + \delta U) - \tau b l r \tag{6}$$

where the logarithmic term on the right side is the elastic energy of interaction between the two dislocation segments separated by a distance r; E_0 is the elastic energy from distortion in the misfit zone; δU is the energy change related to twist motion and the last term is the irreversible work done by the applied stress τ. The same expression is valid for the nucleation of a single dislocation at a distance $r/2$ from the lamella edge because of the existence of image forces.

The critical width of the nucleus r_c corresponds to a maximum of $\Delta G(r)$ and can be found by partial differentiation of Eq. (6) with respect to r. Since the core energy $(E_0+\delta U)$ is assumed to be independent on r for $r>2r_0$, this gives:

$$r_c = \frac{Kb}{2\pi\tau} \tag{7}$$

The activation energy ΔG_c is found by replacing of Eq. (7) in Eq. (6):

$$\Delta G_c = \frac{Kb^2 l}{2\pi}\left[\ln\left(\frac{Kb}{2\pi r_0 \tau}\right) - 1 + \frac{4\pi}{Kb^2 l}(E_0 + \delta U)\right] \tag{8}$$

If the thermal fluctuations are large enough to supply energy ΔG_c, a screw dislocation at a distance $r_c/2$ from the lamella edge could form and eventually expand under the applied shear stress τ.

To our knowledge, there is no continuum theory available for the estimation of the elastic misfit energy E_0 of a twisted PE chain embedded in a perfect PE crystal. Molecular simulations give the maximum misfit strain of such a chain to be about 5% and the total misfit length along the chain direction to be about 70 CH_2 units, or 9 nm [21]. These values suggest that E_0 must be much smaller than the core energy estimated for typical dislocations. Given that the core energy in small-molecules crystals is 5–10% of the total dislocation energy, E_0 related to twists should represent even a smaller fraction of the total energy and can be neglected in a first approximation.

For the stress-induced twist motion, we suggest that this is an Eyring activated rate process for the following reasons. First, the yield stress of semi-crystalline polymers is rate dependent and can be described by the Eyring transition states theory, and more specifically, by the so-called cooperative model of Fotheringham and Cherry [11,12]. Secondly, according to the well-known Orowan equation, the plastic shear rate of the crystal is proportional to the velocity of the dislocations. Thirdly, in the context of migration of twist defects, it is reasonable to assume that the velocity of the [001] screw dislocations is proportional to the velocity of the twists, so that a higher migration rate of the twists results in a higher velocity of the screw dislocations. With these considerations in mind, we can relate the plastic shear rate in the crystal $\dot{\gamma}^p$ to the shear stress τ through the effective energy barrier for twist motion ΔU by an Eyring equation:

$$\dot{\gamma}^p = \dot{\gamma}_0\left[\exp\left(-\frac{\Delta U - \tau V}{kT}\right) + \exp\left(-\frac{\Delta U + \tau V}{kT}\right)\right]^n \tag{9}$$

where $\dot{\gamma}_0$ is a reference shear rate, V is an activation volume, k is the Boltzmann's constant and n is a cooperative exponent expressing the probability for simultaneous (cooperative) movement of n chain segments in the twist zone [11]. The first term in the square brackets is the probability for twist motion along the direction of the applied stress and the second one represents the probability for backward motion. The Eyring theory implies that the effective activation barrier at equilibrium ΔU is lowered in the direction of the applied stress by an amount τV and becomes higher by the same amount for reverse motion. As we consider the yielding process, the stress τ is relatively high so that $\tau V > kT$ and the second term in the square brackets of Eq. (9) can be neglected. This is equivalent to the picture where the twist motion is strictly in direction of the applied stress τ, while the probability for backward motion is practically zero. Then, Eq. (9) simplifies to:

$$\dot{\gamma}^p = \dot{\gamma}_0 \exp\left[-\frac{n(\Delta U - \delta U)}{kT}\right] \tag{10}$$

where $\delta U = \tau V$ is the free energy change related to twist motion. We can express δU from Eq. (10) as:

$$\delta U = \Delta U + \frac{kT}{n}\ln\left(\frac{\dot{\gamma}^p}{\dot{\gamma}_0}\right) \tag{11}$$

It is noted that in our formulation, the activation volume V is not needed as a model parameter.

The effective barrier to relaxation ΔU for a long twisted chain embedded in a perfect PE crystal in the absence of external stress has been derived by Tuijnman [14]. Here we assume that this is also the effective barrier to twist motion. Then, we can write ΔU as [14]:

$$\Delta U = \frac{\pi^2}{4} AB \tan h\left(\frac{Bm}{2A}\right) \tag{12}$$

where A and B are the bond energy and the force constant for twisting of one CH_2 group, respectively; $m = 2l/c$ is the number of monomer units in the crystal stem, which can be obtained from the stem length l and the unit cell dimension c.

The effective barrier ΔU has been derived under the assumption of long chains, or, equivalently, large stem lengths l. Molecular simulations [21,22] show that the twist accelerates when it approaches a chain end. As most chain ends are situated on the lamellae surfaces [23], it is reasonable to expect that twists will accelerate as they approach the lamellae surfaces. Consequently, close to the surface, the effective activation barrier ΔU should be lower than the theoretically predicted in Eq. (12). Therefore, we have to modify the expression for ΔU for lamellae with stem lengths comparable to the length of the twists. We can take these considerations into account by writing the effective barrier for twist motion as:

$$\Delta U = \frac{\pi^2}{4} AB \tan h\left(\frac{\beta B l}{Ac}\right) \tag{13}$$

where the scalar parameter $\beta < 1$ accounts for surface- and chain-end effects, while the theoretical energy barrier for twist motion in very thick crystals remains unchanged. We believe that the effective barrier for twist motion could also depend on the surface morphology, although we are not aware of detailed molecular simulations of polymer crystals with realistic surface morphology that can confirm or reject this assumption. In our model, these effects can be taken into account through the phenomenological parameter β. Such an influence of the morphology of the lamellae fold surfaces on the yield stress has been experimentally observed in Ref. [24].

In order to obtain the expression for the shear yield stress τ_y, we neglect the elastic misfit energy E_0 for reasons already discussed above, and replace δU, given by Eqs. (11) and (13), in Eq. (8). After some manipulations, this yields:

$$\tau_y = \frac{Kb}{2\pi r_0} \exp\left[-\frac{2\pi \Delta G_c}{Kb^2 l} - 1 + f(T, \dot{\gamma}, l)\right] \tag{14}$$

where

$$f(T, \dot{\gamma}, l) = \frac{4\pi}{Kb^2 l}\left[\frac{\pi^2}{4} AB \tan h\left(\frac{\beta B l}{Ac}\right) + \frac{kT}{n}\ln\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right)\right] \tag{15}$$

The effect of the hydrostatic pressure p is not taken into account in Eqs. (14) and (15) but it can be readily included in the context of the Eyring theory in the same way as, for example, in Truss et al. [12].

Assuming that (i) the Tresca yield criterion is valid, i.e. $\tau \le \sigma_y/2$ and (ii) the macroscopic tensile or compressive rate, $\dot{\varepsilon}$, is proportional to the microscopic shear rate, $\dot{\gamma}$, the macroscopic yield stress σ_y is finally obtained from Eqs. (14) and (15) as:

$$\sigma_y = \frac{Kb}{\pi r_0} \exp\left[-\frac{2\pi \Delta G_c}{Kb^2 l} - 1 + \mathcal{F}(T, \dot{\varepsilon}, l)\right] \tag{16}$$

where

$$\mathcal{F} = \frac{4\pi}{Kb^2 l}\left[\frac{\pi^2}{4} AB \tan h\left(\frac{\beta B l}{Ac}\right) + \frac{kT}{n}\ln\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right)\right] \tag{17}$$

and the magnitude of the Burgers vector is $b = c/2$. The above modeling of the yield stress unifies the crystal plasticity approach and the cooperative Eyring theory for viscoplastic flow. Eqs. (16) and (17) contain only one new parameter with respect to the models already reported in the literature, namely, the scalar β accounting for the properties of the fold surfaces. The model is valid for stem lengths greater than the length of a fully developed twist defect, which is about 9 nm as obtained from atomistic calculations [21,22], and for temperatures above the glass transition temperature T_g. Below T_g, the amorphous phase becomes much stiffer and the balance law for free energy change, Eq. (6), should include a contribution from the local elastic deformation of the amorphous phase around the dislocation nucleus.

3. Results and discussion

3.1. Materials and model parameters

In order to compare the predictions of our model to the experiment, we use experimental data for different polyethylene grades investigated in [12,16,25]. For the temperature dependence of the yield stress, we use data from Brooks et al. [16] for three PE grades referred to as materials A, B and C and subjected to tension at a strain rate of $2.08 \times 10^{-3}\ s^{-1}$. The measured lamellar thickness d for materials A, B and C is 10.7, 11.1 and 18.4 nm, respectively; the molecular weight M_w is 126,000; 206,000 and 131,000, respectively; the branch content per 1000 carbon atoms is 21:1000; 6.2:1000 and 0.1:1000 C, respectively. The lamellae thickness d can be converted into a corresponding stem length $l = d/\cos\theta$ based on previous studies of PE showing that the chain axis is tilted at an angle $\theta = 34.5°$ to the lamella normal [26,27]. For the dependence of the yield stress on the stem length, we refer to data reported in Kazmierczak et al. [25]. These authors investigated the yield of high density polyethylene in compression in order to exclude undesirable phenomena observed in tension, such as micro-necking and void generation. The molecular weight and the branch content for the samples used in [25] are $M_w = 120{,}000$ and 5:1000 C, respectively. The deformation is performed at room temperature at a compression rate of 1.1×10^{-3} s^{-1}. For the strain rate dependence, we compare the model predictions for different strain rates and temperatures to the experimental data reported in Truss et al. [12].

The material constants in Eqs. (16) and (17) are chosen as follows: the shear modulus $K(T)$ is computed with Eq. (5); the magnitude of the Burgers vector is $b = 0.127$ nm; the dislocation core radius is $r_0 = 1$ nm; the activation energy is taken as $\Delta G_c = 60kT$ [6] where the Boltzmann's constant is $k \approx 1.38 \times 10^{-23}$ J/K. For the bond energy A and the twisting force constant B of one CH$_2$ unit we use the values identified by Tuijnman [14]: $A^2 = 8.1 \times 10^{-19}$ and $B^2 = 4.3 \times 10^{-21}$ J/mon rad^2, respectively. The reference strain rate is taken as $\dot{\varepsilon}_0 = 2.08 \times 10^{-3}$ s^{-1}. This value is chosen purely for convenience, a physically based reference strain rate could be derived but is beyond the scope of this work. For the simulations with the BM model, we use the same material parameters, except for the magnitude of the Burgers vector, which is taken as $b = 0.254$ nm [6]; the core-energy function $\alpha(T)$ for that model is given by Eq. (3).

3.2. Temperature dependence

We first consider the yield stress as a function of temperature. The experimental data for materials A, B and C are from Ref. [16]. In order to insure a fair comparison with the BM model, we use the same value of β for the materials A, B and C, $\beta = 0.15$, albeit the important differences in the morphologies of the samples would justify a separate fitting for each material.

The yield stress for material A, which is a low density branched polyethylene, is shown in Fig. 3. It is seen that our model gives a fairly good prediction of the yield stress for temperatures $T > 200$ °K. The underestimation of the yield stress at low temperatures can be explained with the increasingly important stress contribution from the amorphous phase, which is not taken into account here. The amorphous phase stiffens considerably below the glass transition temperature, which for polyethylene is $T_g \approx 150$ °K [4].

The model predictions and the experimental data for material B, a medium density polyethylene with low branch content, are plotted in Fig. 4. The model underestimates the experimental data for temperatures $T < 300$ °K. The discrepancy with the experiment can be easily diminished by setting a higher value for β than the currently employed, $\beta = 0.15$. We believe that the apparently higher activation barrier for twist motion in this case is due to the higher molecular weight of the material B with respect to the materials A and C, which results in different properties of the fold surfaces.

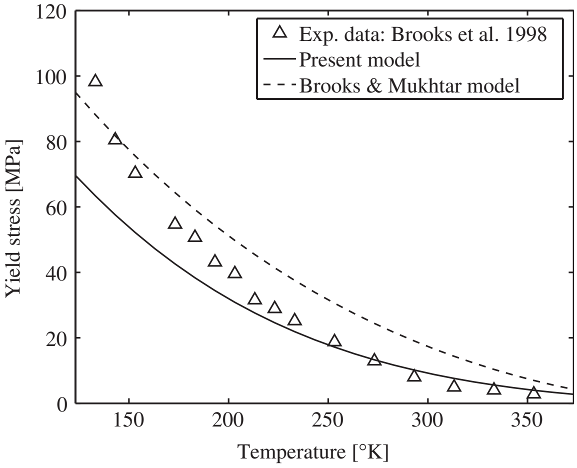

Fig. 3. Yield stress vs. temperature for material A.

The results for material C, which is a high density linear polyethylene, are depicted in Fig. 5. It is seen that the model reproduces well the observed yield stress for temperatures $T < 300$ °K. The overestimation of the yield stress at elevated temperatures is most probably due to a decrease in the intrinsic viscosity within the crystals with approaching the α-relaxation temperature, which for PE is about 330 °K [4].

3.3. Stem length dependence

The evolution of the effective activation barrier for twist motion ΔU with the stem length is shown in Fig. 6.

The theoretically predicted with Eq. (12) evolution of ΔU is too steep and leads to an overestimation of the experimentally observed yield stress for any of the considered polyethylene grades. The corrected activation barriers for the materials studied here are also shown. It is seen that the activation energy for twist motion is of the order of 1 eV ($\approx 1.6 \times 10^{-19}$ J) even for very thick crystals, which suggests that the stress-induced twist motion is an energetically favorable process. Similar

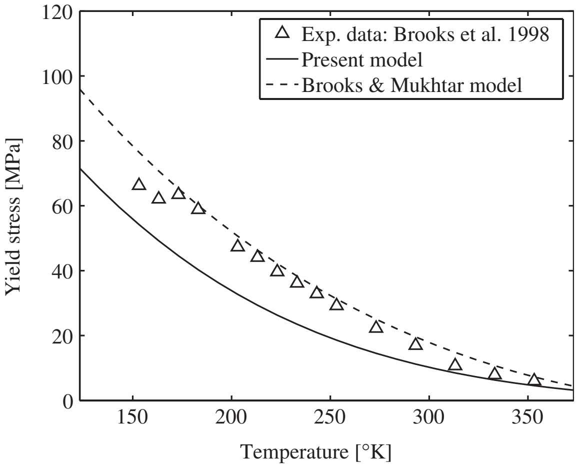

Fig. 4. Yield stress vs. temperature for material B.

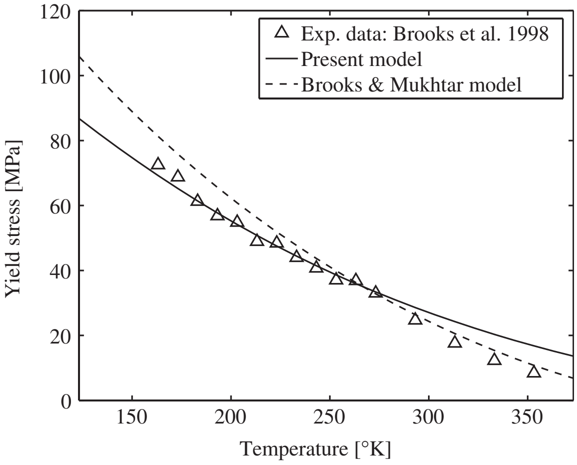

Fig. 5. Yield stress vs. temperature for material C.

values for the activation energy have been obtained by theoretical calculations for thermally activated [001] dislocation generation in polyethylene crystals [23].

In their study of the yield stress of both linear polyethylene and its copolymers, Kennedy et al. [10] performed tensile experiments for samples with different lamellae thicknesses and found that after an initial increase for thinner lamellae, the yield stress remains virtually unchanged over a broad range of thicknesses, which is in contradiction with the predictions of the crystal plasticity approach. In a recent work, Kazmieczak et al. [25] obtained HDPE samples with a broad range of crystal thicknesses by crystallization under high pressure, and their results confirmed the saturation of the yield stress with increasing the lamellar thickness. An attempt to model this behavior has been made by Argon et al. [13]. In addition to pure screw [001] dislocations, these authors considered the nucleation of edge and screw dislocation half loops from the lamellae edges. In [13], the mechanisms for nucleation of dislocation half loops are directly transposed from research made on small-molecules isotropic crystals [28]. However, it is unlikely that such half loops could exist and operate in polyethylene crystals. If we consider that the polymer crystals are made of chain stems where the intra-chain covalent bonds are much stronger than the Van der Waals interactions between the stems, it is unclear what would be the specific molecular mechanism for generation of half loops where the dislocation line crosses the chain direction and whether such a mechanism would be energetically favorable. Here we show that the experimentally observed results can be explained by considering only perfect screw dislocations due to chain twists.

For simulation of the stem length dependence, the parameter β for the HDPE used in [25] is identified as $\beta=0.12$. The cooperative exponent n is set as $n=1.4$ (see the next paragraph). The temperature is $T=293$ °K. The difference between the compressive rate ($\dot{\varepsilon}=1.1\times10^{-3}\ \mathrm{s}^{-1}$) and the strain rate used in the experiments for materials A, B and C ($\dot{\varepsilon}=2.08\times10^{-3}\ \mathrm{s}^{-1}$) is taken into account. The remaining model parameters have the values used for the previous simulations. The results are shown in Fig. 7. It is seen that the complex dependence of the yield stress on the stem length is reproduced better with the present approach compared to the classical crystal plasticity. The experimental data of Kazmieczak et al. [25] show that after an initial steep increase, the yield stress saturates with increasing the stem length. Actually, instead of a simple saturation behavior, our simulation predicts a maximum and a slight overshoot for stem lengths of about 50 nm and this seems to reflect correctly the experimentally observed behavior. This transition stem length is controlled by the parameter β-higher values for β correspond to lower values for the transition stem length. This behavior is naturally obtained with our model, but it is important to note that we did not incorporate any specific a priori assumptions predicting the yield stress saturation with increasing the stem length or the slight overshoot at the transition stem length. Also, the steep increase of the yield stress with increasing the stem length for $l<50$ nm is predicted reasonably well. In contrast, the BM model predicts a monotonic increase of the yield stress and gives less satisfactory results for stem lengths less than 70 nm.

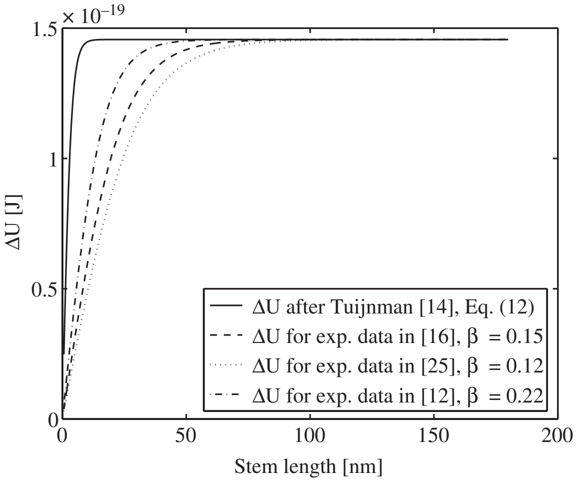

Fig. 6. Activation barrier for twist motion ΔU as a function of the stem length. Tuijnman's (Eq. (12)) and corrected (Eq. (13)) activation barriers for the materials studied here.

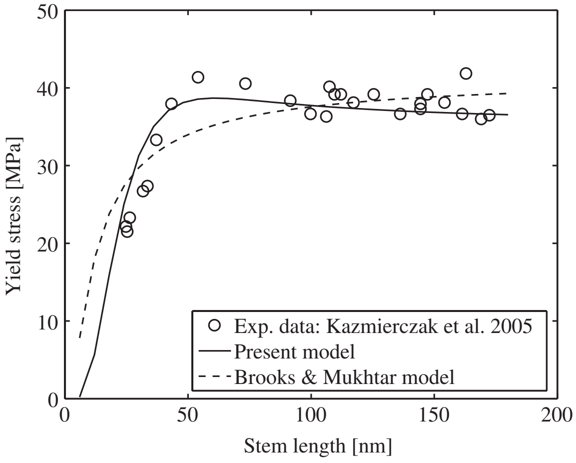

Fig. 7. Compressive yield stress of HDPE as a function of the stem length at room temperature.

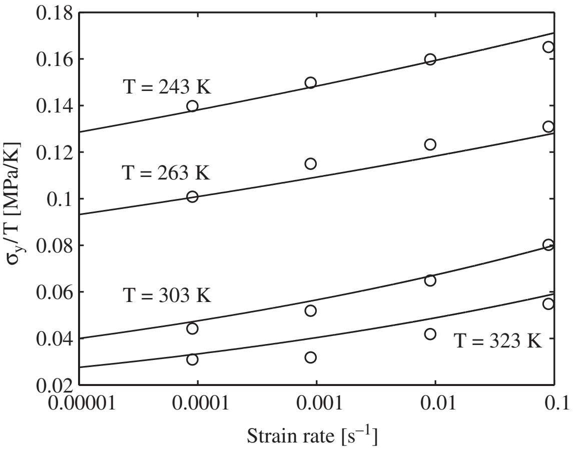

Fig. 8. Eyring plots of the yield stress of PE vs. strain rate at different temperatures: solid lines; model predictions, open symbols: experimental data from [12].

3.4. Strain rate dependence

For the strain-rate dependence of the yield stress, we use experimental data from Truss et al. [12]. The material is linear polyethylene with molecular weight $M_w = 220{,}000$. As the lamellar thickness has been not measured, for this simulation we take the lamellar thickness of material B, which has a similar molecular weight. The parameter β has been identified as $\beta = 0.22$. Four representative sets of data have been chosen at four different temperatures as indicated in Fig. 8. For the simulations at temperatures $T = 243$, 263 °K, the cooperative exponent has been identified as $n = 2.5$. For temperatures $T =$ 303, 323 °K, best fit is obtained with $n = 1.4$. The other parameters of the model have not been modified.

The results are shown in Fig. 8 and are in a reasonable agreement with the experimental data, despite the fact that we use a very simple Eyring model for the rate dependence. The decrease of n with increasing the temperature is in accord with the findings of Brooks et al. [16], who established the existence of a transition temperature above which the viscoelastic behavior prevails, while below that temperature the elastic–plastic type of behavior dominates. For example, for material B, which seems to be similar to the grade studied by Truss et al., the transition temperature is about 253 °K [16]. In the context of propagation of twist defects, the decrease of the cooperative exponent n with increasing the temperature can be interpreted in terms of a corresponding decrease of the twist length along the chains due to increased chain flexibility, lower effective viscosity in the crystal and easier bond rotation. The smaller values of n correspond to a higher strain rate dependence in the viscoelastic regime, while higher n at low temperatures describe the less pronounced strain-rate dependence characteristic for the elastoplastic behavior.

4. Conclusions

We have developed a micromechanical model for the temperature, the stem length and the strain-rate dependence of the yield stress of polyethylene considering only pure screw [001] dislocations. The model is based on the following assumptions: (i) the molecular mechanism for generation and propagation of [001] screw dislocations in polyethylene is the migration of chain 180° twist defects under the applied shear stress with magnitude of the Burgers vector $c/2$; (ii) the twist motion is a dissipative process and can be described by an Eyring activated rate process. The latter assumption allows us to incorporate the strain-rate dependence into the crystal plasticity approach in a physically consistent way, which has not been previously attempted. The effective activation energy for twist motion is found to be of the order of 1 eV. Therefore, twist generation and propagation must be an energetically favorable process at all temperatures. It is found that the theoretical activation barrier for twist motion estimated by Tuijnman [14] gives realistic results for very thick crystals but should be lower for typical thicknesses of PE crystals in order to match the observed values for the yield stress. The lowering of the activation barrier is proposed to be related to easier twist motion close to the fold surfaces. The predicted temperature dependence of the yield stress is in a good agreement with the available experimental data for both low- and high density PE grades. The model predicts that the yield stress of PE levels off with increasing the stem length, as observed experimentally. For stem lengths about 50 nm, our simulation predicts a maximum of the yield stress and a slight overshoot. However, this result is entirely due to the stem length dependence of the activation barrier for twist motion and not to activation of additional dislocation half-loop mechanisms, as recently proposed by Argon et al. [13]. The strain-rate dependence is found to increase with increasing the temperature, in accord with the existence of a transition temperature for the mechanical behavior of PE crystals from an elastoplastic to a viscoelastic regime, as suggested in [16]. In our model, this effect is reflected by the smaller value of the cooperative exponent n at elevated temperatures and is attributed to the smaller relative length of the twist defects due to easier bond rotation, increased chain flexibility and lower intrinsic viscosity in the crystal. Further work is required to extend the model for low temperatures below the glass transition by considering the free energy change due to the elastic deformation of the amorphous phase around the dislocation nucleus.

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