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Plastic deformation of polyethylene and ethylene copolymers

Part I *Homogeneous crystal slip and molecular mobility*

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The plastic behaviour of polyethylene and ethylene copolymers is studied under uniaxial tensile testing in parallel with the viscoelastic properties. Homogeneous plastic deformation is shown to take place at temperatures above the crystalline mechanical relaxation. The activation of homogeneous crystal slip is discussed in relation to the crystal lamella thickness and the molecular mobility of the crystalline chain stems. The thermally activated process of nucleation and propagation of screw dislocations that is proposed for the mechanism of the homogeneous crystal slip relies on the generation of 180° chain twists in the crystal stems of the sheared crystals. This kind of conformational chain defect is the basic link between the plastic and the viscoelastic properties of the materials. Homogeneous crystal slip can take place as long as the applied strain rate is consistent with the strain rate affordable by the screw dislocation propagation. The dependence on draw temperature of the crystal thickness in the fibre structure is ascribed to the stress-induced activation of 180° chain twists which allows an adjustment of the crystal thickness to the temperature of the experiment faster than an annealing treatment will. © *1998 Chapman & Hall*

1. Introduction

The study of the plastic deformation of semicrystalline polymers has long been a matter of controversy. Two different approaches have been developed. One is based on a purely crystallographic standpoint of the problem involving crystal slip and shear [1–5]. The other relies on a melting–recrystallization process, considering that the work of plastic deformation is comparable with the energy of melting [6–10]. The main reason for this controversy is that each of the two approaches can account for some experimental facts that have not found satisfactory explanation in the other approach. In fact, the crystallographic model has no clear explanation for the well-established dependence of the intercrystalline long period on the temperature of deformation. On the other hand, the energy model is unable to describe the crystallographic aspects of the plastic deformation such as the development of preferred crystal orientations, the formation of kink bands, together with the phenomena of crystal phase change and twinning.

There is a profusion of structural studies that support the crystallographic approach. On these bases, theoretical models have been further developed for predicting the yielding and drawing behaviour of semicrystalline polymers, assuming only crystal slip processes [11–15]. Conversely, investigations have been performed to provide experimental evidences to the melting–recrystallization scheme [16–18] which originates from a purely speculative idea [19].

In this paper, we discuss plastic deformation in polyethylene as the result of a crystal slip process fed by homogeneous nucleation and propagation of dislocations in the crystalline lamellae. A correlation is made between plasticity and viscoelasticity owing to a common mechanism for molecular mobility.

2. Experimental procedures

Three ethylene–butene copolymers made from Ziegler–Natta polymerization have been studied. Their molecular and physical characteristics are given in Table I. The materials have been compression moulded into sheets by melting at 160 °C and slow cooling at 20 °C min^{-1}.

True stress–strain measurements have been performed on an Instron tensile-testing machine equipped with a temperature-controlled oven and a video-monitored extensometer [20]. The hourglass-shaped specimens were cut from sheets 3 mm thick by means of a cutting die. The procedure for the determination of the true strains has been described elsewhere [21].

Crystal thicknesses have been assessed from the intercrystalline long period and the volume fraction crystallinity as measured from small-angle scattering (SAXS) and differential scanning calorimetry (DSC),

TABLE I Weight-averaged molar weights, M_w, number-averaged molar weights, M_n, co-unit concentrations, χ, specific gravities, ρ, weight-fraction crystallinities, α_c, volume-fraction crystallinities, ϕ_c, and crystal thicknesses, l_c, of the copolymers

Copolymer	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	χ (mol%)	ρ	α_c	ϕ_c	l_c (nm)
A	157	30	1.2	0.945_5	0.67	0.63	17.8
B	136	31	2.7	0.931_5	0.55	0.51	12.5
C	146	27	7.6	0.910_0	0.35	0.32	8.0

respectively, following previously described methods [22].

Viscoelastic measurements have been carried out on a RSA Rheometrics apparatus at a frequency of 1 Hz, using strips 20 mm long and 4 mm wide, cut from sheets 200 μm thick.

3. Homogeneous crystal slip model

The occurrence of plastic deformation through crystal slip parallel to the chain axis is governed by the critical shear stress of the various slip systems and the crystal orientation with respect to the principal stress. By consideration of the different rates of orientation of the *a* and *b* crystallographic axis, Galeski *et al.* [23] have put forward a very attractive model, making a correlation between the crystal rotation, about the *a* and *b* axis and the activation of the slip systems (1 0 0) [0 0 1] and (0 1 0) [0 0 1], but this does not give information on the mechanism of crystal slip.

3.1. Dislocation nucleation

The plasticity of semicrystalline polyethylene has been previously modelled on the basis of the thermally activated nucleation from the lateral crystal faces of pure screw dislocations parallel to the chain axis, which propagate through the crystal along ($h\,k\,0$) slip planes [22]. This model features homogeneous crystal slip, or alternatively uniform shear of the crystal lamellae, because of the spreading of dislocation nucleation events over the entire length of the crystalline lamellae. Uniform shear is analogous to the so-called "fine slip" described by Bowden and Young [4] that is often referred to as "chain tilt". This model assumes that the molecular mobility is high enough to allow dislocation glide at a rate that could fit with the applied strain rate.

The tensile flow stress, σ_y, derived from the dislocation nucleation theory of Shadrake and Guiu [13] obeys the following equation [22]:

$$\sigma_y = \frac{\mu^b}{\pi r_0} \exp\left(-\frac{2\pi \Delta G}{\mu b^2 l_c} - 1 \right) \tag{1}$$

where μ is the shear modulus of the planes involved in the slip process, b is the Burgers vector, $r_0 = 1.0$ nm is the core radius of the dislocation, l_c is the crystal thickness and ΔG is the energy barrier for the dislocation nucleation. In their model of dislocation nucleation, Shadrake and Guiu take into consideration the equilibrium of a pair of screw dislocations within a crystalline lamellae. These workers emphasized that this situation is equivalent to the state of equilibrium of a single screw dislocation nucleated from a free lateral surface of the lamellae. Notwithstanding, one must keep in mind that ΔG (Equation 1) is the free energy of activation for the nucleation of a pair of dislocations. Derivation of Equation 1 involves the two following assumptions: firstly the resolved shear stress operating on the glide planes is maximum, i.e., crystal slip occurs at an angle of 45° with respect to the tensile axis, and secondly a uniform distribution of the strain on the crystalline and amorphous phases is obeyed. Also, for a dislocation nucleation event to occur within a reasonable experimental time scale, ΔG should be about $40kT$, k being the Boltzmann constant and T the absolute temperature. Finally, one should take into account the theoretical calculations of the shear moduli in crystalline polyethylene as a function of temperature [24].

It turns out that this model can account for the tensile yielding of melt-crystallized polyethylene at room temperature fairly well [25, 26]. We have also shown that tensile yield data of ethylene–butene copolymers covering a wide range of copolymer composition, for either melt-crystallized samples or dried gels recovered from solutions of various concentrations, also fit very well the flow stress versus crystal thickness predictions at a deformation temperature of 60 °C [27]. Kennedy *et al.* [18] have suggested that ethylene copolymers have to be considered separately from homopolyethylenes because of structural differences. Nonetheless, we have shown that the same type of yield behaviour can be effectively observed on ethylene–butene copolymers covering a wide range of crystallinity [28] provided that the draw temperature and strain rate were investigated over large domains. Kennedy *et al.* finally discarded the model of dislocation-governed plasticity for linear homopolyethylenes, but their augmentation relied on measurements of nominal values of the tensile yield stress that have no quantitative relevance.

3.2. Molecular mechanism

Fig. 1 shows a sketch of the three main stages of nucleation, propagation and final exit from the crystal of a screw dislocation in a polyethylene lamellar crystal. In spite of the large amount of evidence of crystal slip which support the models of dislocation-governed plasticity, the mechanisms of nucleation and propagation of the dislocations are still unknown. Dislocations involving chain jogs have been proposed by Predecki and Statton [29] owing to the presence of interstitial chain ends in the crystal lattice. However,

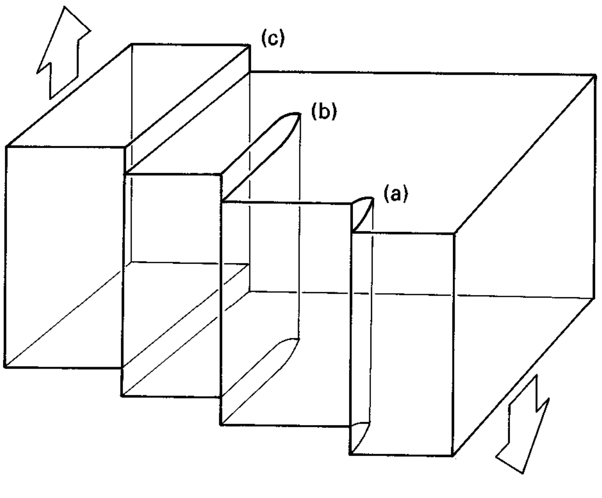

Figure 1 Dislocation model for the homogeneous slip process: (a) nucleation, (b) propagation and (c) exit of the dislocation from the crystal.

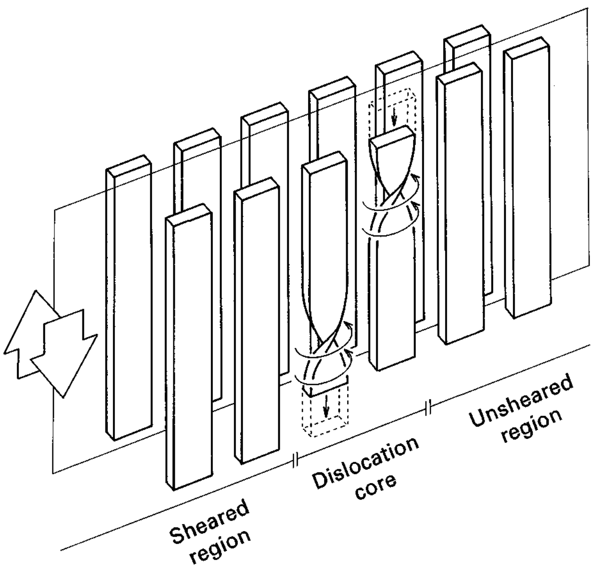

Figure 2 Detailed view of the mechanism of advancement of a screw dislocation.

besides the fact that interstitial chain ends should be infrequent in the case of high molar-weight polymers, such dislocations have an edge component which is unfavorable compared with the screw component as demonstrated by Shadrake and Guiu [13].

A detailed picture of the propagation stage is shown in the enlarged view of the dislocation core of Fig. 2. For clarity, the idealized lattice is represented as ribbon-like crystalline stems with their zigzag plane parallel to the glide plane, but the following discussion applies to the real crystalline lattice of polyethylene. Also, the broadness of the dislocation core over two stems is consistent with a core radius value of 1 nm. It is assumed that 180° twist defects are generated in the crystalline stems [30], this kind of point defect being indeed that most commonly proposed to account for the molecular mobility in polyethylene crystals [30–32]. The detailed picture in Fig. 2 shows that the shear stress acting upon the crystal involves a local compression on the top of the all-*trans* chain stems belonging to the shear interface. The generation of a 180° chain twist is able to relieve this compressive stress owing to the $c/2$ contraction of the chain stem. Then, the stress-activated step-by-step displacement of the point defect along the stem, from one of the twofold surfaces to the opposite surface, finally results in a $c/2$ translation (i.e., the Burgers vector) of the whole stem lying in the dislocation line. The dislocation can thus move forwards by transfer of the dislocation line from one stem to its close neighbour in the glide plane, because the local compressive stress acts on the stem forwards. The dislocation can finally escape from the crystal through the lateral surface opposite to the surface from which it was nucleated.

The eventual dissociation of perfect dislocations having a Burgers vector equal the crystallographic parameter c in the chain direction into partials of Burgers vector $c/2$ has been proposed as a possible mechanism of crystal slip since, when it can work, this phenomenon results in a significant drop in the critical shear stress in the crystal [25, 26]. However, taking into account that the polyethylene chains of planar zigzag conformation in the orthorhombic unit cell fall again into crystallographic register after the half-turn rotation and the $c/2$ translation induced by the twist, the dislocation described above cannot be considered as a partial.

It must be mentioned that Crist *et al.* [26] have previously proposed the 180° chain twist as a molecular mechanism for the advancement of crystal slip in order to account for the discrepancies between experimental data of yield stress and the predicted values of the dislocation nucleation model at high temperatures. Indeed, these workers assumed an elementary chain translation of c since perfect screw dislocations in metallic crystals have a Burgers vector equal to a perfect crystallographic parameter, but they found it very convenient to introduce the chain twist mechanism for the high-temperature slip because of its characteristic $c/2$ translation which causes a reduction in the critical shear stress. In fact, the chain twist is beneficial not only at high temperatures but also at low temperatures for the same reason that a $c/2$ translation of the chains is energetically much less expansive than a c translation. Of course, as emphasized by the above mentioned workers, this kind of conformational chain defect is thermally activated only above the α relaxation temperature. Below the temperature of self-activation, the crystalline defects may be actually stress activated i.e., the critical shear stress acting on the slip planes is likely to promote the generation of defects in order to propagate plastic deformation, step by step in the crystal.

Finally one may wonder what could be the molecular mechanism of screw dislocations having a Burgers vector equal to c.

4. Results and discussion

4.1. Stress-strain behaviour

Fig. 3 shows the true strain–strain curves of the copolymers A and C for a draw temperature $T_d = 20\,^\circ$C

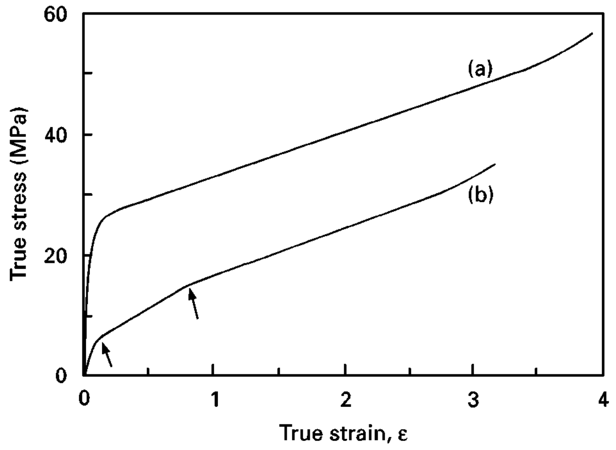

Figure 3 True stress-strain curves of copolymer A (curve (a)) and copolymer C (curve (b)) at $T_d = 20\,^\circ\mathrm{C}$ and a CHS of 0.5 mm min^{-1}.

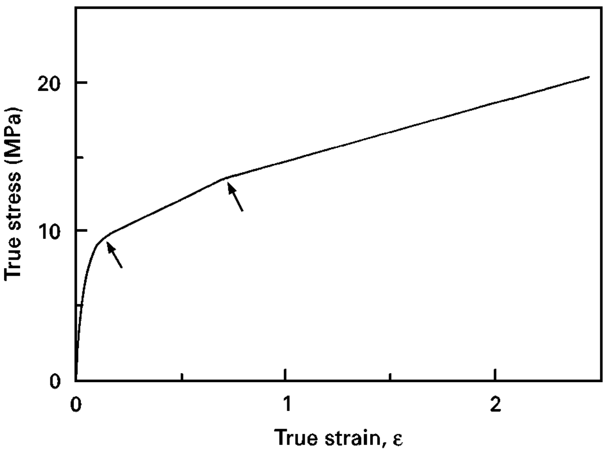

Figure 5 True stress–strain curve of copolymer A at $T_d = 80\,^\circ\mathrm{C}$ and a CHS of 0.5 mm min^{-1}.

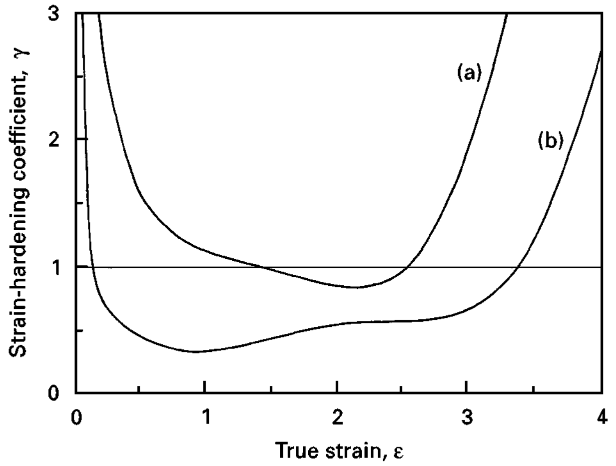

Figure 4 Strain-hardening coefficient versus strain for copolymer A (curve (a)) and copolymer C (curve (b)) for the same conditions as in Fig. 3.

and a cross-head speed (CHS) of 0.5 mm min^{-1}. The significant difference between the shapes of the two curves can be analysed owing to the variation with strain in the true strain-hardening coefficient reported in Fig. 4. Copolymer A displays an elastic deformation in the strain range $0 < \varepsilon < 0.2$ (Fig. 3), after which a monotonic increase in the stress takes place with a true strain-hardening coefficient lower than unity (Fig. 4). This is relevant to the occurrence of a plastic instability i.e. necking. In contrast, copolymer C displays an intermediate homogeneous deformation regime in the strain range $0.2 < \varepsilon < 0.8$ (Fig. 3) with a true strain-hardening rate greater than unity (Fig. 4). Beyond this strain domain, a second yield point occurs for copolymer C which undergoes a plastic instability, with a drop in the true strain-hardening coefficient below unity.

However, increasing the draw temperature to $T_d = 80\,^\circ\mathrm{C}$ promotes homogeneous plastic deformation in copolymer A as can be seen from the true stress–strain curve in Fig. 5 which displays two yield points. This is a piece of evidence for the thermally activated character of plasticity in this kind of semicrystalline polymer.

Fig. 6 shows the variation with temperature in the true yield stress data for the homogeneous plastic deformation of the three copolymers compared with the predictions from the dislocation nucleation model. The calculations are based on the shear modulus of the (0 1 0) glide planes in conformity with our X-ray diffraction observations, indicating that these planes take a better orientation in order to be the preferred slip planes in the plastic deformation process [33]. The Burgers vector is taken as $b = c/2 = 0.127$ nm in consideration of the mechanism proposed for the dislocation line motion, i.e., the 180 °C chain twist which puts the chain into crystallographic register after only a $c/2$ translation. The theoretical curves fit the order of magnitude of the experimental data for the three copolymers fairly well. The double temperature dependence of the model through the shear modulus and the activation energy is not sufficient enough to account for the strong drop in the yield stress with increasing temperature for every copolymer, but it decreases in the right direction. Most remarkable is the ability of the model to account for the drop in the yield stress with the decrease in crystallinity of the copolymers owing to the dependence on the crystal thickness.

The strain-rate sensitivity deserves some particular attention. The model is able to account for it through the activation energy $\Delta G = kT\log(\dot{\varepsilon}_0/\dot{\varepsilon})$ according to the Eyring formalization of plastic flow. Unfortunately, the essentially empirical assessment of $\dot{\varepsilon}_0$ can be only a rough estimation since it involves a number of adjustable parameters [34]. The value of $40\,kT$ chosen in the present study is the lower bound of the ΔG range generally taken into consideration and this makes irrelevant any attempt to predict the strain–rate dependence of the yield stress.

The process of dislocation nucleation, propagation and escape from the crystal is liable to occur repetitively in any favourable slip plane as long as the chain folds that bridge the dislocation glide plane remain slack enough to allow further elementary slip event. However, as the folds are gradually tightened by the progressing crystal slip, nucleation and propagation of dislocations become more and more difficult until

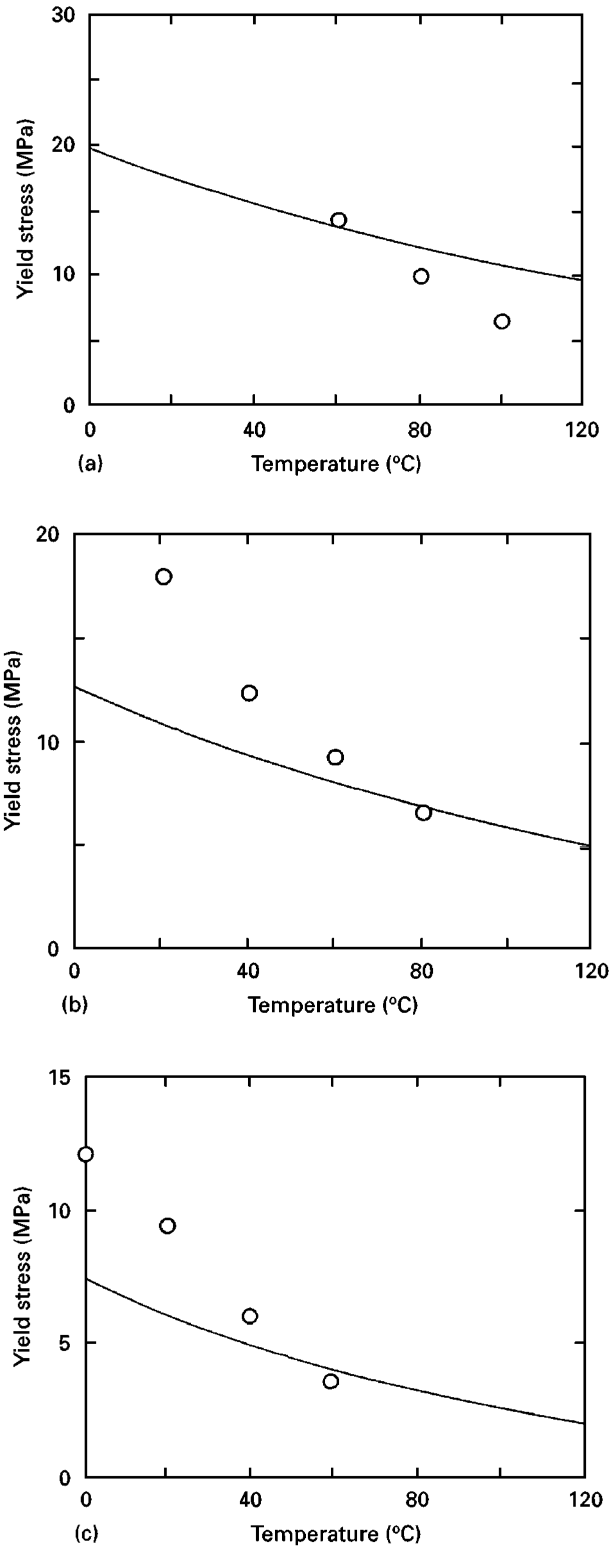

Figure 6 Yield stress versus temperature for the homogeneous plastic deformation for the three copolymers compared with the predicted curves for homogeneous crystal slip according to Equation 1 and using the crystal thickness values of Table I: (a) copolymer A; (b) copolymer B; (c) copolymer C.

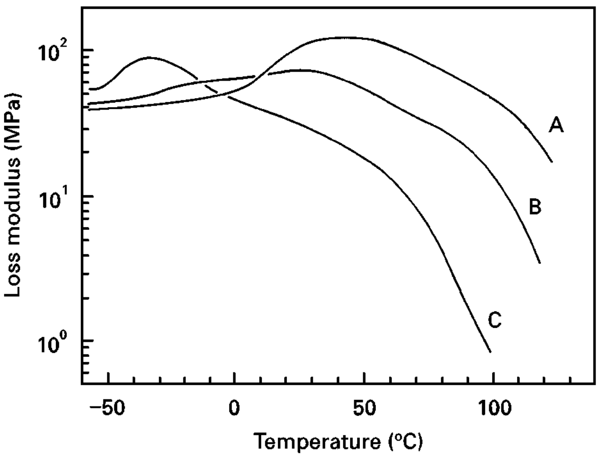

Figure 7 Loss modulus versus temperature for the three copolymers. Curve A, copolymer A, curve B, copolymer B; curve C, copolymer C.

dislocation motion is prevented, leaving the conformational defects frozen in the crystalline matrix. In this connection, it is worth noticing that the remaining defect should contain *gauche* conformations that may perfectly account for the decrease in the *trans* conformation concentration in the crystalline phase at roughly constant crystallinity, as previously reported from the infrared conformational analysis of the homogeneous plastic deformation [22].

At this stage of inhibition of homogeneous nucleation of dislocations due to topological constraints, heterogeneous nucleation should be activated in the regions of stress concentrations. This will result in heterogeneous or localized slip and will entail the occurrence of plastic instability accompanied by fragmentation of the crystalline lamellae. The drawing of copolymer C at $T_d = 20\,^\circ\text{C}$ (Fig. 3) is a typical illustration of this case when the strain goes beyond $\varepsilon = 0.8$. In another connection, reducing the draw temperature will slow down the migration of the chain defects in such a way that the rates of nucleation and propagation of dislocations will be unable to satisfy the applied strain rate. This phenomenon is likely to cause localized slip to initiate at the onset of the plastic deformation. This is the case for copolymer A which yields heterogeneously at for $\varepsilon = 0.2$ for $T_d = 20\,^\circ\text{C}$ (Fig. 3), compared with the drawing at $T_d = 80\,^\circ\text{C}$ (Fig. 5) which allows significant homogeneous plastic deformation prior to plastic instability. A mechanism for the localized slip in polyethylene is discussed in the accompanying paper [35].

4.2. Mechanical relaxation

Fig. 7 shows the loss factor versus temperature curves of the three copolymers. The α relaxation peak temperature drops with decreasing crystallinity. This is a direct consequence of the decrease in the crystal thickness in the copolymers as the co-unit concentration increases. Indeed, it has been shown by several workers that the peak temperature of the α relaxation only depends on the crystal thickness [36, 37]. The thermal activation of 180° chain twists moving through the crystal along the chain stems is perfectly consistent with this finding. In fact, at the same frequency of straining, the thicker the crystals, the higher should be the rate of migration of the chain defects in order to move through the whole crystal thickness in a time scale compatible with the period of a strain cycle. This requirement is fulfilled by a rise in temperature, i.e., a higher α relaxation temperature.

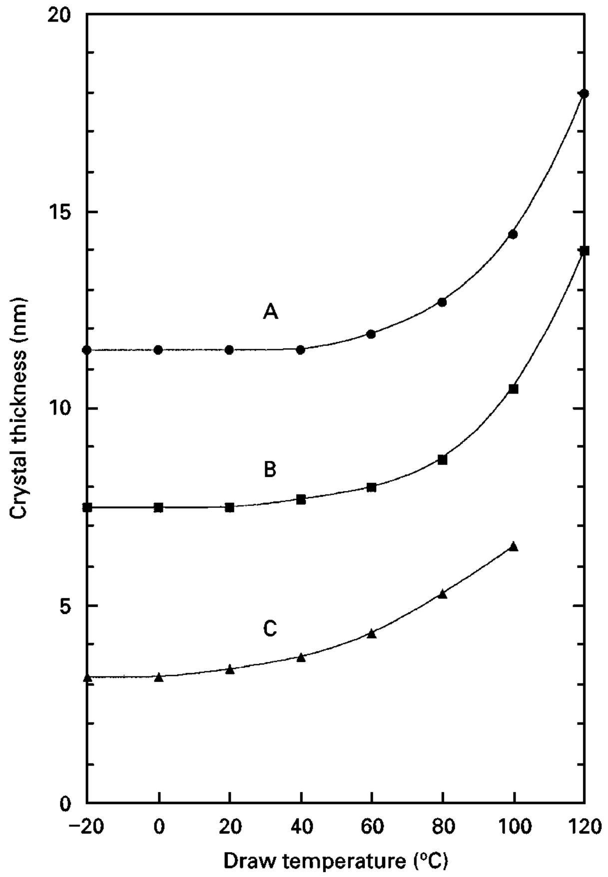

Figure 8 Crystal thickness as a function of the draw temperature for necked samples of the three copolymers. Curve A, copolymer A; curve B, copolymer B; curve C, copolymer C.

There is thus a striking analogy between the α relaxation and the dislocation glide through the fact that both processes can be activated at lower temperature as the crystal thickness decreases. This analogy provides support for the molecular mechanism proposed for the dislocation motion. Additional support comes from the observation of a hindrance to the dislocation nucleation below the α relaxation temperature as will be discussed in the Part II of this series [35].

4.3. Dependence of crystal thickness on draw temperature

Fig. 8 shows the variation in crystal thickness as a function of the draw temperature for the three copolymers drawn up to the necked state. In the low-temperature range, the l_c data for copolymer A are significantly lower than the initial value for the isotropic material (Table I) because of the shearing of the crystal blocks in the fibrillar structure. Indeed, even when plastic instability occurs first, homogeneous slip is likely to take place in the crystalline lamella fragments, owing to its thermally activated character, but at a much lower strain rate than the applied value [22]. This leads to a flattening of the crystal blocks in the fibrils with the chain stems tilted with respect to the fold surface.

Furthermore, for draw temperatures below 60 °C, the crystal thickness of copolymer A remains constant. This finding is inconsistent with the melting–recrystallization process since such a phenomenon should entail a monotonic decrease in the long period with the decreasing draw temperature that is also the crystallization temperature. The critical temperature of 60 °C is roughly the temperature below which the true stress–strain data indicate the occurrence of plastic instability, i.e., heterogeneous plastic deformation, in the case of copolymer A. It is also worth noting that 60 °C is about the peak temperature of the α relaxation of copolymer A, as can be judged from Fig. 7.

The steady increase in l_c, above the critical temperature, is relevant to a great ability of the crystalline phase to undergo a crystal thickness reorganization in the temperature range where homogeneous crystal slip is strongly activated. The molecular mobilities in the crystal which allow easy glide of the dislocations in the crystalline lamellae, above the α relaxation, are strongly suspected to be responsible for the ability of the copolymer to adjust its crystal thickness to the draw temperature.

Similar observations can be made for copolymers B and C (Fig. 8) except that the change from constant to increasing crystal thickness with the draw temperature rise is located at a lower temperature with decreasing crystallinity. This effect perfectly parallels the crystal thickness dependence of the α relaxation peak discussed in the preceding section, i.e., the lower the crystal thickness of the copolymer, the lower is the temperature threshold for the activation of the molecular mobility in the crystalline phase.

The crystal thickness increase with increasing draw temperature is similar to the phenomenon of crystal thickening upon thermal annealing which is well known to occur above the peak temperature of the crystalline α relaxation. However, in the case of drawing, the crystal thickness is allowed to increase within the time scale of the experiment, i.e., a few minutes only. This can be ascribed to a mechanically assisted annealing effect during the tensile drawing owing to the stress activated mobility of the crystalline defects, as previously proposed by Peterlin [38] and Crist [34]. The 180° chain twist defect in Fig. 2 which is the mechanism suggested for the α crystalline relaxation [30–32] is also the mechanism to which crystal thickening has been attributed [39, 40]. However, the rate of migration of such defects during drawing should be much faster than in the case of thermal annealing owing to the additional stress activation.

5. Concluding remarks

The homogeneous plastic deformation of ethylene copolymers is analysed in terms of a homogeneous crystal slip process relying on the nucleation of screw dislocations. The model notably accounts for the large drop in yield stress with increasing draw temperature in the case of tensile testing. The major influence of the crystal thickness on the yield stress level is also fairly well predicted. The usefulness of the model for understanding the properties of semi crystalline polymers has recently been demonstrated in a comparison of the plastic behaviour of chemically homogeneous and heterogeneous ethylene copolymers which display significantly different crystal thicknesses at equivalent crystallinities [41].

The assumption of 180° twists for the molecular mechanism of the dislocation motion is founded on structural considerations about crystallographic slip in crystals consisting of long-chain molecules. It is the basic link between plasticity and viscoelasticity and provides an interpretation for the analogy between the strain-induced crystal thickness rearrangement of drawn materials and crystal thickening due to thermal annealing. Indeed, it is our belief that the occurrence of homogeneous slip during plastic drawing involves the mechanical activation of conformational defects analogous to those that are responsible for the α relaxation process. This phenomenon is the driving force for the short-time crystal thickness adjustment, as long as the draw temperature is close enough to or above the α relaxation temperature.

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