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Polyethylene yielding behaviour: What is behind the correlation between yield stress and crystallinity?

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Yielding in semi-crystalline polymers is generally attributed to crystallite thickness. However, a better correlation is found between yield stress and crystallinity degree. In this paper, it is attempted to clarify this correlation by investigating a set of linear and branched polyethylenes. The polymers were crystallized in order to obtain a wide range of crystallinities and crystallite thicknesses. The influence of these parameters on the yielding behaviour is then studied. A new method that correlates the neck width and the Stress Transmitters (ST) density is proposed and enables to evaluate the ST concentration for each material as close as possible from the initiation of plasticity. The density of ST is found to be dependant on the content of co-unit and on the crystallisation conditions.

To study specifically the initiation of the crystallites shearing, a threshold stress σ_{th} is introduced. σ_{th} appears to be proportional to the crystallite thickness (L_c) at equivalent crystallisation conditions, while it is well correlated to the crystallinity (X_c). This relationship with X_c is explained describing σ_{th} with both parameters L_c and ST.

1. Introduction

Semi-crystalline polymers are used in a large range of applications generally under visco-elastic solicitations. Consequently, small strain behaviour and yielding in particular have been widely studied for the last forty years [1–7]. A large part of these studies has been dedicated to polyethylene mainly because of its massive production and its relative simplicity.

Despite these studies, the initiation of yielding, even on polyethylene, is not fully understood and improvements could be made to clarify the mechanisms involved. Actually it is generally accepted that yielding is controlled by nucleation and motion of screw dislocations [4–11]. Hence a relation between the yield stress (σ_y) and the crystallite thickness (L_c) [4, 6–8] has been put forward. However, the correlation with experimental data is imperfect; therefore the influence of other microstructural parameters has been explored. A phenomenological approach that associates yielding and the crystallinity (X_c) [1–3] has been proposed. A significantly better correlation was highlighted but no physical explanation was brought. Molecular topology and its associated parameters as the molecular weight, the content of co-unit and the density of entanglements were found to influence the plastic behaviour of the polyethylene [1,2,12]. On the contrary, at the mesoscale, the influence of spherulites was found insignificant [1,2,13].

Before reaching the yield stress, the material is first submitted to visco-elastic deformation essentially governed by the amorphous phase [7,8,14]. Crystallites' shearing appears in a subsequent step. In this sequence, the mechanical coupling between crystal and amorphous phase is of course crucial. Coupling or stress transmission is probably carried out by elements of the molecular network such as tie molecules or entanglements. Consequently these Stress Transmitters (ST) have been the subject of several papers [12,15,16]. The main difficulty comes from the experimental quantification of the density of stress transmitters. It is usually evaluated using indicators such as the natural draw ratio or the strain hardening [17,18,19]. However, their reliability can be questioned, especially because the measurements are performed at large strain, far from the initiation of plasticity.

In addition, theoretical approaches have been proposed to evaluate the effect of stress transmitters on mechanical behaviour. Nitta et al. have chosen to calculate the fraction of tie molecules thanks to a statistical model and to compare it versus the yield stress. Finite element calculation was preferred by Bonten and Schmachtenberg [16] to demonstrate that the density of Tie Molecules (TMs) could be determinant on the value of the transmitted force.

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It remains difficult to find a clear relation between microstructure and yielding. These difficulties could originate partially in the measurement methods (of yield stress, tie molecule concentration), whereas numerical modelling is generally performed on ideal and undeformed microstructure.

Consequently, to improve measurements and model consistency, in this article, we first propose new methods to evaluate both initiation of plasticity and stress transmitters concentration. Then initiation of plasticity in relation with microstructural parameters will be analysed. Finally, a possible explanation will be proposed to clarify the experimental correlation between the yield stress and the crystallinity.

The material chosen to carry out this study is polyethylene (PE). Several PE with different molecular parameters were subjected to three different thermal treatments in order to either vary the microstructural parameters (crystallinity, crystallite thickness,…) keeping the same molecular parameters (co-unit content, molecular weight), or keep similar structural parameters and vary the molecular topology. This strategy enables the dissociation of the influence of each parameter on initiation of plasticity.

2. Experimental section

2.1. Materials

Four polyethylenes, obtained using the Philips method with a chromium oxide and with a medium molecular weight Mw (between 180 and 230 kDa) have been studied. This set of industrial material has been provided by Total. They differ from their molecular topology and so can be classified into two different groups: PE A and PE B (respectively with a C6 content of 1.8 mol% and 0.8 mol%) (See Table 1) are considered as “branched” due to their significant C6 co-unit concentration: Popli et al. [20] have shown the influence of C6 concentration above 0.6 mol% on the mechanical properties. The PE C and PE D (respectively 0.1 and 0.2 mol%) are qualified as “quasi-linear” due to their lower C6 concentration. In each category, the polyethylenes differ from their crystallinity: the one of the PE A (49%) is lower than the one of the PE B (54%), and the same gap exists between the crystallinity of the PE C and PE D (respectively 65% and 69%).

2.2. Sample preparation

500-µm thick sheets were obtained by pellets molding between aluminium foils in a press at 170 °C. Then, the polymer sheets were quenched in water at a rate of approximately 30 °C/s. To modify the microstructure, isothermal crystallizations were performed with two different processes. Samples designated hereafter as “annealed” were heated from their quenched state to a temperature close to the crystallisation temperature and were held in these conditions in a thermostatic oil bath for about 15 h.

The samples called “isotherm” were re-melted at 170 °C in an oven before being cooled in a thermostatic oil bath at a temperature close to the crystallisation temperature and held in these conditions during 15 h. Samples were tightly wrapped in order to avoid oil contamination from the thermostatic bath. Moreover, infra-red analysis (detection of carbonyls peak at 1720 cm^{-1}) did not reveal the presence of oxidation.

Table 1
Initial characteristics of the different polyethylene.

Material	C6 (mol%)	M_n (kDa)	M_w (kDa)	M_z (kDa)	I_p	X_c[a] (%)
PE A “branched”	1.8	14.3	231	2770	16.1	49
PE B “branched”	0.8	15.8	187	1770	11.9	54
PE C “linear”	0.1	15.4	216	2770	14	65
PE D “linear”	0.2	15	229	4100	15.3	69

[a] Quenched state.

2.3. Characterization

2.3.1. Differential scanning calorimetry (DSC)

The thermal analysis of the samples was conducted using an indium-calibrated Perkin Elmer DSC7 apparatus. 5–8 mg samples were cut from the polymer sheets, and placed into aluminium pans. The melting thermograms were recorded at a heating rate of 5 °C/min, under nitrogen flow. The crystallinity (X_c) was calculated at ±1% using equation (1):

$$X_c = \frac{\Delta H_F}{\Delta H_F^0} \tag{1}$$

Where ΔH_f is the specific heat of fusion of the specimen and ΔH_f^0 is the heat of fusion of a perfect crystal and equal to 290 J/g [21].

2.3.2. SAXS

An RU-300 X-ray generator with rotating Cu anode (CuKα radiation), with point collimation, was used to record the small angle X-ray scattering (SAXS) patterns by means of a Princeton Instruments CCD camera. Acceptable statistics and quality of SAXS patterns were obtained with an accumulation time of 10 min. The SAXS patterns were analysed by means of circular profiles. The observation range was from $q = 0.024$ to 0.98 nm^{-1}. The long period (L_p) was calculated from the maximum of the diffuse intensity corrected by the Lorentz factor ($Iq^2 = f(q)$) using equation (2):

$$L_p = \frac{2\pi}{q_{max}} \tag{2}$$

q_{max} corresponding to the peak maximum.

The thickness of the lamellae was deduced, with a precision of ±10%, from L_p and X_c using the following relation:

$$L_c = L_p \times \frac{\rho}{\rho_c} \times X_c \text{ and } \frac{1}{\rho} = \frac{X_c}{\rho_c} + \frac{1 - X_c}{\rho_a} \tag{3}$$

Where ρ_c is the crystalline density and equals to 1.003 g cm^{-3}, ρ_a is the amorphous density and equals to 0.850 g cm^{-3} [6] and ρ the density of the sample.

Table 2
Structural characteristics of the different polyethylenes.

Type	Material	Xc (%)	Lc (nm)	Symbol
PE A “branched”	A quenched	49	8	■
	A annealed	52	11	▨
	A isotherm	53	11	□
PE B “branched”	B quenched	54	9	◆
	B annealed	62	13	◈
	B isotherm	65	15	◇
PE C “quasi-linear”	C quenched	65	12	●
	C annealed	73	20	◍
	C isotherm	75	25	○
PE D “quasi-linear”	D quenched	69	14	▲
	D annealed	77	22	◬
	D isotherm	80	28	△

The crystallinity and the crystallite thickness, pulled out from the DSC and SAXS experiments, are summarized in the Table 2. The crystallinity ranges from 49% to 80% and the crystallite thickness ranges from 8 to 28 nm. For each group of PE, the annealed treatment has permitted to increase the crystalline phase in size and in volume but its influence is weaker compared to the one of the isotherm treatment.

2.4. Tensile measurements: discussion on initiation of yielding definition

It is generally accepted that yielding in semi-crystalline polymers is controlled by the nucleation of screw dislocations [4–10]. The dislocation model (equation (4)) gives a relationship between the critical macroscopic tensile stress σ_c to shear a crystallite and the crystallite thickness (or the stem length l). σ_c is often confounded with σ_y [7,8].

$$\sigma_c = \frac{K}{\pi}\alpha(T)\exp-\left[\frac{2\pi\Delta G_c}{Klb^2}+1\right] \text{ and } \alpha(T)=\frac{b}{r_0}\exp\left[\frac{2\pi E_0}{Klb^2}\right] \qquad (4)$$

With K the crystalline shear modulus, b the magnitude of the Burgers vector, l the stem length, r_0 the core radius of dislocation, E_0 the core energy and ΔG_c the critical value of the Gibbs free energy.

Physical parameters involved in this equation are of course evaluated on an undeformed microstructure; therefore it makes sense only for the initiation of plasticity. Experimental measurements have shown a correlation between σ_y and L_c [4,6–8] which is not absolutely convincing. Several theoretical improvements could be proposed; however before modifying a theory, the values of the measurements have to be guaranteed. Indeed, when the dislocation theory describes the very beginning of plasticity, the yield stress is classically measured at the maximum stress where the necking has already affected a part of the sample. Moreover the local deformation is strongly magnified and phenomenona such as cavitation or even beginning of fibrillation could affect the value of σ_y [14,22]. Consequently, a direct evaluation of dislocation theory with such experimental results is not perfectly relevant.

It seems then adequate to define a yielding criterion which is the closest as possible to the initiation of plasticity. Such a parameter already exists and is used in metallurgy. It consists in defining the loss of linearity on a true stress–strain curve using a strain parameter (Fig. 1). This parameter has to be as small as possible, but it has to allow a good precision on the threshold stress measurement. Consequently a true strain parameter of 5×10^{-3} has been chosen to obtain a precision of ±0.5 MPa on the threshold stress σ_{th}. It corresponds to a threshold deformation that varies between 1.5×10^{-2} and 1.9×10^{-2} depending on the considered sample. This kind of yielding measurement is certainly not perfect but is believed to be significantly less dependent on other phenomenona than σ_y. Loading-unloading recovery time experiments were performed during 3 h in order to prove that the plasticity was well initiated around the stress threshold σ_{th}. We can underline as well that Brusselle-Dupend et al. [23] deduced from their experiments that the initiation of the plasticity was happening around a deformation of 1.5×10^{-2}, which is close to our values of σ_{th} respective strains.

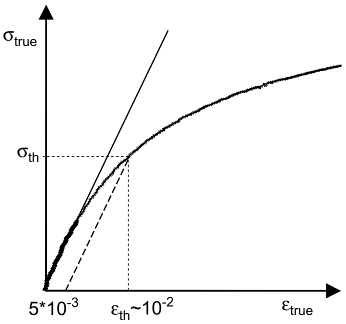

Fig. 1. Method of σ_{th} measurement.

The first series of test were carried out assessing the strain rate at $10^{-3}\,s^{-1}$ thanks to an optical extensometer Apollor Vidéo-Traction composed of a CCD camera and true stress–strain curves were obtained. Dumbbell-shaped samples of 22 mm gauge length, about 5 mm width, and about 0.5 mm of thickness were cut from the sheets. Two types of test were performed with an MTS machine at 23 °C. The aim of the first series was to determine the threshold stress of each sample. A special attention was paid to obtain the best precision on the threshold value, repeating three times the tests.

A second series of test were carried out with a strain rate of $5\times10^{-3}\,s^{-1}$ to obtain nominal stress–strain curves. These tests allow measuring in particular the natural draw ratio (λ_n) and the neck width.

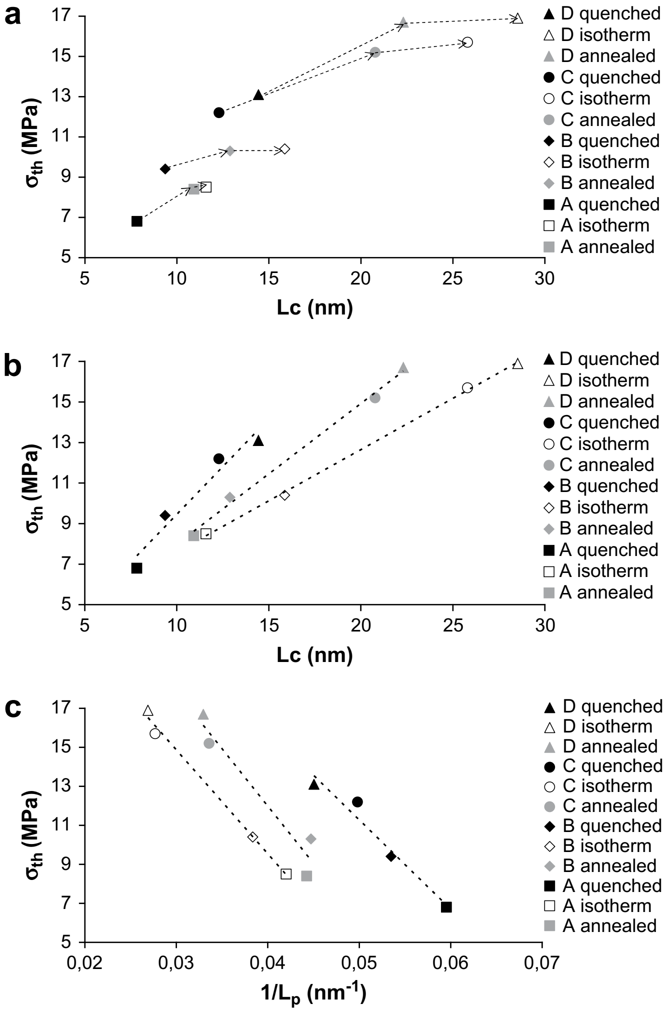

Fig. 2. (a) Plot of σ_{th} versus the crystallites thickness: influence of L_c. (b) Plot of σ_{th} versus the crystallites thickness: influence of L_c and thermal treatments. (c) Plot of σ_{th} versus $1/L_p$: influence of L_p and thermal treatments.

3. Results

3.1. Yield stress

Beyond the dislocation model, some authors have preferred a phenomenological approach associating yielding with the crystallinity [1,2] and a significantly better correlation was highlighted. However, no physical explanation had been brought even if it was furtively explained by Crist et al. [6] by the fact that the crystallinity was itself correlated with the crystallite thickness L_c. Consequently, both approaches were considered for our results: the threshold stress was plotted versus X_c and L_c.

On Fig. 2a and b σ_{th} is first plotted against L_c. The same results are reported on both graphics to highlight distinct tendencies. Furthermore, regarding the values of the error bars (see characterization paragraph) the observed trends are not questionable.

On Fig. 2a, it can be observed that the four groups of PE behave similarly against L_c: the annealed treatment leads to an increase of both L_c and σ_{th}. On the contrary, even if the crystallite thicknesses of the isotherm samples are higher than the annealed ones, they do not lead to higher σ_{th}. This observation reveals that L_c is clearly not the only parameter to describe the yielding behaviour.

On Fig. 2b other tendencies are represented. For a same thermal treatment, a linear trend between σ_{th} and L_c appears: L_c could be the main parameter which affects σ_{th}. Straight lines can be observed so that crystallisation conditions only lead to a slope change. Thus, it seems that the crystallisation conditions would establish a reference value of the stress applied on a crystallite and the molecular topology would affect the crystallite thickness and then increase or decrease the critical stress.

The sole dislocation model is clearly not able to describe all the experimental results even if crystallite thickness plays a significant role on the initiation of plasticity. Considering σ_{th} versus the crystallinity X_c for all samples (Fig. 3), a linear trend is highlighted. Globally, an excellent correlation is observed ($R^2 = 0.960$) so that X_c seems to be the best parameter for all the PE and all the thermal treatments. As suggested previously, a first explanation can be brought:

$$\sigma_{th} = K \times X_c \text{ and } X_c = \frac{L_c}{L_p} \times \frac{\rho_c}{\rho} \tag{5}$$

Consequently, $\sigma_{th} = K \times (\rho_c/\rho) \times (L_c/L_p)$ with K a constant

$$\sigma_{th} = K' \times \frac{L_c}{L_p} \text{ with } L_p = L_a + L_c \text{ and } K' \text{ a constant} \tag{6}$$

σ_{th} appears proportional to L_c/L_p which is not incompatible with the classical theory that correlates σ_{th} and L_c. Indeed, over a range of 5–30 nm dislocation theory predicts an evolution of yield stress versus L_c which is not so far from a linear evolution.

However, it also confirms that L_c is not the only parameter influencing the yielding behaviour: the long period L_p seems to play a direct or indirect role. On Fig. 2c σ_{th} is plotted against $1/L_p$. As previously, the same analysis can be lead: for a same thermal treatment, a linear trend between σ_{th} and $1/L_p$ appears and straight lines can be observed so that crystallisation conditions only lead to a slope change.

To summarize, experimental results lead to the conclusion that both crystallisation conditions and L_c affect σ_{th}. It has been shown (equation (6)) that σ_{th} is linked to L_c and L_p. Therefore L_p and the crystallisation conditions are in connection, but for instance, no physical explanation can be proposed.

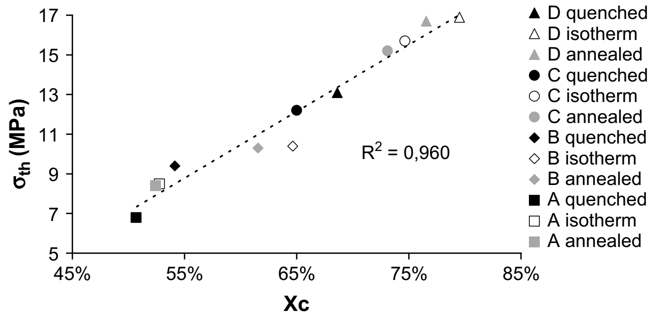

Fig. 3. Plot of σ_{th} versus the crystallinity or the ratio L_c/L_p. Comment: same trend has been found with the yield stress value.

3.2. Role of L_p on yielding behaviour

3.2.1. Definition of stress transmitters

In order to propose a physical explanation for the initiation of plasticity, other parameters in relation with the microstructure have to be taken into account. During a loading sequence, initiation of plasticity appears when the critical local shear stress (τ_c) is reached on a slip plan of a crystallite. This phenomenon depends on the orientation of the crystallite, the external macroscopic tensile stress (σ_{th}) and also on the local stress concentration. The latter is provoked by the inhomogeneous stress transmission from the amorphous phase to the crystal.

Elements as Tie Molecules (TMs), entanglements, interphase (crystal/amorphous) partially ordered and possibly the partial percolation of the crystalline phase participate to the network which is likely essential to transmit the applied stress through the lamella stacks (Fig. 4). Their mechanical contribution can hardly be dissociated by experimental methods. In this paper we consider that they all belong to the same group of elements: the stress transmitters (ST). It has to be noticed that TM concentration has already been considered as an important parameter in the mechanical properties of semi-crystalline polymers. Indeed, TMs can affect the yield behaviour and the σ_y value [12,15,16]. Finite element study was done by Bonten and Schmachtenberg [16] and has demonstrated that the density of TMs is determinant on the stress concentration on crystal phase. It was proved that the fewer TMs there were, the sooner the links failed. Consequently at equivalent crystallite thickness, the yield value increases with the concentration of TMs. Nitta and Takayanagi [15] have studied the dependence of the yield stress on the content of tie molecules calculated by Brown's model. A linear relationship was found and a numerical evaluation revealed that the stress concentration on the lamellar crystals through tie molecules caused their fragmentation. However the direct influence of the crystallite thickness has not been studied in this work.

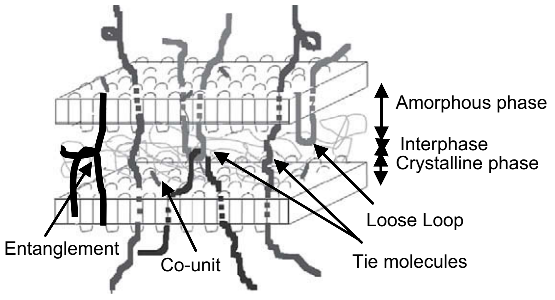

Fig. 4. Scheme of the crystalline and amorphous lamellae with their stress transmitters.

To conclude, our hypothesis is that crystallisation conditions modify the ST concentration and that the ST concentration is in relation with L_p.These propositions would explain both the correlation between σ_{th} and X_c and the discrepancies between σ_{th} and L_c. In the following, we attempt to bring clues to confirm these hypotheses.

3.2.2. *Stress transmitters measurements*

The evaluation of stress transmitter concentration must be addressed in order to succeed in modelling correctly yielding. To our knowledge, direct measurements of the ST concentration cannot be found in literature. However, indirect approaches have been proposed to give information on their density. Strain hardening – measured in compression – is used as an indicator of the macromolecular network [18,19,24,25] as Schrauwen et al. [25] have shown that it can be attributed to both chain entanglement density and TM concentration. The natural draw ratio is also considered as a TMs concentration indicator [12,15–19,21,24–28]; it is also sensitive to the crystallisation kinetics [13,16–18] and the content of co-unit [16,17]. These methods are generally dedicated to measurements of TM concentration while they probably highlight the effect of all stress transmitters.

However, these two parameters present several drawbacks. First, the measurements are performed very far from the visco-elastic strains, the memory of the initial network is possibly partially lost as subsequent strain and hardening could occur even after prior fibrillation. Secondly, these parameters are difficult to evaluate precisely and only indicate roughly a high concentration of stress transmitters. A new indicator can be proposed to reduce the two previous drawbacks. It is proposed to measure the "neck width" to link the intensity of plastic deformation to ST concentration.

Necking is a particularity of the stress–strain nominal curve which has been largely analysed and linked to physical parameters. Indeed, it has been shown that a sharp peak corresponds to an important plastic instability during yielding [14]. Peterlin [29] has proposed that a sharp neck should be due to the sliding of crystal blocks leading to a highly heterogeneous deformation whereas a diffuse neck would originate from shearing of the crystal blocks leading to a more homogeneous deformation. In addition, Crist and Metaxas [30] have linked the neck and the strain hardening: a weak strain hardening follows a sharp neck. On the other hand the chain topology (interphase, chain folding and co-unit) and the crystallisation conditions were found to have an influence on the neck shape and on the homogeneity and stability of the deformation [1,2,13,17]. It can be evoked as well that cavitation (as it can be observed on Fig. 4) takes place during necking and is considered to be coupled with the plastic instability.

From all these results, a relation between ST and neck width can be assumed: the lower the ST concentration is, the sharper the neck is.

The measurement of the neck width can be then chosen as a ST concentration indicator. It is measured, as depicted on Fig. 5b. It must be performed for every sample at constant strain rate, temperature and shape of sample. First, the neck width is a physical criterion because it is measured much closer to the beginning of the plasticity, synchronised with the yield stress measurement. It is consistent with our approach aiming at characterizing the initiation of plasticity before any other phenomenon interacts. Secondly, it turned out that this new indicator is more sensitive to ST concentration than previous indicators. It allows more precise quantitative measurements.

An example is shown on Fig. 5b, the material chosen is PE A with three different thermal treatments. Pictures taken after the end of necking show the difference of plastic instability. The value of the neck width is respectively 0.27, 0.49 and 0.62 for the isotherm, annealed and quenched PE A. The natural draw ratio and the neck width show the same trend however the results of neck width show a strong sensitivity as it is multiplied by a factor 2.3 between isotherm and quenched samples whereas the natural draw ratio varies from 3.5 to 4.75 which corresponds to a factor 1.35.

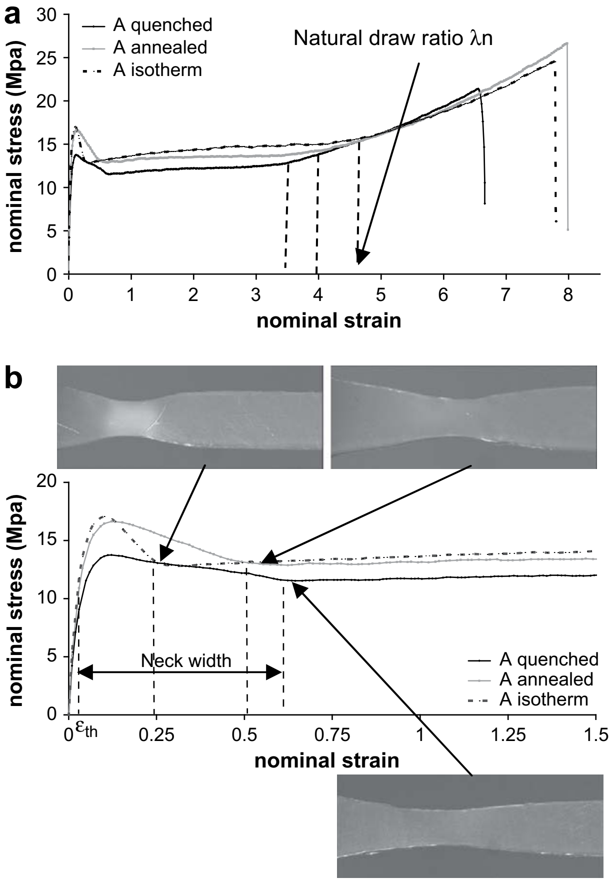

Fig. 5. (a) Drawing and natural draw ratio of the PE A. (b) Necking of the PE A and the corresponding photos.

3.2.3. *Relationship between the stress transmitters density and L_p*

The question of the relation of ST concentration and L_p that was suggested by equation (6) can now be addressed. In fact, the question of the relation between L_p and the ST has been previously evoked in the literature as Brown [31], Yeh and Runt [32] have linked by a statistical model the number of TMs to L_p. Brown's model was based on the hypothesis that the gyration diameter had

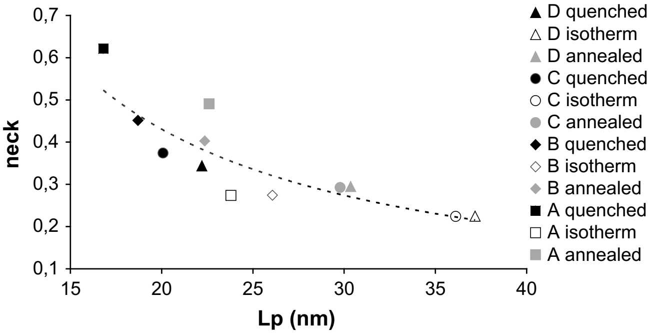

Fig. 6. Width of the neck versus L_p.

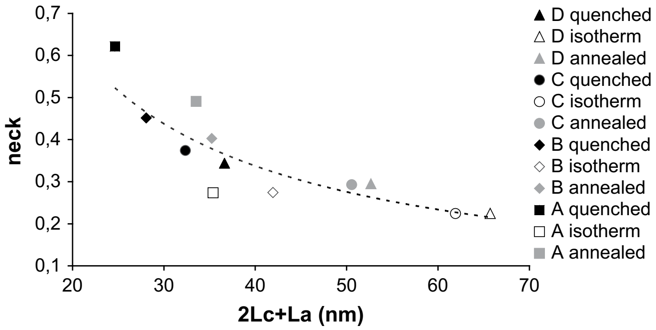

Fig. 7. Width of the neck versus $2L_c + L_a$.

to be superior to $2L_c + L_a$ to make the molecule tying. Yeh and Runt preferred to take into account the entangled molecules: their criterion is in this case $2L_p$ (or $2L_c + 2L_a$).

The neck width is plotted versus L_p on Fig. 6 and versus $2L_c + L_a$ on Fig. 7. A relatively good correlation is observed in both cases; consequently it can simply be deduced that the molecular network is a function of L_c and L_a.

To conclude, it is clear that L_c is not the only parameter that determines the initiation of yielding. Contrariwise, an excellent correlation is observed between σ_{th} and X_c. A simple calculation has shown that it implies that L_p plays also a role. As L_p is not directly correlated to mechanical properties, we have shown that L_p contains indirectly a microstructural information: the ST concentration. Consequently the initiation of yielding should be predicted with a good precision taking into account both L_c and ST concentration.

4. Discussion

4.1. Quantitative analysis

σ_{th} depends on the crystallite thickness L_c: at equivalent ST density, the thicker the crystallites are, the higher the critical shear stress need to be to initiate the plasticity. We have seen that the stress transmitters play also a significant role on the σ_{th} value: a higher ST concentration permits a better distribution of stresses on the edges of the crystalline lamellae and so a lower stress concentration.

Consequently the initiation of the crystallite shearing should be described by a function of σ_c and ST. The following relation was chosen:

$$\sigma_{th} = k \times \left(\frac{\sigma_c}{\sigma_{c0}}\right) \times \left(\frac{ST}{ST_0}\right)^{\alpha} \qquad (7)$$

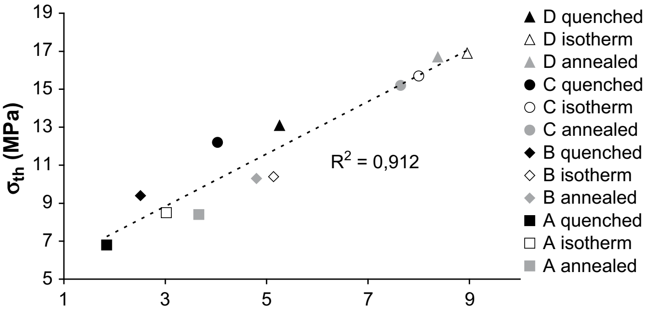

Fig. 8. Plot of σ_{th} versus $(\sigma c/\sigma c_0) \times (\mathrm{ST}/\mathrm{ST}_0)^{\alpha}$.

σ_c over σ_{c0} is obtained from equation (4):

$$\frac{\sigma_c}{\sigma_{c0}} \propto \exp - \left[C_1\left(\frac{1}{L_c} - \frac{1}{L_{c0}}\right)\right] \qquad (8)$$

$$\text{and } C_1 = \frac{2\pi(\Delta G_c - E_0)}{Kb^2} \qquad (9)$$

L_{c0} and ST_0 are the minimal values of all the L_c and ST of the samples.

σ_{c0} is calculated using equation (4) and substituting L_c with L_{c0}.

The aim of such a relation is to evaluate quantitatively the evolution of σ_{th} in relation with the relative evolution of both L_c and ST. Taking $\alpha = 0.6$, a good correlation can be observed (Fig. 8) between σ_{th} and $(\sigma c/\sigma c_0) \times (\mathrm{ST}/\mathrm{ST}_0)^{\alpha}$.

Including the ST in the description of σ_{th}, the three straight lines observed on Fig. 2b are translated, rotated and merged together. Therefore, the correlation factor is comparable to that obtained for σ_{th} and X_c but this correlation can be explained physically. The chosen power $\alpha = 0.6$ could either reveals that σ_{th} is not proportional to ST concentration or that others parameters could affect the initiation of plasticity. The neck method for the measurement of the stress transmitter concentration leads to a better correlation factor than the natural draw ratio method.

Furthermore, this analysis has permitted to estimate the core energy E_0:

C1 is found equal to 2.3×10^{-8} m and taking $K = 2630$ MPa, $k = 1.38 \times 10^{-13}$ J/K, $\Delta G_c = 60$ kT and $b = 1.27$ Å [6–8,11], it leads to $E_0 = 0.93 \times 10^{-19}$ J, which is in the good order of magnitude.

Finally the correlation between σ_{th} and X_c can be interpreted physically:

- a good correlation is obtained between σ_{th} and X_c or L_c/L_p,
- experimental results show that L_p is correlated with ST density,
- dislocation model (equation (4) leads to a quasi-linear relation between σ_{th} and L_c in the experimental range of L_c.

Consequently the good correlation between σ_{th} and X_c can be explained by the fact that X_c represents the products of two factors:

- The crystallite thickness (explained by the dislocation model);
- The stress concentration on the crystallite due to the ST (represented by L_p).

4.2. Influence of the molecular topology on the stress transmitters density

The sensitive ST concentration indicator makes now possible to evaluate the influence of the thermal treatment and molecular

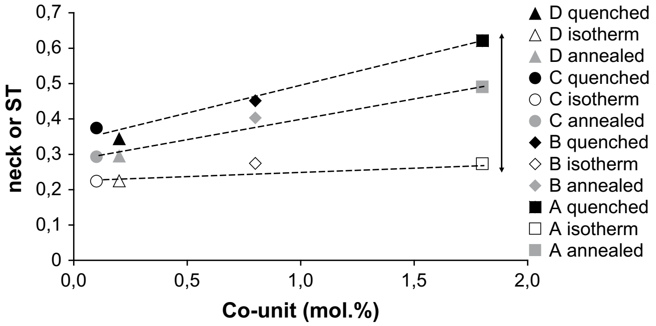

Fig. 9. Width of the neck versus the co-unit content: influence of the thermal treatments.

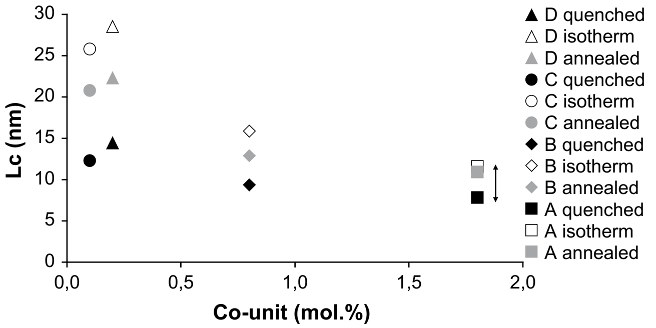

Fig. 10. Crystallite thickness versus the co-unit content: influence of the thermal treatments.

topology of each PE (C6 co-units content) on ST concentration. Indeed, it is classically admitted that the slower the crystallisation is, the less disordered the structure is and consequently the lower the ST concentration is. Therefore the thermal treatments and their associated crystallisation conditions are determinant factors that affect the ST concentration.

On Fig. 9 the ST concentration is represented versus the co-unit content for each PE. Focussing on a same PE (see the arrows on Fig. 9) classical results can be seen: the quenched samples exhibit a higher ST concentration because of the fast cooling and its disordered structure. Annealing and isotherm treatments induce a decrease of ST concentration. It is worth noting that when the isotherm treatment reduces strongly the ST concentration (up to a factor 4 compared to the quenched), the annealing treatment only leads to a 30% decrease of a maximum. It appears that the molecular network is likely fixed during the crystallisation performed from the melt. An annealing, even if it changes the lamellar structure, does not completely disturb the network. The same conclusions can be drawn concerning the evolution of L_c (Fig. 10). While annealing does not lead to a large increase of L_c, the isotherm treatment doubles the quenched value.

Comparing now the results at equivalent treatments (dotted lines) the higher the content of co-unit is, the higher the ST concentration is. It appears clearly that the content of co-unit amplifies the effects of the thermal treatments on ST concentration. In addition, for the isotherm treatment (see open symbols), the same ST concentration is measured whatever the initial molecular topology. These conclusions are in good agreement with previous studies [21,26].

Concerning the crystallite thickness it seems that whatever the thermal treatment, the higher the co-unit content is, the thinner the crystallites are. Contrary to ST concentration, the effect is more pronounced for low co-unit concentrations. It appears that a high co-unit content magnifies the effect of thermal treatments on ST concentration whereas it decreases the effect on L_c.

5. Conclusions

In literature the yield stress (σ_y) is found to be proportional to X_c without any physical explanation. On the contrary the dislocation model predicts a physical relation between σ_y and L_c, which is not consistent with experimental data. To understand these experimental results it is necessary to evaluate the initiation of plasticity by controlling L_c and X_c over large ranges. It has been made possible by varying the co-units content and by using appropriated thermal treatments on polyethylenes.

A first reason of discrepancy between dislocation models and experimental data comes from the choice of σ_y for the initiation of plasticity. Instead of σ_y a new threshold stress has been introduced (σ_{th}). It represents the transition from the visco-elastic to the visco-plastic behaviour. Despite of this improvement, the evolution of σ_{th} can still not be described by the dislocation model. Another parameter has to be introduced: the Stress Transmitter (ST) density which leads to the distribution of stresses on the edge of crystallites. The Stress Transmitters are composed of all the elements that could affect the mechanical coupling between the two phases: tie molecules, entanglements, interphase, … This ST density is determined from the neck width therefore at lower strains than classical indicators (natural draw ratio or strain hardening).

By taking into account this parameter and the dislocation model, all our experimental results can be well fitted. Finally the correlation found between σ_{th} (or even σ_y) and X_c can be understood as X_c includes dislocation model via L_c and stress transmitter density via L_p.

Neck width indicator seems to be suitable parameter to follow the evolution ST density and allows a better understanding of the influence of both co-unit content and crystallisation conditions. As expected, the ST density was found higher for quenched samples with an amplification given by a high co-unit content. A slow crystallisation from the melt has permitted to reduce the ST density to a value which is nearly independent on the co-unit content. Surprisingly, an annealing after quenching did not have a significant influence on the ST density which leads to the conclusion that the molecular network was nearly fixed during the crystallisation performed from the melt.

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