Analysis of the effects of local stress transmission on yielding properties of the polyethylenes

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ABSTRACT: To study the influence of the microstructure on the mechanical properties of the semi-crystalline polymers, heat treatments were performed on polyethylenes in order to, either vary the microstructural parameters (crystallinity, crystallite thickness …) keeping the same molecular parameters, or keep similar structural parameters with different molecular parameters. Tensile tests have been carried out to evaluate qualitatively the presence of tie molecules and entanglements. From these characterisations, it has been attempted to link these different parameters to mechanical properties. It has been shown that tie molecules, as the interface which participates in mechanical coupling between amorphous and crystalline phase, also affect small deformation behaviour of the polymers. It has appeared that for linear polyethylenes, yield stress seems to follow classical correlation with crystallite thickness. On the contrary, polyethylenes with large co-units rate do not obey to this correlation.

Key words: Microstructural parameters, tie molecules, yield, semi-crystalline polymers.

1 INTRODUCTION

Small strain behaviour of the semi-crystalline polymers has been widely studied during the last forty years and general ideas were highlighted. Consensus has appeared concerning on the one hand, the relation between crystallinity and elastic modulus [1-3] and on the other hand, the relation between yield stress and crystallite thickness [3-5]. More recently, it was suggested that different crystallization conditions could affect other microstructural parameters as entanglements, tie molecules concentration or interface between crystal and amorphous phase [6-9]. These microstructural parameters have certainly an effect on small strain mechanical properties, but their contributions are not fully understood yet. In addition, it is now well known that molecular parameters as co-units rate or polydispersity also play a significant role on mechanical behaviour [7,10-11].

2 EXPERIMENTAL SECTION

1.1 Materials

Three 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 in this work. PE A and B (see table 1) are considered as "branched" as Popli et al. [12] have shown the influence of C6 concentration above 0.6%/mol. PE C is quasi-linear because of its lower C6 concentration. Consequently the crystallinity of PE C is higher (65%) than PE A and B (around 50%). An ultra high molecular weight and completely linear polyethylene PE U is also studied. Because of its ultra high molecular weight, it presents a medium crystallinity of 49%.

1.2 Sample preparation

500 µm-thick sheets were obtained by pellets molding between aluminium foils in a press at 170°C (about 30°C higher than the melting temperature of the different polyethylenes). After this step, all the polymer sheets were quenched in

water. To modify the microstructure, isothermal crystallizations were done with two different processes. Samples designated hereafter as "annealed" were heated from their quenched-state to a temperature close to the crystallization temperature and were held in these conditions in a thermostatic bath for about fifteen hours.

The samples called "isotherm" were re-melted at 170°C in an oven before being cooled in a bath at a temperature close to the crystallization temperature and held in these conditions during fifteen hours. Watertightness was made in order to avoid oil contamination from the thermostatic bath.

1.3 Characterization

1.3.a Differential scanning calorimetry

The thermal analysis of the samples was conducted using an indium-calibrated Perkin Elmer DSC7 apparatus. The melting thermograms were recorded at a heating rate of 5°C/min, under nitrogen flow. The crystallinity (Xc) was calculated with a precision of 1% using the value 290 J/g for the specific enthalpy ΔH^0_F of a perfect crystal [7].

1.3.b SAXS

A 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. To improve the statistics and quality of SAXS patterns, accumulation times of 10 min were required. The SAXS patterns were analyzed by means of circular profiles. The observation range in q was from 0,024 to 0,98 nm^{-1}. The long period (Lp) was calculated from the maximum of the diffuse intensity corrected by the Lorentz factor ($Iq^2=f(q)$) with the relation :

$$Lp = \frac{2\pi}{q_{max}} \text{ (nm) },$$

q_{max} corresponding to the peak maximum.

The thicknesses of the lamellae were deduced, with a precision of 1.5 nm, from Lp and Xc thanks to the following relation:

$$Lc = Lp \times \frac{\rho}{\rho_c} \times Xc$$

With ρ_c the crystalline density equals to 1,003 g.cm^{-3} [3] and ρ the density of the sample.

1.3.d Tensile measurements

Dumbbell-shaped samples of gauge length 22mm, width about 5mm, and thickness of about 0,5mm were cut from the sheets. Testing was done with a MTS machine at room temperature and at a draw rate of 6,6mm/min. Yield stress values (σ_y) are defined, with a precision of 0,5 MPa, by the peak stress values and the natural draw ratios (λ_n) with the method of tangents. This method consists in taking the intersection of two tangents: the first is a linear fit of the curve of the neck propagation and the second is a fit of the hardening part.

1.3.d DMA

Small pieces were cut in the different sheets to obtain parallelepipeds with a section about 5*0.5 mm^2 and a length between jaws about 14mm. Experiments were conducted with an inverse torsion pendulum [13]. Measurements were performed at 1 Hz from 100K to 400K at 1K/min. The dynamic strain amplitude is low, about 10-4. It permits to obtain the elastic conservation modulus G', the viscous modulus G'' and the loss factor tanδ.

Table 1. Molecular and structural characteristics of the different polyethylenes

		C6 %wt	C6 %mol	Mn (KDa)	Mw (KDa)	Mz (KDa)	D =Mw/Mn	Xc	Lc (nm)
PE A « highly branched »	A quenched							49%	8
	A isotherm	4,9	1,8	14,3	231	2770	16,1	53%	15
	A annealed							52%	11
PE B « branched »	B quenched							54%	9
	B isotherm	2,3	0,8	15,8	187	1770	11,9	65%	15
	B annealed							62%	13
PE C « quasi-linear »	C quenched							65%	12
	C isotherm	0,3	0,1	15,4	216	2770	14	75%	25
	C annealed							73%	20
PE U « linear »	U quenched							49%	14
	U isotherm	0	0	/	9000	/	/	59%	25
	U annealed							51%	20

3 RESULTS AND DISCUSSION
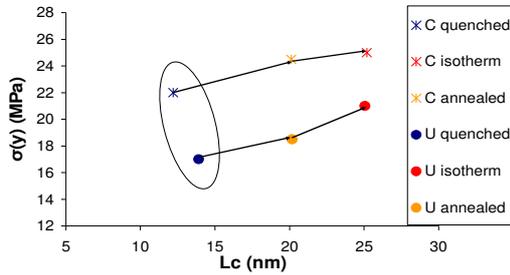
3.1 Yield stress

Fig. 1. Plot of yield stress against the crystallite thickness for the "quasi-linear" PE C and U.
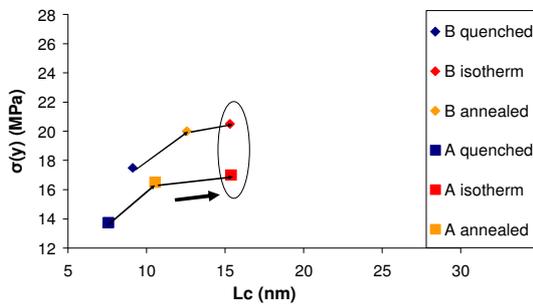

Fig. 2. Plot of yield stress against the crystallite thickness for the "branched" PE A and B.

Some authors have proposed a phenomenological approach associating yielding with the crystallinity [1-2]. However others prefer a theory more physical assuming that σ_y value depends on the crystallite thickness Lc, rather than on Xc, by the dislocation model which establishes a relation between crystallite thickness and critical shear stress. [3-5].

The yield stress is plotted against the crystallite thickness for the quasi-linear polyethylenes figure 1 and for the branched ones figure 2. We can note that there is a difference between the «branched» PE mechanical behaviour and the quasi-linear one.

Concerning the quasi-linear PEs (figure 1), a linear relation between σ_y and the thickness Lc, which fit to the dislocation model, can be observed. So it seems that σ_y is mainly related to Lc. However, for a same Lc, a significant difference between PE U σ_y compared to σ_y of PE C can be seen. It appears that other parameters are required to explain yielding behaviour. The crystallinity could be evoked as PE U crystallinity is around 50% whereas it is around 75% for the other.

On figure 2, a different behaviour can be seen for the branched PEs. They don't obey to the same linear relation. For the PE A (see the arrow), we can note that for an increase of 50% of crystallite thickness (from 10 to 15nm), σ_y remains quasi-constant. In this case, Lc is clearly not the only parameter to describe yielding of the branched PEs.

3.2 DMA analysis

The nature of PEs seems to be predominant in their yielding behaviour, whereas the influence of heat treatments is secondary. On figure 3, the DMA results are represented. Between 200 and 300K, we can note a significant difference of behaviour between branched PEs and the quasi-linear ones. Popli et Al. [12] proposed that this behaviour is related to a transition named β, which could reveal the existence of an interface (link between amorphous and crystal). It is observed that the more branched the PEs are, the more the transition appears. The presence of an interface could be representative of a better stress transmission between crystal and amorphous phase which could have an influence on yield behaviour.
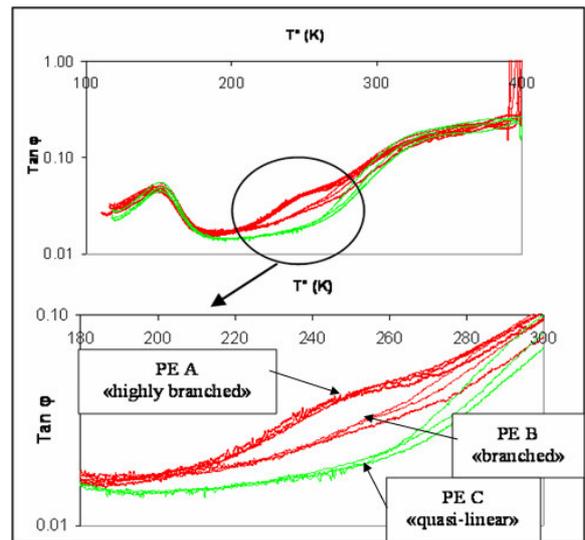

Fig. 3. Plot of the loss factor Tanφ against the temperature for the samples type A, B and C: transition β

3.3 Natural draw ratio

Stress transmission can also be carried out by links between two crystalline lamellae via tie molecules (TMs). Oleinik [9] has shown that TMs could act as stress transmitters in the process of deformation and so could affect the σ_y value. The natural draw ratio (λ_n) is known to be sensitive to the TMs concentration [11,14]. Tests have been performed on PEs A in order to study the influence of heat treatments on TMs concentration and so on yielding. Figure 4 reveals that λ_n increases from a low value for the quenched sample to higher values while applying heat treatments. TMs concentration

depends on the crystallite thicknesses and on heat treatments [15]. For the branched PE A and B, it seems to exist a linear relation between λ_n and Lc. Analysing especially the samples "A annealed" and "A isotherm", λ_n is superior for the isotherm sample to the annealed one, so the isotherm sample presents less tie molecules. We saw that "A isotherm" exhibited a Lc 50% higher than the "A annealed". It should have conferred it a higher σ_y, and yet it is equivalent to the annealed one. To explain this phenomenon, it can be supposed that because of the lack of TMs, the local stresses on crystallites are higher due to stress concentration and so the crystallites can be sheared more easily than expected. That could be the reason why the σ_y value of the sample "A isotherm" is not superior than the σ_y of the "A annealed".
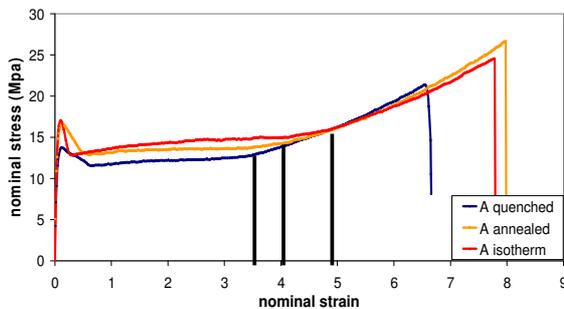

Fig. 4. Plot of the nominal stress against the nominal strain for the samples "A quenched", "A annealed" and "A isotherm".

4 CONCLUSIONS

We have shown that there is an important difference between the yield behaviour of the quasi-linear or linear PEs and the one of the branched PEs. When the linear PEs seem to show a good agreement with the dislocation model, the branched PEs do not show a significant relation between σ_y and Lc.
A first explanation would be found analysing the stress transmission between amorphous and crystalline phase. The β relaxation in DMA reveals that contrary to the linear PEs, the branched PEs present a significant interface between the amorphous and the crystalline phase. So for the branched PEs, the local stresses could be transmitted by the interface and their yield behaviour influenced. A second explanation could be found analysing the network between crystalline lamellae. For the branched PEs, heat treatments can modify their molecular network and especially their TMs concentration. If the crystallization is too slow, like in the case of the isotherm samples, the TMs

concentration would be low because of a good chains folding. This would affect the σ_y.
During mechanical testing, stresses are necessarily transmitted in the material: the interface and the tie molecules play a significant role in this transmission which is certainly decisive in small strain behaviour of the polyethylenes.

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