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

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ABSTRACT

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	△