On the strain-induced fibrillar microstructure of polyethylene: Influence of chemical structure, initial morphology and draw temperature

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Abstract. The influence of crystalline microstructure and molecular topology on the strain-induced fibrillar transformation of semi-crystalline polyethylenes having various chemical structures including co-unit content and molecular weight and crystallized under various thermal treatments was studied by *in situ* SAXS at different draw temperatures. The long period of the nascent microfibrils, L_{pf} , proved to be strongly dependent on the draw temperature but non-sensitive to the initial crystallization conditions. L_{pf} was smaller than the initial long period. Both findings have been ascribed to the strain-induced melting-recrystallization process as generally claimed in the literature. The microfibrils diameter, D_f , was shown to depend on the draw temperature and initial microstructure in a different way as L_{pf} . The evolution of D_f was shown to correlate with the interfacial layer thickness that mainly depends on the chemical structure of the chains. It was concluded that, in contrast to L_{pf} , the microfibril diameter should not be directly sensitive to the strain-induced melting-recrystallization. The proposed scenario is that after the generation of the protofibrils by fragmentation of the crystalline lamellae at yielding, the diameter of the microfibril during the course of their stabilization should be governed by the chain-unfolding and subsequent aggregation of the unfolded chains onto the lateral surface of the microfibrils. The morphogenesis of the microfibrils should therefore essentially depend on the chemical structure of the polymer that governs its crystallization ability, its chain topology and subsequently its fragmentation process at yielding. This scenario is summed up in a sketch.

Keywords: thermal properties, polyethylene, microfibrils, crystallinity, crystalline microstructure

1. Introduction

A general feature of the morphogenesis of semi-crystalline polymers is the regular stacking of chain-folded lamellar crystals alternating with amorphous layers. This stacking is characterized by an intercrystalline long period L_p including the crystalline lamella and amorphous layer thicknesses. The stacking long period is in the range of a few nanometers to a few tens. When crystallization is performed from a quiescent melt, the resulting microstructure is isotropic with a spherulitic arrangement of the lamella stacks as a result of the radial growth of the crystals from a

common multiple nucleus often designated as axi-alite [1]. The size scale of spherulites ranges from a few to several hundred microns.

Upon plastic deformation at large strains, isotropic semicrystalline polymers transform into fibrillar materials that aroused a great interest from both academic and industrial standpoints owing to their remarkable mechanical performances [2–6] to be used as ropes, textile fibers for high performance tissues and fabrics, reinforcing fibers for polymer-based composites, etc.

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The so-called fibrillar microstructure occurs via a plastic instability process, accompanied by a more or less pronounced geometric necking. The fibrillar microstructure consists of bundles of microfibrils parallel to the draw direction, each microfibril being made of a succession of crystal blocs and amorphous layers. It is generally admitted that this microstructure originates from the fragmentation of the crystalline lamellae into blocs during the plastic instability phenomenon [7–11]. These blocks rearrange into *strings of pearls* thanks to the molecular interconnections generated by the partial unfolding of chains. From small-angle X-ray scattering (SAXS) experiments, it was shown that the crystal blocs are regularly arranged with a long period, L_{pf} , along the microfibril axis that is different from the long period of original isotropic material. For various kinds of semi-crystalline polymers, L_{pf} proved to be essentially dependent on the draw temperature in a similar way as L_p depends on the temperature of quiescent crystallization from the melt or from solution, i.e. the higher the temperature the greater the long period [7–10]. Considering this complete reconstruction of the stacking long period, many authors claimed that fibrillar transformation necessarily involves a strain-induced melting-recrystallization process [11, 12]. Several phenomena have been proposed for providing physical support to this hypothesis: the chain-unfolding mechanism that necessarily goes through a transitory state of disordered chain segments analogous to the amorphous state, the conversion of plastic work into heat that may generate significant temperature increase at high strain rates, the stress-induced depression of the melting point, etc. It was even suggested by Mandelkern and co-workers that the initial morphology was completely erased by the strain-induced melting-recrystallization [13, 14].

In parallel, a few SAXS studies have been performed for characterizing the microfibril transverse dimension or width thanks to a Guinier analysis of the transverse intensity profile of the characteristic 2-streak of the one-dimensional fibrillar stacking [7, 15–20]. In this analysis framework, the transverse intensity profile is considered to be governed by the form factor of the scattering microfibrils. It turned out that both draw temperature and draw ratio, and subsequent annealing treatment as well, have an influence of the microfibril width. However, no correlations were made with structural features of the initial semi-crystalline morphology.

The above remarks regarding the fibrillar morphology contrast with the numerous studies dealing with the incidence on the elementary mechanisms of plastic deformation of the initial morphology and molecular topological of semi-crystalline polymers, such as crystallinity, crystal thickness, chain entanglement and tie chain densities, etc. together with deformation conditions [21–36]. It was shown in some cases that these structural or experimental factors could have an impact on the mechanism of fragmentation of the crystalline lamella via the local stress distribution on the crystalline lamellae [22, 25, 30]. So that one may foresee some consequences on the microfibril morphology in spite of the melting-recrystallization process.

In a previous paper [37] we reported an *in situ* SAXS study of the fibrillar transformation at room temperature of a series of polyethylene materials covering a wide range of crystallinity $0.48 < X_c < 0.80$ and long period $17 \text{ nm} < L_p < 37 \text{ nm}$. It was shown that though the fibrillar long period did not depend on the initial morphology, the width of the microfibrils displayed a correlation with the initial semi-crystalline morphology. It was suggested that the microfibril width was related to the average size of the initial crystal fragments via the formation of protofibrils that retained the memory of the crystallization conditions via the density of tie chains and chain entanglements that might survive the strain-induced melting-recrystallization.

The present study is an extension over a large temperature range of our former work of the post-yield drawing of PE. In contrast to most of the previous works dealing with *ex situ* analysis of fibrillar structure at room temperature, SAXS measurements were carried out *in situ* during drawing in order to prevent eventual post-drawing crystallization and topological rearrangements. This is likely to provide information closely related to the morphogenesis of the microfibrils during drawing and help understanding the mechanical behavior of the drawn materials in relation to their processing and crystallization conditions. The morphological changes that occur during ultra-drawing beyond the fibrillation stage [4] are not discussed in this work.

2. Experiment

2.1. Materials and sample preparation

Four linear polyethylenes with different hexene co-unit contents and very close molecular weights

were provided by Total Petrochemicals (Feluy, Belgium). The molecular characteristics are given in Table 1. It is worth noticing that in spite of their very close M_n and M_w values and similar co-units contents, PE-C and PE-D have significantly different M_z values. This is relevant to the presence of a small amount of very long chains in PE-D that is expected to influence the crystallization behavior [38, 39].

The four polymers have been submitted to three different thermal treatments in order to modify their crystalline microstructure and chain-topology. Quenching is expected to keep the entanglement topology of the melt and generate thin crystals. In contrast, annealing in the solid state and isothermal crystallization from the melt are expected to reduce the entanglement density and generate thick crystals, the latter treatment being more efficient than the former one as evidenced through the data of Table 2. The polymer pellets were compression-molded at 170 °C into 500 μm sheets between aluminum foils in a heating press and then quenched into water at room temperature (RT). These samples were called ‘quenched’. Some of the quenched samples were heat treated via two different ways in order to modify the crystalline microstructure. The samples labeled ‘annealed’ were heated up to the temperature $T_c = 122$ °C for 15 hours and subsequently slowly cooled down to RT (see T_c determination below). The samples called ‘isotherm’ were melted at 170 °C and then cooled in a thermostatic oil bath at the temperature T_c and held at this temperature for 15 hours. More details on the sample preparation are given elsewhere [37, 40].

2.2. Differential scanning calorimetry (DSC)

Thermal analysis was conducted on a DSC7 apparatus from Perkin-Elmer using samples of 5–7 mg. The temperature and heat flow scales were calibrated using high purity indium. The heating and cooling scans were recorded at a rate of 10 °C/min. The crystal weight fraction, X_c , was computed from the melting enthalpy of the samples, using the value $\Delta H_m^\circ = 290$ J/g for the heat of fusion of perfectly

crystalline PE [41]. The standard deviation of X_c data is about 1%.

2.3. SAXS measurements

Small-angle X-ray scattering (SAXS) experiments were performed on the BM02 beamline of the European Synchrotron Radiation Facility (Grenoble, France) using a wavelength $\lambda = 0.154$ nm. The 2D-SAXS patterns were recorded on a CCD camera from Princeton Instruments (Trenton NJ, USA) which was set at sample-detector distance of 158 cm. *In situ* recording of SAXS patterns during uniaxial tensile testing was performed using a home-made tensile stage allowing symmetric stretching of the sample. This ensured that all data were recorded from the same location on the sample during deformation. The dumbbell-shaped samples were 11 mm in gauge length, 4 mm in width and 0.5 mm in thickness. The nominal or engineering strain is defined as $\varepsilon = (L - L_0)/L_0$ with L_0 and L the sample gauge length before and during tensile drawing. The strain rate was $6.4 \cdot 10^{-4} \text{ s}^{-1}$ to make sure that the strain increment was less than 0.1% during the 5 s time for every pattern recording. The experiments were performed at several draw temperatures in the range $25^\circ\text{C} < T_d < 100^\circ\text{C}$ for each sample.

The Lorentz-corrected intensity profiles of the isotropic samples prior to straining were obtained by azimuthal integration of the 2D patterns according to Equation (1):

$$I(q) = q_2 \int_0^{2\pi} I(q, \varphi) d\varphi \quad (1)$$

where φ is the azimuthal angle. The average long period of the lamellar stacking, L_p , was then determined from the Bragg’s relation (Equation (2)):

$$L_p = \frac{2\pi}{q_{\max}} \quad (2)$$

where $q_{\max}$ is the scattering vector at the maximum of the correlation peak as determined by a Gaussian fitting. The standard deviation of the L_p data does not exceed 1.0 nm.

The crystal thickness, L_c , of the isotropic samples was computed from Equation (3):

$$L_c = L_p X_c \frac{\rho}{\rho_c} \quad (3)$$

Table 1. Molecular characteristics of the row PE materials

Material	Co-unit [mol%]	M_n [kg/mol]	M_w [kg/mol]	M_z [kg/mol]
PE-A	1.8	14.3	231	2770
PE-B	0.8	15.8	187	1770
PE-C	0.1	15.4	216	2770
PE-D	0.1	15.0	229	4100

where $\rho_c = 1.00 \text{ g/cm}^3$ is the density of the crystalline phase. This relation assumes much larger length and width of the crystalline lamellae as compared with thickness.

Regarding the drawn samples displaying the characteristic two-streak meridian pattern, the one-dimension intensity profile along the meridian was obtained by projection on the meridian of the 2D-pattern according to Stribeck's method [19]. Then the long period along the draw axis, L_{pf} , was estimated by using Equation (2).

The structural data of all isotropic PE samples at RT are reported in Table 2. Also are reported the weight fraction of interfacial zone between crystal and amorphous regions as assessed from Raman spectroscopy, X_i , the concentration of stress transmitters [ST] according to Brown-Huang's theoretical approach, and the natural draw ratio at RT, λ_N , as already determined in a previous study via *in situ* mechanical testing [38, 42].

A convenient way for quantifying the microfibril width is to analyze the transverse intensity profile of the lobes of the 2-streak SAXS patterns. The scattering objects were supposed to be individually embedded in a medium of lower electron density consisting of amorphous chains and cavities, without interference between them. The corresponding model consists of either elongated cylinders or discs. In both instance, the analysis of the transverse intensity profile of the streak-like lobes can be performed via Guinier's approximation of the form factor leading to an estimation of the transverse dimension of the scattering elements. In the case of scattering cylinders, the relevant Guinier's approximation function is given by Equation (4) [43]:

$$I(q) = I_0 \exp\left(-\frac{q^2 D_f^2}{4}\right) \quad (4)$$

where D_f is the cylinder diameter with $D_f = 2R_f$ where R_f is the radius of gyration. Fitting the experimental intensity data with Equation (4) enabled computing only one diameter value for each sample as demonstrated in the previous study [37]. The standard deviation of the D_f data was about 1.0 nm or less.

3. Results

All the SAXS data regarding the fibrillar structure of the materials in the present work are relevant to samples drawn at the same engineering strain $\varepsilon = 1.3$. At this strain level the fibrillar transformation has not reached the whole sample length but the necking process is stabilized at the so-called *natural draw ratio*, λ_N , and propagates along the sample [44, 45]. This enables to study the *nascent fibrillar structure* of each material, irrespective of its macroscopic behavior.

Firstly, it is to be noticed that the λ_N data of Table 2 vary over a very large range and do not display correlation with either X_c or L_p . On the other hand, the λ_N data depend on the thermal treatment for every PE type. This is an evidence that the microfibrillar structure does depend on the initial crystalline microstructure is not thoroughly erased by the strain-induced melting recrystallization process. This strong correlation enabled using λ_N as an indicator of the long-term mechanical properties via the correlation with the initial molecular topology [46, 47].

Figure 1 shows the typical shape of a SAXS pattern recorded from the quenched PE-A after necking at

Table 2. Structural and physical characteristics of the isotropic PE samples at RT

Materials		X_c [%]	[ST]	X_i [%]	λ_N	L_p [nm]	L_c [nm]
PE-A	quenched	48	0.24	13	3.5	17	8
	annealed	52	0.17	14	4.0	23	11
	isotherm	53	0.15	11	4.7	24	12
PE-B	quenched	54	0.19	8	4.2	19	9
	annealed	62	0.14	8	4.7	22	13
	isotherm	65	0.09	4	5.5	26	16
PE-C	quenched	65	0.19	5	4.5	20	12
	annealed	73	0.08	5	6.0	30	21
	isotherm	75	0.03	5	7.5	36	26
PE-D	quenched	69	0.17	3	5.0	22	14
	annealed	77	0.08	5	5.7	30	22
	isotherm	80	0.03	–	7.0	37	29

$T_d = 50^\circ\text{C}$. This figure schematically shows the methodology of calculation of the microfibril long period L_{pf} and diameter D_f . The strong central scattering extending in equatorial direction arises from interfibrillar cavities or low density regions [19]. The electron density contrast between these regions and the microfibrils is so high that this scattering can turn extremely intense and merge onto the streak-like scattering, particularly for high crystallinity materials. In this instance, the analysis of the structural characteristics of the microfibrils is prohibited. However increasing the draw temperature reduces the propensity for cavitation or interfibrillar density fluctuations [48] so that more samples can be inves-

tigated during drawing at elevated temperature than in the case of the drawing at RT. This is one of the major benefits from the present study compared to our previous one [37].

Figure 2 shows the evolution of the meridian intensity profile of quenched PE-A as a function of strain at two different T_d . The SAXS patterns change from isotropic to highly anisotropic patterns with two streak-like scattering patterns during the elongation of samples.

The central SAXS patterns of Figures 2a and 2b show the SAXS patterns about the onset of the streak-like reflections characteristic of the fibrillar structure, for both T_d . The actual strain onset decreases

Figure 1. Schematic SAXS pattern and molecular model of the fibrillar microstructure (borrowed from Striebeck ref. 19)

Figure 2. SAXS patterns and meridian intensity profile of quenched PE-A as a function of strain : (a) $T_d = 50^\circ\text{C}$; (b) $T_d = 100^\circ\text{C}$

with increasing T_d suggesting that the fully oriented structure forms faster at higher T_d . The generation of microfibrils from the crystalline lamella fragmentation should indeed be strongly promoted at higher T_d due to the temperature dependence of the crystal stiffness in the temperature domain of the crystal mechanical relaxation. Besides, at a given T_d , the streak-like scattering intensity strongly increases during elongation due to the gradual conversion of lamellae into microfibrils, and the gradual improvement of orientation as well.

Figure 3 shows L_{pf} as a function of initial L_p for all samples at different T_d . At low T_d , annealed and isotherm samples could not be quantitatively analyzed due to the merging of the intense void scattering onto the microfibrillar scattering. However, more L_{pf} data could be obtained when elevating T_d due to the reduced propensity of the samples for cavitation, as judged from the significant decrease of the scattering about the beamstop (Figure 2).

Figure 3a shows that L_{pf} is generally smaller than the initial L_p indicating dramatic reconstruction of the periodic stacking of amorphous and crystalline phases as a result of the plastic deformation. If considering the SAXS intensity profiles of Figure 2, this phenomenon seems to be rather gradual as a function of increasing strain. In addition, L_{pf} increases with increasing T_d . These findings are in perfect agreement with the melting-recrystallization concept already observed for various semi-crystalline polymers [49–51].

The roughly linear increase of L_{pf} as a function of initial L_p , for every T_d value, may be assigned to the

crystallization potential of the various PEs, i.e. a chemical structure dependence including count content and molecular weight. The chemical structure of the chains indeed governs in a similar way the generation of L_p from the quiescent crystallization in the melt and that of L_{pf} from the strain-induced recrystallization upon drawing.

It appears from Figure 3a that the L_{pf} data at RT (black symbols) are surprisingly close to and even overlap the L_{pf} data at 50 °C (blue symbols). This apparent insensitivity of the fibrillar long period to the draw temperature in the range 25 °C < T_d < 50 °C has been formerly reported by Peterlin and Balta-Calleja for PE materials covering a similar X_c range as the present one and for a similar T_d domain [22]. These authors conjectured that the roughly invariant behavior of L_{pf} for T_d < 50 °C can be assigned to the super-cooling effect consecutive to the strain-induced self-heating and melting of the fibrillated material in the destruction zone during the course of the fibrillar transformation. The reason would be that the crystallization rate turns so high with decreasing temperature that recrystallization of the molten material is almost complete before the actual temperature of the sample reaches the experimental T_d value. It results that L_{pf} gradually turns T_d -independent with decreasing T_d .

Regarding Figure 3b, samples of the same PE material with different crystalline microstructures generated by thermal treatments exhibit very small difference in L_{pf} at given T_d , in the range of experimental accuracy. This finding is an additional evidence of the strain-induced melting-recrystallization process

Figure 3. Microfibril long period versus initial L_p at various T_d : (a) influence of chemical structure for quenched samples; (b) influence of thermal treatment (full colors refer to draw temperatures; symbol shapes refer to the various polymers, declining tint of every color refers to thermal treatments)

Figure 4. Microfibril diameter versus stacking long period: (a) influence of chemical structure for the quenched samples; (b) influence of thermal treatment

that completely erases the initial crystalline microstructure, from the standpoint of crystal stacking in the microfibrils.

Figure 4 shows the microfibril diameter as a function of long period at different T_d . Similar trends could be obtained if using D_f versus L_p . The D_f values perfectly agree with transmission electron microscopy measurements by Tarin and Thomas for high density PE crystallized from the melt under similar conditions [45]. Furthermore, the D_f data of Figure 4a exhibit a linear variation with L_p at a given T_d , that is an evidence of a chemical structure dependence of D_f similar to that of L_{pf} .

Regarding the D_f evolution with thermal treatment in Figure 4b for a given PE type and for a given T_d , it appears a faint increase with increasing L_p , i.e. from quenched to annealed and isotherm sample. The above observations suggest that D_f is slightly correlated to the initial crystalline microstructure. But the most striking feature of Figure 4 is that D_f is temperature-dependent over the whole T_d range, in contrast to L_{pf} that no longer depends on temperature for $T_d \leq 50^\circ\text{C}$. This latter finding lets us foreseeing that D_f is influenced by the melting-recrystallization process in the same way as L_{pf} is. Notwithstanding no global correlation appears between D_f and L_p which is a parameter characteristic of the initial microstructure.

So an attempt has been made to correlate D_f to a parameter characteristic of the chain topology. Figure 5 shows D_f as a function of the natural draw ratio λ_N which is a macroscopic indicator of the concentration of stress transmitters $[ST]$ as deduced from Brown-Huang's model [40, 42]. The reason for

Figure 5. Microfibril diameter versus natural draw ratio at different temperatures

choosing a macroscopic indicator λ_N instead of the actual molecular parameter $[ST]$ is that the occurrence of large scale chain rearrangements such as chain reeling together with regular chain-folding during crystallization at high temperature of highly crystalline PEs likely decreases the occurrence of tie chains and chain entanglements. This phenomenon is not taken into account in the $[ST]$ computation that is performed in the framework of Fischer's model assuming that the global chain coil conformation of the molten state is preserved in the solid state. This point will be further argued in the *Concluding Discussion*. In contrast, λ_N is an experimental parameter that does account for the topological modifications occurring during crystallization. So only the variation direction of $[ST]$ is shown on the x-axis of Figure 5 for the sake of the discussion.

Figure 5 shows that, at a given temperature, the D_f data for the samples having the same thermal treat-

ment linearly increase with increasing λ_N and decreasing $[ST]$. This is again in agreement with the chemical structure dependence. Quenched samples exhibit smaller D_f than annealed and isothermal samples. However, D_f shows little if any dependence on thermal treatment for a given PE material. There is again no global correlation between D_f and the topological parameter, λ_N or $[ST]$, as it was the case for the structural parameter L_p .

Alternatively, we have tried a mixed correlation with crystalline microstructure and chain topology by using Nitta's parameter, $L_c/[ST]^{0.5}$ [52]. Nitta's approach considers yielding as a fragmentation process, the size of the crystal fragment being basically determined by the average distance between tie chains. These topological features are the locus of stress concentration that initiates the lamella fragmentation. From a mechanical standpoint, the L_c factor in this parameter can be seen as featuring the shear stress to which it is roughly proportional according to the dislocation theory at the onset of the lamellae fragmentation [23]. The $1/[ST]^{0.5}$ factor accounts for the distribution of stress on the lamella surface via the density of the stress transmitters. The unreported data displayed no clear correlation between D_f and $L_c/[ST]^{0.5}$ for the various T_d values of the present experiments. This is in agreement with our previous findings at RT.

Finally a correlation was attempted with the interfacial layer thickness which worked fairly well at RT [37]. Figure 6 shows the D_f versus X_i plots at various T_d . For a given T_d value, all the D_f data fall on the same curve, irrespective of the thermal treatment. Moreover, this finding applies to every temperature, each curve being shifted upward with increasing T_d .

Figure 6. Microfibril diameter versus interfacial layer thickness at different draw temperatures

Worth noticing is that X_i is not much dependent on the thermal treatment, but rather on the chemical structure of the polymer. So that it is not clear whether D_f actually depends on the initial crystalline microstructure and chain topology of the samples via X_i or depends on the chemical structure of the polymer in a similar way as X_i (see Table 1).

4. Conclusions

Two major findings have been disclosed regarding the microfibril structure. First, D_f depends on T_d over the whole temperature range $25^\circ\text{C} < T_d < 100^\circ\text{C}$, in strong contrast with L_{pf} that levels off for $T_d \leq 50^\circ\text{C}$. This can be taken as an evidence that the microfibril diameter and long period do not depend in a similar way on the strain-induced melting-recrystallization process. Second, D_f obeys a unique correlation with X_i at every T_d value. This suggests that D_f mainly depends on the mechanism of lamella fragmentation at the onset of yielding, the correlation with X_i being the footprint of the chain topology on the lamella fragmentation process.

However, it is quite surprising that D_f steadily increases with decreasing X_i in parallel to an increase of λ_N as observed in Figure 5. Indeed a greater λ_N value is indicative of a greater drawability of the microfibrils, namely a high potentiality for chain-unfolding. Two mechanisms may be proposed in consideration that high crystallinity PEs develop regular chain-folding during crystallization from the quiescent melt due to the reeling phenomenon. In the case of samples having low X_i that goes along with high crystallinity (Table 2), lamellae may initially break into smaller crystal fragments owing to the high rate of regular chain-folding so that the microfibrils could develop to greater length according to Peterlin's *string of pearls* model. Thereby, their diameter should gradually be reduced at constant crystal volume fraction. Alternatively, the crystal fragments in the protofibrils may display greater capability for chain-unfolding resulting in reduced D_f in the final microfibrils. Both these issues should in principle result in a reduction of D_f which contrasts with the observed increase of D_f .

For reconciling the concomitant increases of D_f and λ_N , one may assume that the chains unfolded during the generation of the microfibrils are able to aggregate onto the lateral surface of the protofibrils. By this process, the final D_f of the microfibrils may grow significantly bigger than the initial D_f of the proto-

fibrils extracted for the fragmented lamellae. Moreover, this process should be more effective for highly crystalline PEs having small co-unit content and high ability for chain unfolding.

This explanation also applies to the observation that D_f increases with increasing T_d at a given X_i value (Figure 6): indeed, the increase of chain mobility with increasing temperature in the present T_d range should promote the gathering of unfolded chains onto the lateral surface of the microfibrils resulting in bigger D_f . To sum up, the morphogenesis of the microfibrils should be essentially dependent on the chemical structure of the polymer that governs its initial crystallization ability and its chain topology and the various stages of the microfibril construction.

At the light of the present data, Peterlin's scenario for the fibrillar transformation may be modified regarding the morphogenesis of the microfibrils as shown in Figure 7, disregarding the classical plastic processes in the crystal such as crystal shear, phase transition and twinning:

- stage 1: protofibrils are generated like *string of pearls* via fragmentation of lamella stacks and subsequent extraction of the crystal fragments via chain-unfolding from the fracture surfaces of the crystal lamellae. The remaining chain-folded crystal fragments undergo a gradual strain-induced melting owing to the self-heating generated by the plastic work or energy delivered by the partial destruction of the crystals via chain-unfolding. The presence of these remaining chain-folded crystal fragments is due to the more or less irregular chain-topology at the crystal/amorphous interface (X_i) that prevents or at least hinders chain-unfolding. These topologically coherent entities are the ones that preserve the protofibril integrity in spite of strain-induced melting. The protofibril should not be as perfectly oriented as shown on the picture and their uniaxial orientation must develop gradually during the protofibril buildup.
- stage 2: benefiting from the self-heating, the partly molten protofibrils undergo elongation and thinning down thanks to further chain-unfolding up to the natural draw ratio. Then, the chain-unfolding potential of the topologically coherent entities is exhausted. The concomitant strain-hardening entails the stopping of plastic deformation. Self-heating stops and the local drop of temperature enables recrystallization of the protofibrils into incipient microfibrils with new long period. At this

stage, incipient microfibrils and protofibrils may coexist for a while.

- stage 3: the completion of recrystallization within the microfibrils together with aggregation and additional crystallization of unfolded chains along the microfibrils finally leads to wider and stable microfibrils. The diameter of the stable microfibrils strongly depends on the material and T_d : the higher are the crystallization potential and T_d , the higher is D_f . An interfibrillar amorphous phase consisting of non-crystallizable unfolded chains should remain due to topological defects such as entanglements and chain defects such as co-units that both prevent the chains to set up in crystallographic register despite good alignment with the microfibrils. This conclusion is consistent with the fact that thermal treatments do not significantly affect D_f .

The question of the long period evolution is somewhat more complex. Figure 3a shows that the fibrillar long period, L_{pf} , is always lower than the initial long period, L_p , in the limits of experimental accuracy. For annealed and isothermal samples, this finding may be rationalized in consideration that the draw temperature, $25^\circ\text{C} < T_d < 100^\circ\text{C}$, is always lower than the temperature of thermal treatment, $T_c = 122^\circ\text{C}$, so that one should expect $L_{pf} < L_p$ after melting-recrystallization (Figure 3b). However, for quenched samples (Figure 3a), it is hardly believable that the structural transformation could occur at a local temperature T_d^* lower than the quenching temperature. This is especially true for $T_d = 100^\circ\text{C}$. Moreover, self-heating is liable to increase the local temperature T_d^* above the T_d value. Thereby, T_d^* is likely to exceed the T_c of quenched samples so that melting-recrystallization cannot account for the finding $L_{pf} < L_p$.

One may thus propose a complementary mechanism to that of the model of Figure 7. One may consider that the melting point could not be reached during the transformation process, so that crystal *destruction-recrystallization* should be more appropriate than *melting-recrystallization* [11]. This implies that only a part of the crystalline phase should be only concerned by the phenomenon. This part should depend on the sample initial crystalline microstructure and chain topology, and experimental conditions as well.

Figure 8 shows a scenario of microfibril generation based on partial strain-induced crystal destruction-

Figure 7. Schematic of the fibrillar transformation upon uniaxial drawing of polyethylene based on Peterlin's model including data from the present study (see text for details)

recrystallization. This model borrows from Thomas and coworkers observations [45, 53] regarding the fibrillar transformation of high density PE in relation to the chain topology, and the correlation with the natural draw ratio. Protofibrils (a) are first formed by fragmentation of the crystalline lamellae stacks. Then the stretched chains between the crystal fragments (b) in the protofibrils are prone to gradually crystallize benefiting from the strain-induced chain orientation. Then, stretching and self-heating promote chain unfolding and thinning down of the protofibrils (c) that gradually turn into microfibrils thanks to further crystallization and aggregation of unfolded chains (d). By this way, the final average L_{pf} value may be lower than the initial L_p value, although the local T_d^* could be higher than T_c . Besides, the amount of new crystal blocks grown under strain is likely to be lower for high T_d than for

Figure 8. Alternative mechanism of microfibril generation in case of partial strain-induced melting (see text for detail)

low T_d owing to lesser density of critical nuclei. This could explain that L_{pf} is higher at high T_d .

The presence of surviving crystal fragments with different crystal thickness than the strain-induced crystal blocks should disrupt the regular stacking in the microfibrils. As a matter of fact, none of the drawn samples displayed harmonics on the 2-streak SAXS patterns.

The amount of surviving crystal fragments may depend on both the sample initial crystalline microstructure and experimental conditions. High T_d and low initial X_c or L_p are favorable to crystal destruction owing to better chain relaxation in the crystalline phase. However, this quantity is hardly accessible to experiments.

The later refinement of the proposed fibrillar transformation model is perfectly consistent with the observation that L_{pf} turns roughly constant for $T_d \leq 50^\circ\text{C}$. Indeed, below the temperature of the crystal relaxation, molecular motions in the crystal are prohibited at usual tensile strain rates. Besides, considering that the β -relaxation in high density PE occurs at about -40°C and the glass transition temperature at -120°C [54], the molecular motions in the amorphous phase are little affected in the range $-40^\circ\text{C} < T_d < 50^\circ\text{C}$. Therefore, the fibrillar transformation process should be practically insensitive to temperature in this T_d range.

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