Rolling and Annealing of Polyethylene

I. David-Boudet[a]; A. C. Grillet[a]

[a] Universite de Savoie Laboratoire Matériaux Polymères et Composites Campus Scientifique, cédex, France

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ROLLING AND ANNEALING OF POLYETHYLENE

I. David-Boudet and A. C. Grillet*
Université de Savoie
Laboratoire Matériaux Polymères
  et Composites Campus Scientifique
73376 Le Bourget du Lac cédex- France

ABSTRACT

Modifications of microstructural and mechanical properties of poly-ethylene (PE) have been investigated by many authors, but nearly always on drawn polymers. Only a few papers deal with rolling of polymers. The aim of this work is to study the changes in morphological and mechanical properties due to cold-rolling, and the evolution of these same properties with thermal treatment after cold-rolling. High density polyethylene (HDPE) with various rolling ratio (0-390%) is analyzed by X-ray diffraction and scanning electron microscopy (SEM). During cold-rolling, the crystalline lattice is partly transformed from orthorhombic to monoclinic structure. This transformation is reversible when the material is annealed one hour at 130°C. A great diminution of the size of the spherulites is observed during rolling. Mechanical properties are analyzed with tensile tests. The strain energy per unit volume is highly increased by rolling due to the raise of the number of links between crystalline and amorphous phase. Contrary to the modification of the crystalline lattice, the changes of morphological and mechanical properties are not reversible.

INTRODUCTION

Microstructural changes in semicrystalline polymers are generally caused by mechanical or thermal treatments. These variations have always been investigated because they govern mechanical properties of materials.

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For polyethylene, many contributions deal with microstructural modifications during drawing and several deformation mechanisms have been proposed to describe the morphological changes occurring in tensile extension, notably by Peterlin [1]. Later on, other research has been performed from the crystallographic scale [2-6] to the spherulitic [2, 4, 7, 8-10], and then to the macroscopic scale [11-18].

A recent review of Lin and Argon [19] about structure and plastic deformation of polyethylene offers a complete resume of all the investigations in this field and especially on the deformation process induced by compression or shear stress.

But very poor literature has been published on microstructure changes due to rolling [20-21].

This work tries to define the influence of this peculiar mechanical treatment on polyethylene properties, combining microstructural, morphological and mechanical characterizations. Moreover, the effect of annealing treatments after rolling is also investigated to determine which modifications are reversible.

Samples and Investigations
Materials and Treatments

The polyethylene used in this study is a very linear PE with a molecular weight of 130 000 g/mole. This material has been provided by Fina Chemicals in powder form and processed by injection molding. Samples are then cold-rolled at three rates: 135%, 325% and 390%.

In order to determine annealing conditions, the crystalline rate has been measured for the non cold-rolled and the most cold-rolled samples (Table 1). Results are gathered in Table 1 for samples annealed 1 hour at three different temperatures (120, 125, 130°C) or after annealing at 130°C during times varying from 1 to 24 hours.

The most significant evolution is due to an annealing at 130°C (especially for the sample cold-rolled up to 390%), but one hour is sufficient to obtain this result. So the annealing conditions used for this study are 1 hour at 130°C.

EXPERIMENTAL

The differential scanning calorimetry used to determine the crystalline amount was a Perkin Elmer DSC7. Analysis has been performed in the 50°C-180°C temperature range with a heating rate of 10°C/min.

Materials morphology has been visualized using a scanning electron microscope JEOL 810A on gold plated samples. At first, microslices were cut with a

TABLE 1. Determination of Annealing Conditions

a- variations of crystalline rate for one hour of annealing at various temperatureS

b- variations of crystalline rate with the annealing time for the unrolled sample

annealing time at 130°C	Xc (%)	a
unannealed	71	
1h	78	
3h	81	
6h	81	
24h	84	

annealing T rolling rate	unannealed	120°C	125°C	130°C	b
unrolled	71%	72%	77%	78%	
390%	64%	75%	76%	82%	

thickness of about 180 μm. Next, a chemical treatment partially removed the amorphous phase in order to throw the crystalline phase into relief. The chemical solution was a blend H2SO4/KMnO4 with 3.8% by weight of KMnO4 [22-23]. The samples stayed 15 minutes in the solution and were rinsed through four steps: H2O/H2SO4 with two parts of H2SO4 for seven parts of H2O in volume, H2O2 30 volumes, H2O and then acetone [22]
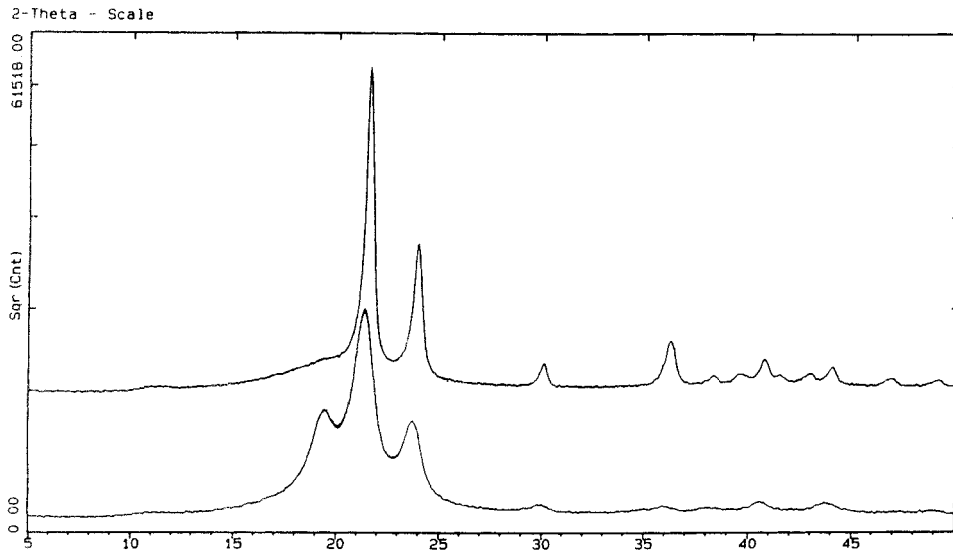
Figure 1.   X diffraction analysis of unrolled and 390% cold-rolled samples.

Mechanical behavior has been tested at room temperature on a JJ-MK30 with a 1kN force sensor. The test speed was 60 mm/min and the samples were cut according to ISO standard.

Diffraction X analysis was obtained using a Siemens 500 diffractometer in reflection mode and at room temperature.

RESULTS AND DISCUSSION

Crystal Lattice and Crystalline Microstructure

The patterns of diffraction for non cold-rolled and 390% cold-rolled samples are given in Figure 1. The peaks appeared for non cold-rolled samples are typical of orthorhombic lattice. The 390% laminated sample exhibits a peak at 2Θ =19.48 which is characteristic of monoclinic phase (<001> reflections) but the other peaks could be due either to orthorhombic lattice or to the superposition of the peaks typical of the two phases.

According to Ingram [5] and Akiyoshi [6], the crystalline lattice is partially modified and, in the laminated material, two crystalline structures exist in the same time.

After annealing for 1 hour at 130°C, the lattice has still been modified (Figure 2a). The signal characteristic of monoclinic lattice has disappeared. The
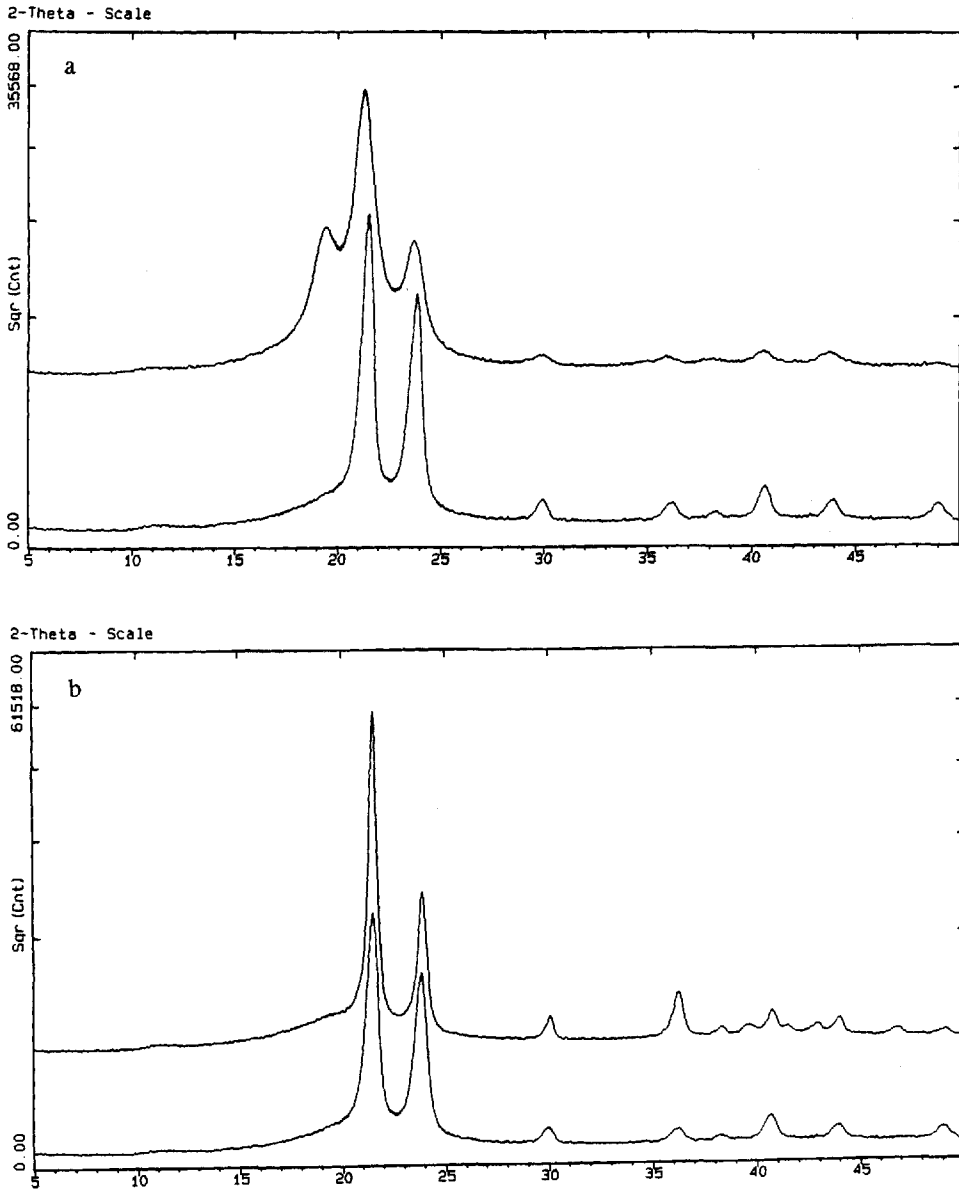
Figure 2. X diffraction analysis of annealed material.

a - comparison between 390% laminated samples annealed or not

b - comparison between untreated and 390% laminated and annealed
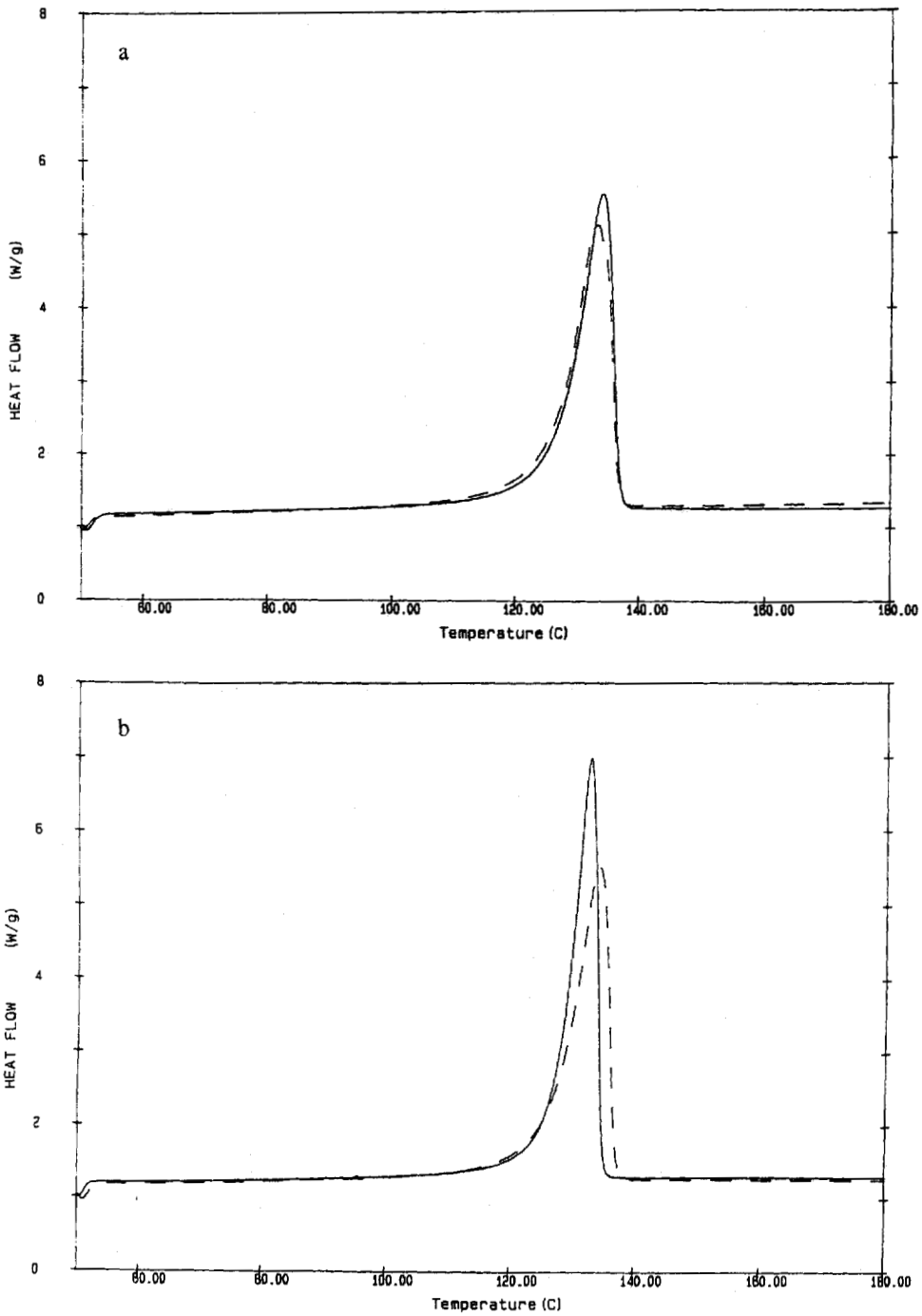
samples

Figure 3.   DSC analysis of unrolled and rolled samples.

a -   -----   unrolled

_____135%

b -   ----   135%

_____325%

TABLE 2. Crystalline Amount of Unrolled, Rolled, and Annealed Materials

annealing T rolling rate	unannealed	130°C
unrolled	71%	78%
135%	72%	78%
325%	69%	78%
390%	66%	80%

super-position of the nontreated sample diffraction pattern with that of 390% laminated and annealed sample shows the same diffraction graph for the two materials (Figure 2b). So, annealing permits the sample to recover the initial ortho-rhombic lattice. Buckley and Mc Crum mention in their study on drawn PE [10], that after annealing there is a remarkable recovery of the microstructure.

The crystalline microstructure has been performed by differential scanning calorimetry (Figure 3). For a laminating rate over 135%, melting of crystalline phase ends at a lower temperature. According to the Gibbs-Thomson law, the melting temperature depends on crystalline lamellae thickness. So, the decrease of the melting end temperature led us to speculate that the thickest crystalline lamellae have disappeared.

The crystalline amounts have also been calculated from enthalpy values (Table 2). They are reduced only from the rolling rate of 325%. For these samples, the crystalline phase disappears partially but not for PE laminated up to 135%. This crystalline amount evolution agrees with Alberola et al. [20]. But generally, however, the results reported about drawn materials mention an increase of the crystalline amount with the drawing ratio, due to crystallization during drawing [11, 15, 17]. So, rolling seems to have a different influence on materials than drawing.

Annealing produces classical effects on microstructure, i.e. a crystalline amount increase due to easier diffusion near melting (Table 2) and a total shift of the melting peak to higher temperatures. Lamellae thickness increases with annealing and their size distribution could be modified [1 , 20, 24-25].
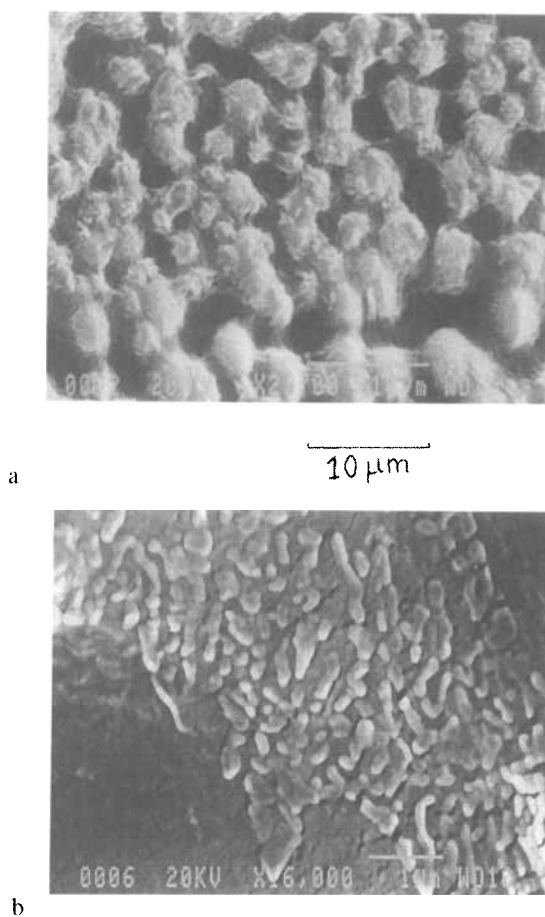
Figure 4.   Morphology of rolled polyethylene.

a - unrolled

b - 390%

After annealing, the difference between the crystalline amount of non-flattened and flattened material is scarcely visible. Thermal treatments tends to give a similar crystalline rate to all samples and to cancel the mechanical treatment effect.

Morphology

Morphology of samples has been investigated by scanning electron microscopy after chemical treatment of microslices. Only materials that have been submitted to rolling rates of 135% and 390% have been observed. The morphology of an unrolled sample is presented in Figure 3. An analysis of composition performed on the "small balls" seen in the material permits us to conclude that they are
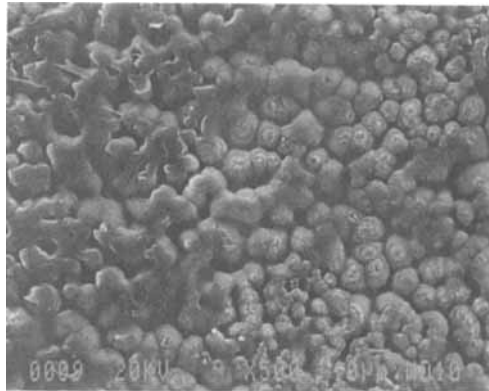
Figure 5. Morphology of the 390% rolled material surface

constituted only by carbon and hydrogen. Therefore, they are formed by polyethy - lene and not caused by the chemical treatment [22].

Flattening has great consequences on polyethylene morphology. Since the first rolling rate, spherulites size decreases from 3-5 μm for the unrolled to around 1 μm for the one rolled to 135% (Figure 4). If the laminating rate still rises, spherulites size carries on to diminish. For the samples rolled up to 390%, the morphology looks like small sticks which have a width of about 0.3 μm (Figure 4).

If the observations are realized, not on the microslices but on the poly- ethylene surface (always after chemical treatment), the morphology seems to be similar to the one before laminating (Figure 5). The material surface has not under- gone morphological modifications due to mechanical treatment. The rolls of the flatting mill are lightly lubricated and the sample surface could have tendency to slip. Then, the stresses are concentrated on material core.

Thus, a spherulites orientation, such as described by Reed and Zhao [8] for a drawing material, has not been shown. But, independently of rolling problems, the orientation effects can be different whether treatment is drawing or laminating. Drawing favors only one deformation direction, whereas during rolling, the material is deformed along two directions: lengthwise and transverse.

The morphological observations can be linked to the microstructure modif- ications determined before. For the sample rolled up to 135%, the spherulites size decreases without any modification of melting temperature, crystalline amount or lamellae thickness. This result could be explained by a fracture of the lamellae tips into tiny crystalline units [7]. However, it could be also due to the morphological heterogeneousness of the material. Differential scanning calorimetry analysis in- volves both core and surface crystalline units.
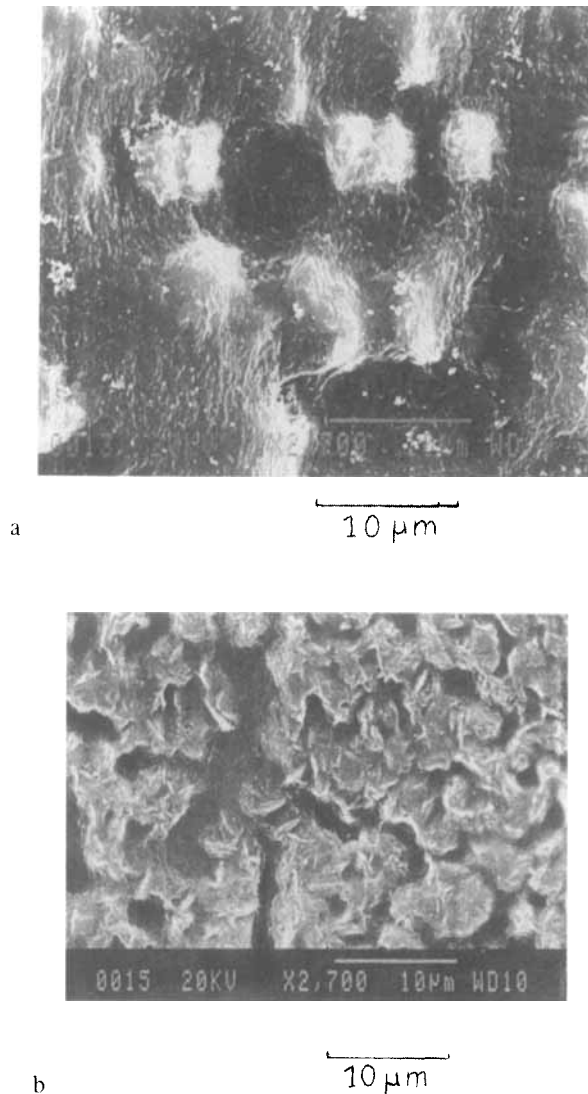
Figure 6.   Morphology of annealed materials
            a - unrolled
            b - rolled until 390%

When the flattening rate increases, the thickest lamellae disappear and the spherulites size diminishes. This explains the narrowing of enthalpic signal and the crystalline amount reduction.

The same type of analysis has been performed on annealed polyethylene (Figure 6). A great increase in the crystalline units (spherulites or sticks) has been

TABLE 3. Size of Crystalline Units for Unrolled, Rolled, and Annealed Materials

annealing T rolling rate	unannealed	130°C
unrolled	4 μm	6-7 μm
135%	3 μm	7 μm
390%	0,3 μm	3 μm

TABLE 4. Strain Energy Per Volume Unit for Laminated and Annealed Samples

rolling rate annealed T	unrolled	135%	325%	390%
unannealed	2 MPa	3 MPa	22 MPa	27 MPa
130°C			33 MPa	37 MPa

observed, especially for the highest rate laminated sample (Table 3). This increase reaches 1000% for the most rolled material but only respectively 133% and 50-75% for the 135% rolled and unrolled samples. Furthermore, the crystalline units of the most flattened material lose sticks shape and become spherulites again. But for the same annealing time their size is far from the one of the other polyethylene.

Mechanical Properties

One original feature of mechanical behavior is the strain energy per volume unit: $U_y = \sigma_y \, d\varepsilon$. The flattening treatment to 325% and 390% leads to a value of U_y around ten times as high (Table 4). The crystalline units of these materials are very small and even though the crystalline amount is lower, the number of links between amorphous and crystalline phases could increase. and so, energy used to deform one volume unit becomes higher.

After annealing 1 hour at 130°C, the strain energy has still increased (Table 4) due to the great rise of the crystalline amount: crystalline units acts as stiffening

materials and the strain energy required to deform one volume unit is more considerable.

CONCLUSION

The microstructure changes in the material properties due to rolling are different from those induced by drawing. Rolling leads to an increase in the crystalline rate and a disappearance of the thickest lamellae.

Spherulites size decreases more and more until crystalline units becomes sticks. The orthorhombic crystallographic lattice is partially transformed into a monoclinic lattice. This last modification is reversible when the polyethylene is annealed. In the same way, the thermal treatment erases the rolling effects on the crystalline rate but the morphology is different between rolled and unrolled material after annealing. Then, mechanical properties and morphology are not reversible characteristics.

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