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Microstructural changes induced in linear polyethylene by plastic deformation (rolling)

N. ALBEROLA*, J. PEREZ
INSA, GEMPPM, URA CNRS 341, Av. A. Einstein, 69621 Villeurbanne, France

Mechanical spectrometry and differential scanning calorimetry analysis completed by wide-angle X-ray diffraction and density measurements were performed on linear polyethylene in order to characterize the influence of a plastic deformation (rolling) on the microstructure. Thus, rolling performed at room temperature results in the breaking of the thicker lamellae. The changes in the microstructure in polyethylene induced by rolling are in agreement with those suggested by other authors. A phenomenological model, applied to the α' relaxations exhibited by polyethylene, allows quantitative analysis of the microstructural changes due to plastic deformation. Thus, rolling induces an increase in the interactions between phases through an increase in the number of tie molecules connecting the broken crystallites. Moreover, rolling results in an increase of crystallographic defect concentration within the crystalline phase and this plastic deformation induces phase transformation from orthorhombic to monoclinic lattice, which is preferentially developed for thicker lamellae.

1. Introduction

Plastic behaviour of polymers depends not only on the applied stress, the deformation rate and on the temperature, but also on the initial microstructure and on microstructural changes induced by strain.

According to Peterlin [1], the morphology results from the magnitude of the draw ratio λ ($\lambda = l/l_0$ where l_0 is the initial dimension and l that of the sample after deformation). At low draw ratio ($\lambda < 3$), spherulitic structure remains unchanged but the crystalline lamellae are deformed and chain axes are tilted with respect to their initial direction. With increasing deformation ratio, spherulitic structure is progressively destroyed. Crystalline lamellae are broken to a large number of small crystallites. This leads to an increase in the number of molecules connecting the blocks. All these small crystallites and tie molecules form the characteristic fibrillar structure observed by transmission electron microscopy [2]. Moreover, Peterlin [1] has suggested that Young's modulus and stress at break also change the number of tie molecules with increasing draw ratio. Phase transformation from orthorhombic to monoclinic structure has been observed for polyethylene undergoing high deformation [3].

The present work attempts to make some contributions to the knowledge of changes in the microstructure of polyethylene induced by plastic deformation. We have previously [4, 5] developed analysis tools of the microstructure of polyethylene based on differential scanning calorimetry (DSC) and mechanical spectrometry. Thus, based on DSC experiments, we have developed a model to determine the lamellar thickness distribution curves from thermograms [4, 5]. We have shown that the width of the distribution curves depends on the thermal history of the samples and the presence of a bimodal lamellar distribution curve could result from a thermal gradient occurring within the sample on cooling from the crystallization temperature to room temperature. Mechanical spectrometry experiments carried out under isochronal and isothermal conditions performed on high-density polyethylene have shown the presence of two mechanical α relaxations, designated α_1 and α_2, with increasing temperature, and located at about 60 and 100 °C, respectively. Because α_1 and α_2 peak temperatures are correlated to the average thickness of thin and thick lamellae, respectively, it was suggested that the α_1 and α_2 relaxations could result from some molecular mobility within the crystallites and, thus, from the diffusion of some crystallographic defect within the thickness of the thin and thick crystalline lamellae, respectively [4, 5]. Among the great variety of crystallographic defects [6] (kinks, jogs, dislocations, disclinations), it was not possible, from these results, to pin-point the type of defects involved in the α processes. However, according to important work carried out on dielectric measurements in polyethylene by Reneker and Mazur [7], the involved defect could be a "Reneker's defect", i.e. a "dispiration" which is a combination of a partial dislocation and a partial disclination involving six

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* Also at Ecole Centrale de Lyon, Laboratoire de Technologie des Surfaces, URA CNRS 855, 36 avenue Guy de Collongue, BP 163, 69131 Ecully Cedex, France

carbon atoms. Thus, when a lamella is bent by an elastic deformation, defects tend to move to the uncompressed region, producing an additional inelastic deformation. Another type of defect has been proposed by Boyd [8] to take account of dielectrical α relaxation of polyethylene: "Boyd's defect" is a smoother twist involving about twelve carbons, which fits better into the lattice and moves easily without producing inelastic deformation of the lamellae. This defect has the character of a solitary wave (solution) [9].

As the mechanical relaxation time distribution is much broader than the dielectric one and locates at higher values, Boyd [8] assigned the mechanical relaxation to the amorphous phase: the inelastic deformation of the amorphous phase being the consequence of the "Boyd's defect" migration within the crystalline phase. In order to elucidate the role played by the "tied" amorphous phase, i.e. to analyse the role of connecting molecules. Jourdan *et al.* [10] have proposed a phenomenological model to interpret the mechanical α relaxation displayed by polypropylene and based on Reneker's assumption: mechanical α relaxation originates from crystalline phase, but in order to take into account (i) the high value of the measured activation energy of the mechanical α process (more than $80\,\mathrm{kJ\,mol^{-1}}$ in the case of either polypropylene [10] or polyethylene [4]) which is not usually observed for simple thermally activated process, i.e. thermally activated diffusion of crystallographic defects within the crystallites, and (ii) the low value of the pre-exponential time in the Arrhenius law giving the time–temperature relation through

$$\tau_\alpha = \tau_0 \exp(\Delta H_\alpha / RT) \tag{1}$$

which has no physical meaning (τ_0 as low as 10^{-35} s), it was assumed that the amorphous phase also contributes to the mechanical process induced by the migration of crystallographic defects [5, 10]. Thus, in this model, the mechanical α process is assigned to crystallographic defect diffusion within the crystalline phase, in agreement with Reneker's hypothesis. But unlike Reneker's approach, it is assumed that the amorphous phase also contributes to the mechanical relaxation because of the connections between phases in such a macromolecular system. According to this model, the behaviour of the crystalline phase in the α relaxation region can phenomenologically be described by a "Cole–Cole" law

$$G^* = G^R + \frac{G^U - G^R}{[1 - (iw\tau_\alpha)^{-k_\alpha}]} \tag{2}$$

where G^U and G^R are the unrelaxed and relaxed dynamic moduli, respectively, and are given by extrapolation of the Cole–Cole diagram; τ_α is the mechanical relaxation time measured under isothermal conditions; $0 < k_\alpha < 1$ has been related to correlated motions characterizing the mobility in the amorphous phase according to a physical model previously developed to describe the inelastic and plastic deformation of amorphous materials near T_g [11]. The k_α value is governed by the effectiveness of the correlation effects, i.e. by the magnitude of interactions between phases. Thus, with increasing connection between phases, k_α decreases [11]. k_α is determined from the slope of the tangent at the origin of the Cole–Cole diagram. For polypropylene [10], k_α was found to be about 0.30. According to the model, the activation energy of the crystallographic defect diffusion (ΔH_1) can be determined from the measured apparent activation energy of the mechanical α process (ΔH_α) through:

$$\Delta H_1 = \Delta H_\alpha k_\alpha \tag{3}$$

The intensity of the α relaxation given by the ratio G^U/G^R ($G^U < G^R$) varies with the relaxing site density, i.e. as the defect concentration in the crystalline phase.

In this work, the changes in the microstructure of high-density polyethylene induced by a peculiar mechanical treatment (rolling) were analysed by such microstructural characterization tools, based on differential scanning calorimetry and mechanical spectrometry experiments. The work was carried out on polyethylene having undergone different thermal histories and then exhibiting different initial microstructures. Moreover, the sample characterizations were completed by wide-angle X-ray diffraction and density measurements before and after rolling.

2. Experimental procedure

2.1. Material

The high molecular weight linear polyethylene used in this work had an average molecular weight, M_W, given as 6×10^5. The density was 0.939.

2.2. Thermal treatments

As-received polyethylene sheets were heated for 30 min at 170 °C and then one of these sheets was isothermally crystallized at 110 °C for 24 h. Three of these sheets were quenched from 170 °C in water at 15 °C. One of these specimens, the so-called quenched sample, was kept at room temperature. The other quenched samples were annealed for 24 h at 100 and 130 °C, respectively, and then rapidly cooled in water to 15 °C. For experimental works, all samples were cut to the following dimensions: $40 \times 6 \times 1.3\,\mathrm{mm^3}$ for dynamic mechanical analysis, $2 \times 2 \times 1.3\,\mathrm{mm^3}$ for calorimetric experiments and $25 \times 25 \times 1.3\,\mathrm{mm^3}$ for X-ray scattering experiments. Rolling of the samples was carried out at room temperature. For all specimens the rolling ratio was about 0.3.

2.3. Dynamic mechanical spectrometry

The inverted torsion pendulum [12] was used in this study. This set up provides the real, G', and imaginary, G'', parts of the dynamic shear modulus and $\tan\phi = G''/G'$ as a function of temperature (for one or several fixed frequencies) or frequency (under isothermal conditions).

2.3.1. *Isochronal measurements*

Runs were performed at increasing and decreasing temperature in the 20–120 °C temperature range and at two fixed frequencies 1 and 0.1 Hz. The heating (and cooling) rate was about 35 °C h^{-1}.

2.3.2. Isothermal measurements

Frequency scans were carried out under isothermal conditions in the 30–100 °C temperature range over a wide range of frequencies (10^{-4}–1 Hz).

2.4. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction spectra were recorded on a Siemens D500 diffractometer using CuK_α radiation ($\lambda = 0.154$ nm) between 5° and 20° with 0.02 (2θ) scan increments. The crystalline structure was defined by the position and the relative intensity of the different rays.

The crystallinity content (X_C) was obtained from the area of crystalline X-ray diffraction peaks. Crystal thickness, l, was obtained from the reflection profile (1 1 0). X-ray diffraction experiments were performed at room temperature.

2.5. Differential scanning calorimetry

Thermograms were recorded using a Perkin Elmer DSC 1B apparatus over the temperature range 20–150 °C at a heating rate of 8 °C min^{-1}. The crystallinity index, X_C, was determined from the area of the melting endotherm. Furthermore, according to a model described in a previous paper [4], lamellar thickness distribution curves were determined from thermograms.

2.6. Density measurements

Sample density was measured in a water/alcohol gradient density column at 20 °C. Weight fraction crystallinity is determined from [6]

$$X_C = \frac{d_C}{d}\left(\frac{d - d_a}{d_C - d_a}\right) \qquad (4)$$

where d_C is the density of 100% crystalline polyethylene ($d_C = 0.997$), and d_a the density of amorphous phase ($d_a = 0.854$).

3. Results

3.1. Morphological characterizations

3.1.1. DSC measurements

Rolling of polyethylene samples induces a weak decrease in the crystallinity ratio as shown by Table I. However, patterns of lamellar thickness distribution curves determined for rolled samples are very different from those displayed by the unrolled specimens (Fig. 1). The distribution curves of rolled samples are narrower than those of unrolled specimens. This suggests that the rolling induces breaking of the larger crystallites and the destruction of a few small crystallites. Characteristic values of lamellar thickness distribution curves are reported in Table I.

3.1.2. Wide-angle X-ray diffraction measurements

X-ray spectra determined for rolled samples are given, for example, in Fig. 2. In addition to the (1 1 0) and (2 0 0) reflection profiles characteristic of the orthorhombic phase, rolled samples display another reflection profile located at about 19.4° (2θ) which could be characteristic of the presence of a new phase, the monoclinic phase [3]. This ray should be due to the (0 1 0) reflecting plane of the monoclinic structure.

Moreover, for any thermal history of the specimens, the parameters of the orthorhombic lattice remain unchanged after rolling.

Rolling induces a weak decrease in the crystallinity content (Table II) measured from X-ray experiments in agreement with DSC measurements. The relative amount of monoclinic phase estimated by the ratio of (area of the $(0\,1\,0)_M$ reflection profile)/(areas of the $(1\,1\,0)_O$ and $(2\,0\,0)_O$ diffraction rays) seems to increase with increasing lamellar thickness of the thicker lamellae. The relative amount of monoclinic phase is about 10% for the quenched sample which shows an average thickness of 11 nm, while the annealed sample at 130 °C exhibits a greater amount of monoclinic phase, about 15%, and shows thicker crystalline lamellae ($l \approx 22$ nm). It can be assumed that the phase transformation induced by rolling preferentially occurs in thick lamellae.

3.1.3. Density measurements

Table III shows density values and crystallinity indexes determined from these measurements.

The rolling produces an apparent decrease in the crystallinity more important than the X_C decrease shown by DSC and X-ray measurements. Therefore, we can suggest that the decrease in the density induced by rolling is not only due to the decrease in the crystallinity content but also to another structural change, which will be discussed in Section 4.

TABLE I Characteristic values of lamellar thickness distribution curves

Systems	Before rolling				After rolling			
	X_C (%)	l_{max} (nm)	$l_{1/2}$ (nm)	l_{end} (nm)	X_C (%)	l_{max} (nm)	$l_{1/2}$ (nm)	l_{end} (nm)
Quenched	40	11	5–16	23	36	11	7–14.5	19
Annealed at								
100 °C	50	13	5–20	30	43	12	6.5–20	24
130 °C	70/–	22	4–40	70	62	17	4.5–27	43
Isoth. cryst.								
at 100 °C	65	14	4–26	65	57	14	8–22.5	30

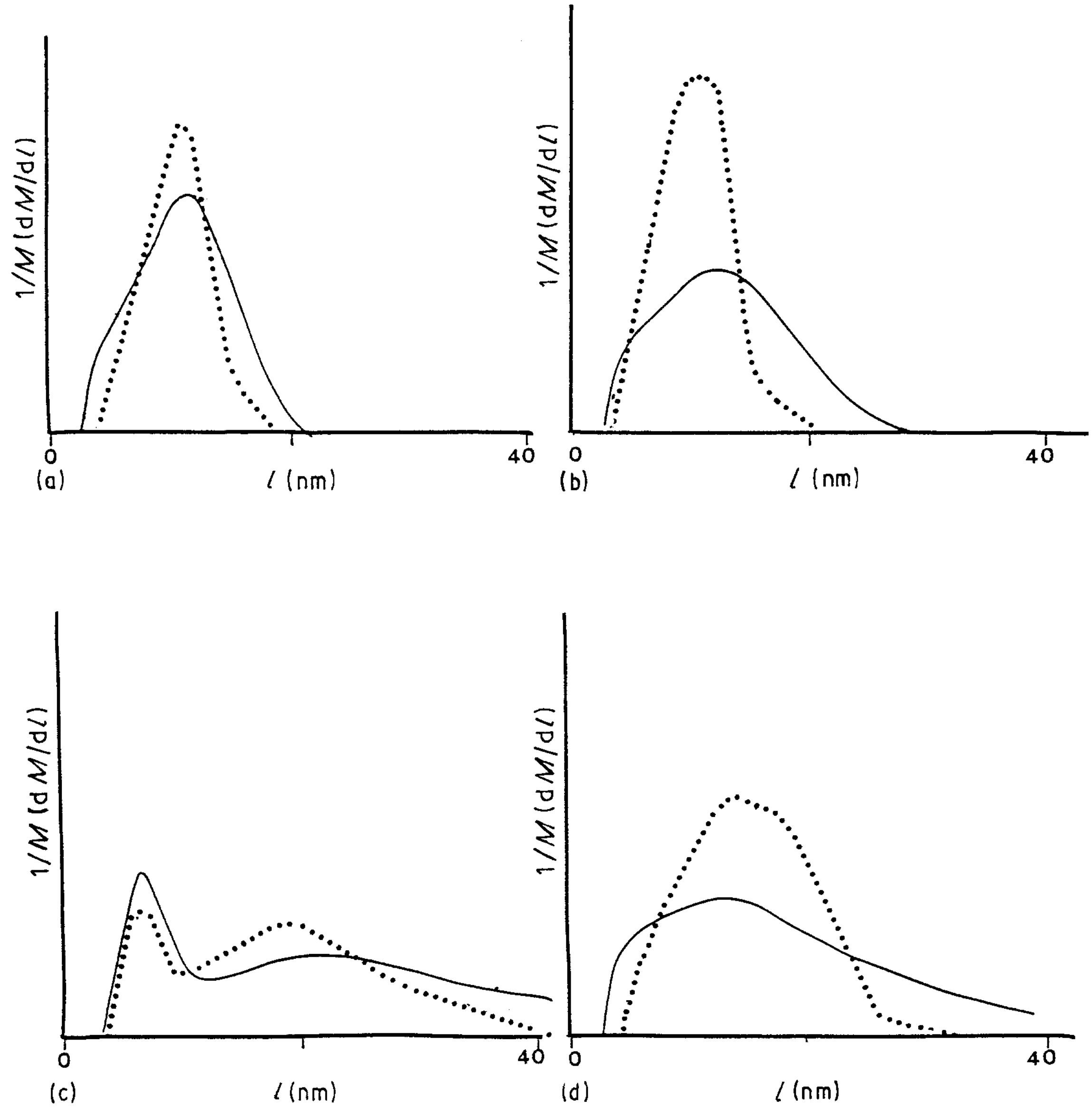

Figure 1 Lamellar thickness distribution curves of (●) rolled and (——) unrolled systems: (a) quenched from 170–15 °C, (b) quenched and then annealed at 100 °C, (c) quenched and then annealed at 130 °C, (d) isothermally crystallized at 110 °C.

3.2. Mechanical spectrometry

Plots of log G' and tan ϕ at increasing and decreasing temperature at 0.1 Hz for unrolled and rolled samples are shown in Fig. 3. From a comparison of the spectra recorded at increasing temperature, we can see that rolling induces:

(i) first, an increase in the magnitude of the α_1 and α_2 peaks;

(ii) second, a shift of the α_2 peak towards the lower temperatures, the temperature of the α_1 maximum remaining almost unchanged;

(iii) third, a slight decrease in the modulus of the samples over the analysed temperature range.

After rolling, the spectra recorded at decreasing temperature are different from those obtained at increasing temperature according to: (i) the maxima of the α_1 and α_2 peaks are weaker; (ii) the α_2 relaxation is located at higher temperature; and (iii) the elastic modulus is higher over the analysed temperature range. Unrolled samples exhibit a similar behaviour with decreasing temperature but the magnitude of the changes is lower than for rolled specimens.

Fig. 4a shows the temperature cycles performed on the sample isothermally crystallized for 24 h at 110 °C then rolled. The different cycles recorded between 20 and 90 °C lead to a progressive decrease in tan ϕ. This evolution appears as early as 30 °C. For the unrolled sample, the decrease in tan ϕ during the temperature cycles begins at a higher temperature, from about 80 °C (Fig. 4b). Measurements of tan ϕ as a function of frequency between 10^{-4} and 1 Hz performed under isothermal conditions can be represented as shown in Fig. 5 in the form of a so-called "Cole–Cole diagram" with the same experimental data G'' as a function of G'. As can be seen, the time–temperature superposition principle is not correct because all the plots for each sample do not fall on one curve. A similar deviation from the time–temperature superposition principle was also observed for unrolled polyethylene specimens [4, 5] and for the polypropylene system [10]. In the following section possible reasons for

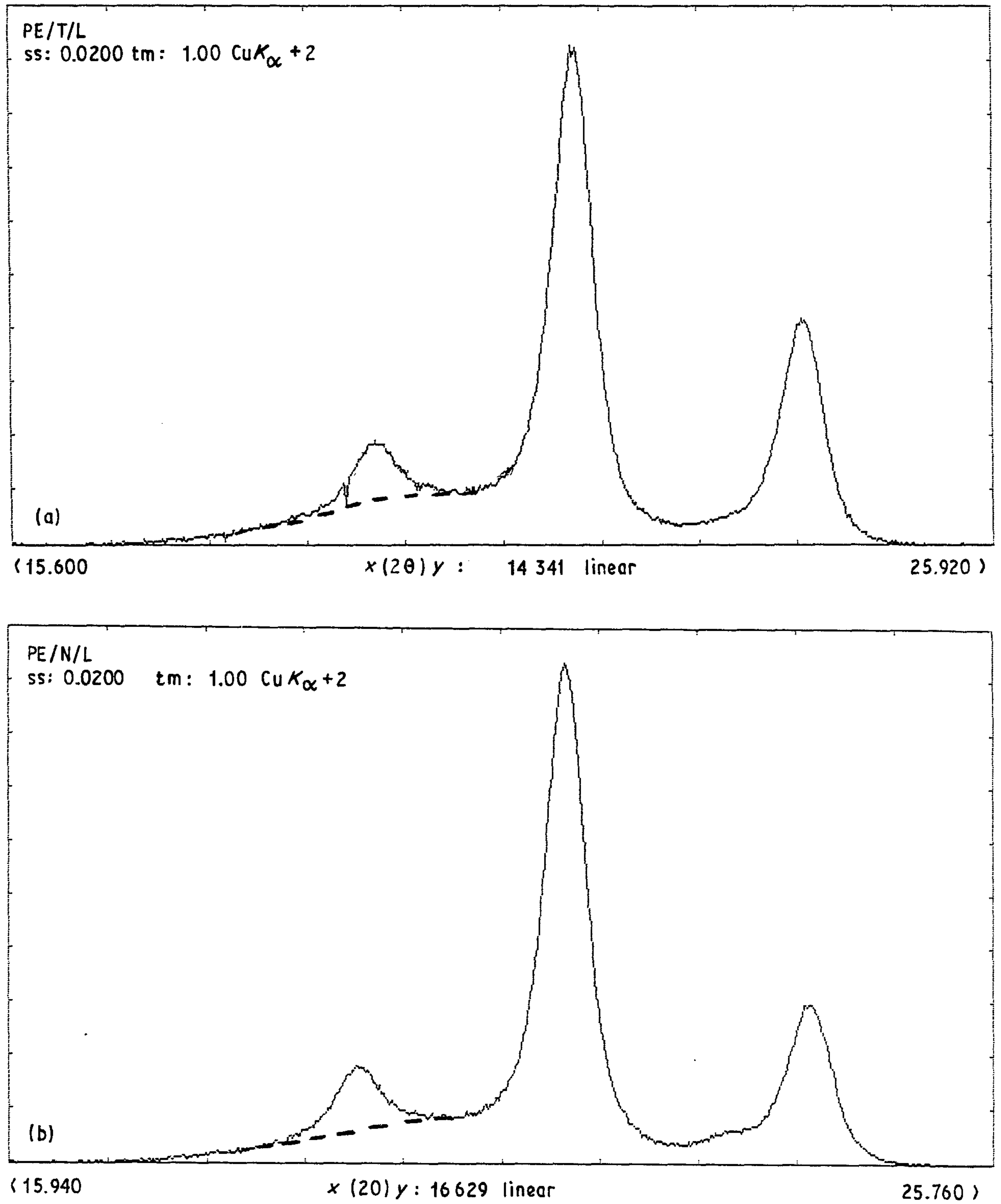

Figure 2 Wide-angle X-ray diffraction profile of rolled systems: (a) quenched from 170–15 °C, (b) quenched then annealed at 130 °C. (– – –) X-ray profiles of the corresponding unrolled specimens in the angle range.

TABLE II Characteristic values from X-ray diffraction experiments ($l_{1\,1\,0}$ crystallite thickness determined from the (1 1 0) reflection profile of the orthorhombic structure; $l_{0\,1\,0}$ thickness in the (0 1 0) direction of crystallites in the monoclinic structure)

Systems	X_C (%)		l (nm)			O → M (%)
	Unrolled	Rolled	Unrolled	Rolled		
			$l_{1\,1\,0}$	$l_{1\,1\,0}$	$l_{0\,1\,0}$	
Quenched	45	42	15	14.5	12	10
Annealed at:						
100 °C	47	43	17	16	12	12
130 °C	65	60	22	18.5	12.5	15
Isoth. cryst.						
at 110 °C	58	52	20	15	13.5	15

TABLE III Density values, d, and crystallinity indexes, X_C, determined from density measurements

Samples	Unrolled		Rolled	
	d	X_C (%)	d	X_C (%)
Quenched	0.908	41	0.899	35
Annealed at:				
100 °C	0.914	46	0.906	40
130 °C	0.945	67	0.927	55
Isoth. cryst at 110 °C	0.939	62	0.918	49

deviation from the time–temperature superposition principle will be discussed.

The apparent activation energy (ΔH_α) of the α relaxations calculated from the locations of the maxima of tan ϕ of isothermal spectra are reported in Table IV. We can see that apparent activation energies of α relaxations are high for both types of specimen and the apparent activation energies of rolled samples are about twice those determined for unrolled samples.

4. Discussion

As recalled in Section 1, we have suggested in a previous paper [4] that the α_1 and α_2 mechanical relaxations are due to crystallographic defect diffusion within the thickness of thin and thick lamellae, respectively.

According to this assumption, the shift towards the lower temperatures of the α_2 relaxation (isochronal measurements) induced by rolling and observed for all samples on heating could be due to the breaking of the thicker crystallites in agreement with DSC results (cf. Fig. 3). In fact, a decrease in the crystallite thickness leads to a decrease in the diffusion time of the crystallographic defects and then, in terms of time–temperature equivalence, to a decrease in the α_2 peak temperature. From similar considerations, the increase of the α_2 relaxation temperature observed on decreasing the temperature from about 120 °C for

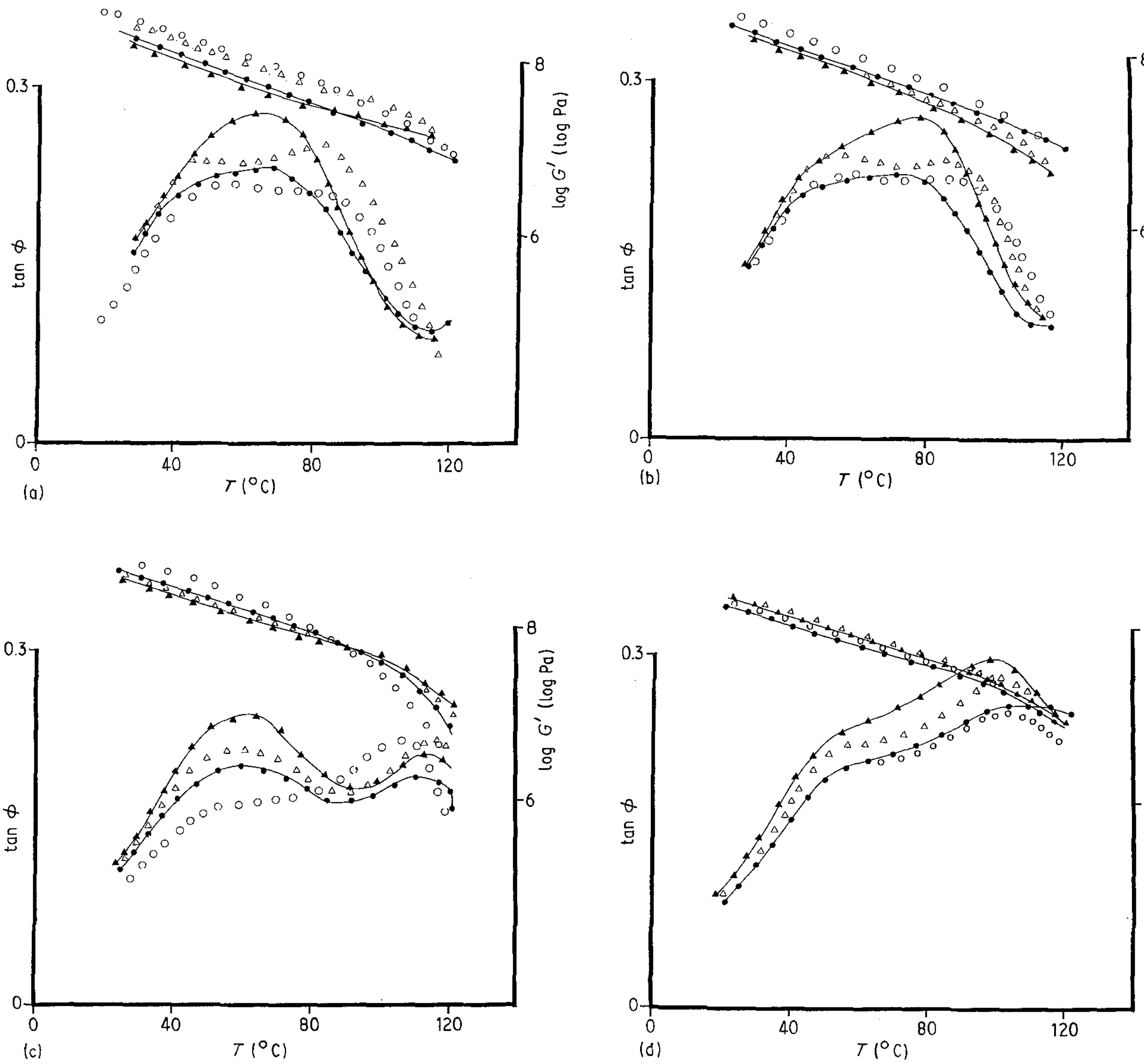

Figure 3 Isochronal spectra carried out at 0.1 Hz of (●, ○) unrolled and (▲, △) rolled samples recorded at (●, ▲) increasing and (○, △) decreasing temperature; (a) quenched from 170–15 °C, (b) quenched and then annealed at 100 °C, (c) quenched and then annealed at 130 °C, (d) isothermally crystallized at 110 °C.

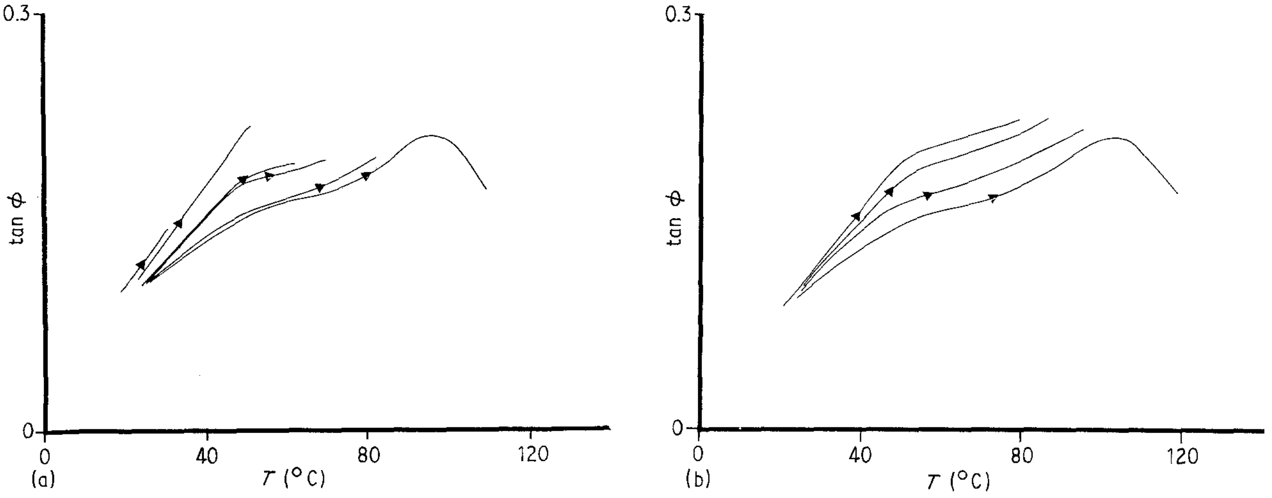

Figure 4 Temperature cycles at 0.1 Hz over 20–120 °C temperature range recorded for a sample isothermally crystallized at 110 °C: (a) rolled, (b) unrolled.

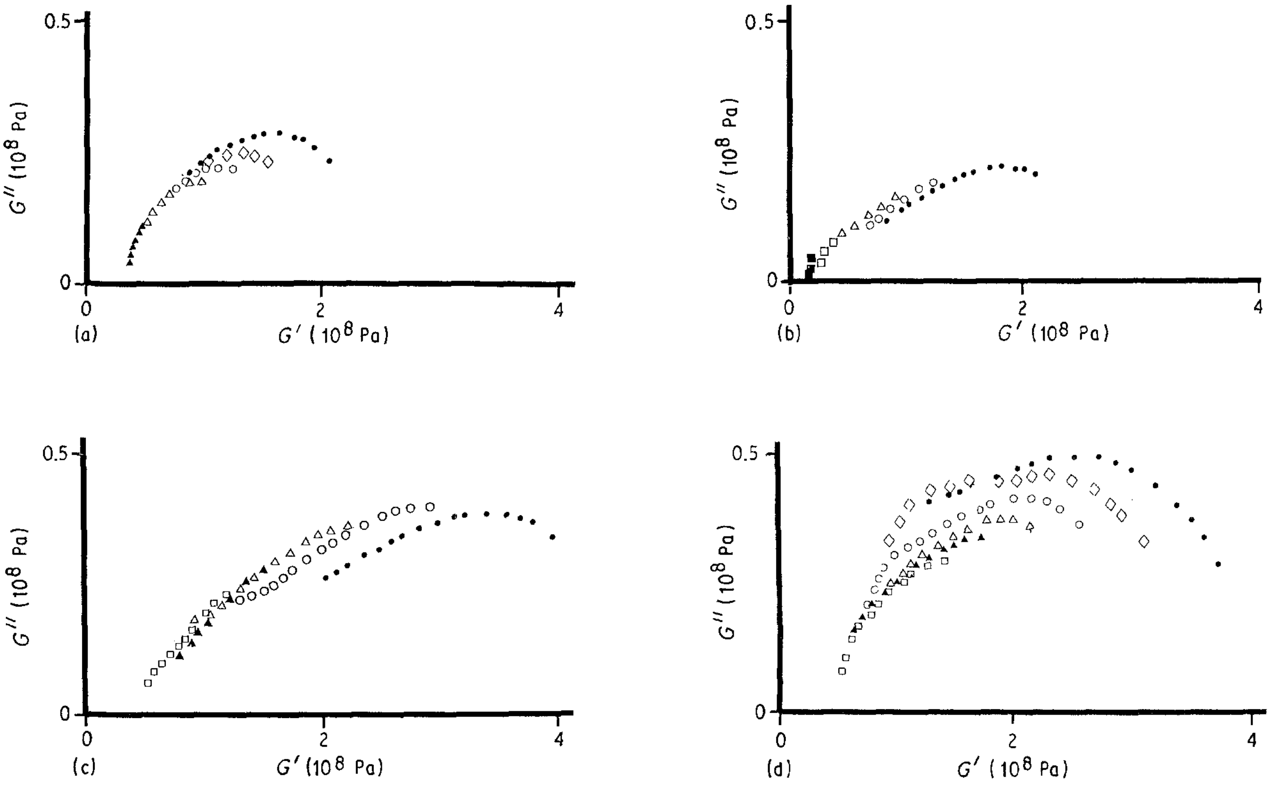

Figure 5 Cole–Cole diagrams determined for the following rolled systems: (a) quenched from 170–15 °C, (b) quenched and then annealed at 100 °C, (c) quenched and then annealed at 130 °C, (d) isothermally crystallized at 110 °C: (●) 30 °C, (◇) 40 °C, (○) 50 °C, (△) 60 °C, (▲) 70 °C, (□) 80 °C.

TABLE IV Characteristic values of the α mechanisms determined from the phenomenological model

Samples	Unrolled				Rolled			
	ΔH_α (kJ mol^{-1}) α_1/α_2	k_α α_1/α_2	ΔH_1 (kJ mol^{-1}) α_1/α_2	I_R α_1/α_2	ΔH_α (kJ mol^{-1}) α_1/α_2	k_α α_1/α_2	ΔH_1 (kJ mol^{-1}) α_1/α_2	I_R α_1/α_2
Quenched	–/87	–/0.42	–/36	–/3.7	–/136	–/0.22	–/30	–/7.5
Annealed at:								
100 °C	109/–	0.32/–	35/–	4.3/–	200/–	0.23/–	46/–	7.9/–
130 °C	136/–	0.31/–	42/–	4.7/–	226/–	0.20/–	45/–	8.5/–
Isoth. cryst.								
at 110 °C	70/89	0.46/0.43	32/38	2.1/3.2	–/153	–/0.28	–/44	–/6.4

both types of sample with respect to the location of this relaxation on the heating run could be due to a thickening of crystallites which could occur in the temperature cycle during the experiment as early as 100 °C. The increase in the magnitude of the α_1 and α_2 peaks produced by rolling and observed for all samples is related to an increase of the concentration of relaxing entities, i.e. according to the previous discussion, to an increase in the crystallographic defect concentration. This hypothesis is consistent with density measurements. By comparing values of crystallinity index after rolling determined from DSC, WAXS and density measurements, we have shown that the decrease in density produced by rolling is not only due to the weak decrease in crystallinity but also to another structural change which could be the decrease in the perfection of crystalline phase, i.e. an increase in the crystallographic defect concentration. The progressive decrease in $\tan \phi$ values observed in the temperature cycles (cf. Fig. 4) can be interpreted as the result of "annealing effects" leading to a progressive removal of crystallographic defects and then to a more perfect crystalline phase. Such "annealing effects" occurring on temperature cycles begin as early as 30 °C for the rolled sample and at about 80 °C for the unrolled ones: rolling could produce a great variety of crystallographic defects and the more thermodynamically unstable defects are rapidly removed on heating.

The phenomenological modelling of α relaxations [5, 10], previously described, is now applied to give some semiquantitative evaluation in the changes in (i) the magnitude of interactions between the crystalline phase and the amorphous region located in the interfacial regions and then in the influence of tie molecules connecting adjacent crystalline lamellae, through the k_α value modifications, and (ii) the concentration of relaxing sites which can be likened to the crystallographic defect density induced by the mechanical treatment, through the intensity of relaxation ($I_R = G^U/G^R$).

Table IV gives the values of the parameters determined from the phenomenological model. As the failure in the time–temperature superposition principle for rolled and unrolled samples is traduced by a decrease in the values of G^U, G^R and I_R (cf. Fig. 5) with increasing temperature, only average values (when they can be determined) of these parameters are reported in Table IV. No significant change in the values of k_α is detected on increasing the temperature of isothermal measurement. Thus, the rolling of specimens results in an increase in the interactions between phases as shown by the decrease in the k_α values. The increase in correlation effects induced by rolling could be due to the increase in the number of tie molecules resulting from the breaking of thicker lamellae (cf. lamellar thickness distribution curves, Fig. 1). For any thermal treatment and for samples rolled and unrolled, the activation energy, ΔH_1, of the primary process, i.e. defect diffusion within crystallites, is constant and approximately the value of the activation energy of the α process shown by the dielectric relaxation (35 kJ mol^{-1}) [13]. Moreover, rolling leads to an increase in the magnitude of the α relaxation which could be due to an increase in concentration of crystallographic defects. This result is in agreement with (i) changes induced by rolling on the isochronal spectra, i.e. an increase in the height of the α peaks (see above), (ii) the progressive decrease in the $\tan \phi$ values on temperature cycles traducing the removal of some crystallographic defects, and (iii) the decrease in density values after rolling and which could be due to a decrease in the perfection of the crystalline phase.

Another interesting feature is the failure of time–temperature superposition of the α relaxations shown by polyethylene and also observed for α relaxation in polypropylene [10]. In agreement with Jourdan *et al.*'s hypothesis [10], it can suggest two possible mechanisms: (i) the crystallinity index should apparently decrease on increasing the temperature because the thermal expansivity of the amorphous phase is higher than that of crystalline phase; (ii) as the temperature is increased, some premelting of crystallites could occur on the first layers of chains. Both phenomena lead to a decrease in the crystallinity index which was estimated by Jourdan *et al.* [10] to be about 10%, and then could result in a decrease of elastic moduli with increasing temperature.

5. Conclusion

The consequences of rolling on the microstructure of linear polyethylene were found to be as follows:

1. breaking of the thicker lamellae, as shown by the changes in lamellar thickness distribution curves determined from DSC experiments,
2. an increase in the interactions between phases which could be due to the increase in the number of tie molecules according to the decrease in the value of k_α determined from the phenomenological modelling of the mechanical α relaxations.
3. an increase in the defect concentration within crystallites according to mechanical spectrometry data: the increase in the intensity of the α relaxation shown by isochronal experiments; the progressive decrease in the $\tan \phi$ values on temperature cycling characterizing the progressive removal of defects induced by rolling; the increase in the relaxation intensity determined from phenomenological model; and the density measurements,
4. the phase transformation of orthorhombic → monoclinic structure which is preferentially developed in thick lamellae, according to wide-angle X-ray diffraction experiments.

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