Crystallinity Variations in the Double Yield Region of Polyethylene

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ABSTRACT: Numerous specimens of a linear low density polyethylene sample were uniaxially deformed up to different elongations to study the double yield phenomenon. Extruded samples were analyzed to calculate the crystallinity and to estimate the mean crystal size, under stressed state and released state (after removal of the stress), using the wide angle X-ray scattering technique. The crystallinity degree and the mean crystal dimension associated to the (110) orthorhombic reflection of the specimen without deformation were of 55% and 16 nm. These parameters in the stressed state, as functions of the elongation, presented a multi-step behavior. A decrement after the first yield point (48%, 13 nm), then another decrement, and an abrupt increment followed by a decrement at higher strain values around the second yield point (28, 40, and 30%; 12, 14.5, and 11 nm). The behavior was more notorious in the stressed state than in the released state. The latter results were interpreted in terms of a partial melting followed by a recrystallization process. These experimental findings show that the second yield is not only associated with the deformation of the crystalline region. This partial melting–recrystallization process is one of the main mechanisms of the double yield phenomenon. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3103–3111, 2007

Key words: linear low density polyethylene (LLDPE); stress–strain; crystallinity; mean crystallite size; melting-recrystallization

INTRODUCTION

A yield point in polymers is conventionally accepted as the point where a local maximum is shown in the stress–strain curve. At this point a material ceases to deform elastically in a recoverable manner and undergoes permanent (irreversible) plastic deformation. Traditionally, the yielding phenomenon of semicrystalline polymers has been associated with a change in the morphology of the material where a spherulitic structure transforms into a fibrillar one.[1–3] This change occurs through shearing and fragmentation of the crystalline lamellae into blocks that rearrange into the form of parallel microfibrils.

Works published for polyethylenes under tensile loading have demonstrated the existence of double yield points.[4–16] This double yield phenomenon has been studied (a) in a variety of systems: polyethylene and related copolymers, binary blends of two polyethylenes, and ternary blends of two polyethylenes and an elastomer; (b) in polyethylenes with a variety of properties: linear or branched, different molecular weight, crystal thickness distributions, and degrees of crystallinity; (c) under different conditions of tensile loading: deformation temperature and strain rate; and (d) in samples with different thermal history caused by varying crystallization conditions.

Double yielding has also been reported for other semicrystalline polymeric systems such as poly(tetramethylene terephthalate) and its copolymers,[17] polyamide 6 and glass bead filled polyamide 6 composites,[18,19] polybutylene terephthalate,[20] polypropylene,[11] polycarbonate/polyethylene blends.[21] It has been thought for a long time that the double yield phenomenon is a characteristic of semicrystalline polymers. However, the existence of double yielding in nanostructured amorphous polymer was reported recently.[22]

The shape of the stress–strain curve (σ-ε) in the double yield region may exhibit comparable values of the stress of the two maxima or a dominant value of either maximum. The stress of the first yield process becomes dominant under extreme conditions of low temperatures, high strain rates, or high crystallinities. The second yield process becomes dominant under the opposite extreme conditions. The existence of double yield points is clearly demonstrated and, also, it is expected that different deformation mechanisms exist for each yield process. However, the proposed explanation has not been unique.

Some possible deformation models and mechanisms have been postulated to explain the origin of the special phenomenon. For example, an explanation[5,7,10] was in agreement with the proposal[23] that the onset

of plastic deformation in semicrystalline polymers is governed by two structurally well-defined processes: a slip of the crystal blocks past each other in the mosaic crystalline structure (called heterogeneous slip) and a homogeneous shear of the crystal blocks (called homogeneous slip). These features were discussed in terms of two thermally activated rate processes of plastic deformation.[7] Some authors have referred to these types of deformation as fine slip and coarse slip.[11,16] Both processes could explain the two yield maxima observed. Analogous findings from tensile experiments were reported[6,14] and showed besides that the mechanism operating at the first yield point marked the onset of plastic strains, which are slowly recoverable at least in part, while the one that governs the second yield point is effectively irrecoverable and was associated with a sharp necking of the samples.

The yield points have been interpreted mechanically as the yield of two dashpots and the model used to describe the yield is of two Voigt elements (a spring in parallel with a thermally activated Eyring dashpot) in series,[10] two nonlinear Maxwell elements in parallel,[6] or as two distinct thermally activated rate processes (parallel association of two Eyring dashpots).[24]

Another important possible explanation for the mechanisms involved in the double yield phenomenon has been proposed.[4,8] From the experimental results in a set of linear polyethylenes and well-characterized ethylene copolymers of narrow molecular weight and composition distribution, and varying molecular weight, crystallinity, deformation rate, and temperature, a qualitative explanation was based on the postulate of a partial melting–recrystallization process during deformation. However, no experimental data had been reported to evidence the recrystallization.

Most previous work on the double yield phenomenon has concerned itself with the correlation of stress–strain behavior and the deformation of the crystalline portion of the material, and little effort has been made to understand the behavior of the crystallinity degree and crystal size. Since there is a strong correlation between the nature of the yield region and the permanent deformation of the material, understanding of the origin of double yielding is very important to understand the mechanisms involved in the complete deformation process. To our knowledge, there is no published work with a quantified evidence of the melting–recrystallization process for different states of deformation in the double yield region.

The basic idea in this paper is to take a semicrystalline polymer exhibiting the double yield phenomenon. If melting and recrystallization occurs during the deformation, some change in the crystallinity

degree is expected. We analyze the yield behavior of a linear low density polyethylene (LLDPE) by determining the crystallinity and mean crystal size as a function of uniaxial elongation, for both the stressed state and released state, using the wide angle x-ray scattering technique (the released state is obtained from the stressed state when the stress is removed). For the determination of these crystalline properties, to maintain the sample in the stressed state is necessary to prevent the relaxation that inevitable occurs after removing the load. The experimental approach that is being taken here should be of help in resolving some of the controversies with respect to the possible mechanisms. The results should set the basis, in part, for progress in the understanding of the deformation process in the yield region.

EXPERIMENTAL

Mechanical testing specimens

The commercial polymer obtained from Dow Chemical (Dowlex 2101) has a melt index of 1.6 dg/min and a density of 0.924 g/cm^3. The polymer was used without any modification. Sheets with a uniform average thickness of 1.1 mm were prepared using a single-screw Brabender extruder, in which temperatures at the different zones (two in the barrel and one in the die) were set at the value of 150°C and the screw at an angular speed of 70 rpm. From these sheets, samples with the standard dumbbell shape with an average width of 7.5 mm were punched out for tensile tests.

The uniaxial deformation was carried out at 25°C in an Instron tensile testing machine (model 4502). The clamp-to-clamp distance was fixed at 25.0 mm. To determine the adequate crosshead speed at which the two yield points are well defined and have comparable values of stress, experiments were carried out at 50, 10, and 1 mm/min. Then, subsequent specimens were stretched with a fixed deformation rate of 10 mm/min up to predetermined elongations in the range where the two yield peaks occur. Every time a new specimen was used. A special X-ray sample holder, built to maintain the applied stress, was placed in the middle part of the stretched sample; then the sample was cut for X-ray analysis.

WAXS measurements

Wide angle X-ray scattering (WAXS) patterns of the specimens were recorded with a Philips horizontal goniometer model PW 1380/60 fitted with a scintillation counter, pulse-height analyzer, and a graphite crystal monochromator placed in the scattered beam. Cu Kα radiation generated at 30 kV and 20 mA was

used. The angular position (2θ) was scanned with a speed of 1°/min and the scattered radiation was registered in the interval from 5° to 35°. The X-ray measurements were recorded using stretched samples with the elongation axis held perpendicular to the plane defined by the incident beam and direction of scanning. The elapsed time between the end of the stretching experiment and the beginning of the WAXS experiment in the stretched state was around 10 min.

The WAXS pattern was obtained for the specimen in the stressed state; immediately after this run, the stress was removed (released state) and a second pattern was obtained. This procedure was repeated for new specimens stretched up to different predetermined elongations. After subtracting background scattering and smoothing each pattern, deconvolution using Lorentzian functions was applied to separate the contribution of amorphous and crystalline parts in the angular interval from 15.0° to 27.5°. For both stressed and released states the mean size of the crystalline particles was estimated by using the Scherrer equation, and the degree of crystallinity was calculated in the standard way.[25,26]

RESULTS AND DISCUSSION

Stress–strain

Samples stretched at room temperature and at rates of 50, 10, and 1 mm/min, have stress–strain curves (σ-ε) as shown in Figure 1. A yield maximum takes place at the highest stretching rate. On the right-hand side of the yield maximum, a hump appears and develops with decrease in stretching rate. This hump turns into a second yield maximum, and at a stretching rate of 10 mm/min, its stress value is comparable to that of the first yield maximum, then this second, broader maximum becomes predominant at the smaller stretching rate. This indicates that in the yield process there are two mechanisms that are strongly affected by the stretching rate. At high stretching rate the first mechanism predominates over the second mechanism, while at slow stretching rate the second mechanism predominates. In the figure it is evident that at higher strain rate the polymer exhibits higher yield stress and, also, that the elongation interval of the double yield region is smaller. These effects were explained in terms of the stress relaxation, which always is present.[13] When the deformation takes place in a short time (i.e., high strain rate), the effect of the stress relaxation is small. In the opposite extreme case, when the deformation is applied slowly (50 times smaller), the stress value is smaller because the relaxation has sufficient time to reduce the stress. On the other hand, the magnitude of the stress corresponding to the second mech-
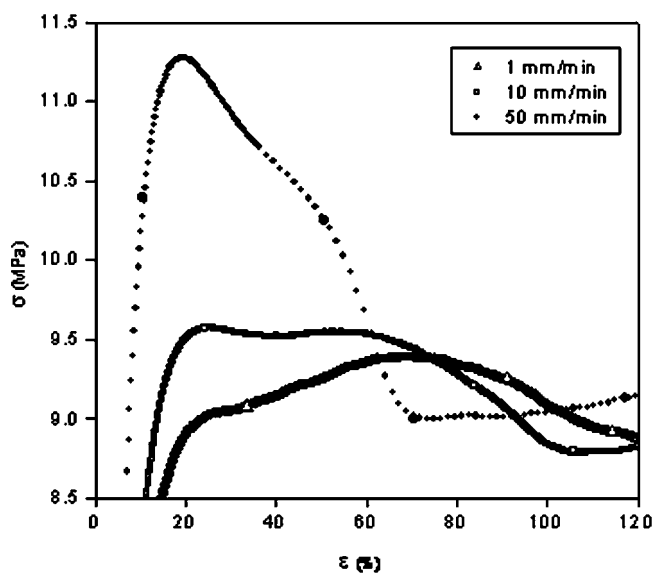

Figure 1 Stress–strain curves in the double yield region for three stretching rates.

anism is relatively less rate dependent as is evidenced in the σ-ε curves. Similar curves have been reported.[6–8] Visual observations of the deformation process also detected the onset of necking around the second yield, as reported.[6–8,12]

The behavior shown here for the σ-ε curves at a fixed temperature and varying the deformation rate has also been observed for polyethylenes at different experimental conditions, for example, different values of deformation temperature and different initial degree of crystallinity, as has been documented by a number of authors.[5–8] For a fixed strain rate at low temperatures a sharp first yield point is seen, but as the temperature increases, this gradually becomes less pronounced and a broader second yield dominates at higher temperatures. When both temperature and strain rate are varied, the first yield point is the major factor at low temperatures and high strain rates; the second yield point is more pronounced than the first at high temperatures and low strain rates. The influence of initial crystallinity on the yield region has also been examined at constant deformation temperature and strain rate.[7,8] The changes in the shape of the stress–strain curve with decrease in crystallinity degree are very similar to the changes observed with decrease in stretching rate; changes from a predominant first yield, to equal double yields, to a predominant second yield as the crystallinity is reduced.

WAXS

To correlate the mechanical properties shown in the σ-ε curve and the changes of crystalline properties
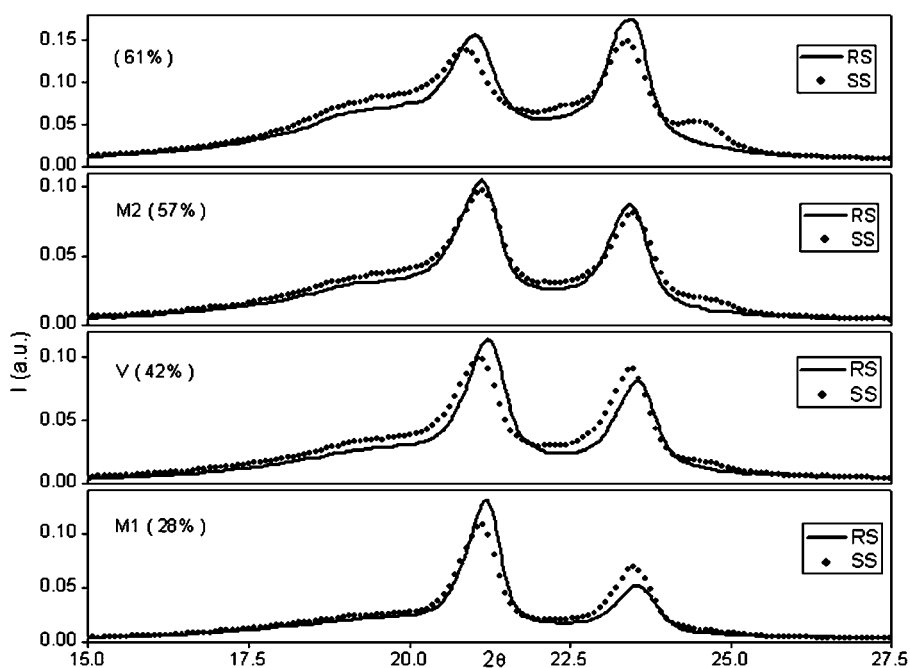
Figure 2 WAXS spectra of specimens in the stressed state (SS) at the indicated elongation and in the released state (RS) (before removing the stress they were deformed at the indicated elongation).

during deformation, the crystallinity degree and mean crystal size were analyzed as a function of elongation. The relaxation effects in the stressed state during the WAXS experiment can be ignored, since for a specimen stretched to an elongation of 60% the X-ray spectra did not appreciably change in 15 h. Figure 2 illustrates the evolution of some of the WAXS patterns in both the stressed state (SS) and the released state (RS) at the indicated elongation values. Here, curves denoted as M1 (28%), V (42%), and M2 (57%) represent specimens stopped at elongations related to about the first yield maximum, the valley, and the second yield maximum of the σ-ε curve. The different spectra that were obtained vary in a very systematic manner with the level of deformation. The figure gives examples, selected from among the specimens, which demonstrate the different shapes of the spectra that can be observed and the important influence of the deformation level.

The spectra show the two sharp characteristic peaks (110) and (200) of the orthorhombic structure.[26] In general, as a consequence of the deformation, the intensity of the (110) reflection in the stressed state slightly decreases whereas that of the (200) reflection shows important increases. However, when the tension is released, the intensity of (110) peak increases for all elongations, while the intensity for the (200) peak decreases for elongations below the second yield but increases for higher elongations. In the released state the intensity of the (110) reflection at the first yield point almost restores its value in the unstretched specimen, which means that the original

properties are almost recoverable. Most noticeable is that the (200) peak increased in intensity with the elongation for both states, with respect to the (110) reflection.

These changes in the intensities of the orthorhombic peaks may be explained in terms of the orientation. It was reported for LLDPE samples that there was no discernible orientation until the first yield point was reached.[16,27] The decrease in orthorhombic (110) intensity was directly correlated with the increase in monoclinic ($\bar{2}$01) intensity. At the first yield point the orthorhombic (200) reflection oriented rapidly towards the equator, its intensity increased up to elongations beyond the second yield point but remained constant when reaching the plateau region of the load–extension curve.

In the WAXS patterns corresponding to the stressed state, coincident with the second yield part of the σ-ε curve, a small extra reflection was registered at $2\theta = 24.6°$ in all the specimens, initiating from the elongation at $\varepsilon = 51\%$ due to the monoclinic phase. Some authors have reported this phase as a martensitic transformation from the orthorhombic to the monoclinic phase. The indexes associated to this reflection are ($\bar{2}$01) as reported elsewhere.[27,28] This monoclinic ($\bar{2}$01) reflection increased in intensity until a certain strain was reached ($\varepsilon = 65\%$) and then remained constant or decreased as deformation continued. This behavior agrees with that reported for LLDPE by these same authors. This monoclinic peak is not stable, since it only appeared in the stressed state but disappeared after the removal of

the stress (see Fig. 2). The strain at which the martensitic transformation starts to occur depends on the degree of crystallinity of the sample and on the strain rate.[28] This monoclinic reflection has little contribution to the total crystallinity because its intensity is very small as compared to those of the orthorhombic reflections.

Crystallinity

The degree of crystallinity in the stressed and released states was determined from the WAXS spectra in the angular interval from 15.0° to 27.5°, which only encompasses the very intense (110) and (200) reflections from the orthorhombic structure. We are interested to determine the evolution of the crystallinity associated to these orthorhombic reflections as a function of the elongation. The crystalline fraction Φ was calculated from the spectra as the ratio of integral of the orthorhombic crystalline peaks over the sum of integrals of the crystalline and amorphous peaks. That is, Φ was obtained from each spectrum using the following relation

$$\Phi = \frac{A^{110} + A^{200}}{A + A^{110} + A^{200} + A^{\bar{2}01}} \quad (1)$$

where A and A^{hkl} are the areas under the amorphous halo and the hkl reflections, respectively.

The degree of crystallinity values, calculated according to eq. (1), in the stressed and released states are presented in Figure 3. For the stressed states are represented by the squared-shape symbols and for the released states by the empty circles. The crystallinity values changed considerably at different strain stages and showed a multi-step plot. Comparing the behavior of the Φ values to the stress–strain curve, the plot in this Figure 3 can be schematically subdivided into three zones of the elongation. We call the first yield zone that with elongations smaller than $\varepsilon = 35\%$, the valley zone that between 35 and 55%, and the second yield zone for elongations higher than 55% but smaller than that where strain-softening ends and the curve plateau starts.

The crystallinity of the specimen without deformation was of $\Phi = 55\%$. In the first yield zone the crystallinity for SS increased to 65% at small elongations (below the first yield point). This increment can be explained by the process of strain-induced crystallization because on initial deformation, the crystallites act as hard inclusions, and the strain in the material is carried predominantly within the amorphous fraction. But as deformation continued the Φ value decreased to 58% and remained constant in this first zone, within experimental errors. In the valley zone the crystallinity shows a significant decrement to a value of 48%, which may be associated
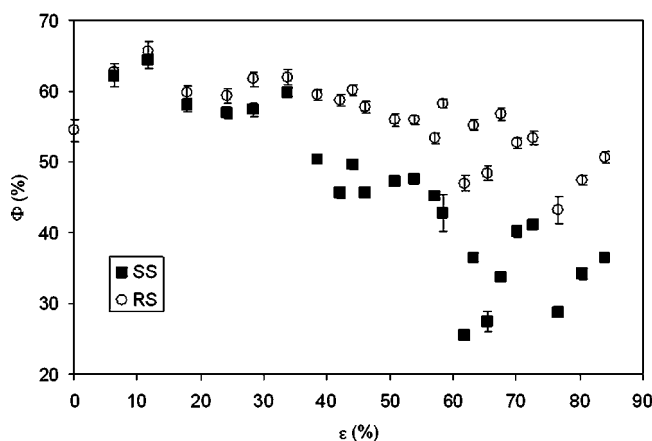

Figure 3 X-ray degree of crystallinity of specimens as a function of the elongation for stressed and released states.

to the fragmentation of the crystalline lamellae which in turn possibly may cause stress-induced decrystallization. In the second yield zone the crystallinity has an additional significant decrement to 28% followed by an important increment to 40% and then decreased to about 30%. The first decrement may be associated to partial melting of the less perfect crystallites. However, the increment can only be associated to a recrystallization process. The final decrement in the second yield zone is also related to the neck formation observed, where a temperature rise may occur (Ref. 2, Chapter 11); with the increase of temperature the decrement of crystallinity is expected. The crystallinity evolution with the uniaxial deformation was analyzed only for specimens stretched at 10 mm/min because the associated σ-ε curve showed that the values of the stress in both yield points were equivalent. The appearance of the second yield point seems to be related to the increment of crystallinity observed in the second yield zone.

These results seem to identify three well-defined zones associated with the first yield, valley, and second yield points, which appear at approximately the same elongation intervals observed in the stress–strain curve obtained at 10 mm/min. Two most noticeable features are seen in the crystallinities plots: (1) the fact that significant decrement occurs at the very beginning of the second yield zone ($\varepsilon > 55\%$) may be caused by partial melting of the crystallites, and (2) the significant increment for elongations in the region of the second yield point may be associated to a recrystallization process.

A melting–recrystallization process was discussed and postulated as a possible explanation for the double yield phenomenon. In semicrystalline polymers chain units are present that are still potentially crystallizable. Further crystallization can be induced

in such systems by a uniaxial deformation. On the other hand, partial melting involves the fusion of the less perfect crystallites. It was proposed that during deformation the energy for partial melting comes from the concentration of stress on these less perfect crystallites; thus, it is not necessary for a large temperature increase to take place in order for partial melting to occur.[4] With deformation, the melted material will recrystallize. This crystallization process may be further augmented by the crystallization of some of the initial crystallizable but not already crystalline units. Thus, with the tensile deformation there is the possibility of two yields based on the original and on the newly formed crystallites.[8] Some authors have cited evidence for partial melting in the yield region using transmission electron microscopy,[29] whereas partial melting and recrystallization process in the deformation of polyethylene has been inferred from neutron scattering experiments.[30]

The crystallinity for the released state shows a similar tendency but in a minor extent. We considered important to include the crystallinity values in the released state because, being free of the influence from the monoclinic phase, they allow to examine the crystallinity variations due to the exclusive contribution of the history imposed by the plastic deformation. In all cases the Φ values for the released state are higher than those for the stressed state. Crystallinity values measured using differential scanning calorimetric technique in a necked specimen, 1 h after unloading, of several LLDPE samples have been reported.[16] For some samples this crystallinity was higher than the crystallinity in the undeformed state and was attributed to stress-induced crystallization, but the value for this unique elongation was not established. Since the necking is presented in the second yield zone, and taking into account our results, we think that this higher crystallinity in necked specimens may be due to recrystallization. The precise mechanisms associated with this behavior (RS values higher than SS values) are still not well understood. However, it may be reasonable to expect higher crystallinity values in the released state than in the stressed state because of the absence of the constraints imposed by the stress on the molecular chains.

It is interesting to compare the contribution of the orthorhombic (110) reflection to the total crystallinity; this contribution is presented in Figure 4. A great parallelism is observed in the second yield zone between the behaviors of these data with those presented in Figure 3. It was reported that the decrease in this equatorial orthorhombic intensity corresponded to the formation of monoclinic material.[16,27] However, the intensity of the monoclinic ($\bar{2}01$) peak is very small as compared to the orthorhombic (110) peak. Its highest contribution to the
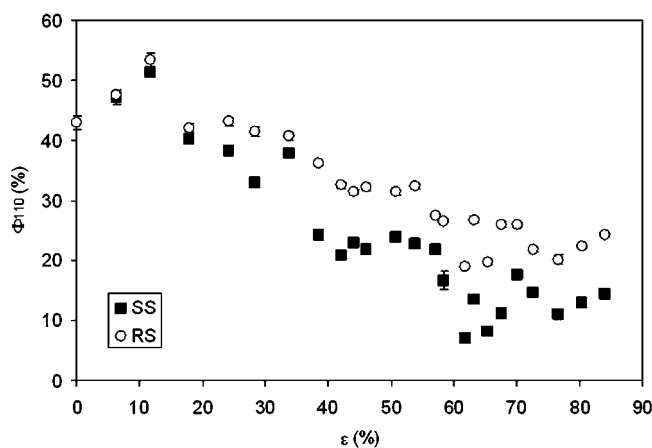

Figure 4 Crystallinity associated to the orthorhombic (110) reflection as a function of elongation for stressed and released states.

total crystallinity was of 2.62% $\pm$ 0.04% at $\varepsilon = 61.7\%$, this value in terms of the scale used in this figure is less than two times the size of the symbol used, which in most data is greater than the uncertainty associated to this orthorhombic reflection. Therefore, the abrupt decrement observed at the start of the second yield zone is mainly due to the effect of melting.

Mean crystal size

Since the intensities of crystalline peaks are related (in principle) through unit-cell structure factors, their ratios should be constant.[26] However, the intensity ratio of (110) to (200) crystal reflections decreases for elongations beyond the first yield point (see Fig. 2). This change in the intensity ratio may be due to the crystal orientation along the stretching direction or to the monoclinic structure observed in the yield region. Comparison of the two spectra for elongation at 28% shows that about the first yield point after unloading the (110) peak increases while the (200) peak decreases. This indicates the tendency to recover the original shape (ratio of intensities) of the sample. However, at the second yield point ($\sim 57\%$) and beyond this tendency disappears, which may indicate that the deformation is irreversible. This observation agrees with results reported for residual strain.[6]

The effect of the deformation on the crystalline portion is illustrated by the selected X-ray spectra shown in Figure 2. The shape of the reflections changes with the progress of the deformation. The intensity of the (200) peak increases with elongation with respect to the intensity of the (110) peak. The width of both reflections changes with the deformation for samples under SS. To a minor extent the released specimens show the same trend. The width

of the wide-angle reflections is correlated with the imperfection of the crystallites. Decreasing crystallite size and increasing crystallite distortions as well as increasing disorientation of the crystallites broaden the reflection.[25] Therefore, the width changes of the reflections may indicate changes in the crystallite size.

The estimation of the mean size of the crystalline particles was made by using the Scherrer equation, which is given by[25]

$$L_{hkl} = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where L_{hkl} represents the mean crystal dimension normal to the corresponding hkl plane, β is the half-height width of the scattering peak, 2θ is the scattering angle, λ stands for the radiating wavelength, and K is a constant of the order of 1. This equation does not consider instrumental broadening corrections, but for the purpose of this study, it is used as a practical reference to estimate the average dimension of the crystalline particles. With $\lambda = 0.15418$ nm the mean crystal size as a function of elongation was estimated.

The L_{110} values of the (110) reflection for specimens stretched at 10 mm/min, under stress and in the released state are shown in Figure 5. The size of crystallites also changed considerably at different strain stages. Comparing the behavior of the mean size values to the stress–strain curve, the plot in this Figure 5 can also be subdivided into the three zones mentioned earlier, although now are less clearly defined. The mean size values in the first yield zone are around 14.5 nm for the SS state; in the valley zone they are abruptly reduced to less than 13 nm; in the second yield zone they increase up to 14.5 nm and later decrease more abruptly to about 11 nm. These values for the crystal size fall in the range of sizes (4–30 nm) reported for polyethylene.[31] Although the uncertainty for each point is small, in almost all cases of the size of the symbol, the dispersion of the values comes from the stress–strain curves that do not exactly coincide in a same curve for all the stretched specimens at different elongations.

Below the first yield point ($\varepsilon = 25\%$) it is expected that the amorphous fraction has been sufficiently stretched, such that the tie molecules have become taut and so are able to transfer the load to the crystallites. Up to the first yield point, the material is elastic and deformations are fully recoverable. This process has been associated with an interlamellar shear process and leads to a reorientation of the lamellae, with little or no destruction of the lamellae themselves.[1,14] The fracture of the lamellae occurs in the valley zone causing a reduction of the crystal dimension, as is observed in Figure 5. Here hetero-
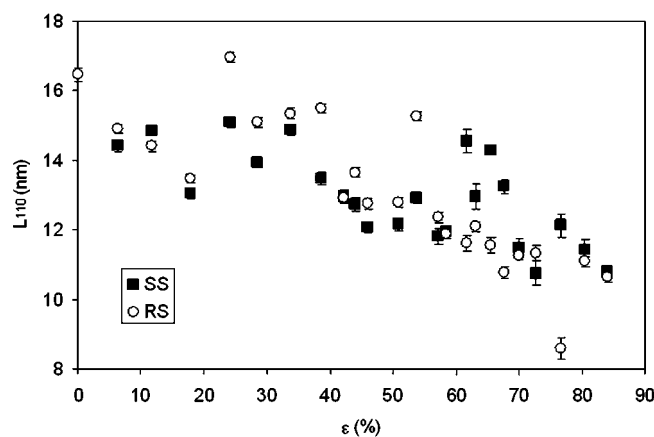

Figure 5 Mean size of the crystalline particles associated to (110) reflection for specimens in stressed and released states as a function of elongation.

geneous slip accompanied with lamella fragmentation begins to take place before the occurrence of the second yield point, leading to partial transformation of the material into a fibrillar structure.[10] The second yield zone occurs at higher strains and marks the onset of permanent plastic deformation and is generally associated with the formation of a neck, lamella destruction and to the beginning of the spherulitic to fibrillar morphological transformation.[6–9,14] The second yield point is related to permanent deformation in the specimens, and so this yield is associated with a more drastic breakdown in the structure of the polyethylene.[6,16]

These decrements in the mean crystallite size (occurring before the second yield point) may indicate that the crystalline lamellae, constituting the unoriented material, deform until they fragment; the fragments form much smaller crystalline blocks. However, the increment of the L_{110} values with the elongation in the second yield zone only can be ascribed to the partial melting associated to the crystallinity decrement. A detailed inspection of Figures 3 and 5 revealed that, in the range of 60–65% for elongation, the crystallinity value had the highest decrement and the crystallite size had the highest increment. This may indicate that, as the partial melting is produced on the smallest or less perfect crystallites, the L_{110} value increased because the remained crystallites have higher size. Although distortion and disorientation may be present, as deformation continues their effect is expected to remain constant or to increase the width of the crystalline reflections. Therefore, the reduction in the width of the peak reflections is caused by the increment of the crystallite size. It is known that for linear polyethylene the yield stress increases with the initial crystallite size[4] (i.e., without deformation); therefore it is reasonable to expect that the magnitude of the yield stress at

the second yield point also increases due to the increment of crystallite size. The subsequent decrement of the L_{110} values with the elongation in the second yield zone can be ascribed to the fracture of the newly formed crystalline lamellae.

The L_{110} values for the released state are also presented in Figure 5; they have similar tendency as those corresponding to the SS state. The values for RS are larger than those for SS in the first yield and valley zones. The opposite is observed in the second yield zone. These behaviors indicate that the released specimens have the tendency to recover the initial size only in the first two zones. This finding agrees with the reported observations[6,32] that below the first yield point the deformation is completely recoverable on unloading; at strains greater than the first yield point, but less than the strain of the second yield point, are largely recoverable over a longer time scale; all deformation beyond the second yield point is effectively permanent plastic deformation.

We have been able to draw some information of the relation between the mechanical behavior of the double yield phenomenon and crystalline properties from the experimental findings of the crystallinity and mean crystal size. In the first yield zone appears a strain-induced crystallization. The valley region is associated with fragmentation of crystalline lamellae. The second yield zone is associated with partial melting, recrystallization, martensitic transformation, fragmentation, and necking. The experimental evidence presented in this paper indicates that the partial melting–recrystallization process is one of the important mechanisms of the double yield phenomenon and helps to explain the appearance of the second yield point.

CONCLUSIONS

The double yielding phenomenon was observed in specimens of LLDPE. The stress–strain curves confirmed that this phenomenon was in correlation with the stretching rate and showed that it occurred much more easily and distinctly at lower stretching rates.

The wide angle X-ray scattering analysis showed the martensitic transformation from orthorhombic phase to monoclinic phase. This phase was observed in the stressed state around the second yield point, but disappeared when the applied stress was removed.

The WAXS experiments indicated that the double yielding behavior is related to changes of both the crystallinity of the stretched specimens and the mean crystallite dimension at different stages in the course of a tensile test. The uniaxial deformation is a complex, multistep process, and at various deformation stages some additional mechanisms are activated. The crystallinity as a function of elongation allowed subdividing the double yield phenomenon into three zones: first yield, valley, and second yield. At small strains in the first yield zone strain-induced crystallization was observed. Later, the crystallinity and the mean size of crystallites of the orthorhombic phase decreased abruptly in the valley region, associated with fragmentation of crystalline lamellae. In the second yield zone the crystallinity again decreased and presented an increment followed by an approximately equal decrement. This last behavior is associated with partial melting followed by recrystallization, and the final decrement may be associated to fragmentation of the newly formed crystals. The mean size of crystallites also detected the partial melting. The crystallinity and mean crystallite size for specimens in the released state (after removing the applied stress) do not have the influence of the monoclinic phase and show similar behavior as the stressed specimens, although to a relative minor extent.

These experimental results show that the second yield point is not only associated with the deformation of the crystalline portion. They indicate that a process of partial melting of the crystallites followed by a recrystallization takes place in the second yield region. This partial melting–recrystallization process is one of the main mechanisms in the double yield phenomenon. The behavior of the crystallinity and crystallite size are of considerable importance in the understanding of the mechanical behavior of polyethylene.

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