

# RECRYSTALLIZATION OF POLYETHYLENE IN THE DOUBLE YIELD REGION

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## INTRODUCTION

A yield point in polymers is conventionally accepted as the point where a local maximum is shown in the stress-strain curve. 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 [1-2]. This change occurs through shearing and fragmentation of the crystalline lamellae into blocks which rearrange into the form of parallel microfibrils. Investigations of the yield process in polyethylene have also been performed from a phenomenological point of view to establish the constitutive equations of the plastic flow [3-4].

Works published [5-10] for polyethylenes under tensile loading demonstrated the existence of double yield points. This double yield phenomenon has been studied (a) in a variety of systems: pure polyethylenes, binary blends, and ternary blends of two polyethylenes and an elastomer; (b) in polyethylenes with a variety of properties: linear or branched, different crystal thickness distributions, different degrees of crystallinity, and ternary blends with different types of elastomer; (c) under different conditions of tensile loading: deformation temperature, and strain rate; and (d) in samples with different thermal history caused by processing conditions, and cooling rates.

The shape of the stress-strain curve ( $\sigma$ - $\epsilon$ ) in the double yield region may exhibit comparable values of the stress of the 2 maxima or a dominant value of either maximum. The first yield process becomes dominant under extreme conditions of low temperature, high strain rate or high crystallinity. The second yield process becomes dominant under the opposite extreme conditions. A different deformation mechanism exists for each yield process; but the proposed explanation has not been unique.

The double yield behavior of a medium density polyethylene with a narrow crystal thickness distribution was studied [6]. The explanation was in agreement with the proposal [11] 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 and a homogeneous shear of the crystal blocks. The yield behavior in polyethylene samples with different degrees of branching was investigated [7,9]. The first yield point marked the onset of plastic strains which are slowly recoverable at least in part. Deformation beyond the second yield point is effectively irrecoverable and was associated with a sharp necking of the samples. The yield points were interpreted mechanically as the yield of two dashpots and the model used to describe the yield is of two non-linear Maxwell elements in parallel. The double yield phenomenon was studied [10] in a set of linear polyethylenes and well-characterized ethylene copolymers of narrow molecular weight and composition distribution, as a function of molecular weight,

crystallinity, stretching rate and temperature. A qualitative explanation was based on the postulate of a partial melting-recrystallization process during deformation.

Since there is a strong correlation between the nature of the yield region and the permanent deformation of the material, understanding the yield process is very important to understand the complete deformation process. To our knowledge, there is no published work with any quantified evidence of the melting-recrystallization process in the double yield region. In this paper we analyze the yield behavior of a linear low density polyethylene by determining the crystallinity in both the stressed and released states, using the wide angle x-ray scattering technique (the released state is obtained from the stressed state when the stress is removed).

## **EXPERIMENTAL**

The commercial polymer was obtained from Dow Chemical (Dowlex 2101). The polymer was used without any modification. Sheets with a uniform thickness were prepared using a single-screw Brabender extruder. From these sheets, samples with the standard dumbbell shape were punched out for tensile tests. To determine the values of the elongation at which the two yield maxima occur, in a first experiment the deformation was carried out up to rupture. Then, the subsequent specimens were stretched up to a predetermined elongation. The uniaxial deformation was carried out at 25 °C in an Instron tensile testing machine (4502) at the stretching rates of 50, 10, and 1 mm/min. A special x-ray sample-holder, built to maintain the applied stress, was placed in the central portion of the stretched sample; then the sample was cut for x-ray analysis.

Wide angle x-ray scattering (WAXS) patterns of the samples 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 K $\alpha$  radiation generated at 40 kV and 30 mA was used. The angular position ( $2\theta$ ) 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 of 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 minutes. The WAXS patterns were obtained for samples in the stretched state; immediately after this run, the stress was removed (released state) and a second pattern was obtained. This procedure was repeated for specimens stretched up to a different predetermined elongation. The degree of crystallinity was calculated in the standard way [12,13].

## **RESULTS AND DISCUSSION**

The relaxation effects in the samples during the WAXS experiment can be ignored, since for a sample stretched to a high elongation of 400% the x-ray spectra did not change in 22 hours. Only the sample stretched at 10 mm/min showed the double yield phenomenon, with comparable stress values of each maximum; at the stretching rate of 50 mm/min the first yield maximum was dominant, but at 1 mm/min the second yield maximum dominated. As a consequence of the deformation, the intensity of the (110) reflection in the stressed state decreases whereas that of the (200) reflection increases in both states of

deformation. In the released state, the intensity of the (110) reflection for the first yield point almost restores its value in the unstretched state. Most noticeable is that the (200) peak increased in intensity with the elongation for both states, although much less for the released state.

In the WAXS pattern corresponding to the stretched sample around the second yield point, an extra reflection is registered due to the stress-induced monoclinic phase. Some authors have reported this reflection as a martensitic transformation from the orthorhombic to the monoclinic phase. The indexes correspond to the reflection ( $\bar{2}01$ ) as reported elsewhere [14]. This monoclinic peak is not stable, since it only appeared in the strained state but disappeared after the removal of the stress.

Since the intensities of crystalline peaks are related (in principle) through unit-cell structure factors, their ratios should be constant [13]. However, the ratio of the intensities of the (110) and (200) reflections decreases for elongations higher than that for the first yield point. This change in the intensity ratio may be due to the crystal orientation along the stretching direction or to the stress-induced monoclinic structure observed for polyethylenes in the yield region [9,14].

Comparison of the spectra shows that at the first yield point the original shape of the sample is almost recoverable, but at the second maximum the deformation is irreversible. This observation agrees with results reported for residual strain [7].

The mean size of the crystalline particles was estimated as a function of the deformation. In the stressed state, the  $L_{110}$  values decrease gradually, but immediately after the second yield point show abrupt decrements; the crystal size  $L_{200}$  has almost a constant value, except after the second yield point where has a high decrement. These decrements indicate that the crystalline lamellae, constituting the unoriented material, deform until they fragment. The fragments form much smaller crystalline blocks.

The degree of crystallinity, as a function of the elongation in both the strained and released states, was determined in the angular interval  $12.5-30^\circ$ , which encompasses the very intense (110) and (200) reflections from the orthorhombic structure. The crystallinity was obtained from the spectra as the ratio of integral of the crystalline peaks over the sum of integrals of the crystalline and amorphous peaks. The crystallinity values decrease gradually with the elongation, but after the first yield point (between the valley and the second yield point,  $\epsilon=45\%$ ) an abrupt increment is observed almost to the value of the initial unstrained state; after this elongation the crystallinity continues decreasing. The decrement may be caused by a partial melting of crystallites, and the significant increment at a higher elongation may be associated with a recrystallization process. The crystallinity of the (110) reflection also decreases with the elongation and has an increment at the same elongation as the total crystallinity; whereas that of the (200) reflection increases up to  $\epsilon=45\%$  and remains almost constant for higher elongations.

## CONCLUSION

The wide angle x ray scattering analysis showed the stress-induced monoclinic phase. This phase was observed in the stressed state around the second yield point, but disappeared when the applied stress was removed.

The crystallinity of the orthorhombic phase decreased in the first yield point and presented an abrupt increment before the second yield point. These experimental results indicate that a process of partial melting of the crystallites followed by a recrystallization takes place in the double yield region.

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