Polymer Bulletin 39, 125–132 (1997)

Polymer Bulletin

# The phenomenon of double yielding in blown polyethylene films

**J. L. Feijoo, J. J. Sánchez, A. J. Müller***

Grupo de Polímeros USB, Departamento de Ciencia de los Materiales,
Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

Received: 25 March 1997/Revised version: 19 May 1997/Accepted: 23 May 1997

## Summary

The plastic deformation mechanisms of isotropic and blown High-Density Polyethylene (HDPE) and Linear-Low Density Polyethylene (LLDPE) films were studied. The deformation process was followed in stages using dichroic FTIR measurements. Our results indicate that the mean orientation direction of the crystalline regions determines whether or not the polyethylene sample exhibits double yielding behavior in a particular stretching direction, regardless of its crystalline content.

## Introduction

The double yielding process was first explicitly reported for branched polyethylenes in 1987 (1), even though earlier examples exist in the literature but were not recognized previously as such (2-4). Many recent studies have tried to understand this complex phenomenon (5-15).

A typical engineering stress-nominal strain curve for a Linear-Low Density Polyethylene (LLDPE) exhibits two maxima associated with the double-yielding phenomenon (see Fig. 1*a*) as opposed to the behavior exhibited by isotropic High-Density Polyethylene (HDPE), in which only one yield point is observed. All the recent published reports quoted above agree that the first yield is not associated with extensive permanent plastic deformation of the specimen since necking only starts after the second maximum in the stress-strain curve for LLDPE. However, the microstructural origin of the two maxima is still under discussion. According to Mandelkern *et al.*, the two yield points result from the tensile deformation of the original crystallites present in the sample and from the deformation of newly formed crystallites produced by a mechanically induced melting and recrystallization process that occurs during the tensile test (1,12). This model has been questioned by the absence of evidence of partial melting during tensile deformation and by the fact that it presupposes that the polymer must have a wide distribution of lamellar thickness in order to show double yielding (5-8,10-11).

Séguéla *et al.* (5,10) have postulated that the two yield points are due to the slip of crystalline blocks past each other and the homogeneous shear of the crystal blocks for a model comprising mosaic crystalline structures. The two yield points were found to be independently activated by temperature and strain rate. Balsamo and Müller (7-8) also found that the two yield processes in LLDPE, LDPE and their blends were independently activated by strain rate

---

* Corresponding author

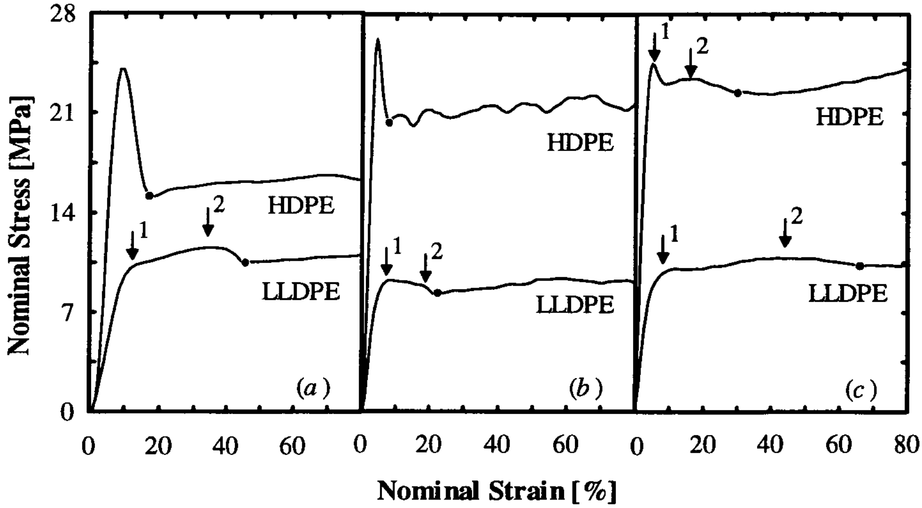

**Figure 1.** Typical stress-strain curves in the yield zone obtained (*a*) for compression molded samples; for blown films: (*b*) TD: Transverse direction, (*c*) MD: Machine direction. (1) First yield point and (2) Second yield point. The strain at which necking appears is indicated with a filled circle in each curve.

and calculated the activation volumes using the Eyring treatment. Even though the Séguéla-Rietsch model can help to explain qualitatively how the two yield points vary with degree of crystallinity, strain rate and temperature (5,7-8,10,13-14) the assumption of a crystalline mosaic structure only considers the amorphous chains as defective intracrystalline regions. This assumption is more suitable for highly crystalline materials but not for LLDPE or Low-Density Polyethylene (LDPE) where the amorphous regions can amount to 65% of the material. Brooks *et al.* (6,11) have made a comprehensive study on the structural changes that occur during the double yielding behavior of isotropic polyethylenes; their results show that the first yield point signals the onset of a recoverable reorientation process (a non-linear viscoelastic process that can nearly completely recover upon unloading after 3 to 9 days depending on the density of the sample) of the lamellae within the spherulites that leads to a final orientation of the lamellae at approximately 45° to the draw direction. The second yield point is related to the destruction of these lamellae by *c* shear, a process related to the onset of necking and to the beginning of the spherulitic to fibrillar morphological transformation.

In this work, we follow the changes in the mean orientation of the crystalline regions of oriented blown films of HDPE and LLDPE during the double yielding process under tension by dichroic infra-red measurements before and after each yield process.

## Experimental

The materials used in this study were a 11F1 1-butene LLDPE ($\rho$ = 0.919 g/cm$^3$, MFI = 0.75 dg/min, $\overline{M}_n$ = 32,400 g/mol, $\overline{M}_w$ = 132,000 g/mol) kindly supplied by *RESINAS LINEALES RESILIN* (Venezuela), and an ALTAVEN 7000F HDPE ($\rho$ = 0.956 g/cm$^3$, MFI = 0.05 dg/min,

$\overline{M}_n = 12{,}500$ g/mol, $\overline{M}_w = 230{,}000$ g/mol) manufactured in Venezuela by *POLIOLEFINAS INDUSTRIALES*. The isotropic samples were compression molded into 0.5 mm thick sheets (from which ASTM D638 dumbbell specimens were cut) at 170°C and then quenched in ice water. The blown films were prepared by extrusion blow molding at 240°C for the HDPE and 210°C for the LLDPE. The blow up ratio (BUR) was 1.6 and 2.2 for the HDPE and the LLDPE respectively and the film thickness obtained varied between 50 to 80 µm. Nominal stress-strain curves were obtained using a *JJ LLOYDS T5003* universal testing machine at a strain rate of 50 mm/min and 23 °C.

The IR measurements were performed with a ***BRUKER*** *IF55* Fourier Transform Infra-red (FTIR) spectrometer fitted with a gold-wire-grid polarizer, which allowed dichroic measurements. Further experimental details are given elsewhere (15). The band doublet observed in the spectrum of polyethylene at 720/730 $cm^{-1}$ (see Fig. 2) have been analyzed in order to characterize the mean orientation of the crystal unit cell as a function of applied deformation (16). This band doublet has been assigned to in- and out-of-phase $CH_2$-rocking vibrations, respectively, of the crystal phase with the 730 $cm^{-1}$ band polarized along the crystallographic *a*-axis and the 720 $cm^{-1}$ band polarized along the *b*-axis (17). We have followed the assumption that the contribution of the amorphous regions to the 720 $cm^{-1}$ peak maximun absorbance is comparatively small for LDPE and that there is uniaxial symmetry within the sample (16,18). We have attempted to monitor the orientation of the crystallographic *a*-, *b*-, and *c*-axes, respectively, relative to the stretching direction by their corresponding orientation functions $f_a$, $f_b$ and $f_c$ using static FTIR measurements. Onogi and Asada (18) have shown that static and dynamic FTIR yield almost identical results in the study of stretching of LDPE because the structural units that cause the relevant absorption bands can attain their equilibrium in times shorter than 1 s after stretching. The orientation functions of crystal axes *a* ($f_a$) and *b* ($f_b$) may be evaluated from the FTIR dichroic ratios for the 730 and 720 $cm^{-1}$ bands, $D_{730}$ and $D_{720}$ respectively, by the method used by Siesler (16). The orientation function of the *c*-axis ($f_c$) was derived from the values of $f_a$ and $f_a$ also following Siesler. We are aware of the common difficulties associated with the determination of orientation functions, however in the case of the band doublet used here these effects are negligible (19).

## Results and Discussion

The results presented in Fig.1*a* agree with the observations of Lucas *et al.* (12), who claim that double yielding is only observed in samples with crystallinity degrees between 20 and 50%, since only the LLDPE displays a clear double yield phenomenon (the DSC crystallinity degrees of the isotropic samples of Fig. 1*a* were 64 and 42% for the HDPE and the LLDPE respectively). However, when we examined the yielding behavior of the blown film samples the results were quite different. Figures 1*b* and 1*c* show the yield zone section of the nominal stress-strain curve for both HDPE and LLDPE films tested along the machine direction (MD) and along the transverse direction (TD), respectively. The LLDPE still exhibits double yielding when tested along MD. Along TD the LLDPE films presented the double yielding process in a much narrower range of strains (necking was observed at around 20% nominal strain for TD and at around 65% for MD direction). The HDPE films show a

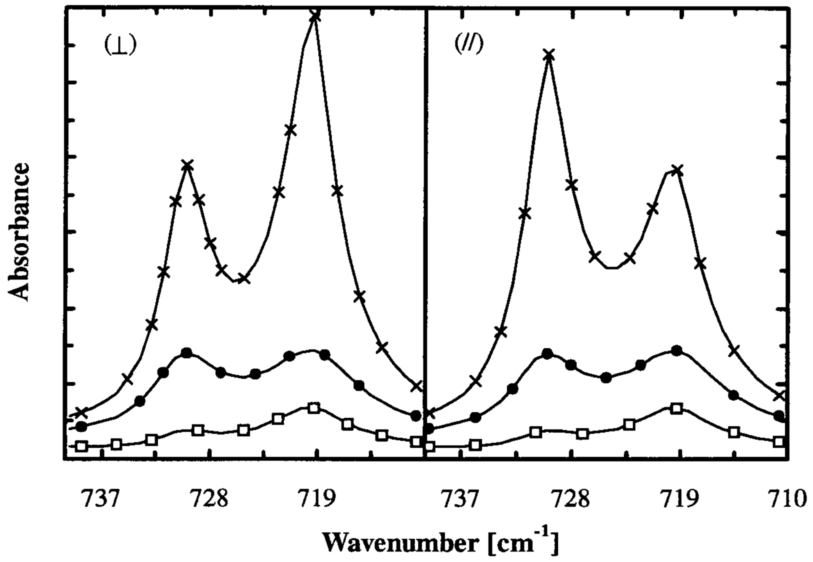

**Figure 2.** FTIR spectra of blown LLDPE films, undeformed and after deformation along MD. The light was polarized alternately perpendicular and parallel to MD: (x) Undeformed, (●) Between 1st and 2nd yield (20% nominal strain), and (□) Neck region (65% nominal strain)

single yield point along TD and a remarkably clear double yielding along MD. These results indicate that the orientation produced during the extrusion blow molding process affects yielding in such a way that even HDPE, with a high degree of crystallinity, can exhibit double yielding at room temperature (15). In order to explain these results we determined the mean orientation direction of the crystallites by FTIR within the blown films.

The determination of crystal axes orientation in blown polyethylene films by Wide-Angle X-ray Scattering (WAXS) measurements has been extensively discussed by several authors (20-21). Stress-induced crystallization of an oriented melt leads to a typical texture with the lamellar growth direction (crystalline *b*-axis), perpendicular to the extrusion direction, while the other two crystalline axes are distributed around the extrusion direction. This phenomenon has been called an "*a*-axis texture" because of the observation of strong (200) meridional maxima in WAXS photographs. Additionally, it has been shown that the average angle of *a*- and *b*-axes with respect to MD has a strong dependence on extrusion temperature. At relatively low extrusion temperatures the *a*-axis mean direction points along TD, while the *b*-axis distribution is completely fiber symmetric; and for higher extrusion temperatures *a*-axis preferentially point in the machine direction while *b*-axis show a mean direction normal to the film plane (22). Early static IR studies devoted to the necking of polyethylene (blown LDPE films) have shown that the crystalline phase deforms according to shear processes that progressively bring the chain axis parallel to the stretching direction, in order to promote chain unfolding (18). More recently, Dupuis *et al.* (23) carried out static and dynamic FTIR spectroscopy in order to study hot drawing of blown LLDPE films, their investigation performed in static mode has shown that the crystalline phase undergoes a quick reorientation of the *c* axis towards the draw direction, apparently involving the untwisting of the lamellar ribbons. From their dynamic study they distinguish a transient orientation of the amorphous chains, which arises from the dynamic crystal block rearrangements during necking. Dynamic FTIR spectroscopic studies have been carried out previously on blown HDPE films, where transient regime studies of the plastic deformation have been reported. In particular the process of martensitic transformation has been well emphasized (16,25).

Figure 2 shows an example of a series of selected IR spectra for perpendicular ($\perp$) and parallel (*//*) polarization direction with respect to MD in the region of the $CH_2$-rocking vibrations. The spectra corresponding to the undeformed samples show a preferred orientation of the *a*- and *b*-axes of LLDPE unit cells parallel and perpendicular to the stretching direction respectively. Therefore the average orientation of the *c*-axis is along TD. The IR dichroic ratios ($D_{730} = 1.38$ and $D_{720} = 0.66$, see Table 1) for the undeformed sample confirm the latter conclusion. As strain was applied to the sample up to 10% (first yield point), the changes in the values of dichroic ratios and in the intensity of the relevant bands indicate that there is an appreciable modification in the mean orientation of the crystals. These changes might be related to the lamellar reorientation process associated by Brooks *et al.* (8) to the first yield. From *circa* 10-65% strain induced characteristic changes in the dichroic ratios (see Table 1) occur, which correspond to a rotational motion of the crystals that leads to a mean orientation of the *c*-axis along the stretching direction and to the *a*-axis being perpendicular to the stretching direction. Our dichroic measurements are in agreement with similar results reported by Onogi and Asada on the tensile deformation of blown LDPE films using static FTIR spectroscopy (18). Qualitatively similar changes in the mean orientation direction of HDPE crystallites are reflected in the values of the dichroic ratios shown in Table 1 and discussed in our previous work on the subject (15).

From the dichroic FTIR results and the stress-strain curves we can gathered that before the tensile deformation, the blown LLDPE films possess an "*a*-axis texture" type of orientation along MD with a morphology that can be described by the Keller and Machin row nucleated model presented in Fig. 3. Along TD the films have a *c*-axis type of mean orientation before the tensile tests. To correlate the macroscopic properties and the structural changes occurring during deformation, the orientation functions ($f$) have been plotted as a function of strain in Fig. 4.

The FTIR dichroic results presented in Fig. 4 and the stress-strain diagram for uniaxial elongation (MD) can be separated into different regions. The first region corresponds to the increase in deformation up to the first yield point (0-10%), where $f_b$ increases and $f_a$ decreases with strain indicating a small rotation of the *b*-axes towards the stretching direction and a movement towards the opposite direction of the *a*-axes (18, 24). These changes might be related to the reorientation of the lamellar units within the polymer superstructure during stretching (up to the first yield region) as indicated by Brooks *et al.* (11). The second region spans strains from 10 to 45% (second yield) at which $f_c$ exhibits a relative increase as strain increases while $f_a$ decreases. In this case, these changes might be associated to the process of intralamellar rotational motion or untwisting around the *b*-axes (23) of the crystals with their *c*-axes oriented along the stretching direction and their *a*-axes perpendicular to it. The untwisting process mentioned above could be responsible for bringing the chain axes to the best possible orientation for the subsequent shear of crystal blocks past each other (or *c*-shear deformation that leads to necking and the ultimate fibrillar transformation). In the stress-strain curve this second region corresponds to small changes in the nominal stress whilst the strain

**Table 1.** Infrared Dichroic Ratios in blown LLDPE and HDPE films undeformed and after deformation in the yield zone along MD.

| **Description** | **Nominal Strain** [%] | **IR Dichroic Ratios, *D*:** 730 [cm$^{-1}$] | 720 [cm$^{-1}$] |
|---|---|---|---|
| LLDPE RESILIN 11F1: | | | |
| Undeformed | 0 | 1.38 (*a*) | 0.66 |
| First yield point | 10 | 0.97 (*a-b*) | 1.03 |
| Between first and second yield | 20 | 1.00 (*a-b*) | 1.00 |
| Second yield point | 45 | 0.84 (*c*) | 1.00 |
| After second yield (Neck region) | 65 | 0.47 (*c*) | 0.72 |
| HDPE ALTAVEN 7000F: | | | |
| Undeformed | 0 | 1.70 (*a*) | 0.38 |
| First yield point | 6 | 1.16 (*a*) | 0.82 |
| Between first and second yield | 10 | 1.08 (*a*) | 0.87 |
| Second yield point | 15 | 0.81 (*c*) | 0.86 |
| After second yield | 20 | 0.80 (*c*) | 0.98 |

*a*, *a-b*, *c*: Indicate the mean axis orientation in the crystalline regions in the machine direction.

accumulates irrecoverable plastic deformation (11). The third and final region extends beyond the second yield maximum (onset of neck formation), here $f_a$ starts to decrease drastically, while $f_c$ increases sharply, indicating that the process of fibrillar transformation has started. At the same time (as can be seen in Fig. 2) the intensity of the 730 cm$^{-1}$ band decreases in comparison to the 720 cm$^{-1}$ band (especially after the second yield on the neck region), which could be taken as evidence of the distortion of the unit cells by the process of chain unfolding from the lamellae (16,24).

After necking all samples possess a *c*-axis type of orientation since the typical fibrillation process in the neck has occurred. A very clear picture of the yield process in the blown films can be deduced by careful consideration of the model by Brooks *et al.* (11). For the deformation along MD the two yield points can be explained, since the first yield point is due to the reorientation of the lamellae to a more favorable orientation for the subsequent *c*-shear deformation that will occur during the second yield. When the chains are already oriented along the *c*-axis, i.e. when the test is performed along TD, then only the second yield is observed since only minor chain reorientation will occur during the fibrillar transformation.

In the isotropic HDPE compression molded sample, only one yield is observed since the crystallinity degree is so high that most of the amorphous chains will be connected somehow to the radially oriented lamellar structure within the spherulites. Upon deformation, when the lamellar rotation (at low strains) induced by the deformation of the amorphous regions is occurring, a simultaneous *c*-shear of the lamellae induces plastic deformation and necking (i.e., the characteristic second yielding process of the material). In the case of the blown HDPE films, the row nucleated "*a*-axis texture" type of structure makes possible the separation of the two yield processes when the tensile test is performed along MD in view of the reorientation mechanisms involved and explained above. FTIR dichroic spectroscopy is capable of discerning between the two contributions in the latter case.

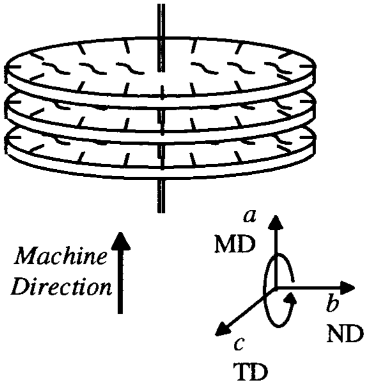

**Figure 3.** Schematic representation of a row-nucleated morphological model for blown PE film (*a*-axis texture). ND, normal direction (Based on Keller and Machin, Ref. 20)

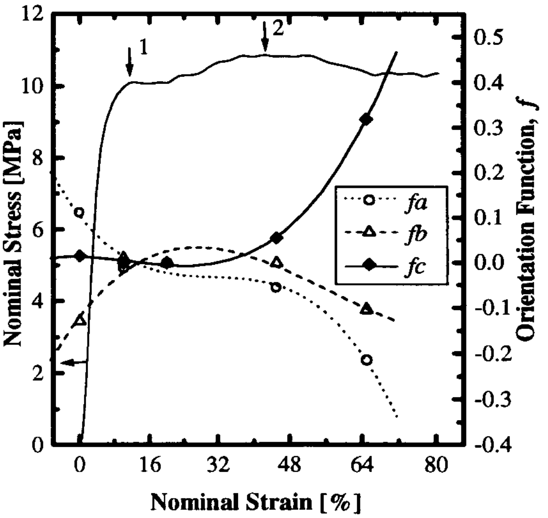

**Figure 4.** Variation of orientation functions for *a*-, *b*-, and *c*-axes ($f_a, f_b, f_c$) and the nominal stress-strain curve along MD for blown LLDPE film.

## Conclusions

According to the results presented above, double yielding is a general phenomenon for polyethylene irrespective of its crystallinity degree, and the deformation model put forward by Brooks *et al.* (11) can satisfactorily explain the structural morphological transformation that cause double yielding in this material. It is suspected that the double yielding process could also be the general plastic deformation mechanism of semi-crystalline polymers that exhibit shear yielding but in many cases only one yield point is observed (the second yield process), as in isotropic HDPE deformed under tension at room temperature or in blown HDPE films strained along TD. As a matter of fact, double yielding has been also reported in the tensile deformation of Nylon 6 and poly(butylene terephtalate) (26-27).

## Acknowledgments

We would like to gratefully acknowledge the financial support of the *CONICIT* through grant NM-43. We would also like to thank I. Rodríguez and G. Orellana for their invaluable help with the FTIR measurements. The use of the *BRUKER* FTIR Spectrometer was made possible by J. Mostany and B. Scharifker, through grant NM-12 (also by *CONICIT*). Blown HDPE films were extruded at *PLÁSTICOS MLM* by courtesy of F. Massott. The help of M. Urbina from *RESILIN* with the extrusion blow molding process of the LLDPE and of D. Rizzi with the tensile properties of the blown LLDPE film is gratefully acknowledged.

## References

1. Popli R, Mandelkern L (1987) J Polym Sci, Polym Phys Ed 25: 441
2. Sperati CA, Franta WA, Starkweather HW (1953) J Am Chem Soc 75: 6127
3. Vincent PI (1960) Polymer 1: 7
4. Takayanagi M, Kajiyama T (1973) J Macromol Sci Phys B8: 1
5. Séguéla R, Rietsch F (1990) J Mater Sci Lett 9: 46
6. Brooks NW, Duckett RA, Ward IM (1992) Polymer 33: 1872
7. Balsamo V, Müller AJ (1993) J Mater Sci Lett 12: 1457
8. Balsamo V, Müller AJ (1993) Mat Eng 4: 207
9. Springer H, Hengse A, Hinrichsen G (1993) Colloid Polym Sci 271: 523
10. Séguéla R, Darras O (1994) J Mat Sci 29: 5342.
11. Brooks NW, Unwin AP, Duckett RA, Ward IM (1995) J Macromol Sci-Phys B34: 29
12. Lucas JC, Failla MD, Smith FL, Mandelkern L (1995) Polym Eng Sci 35: 1117
13. Plaza AP, Ramos E, Manzur A, Olayo R, Escobar A (1997) J Mat Sci, In press
14. Manzur A, Olayo R, Ramos E (1997) J Appl Polym Sci, Accepted for publication
15. Feijoo JL, Sánchez JJ, Müller AJ (1997) submitted to J Mat Sci Lett
16. Siesler HW (1984) Adv Polym Sci 65: 1
17. Snyder RG (1967) J Chem Phys 47: 1316
18. Onogi S, Asada T (1967) J Polym Sci Part C No 16: 1445
19. Myers CW, Cooper SL (1994) Appl Spectroscopy 48: 72
20. Keller A, Machin MJ (1967) J Macromol Sci-Phys B1: 41
21. Choi K-J, Spruiell JE, White JL (1982) J Polym Sci: Polym Phys Ed 20: 27
22. van Gurp M, Kip BJ, van Heel JPC, de Boer S (1994) J Plast Film Sheet 10: 156
23. Dupuis J, Legrand P, Séguéla R, Rietsch F (1988) Polymer 29: 626
24. Holland-Moritz K, Holland-Moritz I, van Werden K (1981) Colloid Polym Sci 259: 156
25. Holland-Moritz K, van Werden K (1981) Makromol Chem 182: 651
26. Hoashi K, Kawasaki N, Andrews RD (1973), in Lenz RW, Stein RS (eds) Structure and Properties of Polymer Films. Plenum Press, New York (pp 283)
27. Muramatsu S, Lando JB (1995) Polym Eng Sci 35: 1077