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Bending Behaviour of LLDPE Monofilaments Depending on Cold Drawing and Composition of the LLDPEs

Abstract

The behaviour of the pile layer of artificial turf is an important element for the performance of artificial turf. As a top layer, it is constantly under deformation, with the most possible being bending. The bending behaviour of monofilaments of linear low density polyethylene (LLDPE) is strongly influenced by the processing parameters, the type of polymer, and geometrical factors, which in combination with each other seem to have a strong influence on the behaviour of the final product. From the results obtained, the use of octene instead of hexene as a monomer yields better results for resilience due to a higher concentration of intrafibrillar tie molecules for the same degree of DSC crystallinity of the LLDPEs. The increase in the final cross section of monofilaments based on the same LLDPEs resulted in a decrease in the intrafibrillar tie molecules due to a slower cooling after melt extrusion.

Key words: polyethylene, draw ratio, resilience, monofilaments, tie molecules.

Introduction

Linear low density polyethylene is the polymer most used for monofilaments composing the pile layer of artificial turf and has been the subject of several publications [1 - 5]. The pile layer, used as a top layer, is responsible for the performance of the ball behaviour in terms of the rolling distance and speed of rolling. When the pile layer becomes flat, these two parameters change [6] and have a strong influence on the performance of the entire artificial turf field.

As a polymeric material, the behaviour of monofilaments is related to their internal structure, which is influenced by the production parameters and processing conditions [7]. The stretching ratio has a negative influence on the deformation recovery of monofilaments [3], described as the most possible deformation happening in the real field. Samples with a low value of stretching have better recovery compared to the one more highly stretched. This was explained as a function of the 3rd phase structure composing the structure of the product [4]. Different from the bending test, the mechanical properties were significantly improved with respect to the stretching ratio. Based on literature, this could be explained due to the increase in the degree of crystallinity or the molecular orientation of the product [7 - 9]. From the results obtained [3, 4], the amount of crystallinity was almost constant for different values of stretching ratio(s); however the molecular orientation was increased and could be correlated with the mechanical improvements [3].

There is evidence, particularly from studies of non-crystalline polymers, that the natural stretching ratio depends on the degree to which the polymer is already oriented prior to cold stretching. Without cold stretching, the structures of the monofilaments are characterised by an interphase composed of tie molecules containing only gauche bonds [10]. On cold stretching, the tie molecules are stretched, become tauter and the gauche (G) bonds are transformed into trans bonds. This is the origin of the increase in the elastic modulus, being related to the transition of the gauche bonds into trans bonds, known as the most stable structure [9] in the 3rd phase of polyethylene. The influence of the interphase and its structure variations can be linked to the semi-empirical models of taut tie molecules. At the limit of the high stretching ratio, the intrafibrillar taut tie molecules of LLDPE are completely transformed into long (zig-zag) sequences of all-trans bonds. This transformation of gauche bonds into trans bonds was observed and analysed during the cold stretching of LLDPE monofilaments and the linear relationship between the elastic modulus and content of trans bonds was proven [4]. In the first approximation the elastic modulus is related to the content of the gauche (G) and trans (T) bonds [8, 11]. The extra structure variation in the interphase, taking place during the cold stretching, is the transformation of gauche bonds into trans bonds.

According to the model of taut tie molecules [12], the fibre structure of stretching polyethylene monofilaments is constituted by microfibrils, in which crystal-

line and amorphous layers are periodically arranged. Some taut tie molecules exist between these two structures and others inside the microfibrils, which improve the mechanical properties of the monofilaments.

The precise mechanism of orientation inside the product [9] depends on the polymers used, depending on the monomers utilised, molecular weight and molecular weight distributions [6]. In this paper the behaviour of monofilaments is studied in relation to monomers of LLDPEs (octene and hexene) and to the thickness of the monofilaments produced.

Experimental

Materials

The two polymers used in this study were obtained from the Dow Chemical Company, namely low linear density polyethylene DOWLEX™ 2035G and DOWLEX™ 2606G [13]. DOWLEX™ 2035G is a low linear density polyethylene (LLDPE) with a density of 0.919 g/cm³ and a melt index of 6g/10 min, with octene as a monomer. DOWLEX™ 2606G is also a low linear density polyethylene, with a density of 0.92g/cm³, a melt index of 4g/10min, but with hexene as a monomer.

Monofilaments production

Extrusion of monofilaments

The monofilaments investigated were extruded in two different extruders. The first extruder, HaakePolydrive Extruder by the Thermo Electronic Corporation, was a single screw extruder of 25D in length and screw diameter of 19 mm. The temperature in the die was 220 °C. The die has diamond-shaped openings with a cross section of 2.36 mm² each. From this extruder, two series of monofilaments with the same production pa-

rameters but with different thicknesses were produced.

The other extruder used for monofilament production, comparable with industrial lines, is an OerlikonBarmag type 3E/24D extruder with a screw diameter of 30 mm and length of 25D. The temperature in the die was 220 °C. The die has diamond-shaped openings with a cross section of 5.7 mm² each. For both cases, after the melt stage monofilaments were pulled through a water bath and then passed through an oven at a higher temperature.

The temperature in the oven for the samples produced with the small extruder was 95 °C and the oven was 40 cm long. For the industrial line, the temperature in the oven was 100 °C and the length of the oven 3 m.

The drawing ratios and physical characteristics of all the samples produced are summarised in *Table 1*.

Characterisation techniques

Mechanical properties, tensile testing

A tensile test was performed on Instron 3369 tensile equipment at a room temperature of 23 ± 2 °C. The cell load was 500 N and the initial gauge length 50 mm, with a test speed of 500 mm/min. For each sample, five repetitions of tensile deformations were made and the elastic modulus was calculated from the mean values of these measurements. The stress and strain obtained during the tensile deformations were the engineering stress and engineering strain measured directly between the clamps. The tensile strength and elasticity modulus were calculated from the stress-strain curves obtained.

Bending behaviour, resilience and deformation recovery

The bending behaviours of the monofilaments were evaluated in the dynamic and

static bending modes as described in the previous article [3, 4, 14]. The experiments were performed at ambient conditions (23 ± 2 °C). The resilience (R) and deformation recovery are calculated using formula (1 and 2). For each sample three replications were performed. In both cases the length of the samples was 17.5 mm, which corresponds with the average free pile length in an artificial turf system.

$$R = (F_{300}/F_1) \cdot 100, \text{ in } \% \quad (1)$$

where: R is the resilience, in %, F₁ is the maximum force encountered during the first cycle, in cN, F₃₀₀ is the maximum force encountered during the last cycle, the 300th cycle, in cN.

$$\text{Deformation recovery} = (\Theta_{(t_x)} / 90) \cdot 100, \text{ in } \% \quad (2)$$

where: 90° is the maximum angle, which corresponds to the perpendicular position of the filament at the beginning (t₀), Θ_(t_x) is the value of the angle measured after five minutes relaxation time (t_x).

The maximum and minimum angles of the yarn were measured for each sample and a mean value was calculated.

Structural characterisation

Dynamic scanning calorimetry (DSC)

Dynamic scanning calorimetry (DSC) was performed on a DSC Q 2000 (TA Instruments), with a standard heating rate of 10 °C/min in a nitrogen environment. Calibration of the temperature and melting enthalpy was performed with an indium and tin sample. An enthalpy of 290 J/g for perfect crystalline polyethylene [7] was used to calculate the percentage of crystallinity (CRY_{DSC}) using the following *Equation 3*:

$$\% \text{CRY}_{\text{DSC}} = (100 \times \Delta H_{\text{exp}}) / \Delta H \quad (3)$$

where: ΔH_{exp} is the experimentally determined heat of fusion, ΔH° is the heat of fusion of perfect crystalline polyethylene (290J/g).

Raman measurements

Raman measurements were performed on a FT-Perkin Elmer instrument. The measurement range was from 300 to 3500 cm⁻¹. Three repetitions were made for each sample, consisting of 32 scans, and a laser power of 800 mW was used. The raw Raman spectra were smoothed and the baseline corrected. The total integral intensity of the CH₂ twisting region (1350 - 1250 cm⁻¹) is not dependent on the degree of crystallinity and is used as

Table 1. Characteristics of the monofilaments produced with the two extruder lines (Haake-Polydrive and OerlikonBarmag, respectively), with two LLDPEs (DOWLEX 2035G and DOWLEX 2606G); * CDR is the stretching ratio of the product in a solid state (λ).

HaakePolydrive DOWLEX 2035G						OerlikonBarmag DOWLEX 2606G		
CDR	Linear density, tex	cross section, mm ²	CDR	Linear density, tex	cross section, mm ²	CDR	Linear density, tex	cross section, mm ²
7.2	85	0.09	7.2	181	0.20	7.2	195	0.21
6.2	86	0.09	6.1	187	0.21	6.2	196	0.21
5.7	85	0.09	5.3	195	0.21	5.5	199	0.22
4.5	84	0.09	4.8	170	0.19	---	---	---
3.7	86	0.09	3.8	188	0.21	3.3	207	0.22

an internal standard [15]. The mass fraction of the crystalline phase (C_R) contained in the samples investigated was calculated using the formulas (4 - 6) proposed by Strobel [15 - 18].

$$C_R = I_{1417}/I_{TW}; \quad (4)$$

where: I_{1417} is the intensity at 1417 cm^{-1} corresponding to the crystalline structure, I_{TW} is the integral intensity of the whole twisting vibration region (1250 – 1350 cm^{-1}) and was used as an internal standard.

The percentage of Tran's structure calculated from Raman:

$$\% \text{ Trans} = I_{1295}/I_{TW} \times 100 \quad (5)$$

where: I_{1295} is the intensity at 1295 cm^{-1} corresponding to Tran's structure, The percentage of Gauche structure calculated by Raman was as follows:

$$\% \text{ Gauche} = I_{1305}/I_{TW} \times 100 \quad (6)$$

I_{1305} is the intensity at a 1305 cm^{-1} peak corresponding to the Gauche structure.

As was mentioned in the previous article [4], the difference between the non-crystalline fractions calculated from DSC and the amorphous phase calculated by X-ray yields the percentage of the intermediate phase present in the different samples. The difference between the gauche content from Raman and the fraction of the amorphous phase by X-ray corresponds to the amount of gauche molecules present in the 3rd phase.

X-ray measurements

Measurements were performed on an X-ray diffractometer from Thermo Fisher Scientific by the COMOC Research Group (University of Ghent). The measurements were used to characterise the crystalline microscopic structure of the polymer. The radiation source Cu K_1 was operated at 45 kV, 40 mA. The scanning angle ranged from 5 to 50° (2 theta), with a wave length of 54 Å, 0.02° step-size. The percentage of amorphous, orthorhombic crystalline phase and monoclinic phase were calculated afterwards using the Gaussian fit procedure.

Results and discussions

Degree of crystallinity determined by means of DSC

From the DSC measurements, it was observed that the range of melting temperatures and the final melting temperature

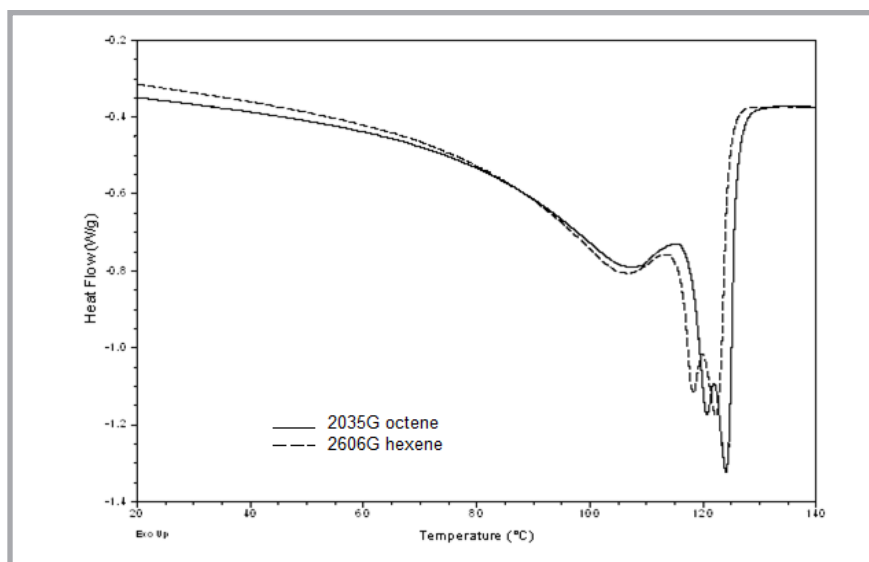


Figure 1. DSC curves for LLDPE-s products, 2035G with octene and 2606G hexene as monomers.

were nearly constant for both LLDPEs, irrespective of the monomers and drawing ratios. The DSC melting endotherms are characterised by a broad melting range of temperatures between 20 °C and 140 °C (see **Figure 1**).

Such broad melting ranges of temperatures are characteristic of LLDPE materials and are the result of the presence of a broad distribution of crystal sizes. This is further attributed to the highly heterogeneous structure that results from non-random incorporation of the monomers during the polymerisation with a Ziegler-Natta catalyst.

The three series of monofilaments show no difference in the amount of DCS crystallinity despite the fact that they have different thicknesses and the LLDPEs are composed of different monomers. This confirms that the rate of crystallisation is controlled by the production parameters within the limits imposed by its molecular character [6]. The percentage of crystallinity was increased by a small fraction

by increasing the stretching ratio(s) for all of the samples produced.

The DSC curves show that for both cases the highest melting peak temperature was around 123 °C, which was the same for all LLDPE monofilaments. However, the melting enthalpies show a slight difference in values affected by cold drawing. **Table 2** summarises results for the crystallinity fraction (crystallinity_{DSC}) for the three series of monofilaments.

Tensile properties of the monofilaments

The tensile behaviour of LLDPE monofilaments with different stretch ratios were studied at room temperature and engineering stress-strain curves of the different LLDPE monofilaments were recorded during uniaxial tensile deformation. For each sample, the elastic modulus and maximum tensile force were calculated from the stress-strain curves, the results of which are summarised in **Table 3** (see page 26).

As can be seen from **Table 3** and **Figures 2 & 3** (see page 26), the elastic mod-

Table 2. Thermal properties of all series of samples produced with two different LLDPEs (DOWLEX 2035 G and DOWLEX 2606 G) at different drawing ratios (CDR).

HaakePolydrive				OerlikonBarmag	
DOWLEX 2035 G				DOWLEX 2606 G	
CDR	Crystallinity, %	CDR	Crystallinity, %	CDR	Crystallinity, %
7.2	51	7.2	51	7.2	53
6.2	50	6.1	52	---	---
5.7	47	5.3	50	5.7	51
4.5	47	4.8	50	4.5	50
3.7	46	3.8	45	3.3	47
pellet	45	T _m = 124 °C		pellet	45. T _m = 122 °C

Table 3. Elastic modulus, maximum tensile force and tensile stress at a maximum load of the monofilaments produced from Dowlex2035G and 2606G of LLDPE.

DOWLEX 2035G	0.09 mm ²	CDR	E-Modulus, MPa	Maximum tensile force, N	Tensile stress at maximum load, MPa
		7.2	270 ± 3	100 ± 9	219 ± 21
		6.2	203 ± 8	75 ± 5	169 ± 5
		5.7	165 ± 9	57 ± 4	129 ± 6
		4.5	125 ± 5	45 ± 5	114 ± 10
		3.7	103 ± 3	45 ± 3	101 ± 8
	0.2 mm ²	7.2	176 ± 11	208 ± 13	109 ± 9
		6.1	165 ± 6	132 ± 9	128 ± 9
		4.8	115 ± 3	71 ± 3	75 ± 4
		3.8	79 ± 5	59 ± 3	58 ± 3.2
DOWLEX 2035G		7.2	216 ± 3	346 ± 21	203 ± 5
		6.2	177 ± 5	245 ± 4	145 ± 4
		5.5	159 ± 4	197 ± 13	134 ± 3
		3.3	63 ± 4	85 ± 4	58 ± 2

ulus increases when the stretching ratio is increased for all the series of samples produced.

As presented in **Figures 2 & 3**, the elastic modulus (E) shows a linear increase with the rubbery deformation ($\lambda^2 - 1/\lambda$), recalculated from the stretching ratio (λ), within the limits of experimental error. The two series presented in **Figure 2** show a difference in values but the relation with the stretching ratio is similar. The series of monofilaments of 0.09 mm² thickness shift toward higher values of elastic modulus compared with the series of monofilaments of 0.2 mm² thickness. Comparing the values of elastic modulus for non-stretched samples, it can be observed that both series show different values. The first series, with a 0.09 mm² thickness, shows a value of 50 MPa and the second series, with a 0.2 mm² thickness, - a value of 32 MPa.

The two series with the same thickness (0.2 mm²) but produced from LLDPEs

with different monomers are presented in **Figure 3**. Different from **Figure 2**, these two series do not show a difference in values of E-modulus, as can be observed in **Figure 3**. This is an indication of the importance of heat transfer and cooling conditions during the cooling of the extruded monofilaments in the water bath.

From the DSC measurements the degree of crystallinity for the three series of samples produced (different thicknesses and monomers) does not show significant changes (**Table 2**).

Considering the processing conditions, the orientation of the product, theoretically, has a strong effect on the properties of the crystalline polymers. The mechanical properties of semi-crystalline polymers depend on non-crystalline components and the orientation of tie molecules.

The content of tie molecules in the product can be calculated from the values of their elastic modulus measured [11].

The elastic modulus of tie molecules containing 100% gauche bonds equals 2600 MPa. This content of tie molecules for monofilaments with a 0.09 mm² thickness is 1.9% and 1.3% for those with a cross section of 0.2 mm². For the cold drawing, tie molecules were stretched and became tauter and the gauche bonds were transformed into trans bonds, as was observed in the previous article [3].

The processing conditions under which the starting products of the two series of monofilaments were produced are comparable, including the cooling conditions as well. The content of tie molecules are the same (1.3%), proving the influence of the cooling phase on the structure of the polymers [3].

The elastic modulus is in good correlation with the stretching ratio for both series of monofilaments. The elastic modulus (E) increases linearly with (λ^2-1/λ) instead of λ , which means that other structure variations still accompany the stretching of flexible units between the entanglements.

The extra structure variation taking place during the cold drawing is the transformation of gauche bonds, present in the interphase, into trans bonds. This is the origin of the stronger increase in the elastic modulus and is related to the transition of the gauche bonds into trans bonds in the interphase or 3rd phase of the polyethylene.

The influence of the interphase and its structure variations can be linked to the semi empirical models of taut tie molecules. According to the model of taut

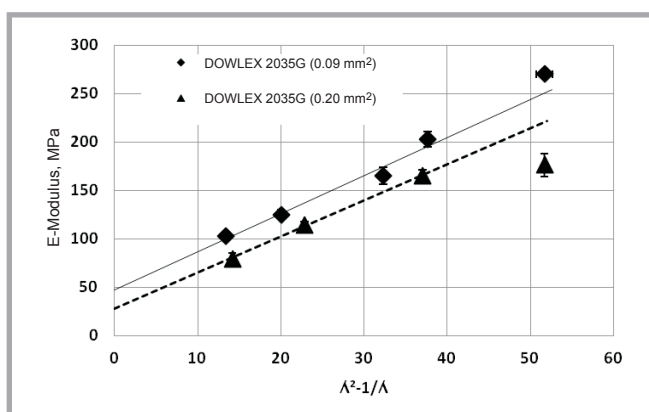


Figure 2. Relation of elastic modulus (E) and recalculated stretching ratio (λ^2-1/λ) for samples with different thicknesses produced with the same production parameters and from the same LLDPE DOW 2035G.

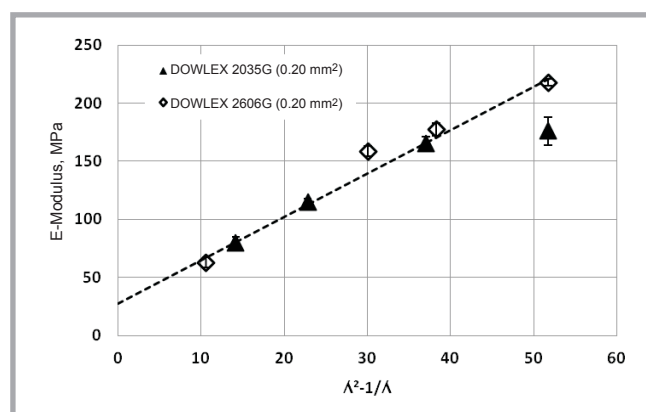


Figure 3. Relation of elastic modulus (E) and recalculated stretching ratio (λ^2-1/λ) for samples with the same thickness (0.2mm²), produced with the same production parameters but from different LLDPE-s (DOW 2606G and DOW 2035G).

tie molecules, the fibre structure of the drawn polyethylene monofilaments is constituted from microfibrils, in which crystalline and amorphous layers are periodically arranged. Some taut tie molecules exist between and others inside the microfibrils, which makes the monofilament have good mechanical quality.

The use of true stress-strain measurements has promoted the development of semi empirical models for large deformations of thermoplastics. Most of these semi empirical models can be represented by equations derived from the theories of rubber elasticity. This is based on the entropic force associated with the deformation of the macromolecular network, which may be estimated according to the theories of rubber elasticity.

X-Ray and Raman analysis of the starting products before cold drawing

The Raman spectra measured were decomposed into individual bands using Gauss functions in the region between 1250 and 1500 cm^{-1} . The total integral intensity I_{TW} of the CH_2 -twisting region (1250-1303 cm^{-1}) is not dependent on the degree of crystallinity and is used as an internal standard [15]. The spectrum in this twisting region can be deconvoluted into a narrow band centred at 1295 cm^{-1} and a broader component with the maximum intensity at 1303 cm^{-1} . The mass fraction of the crystalline phase (C_R) is calculated using the integral intensity of the band located at 1416 cm^{-1} [16]. In another approach the integral intensity of the band located at 1295 cm^{-1} is used to calculate the all-trans molecules [17, 18].

From a previous article [4] the gauche and trans-conformations are calculated using the formulas (5) and (6).

The results calculated for the different LLDPE monofilaments are summarised in **Table 4**. The X-ray spectra recorded were used to calculate the amount of amorphous phase in the different LLDPE monofilaments after the Gauss curve fitting of diffraction. The peak band of the amorphous phase at 19.5° , which is typical for polyethylene polymers, was used to calculate the amount of amorphous phase. Both crystalline peaks and amorphous halos were represented by Gauss profiles. These results showed that the monoclinic phase was present in the starting material before the cold drawing. However, the amount of monoclinic

Table 4. X-Ray and Raman analysis of the morphology structure of monofilaments before cold stretching (CDR).

Product samples	X-Ray			Raman		
	Orthorhombic, %	Monoclinic, %	Amorphous, %	T, %	G, %	Orthorhombic, %
2035G (0.09 mm ²)	52	11	37	45	55	41
2035G (0.2 mm ²)	45	10	45	56	44	43
2606G (0.2 mm ²)	48	10	42	56	44	43

material, determined by X-ray measurements, is rather small. But the presence of this monoclinic structure is an indication of a partially ordered component of the polymer structure, with a lower degree of order than the true crystalline structure. The results of the X-ray and Raman measurements are summarised in **Table 4**. For both cases for X-ray and Raman spectra the 100% Gauss curve fitting was used as explained in previous articles [3, 4].

The degrees of crystallinity of the starting products before the cold drawing, measured by X-ray as orthorhombic crystallinity and by DSC, are comparable and practically equivalent. The degree of orthorhombic crystallinity measured and analysed by Raman spectroscopy are lower than the DSC crystallinity, and these values are practically the same for the three series of monofilaments. In general, it should be mentioned in this context that different methods of the determination of the crystallinity do not necessarily yield the same crystallinity value for exactly the same sample. These differences can be related to the amount of rigid fraction of the polyethylenes composed of the real crystalline phase and that of the amorphous phase, also described as the interphase, 3rd phase or monoclinic phase in X-ray measurements. The most important differences between the three series of monofilaments are in the contents of the Gauche and Trans bonds of the starting products with different cross sections.

Bending behaviour

The maximum bending force of the first cycle (F_1) and of the last one (F_{300}) is plotted vs. the recalculated drawing ratio ($\lambda^2 - 1/\lambda$), presented in **Figures 4, 5, and 6** (see page 26) for all the series produced.

From all the Figures presented above, the bending force of the first cycle (F_1) significant increases with an increase in the stretching ratio for all of the series. The bending force F_1 plotted vs ($\lambda^2 - 1/\lambda$) gives a straight line, which is the same as in the

case of the elastic modulus. In contrast to the maximum bending force of the first cycle (F_1), that of the last cycle (F_{300}) is characterised by nearly constant values irrespective of the stretching ratio(s) and final orientation in the monofilaments.

The increase in F_1 in relation to the drawing ratio, as with the elasticity, could be explained as a result of an increase in the molecular orientation, as the DSC crystallinity is nearly constant. This is also proved with the ratio of (I_{1130}/I_{1060}) from the Raman spectrum by showing a good correlation with the drawing ratio. As a result of increasing the orientation of taut tie molecules between lamellas and connecting them, an increase in the mechanical properties under bending was also measured and related to the mechanical properties under tensile deformation. The higher the concentration of taut tie chains and their orientation in the drawing direction, the greater the connectivity between neighbouring lamellas and the greater the load that can be carried will be.

The deformation of the randomly oriented spherulitic structure in thermoplastics, such as in PE, results in a change from the stacked lamellae (ca. 20 nm thick) to a highly oriented microfibrillar structure (micro fibrils 10 nm wide and very long) with molecular chains oriented along the drawing direction [19]. The molecules, links between the adjacent crystal plates in the spherulites, also appear to orient and yet still connect the stacked plates in the final fibril structure.

Polyethylene crystallites deform by a combination of three mechanisms: fibrillar slip, lamellar slip, and chain slip. These mechanisms are based on a morphological model that assumes a high degree of adjacent re-entry of chains at the lamellar surfaces. Lamellar slip is the process by which lamellae slide over the surface of one another [20].

During these slips, the taut tie chains spanning wide inter-lamellar regions are

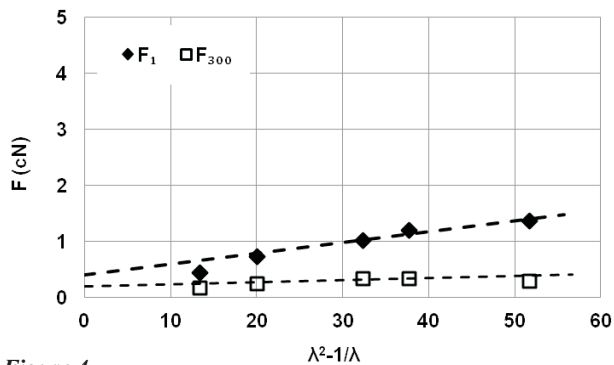


Figure 4.

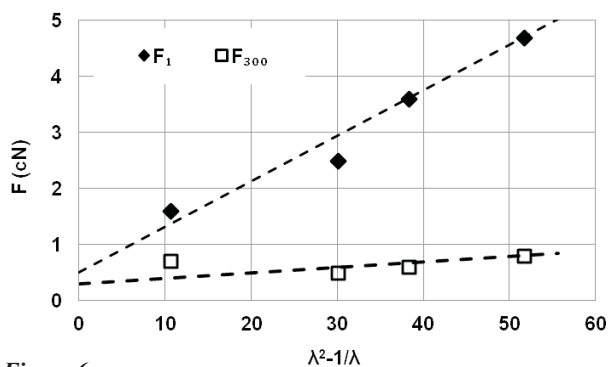


Figure 6.

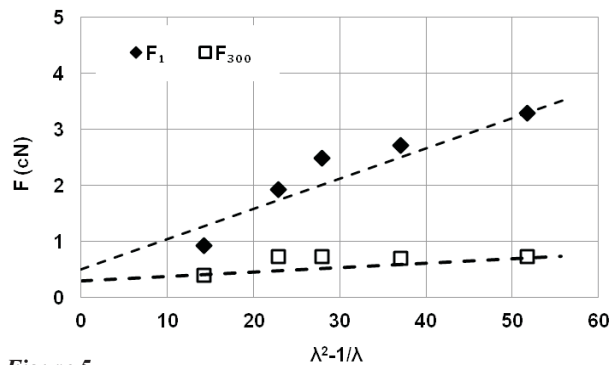


Figure 5.

Figure 4. Variation in bending forces of the first cycle (F_1) and last cycle 300 (F_{300}) vs. the recalculated drawing ratio ($\lambda^2 - 1/\lambda$) for the monofilaments of 0.09 mm^2 thickness produced by Dowles 2035G.

Figure 5. Variation in the bending forces of the first cycle (F_1) and last cycle 300 (F_{300}) vs. the recalculated drawing ratio ($\lambda^2 - 1/\lambda$) for monofilaments of 0.2 mm^2 thickness produced by Dowlex 2035G LLDPE.

Figure 6. Variation in bending forces of the first cycle (F_1) and last cycle 300 (F_{300}) vs. the recalculated drawing ratio ($\lambda^2 - 1/\lambda$) for monofilaments of 0.2 mm^2 thickness produced with LLDPE 2606G.

less likely to be taut than those spanning narrow regions. As a result of the bending, some of the taut tie molecules might lose connection with their original lamellae as a result of a cyclic bending (in our case the maximum is 300 cycles of bending). The taut tie molecules (TTM) might lose some of their connections by creating new ones and so changing the length of taut tie molecules. The bending force after a certain number of cycles decreases significantly, after which the changes are very small, considered almost constant, irrespective of the number of cycles and stretching ratio.

The non-dependence of F_{300} on the stretching ratio is a result of decreased taut tie connections between microfibrils. Important for the bending force are the taut tie molecules, which create links between lamella from different microfibrils, marking the difference with tensile deformations, dominated by taut tie molecules between lamella from the same micro-fibril. The values of bending force F_{300} are practically constant, which means that the structure of the taut tie molecules, responsible for the connection between the microfibrils, has changed. This change is the result of the increased length of these taut tie molecules, proving that after a certain amount of bending the taut tie molecules which are folded

between lamellae will lose some connectivity therewith, but not be broken, as the products show the same values of F_1 after a certain time of relaxation.

By comparing samples with different thicknesses but produced from the same polymer (LLDPE 2035G), a significant difference is observed in the values of F_1 measured. Samples with a thickness of 0.2 mm^2 show higher values of F_1 , compared with those with a thickness of 0.09 mm^2 . Theoretically, by considering the deflection formula [21], the bending force of the beam will be eight times higher for a double increase in thickness. However, this could not be precisely the case for our samples due to the complex geometry and composition.

By comparing samples with the same area of cross section but produced from two LLDPEs (LLDPE 2035G with octane as a monomer and LLDPE 2606G with hexane as a monomer) and having almost the same density (0.919 and 0.92 g/cm^3), the values of F_1 are different, but the values of F_{300} are almost the same for the same stretching ratio. This could be explained by the amount of intrafibrillar tie molecules present in the fibrils in the outer layer of the monofilaments resulting from the temperature gradient during cold drawing in a hot air

oven. However, the amount of interfibrillar tie molecules appears to be the same as they show the same force in the last cycle (F_{300}) irrespective of the composition of the two products, for the same degree of crystallinity, which was around 50%.

In Figure 7, the resilience of the three series is presented vs. the recalculated drawing ratio, expressed as $\lambda^2 - 1/\lambda$. In general, they show almost the same relationship. The resilience decreases by increasing the stretching ratio (s).

The resilience of the first series of samples produced from 2035GLLDPE with a 0.09 mm^2 thickness is a decreasing function of the stretching ratio with an almost constant slope.

For the other two series with the same thickness (0.2 mm^2) but produced from different LLDPEs (2035G and 2606G), the resilience is a decreasing function of the stretching ratio up to the value of $\lambda = 5.7$, ($\lambda^2 - 1/\lambda = 32$), after which the values of resilience are almost constant, irrespective of the orientation. Monofilaments produced by 2035GLLDPE show higher values of resilience compared to 2606GLLDPE, different from the elastic modulus (see Figure 3), which is the same for two series. This could be explained by the deformation model, in

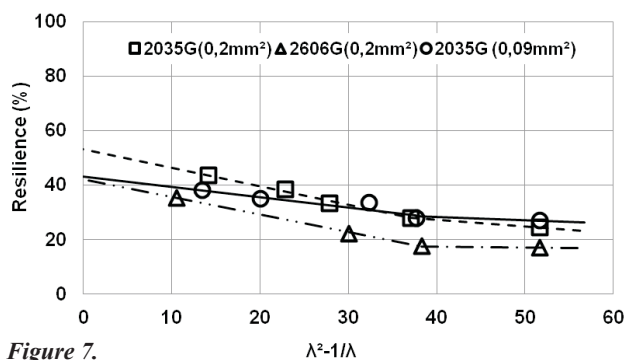


Figure 7.

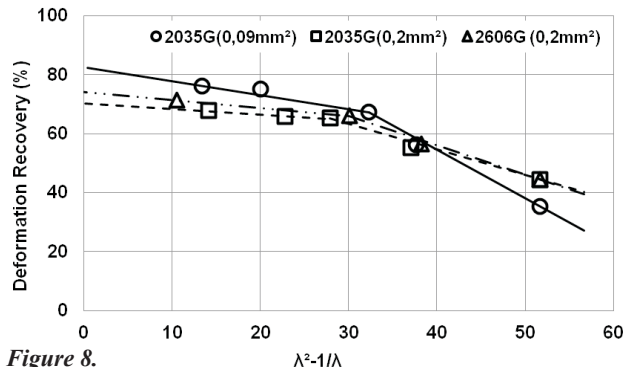


Figure 8.

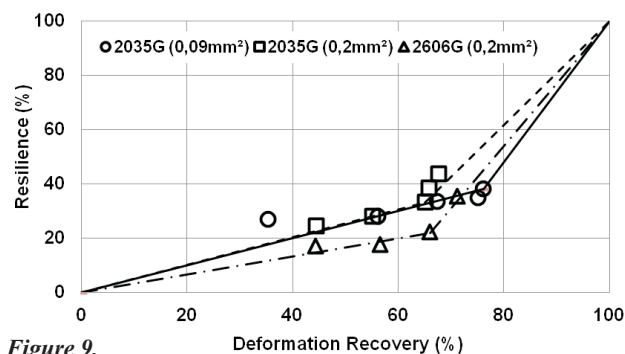


Figure 9.

Figure 7. Resilience of monofilaments for the three series vs the recalculated drawing ratio, represented by the formula $\lambda^2 - 1/\lambda$.

Figure 8. Deformation recovery of monofilaments vs drawing ratio (represented by using formula $\lambda^2 - (1/\lambda)$, for the three series of monofilaments produced.

Figure 9. Relation between resilience and deformation recovery for all of the samples tested.

which the sliding and gradual tilting of macromolecules results in the destruction of lamellae and the formation of crystalline blocks organised into microfibrils. These crystalline blocks consist of folded macromolecules and are connected by intrafibrillar tie molecules within the microfibril. The neighbouring microfibrils are connected by interfibrillar tie molecules. The microfibril is represented as a periodic alternation of the crystalline blocks and amorphous layers.

The mechanical properties in tensile deformation are a function of the intrafibrillar tie molecules connecting the crystal structures inside the microfibrils, created during the production of the monofilaments, which are the same for both polymers; however, the numbers of interfibrillar tie molecules connecting neighbouring microfibrils might be different. This difference could be explained by the different monomers used to produce the LLDPEs.

It is mentioned in [22] that octene is more effective in building tie molecules than hexene or butene. After drawing, the number of interfibrillar tie molecules is much smaller than that of intrafibrillar tie molecules [23].

The same trend as for the resilience is observed for the deformation recovery (Figure 8); however, the values are dif-

ferent, because they are two different techniques, as explained in a previous article [3].

Samples of 0.09 mm² thickness show better behaviour for deformation recovery compared to samples of 0.2 mm² thickness, which could be a result of the thickness or the composition of LLDPEs (different monomers). For both cases, there is a difference in behaviour. Less stretched samples show better behaviour for small thickness but more highly stretched samples show better behaviour for thicker samples. Nevertheless more measurements are needed to support this conclusion.

What seems to be interesting and in line with previous measurements is the change in slope. For all the series the changes are all located at the same point of stretching $\lambda = 5.5$ or $(\lambda^2 - 1/\lambda) = 32$.

Correlation between the two bending methods

The resilience and deformation recovery have been calculated for all the samples using the two test methods: dynamic bending and static bending. As can be concluded from Figure 9, there is a correlation between the two methods, which proves that both methods are necessary in order to obtain a good indication of the bending behaviour of monofilaments based on polyethylene.

For the monofilaments produced from LLDPE DOW 2606G, the relationship between the resilience and deformation recovery gives the result that the resilience is only 33.3% of the deformation recovery, whereas measurements of the resilience versus deformation recovery for the monofilaments based on LLDPE DOW 2305G show that the resilience is 50% of the deformation recovery. These two relationships between the resilience and deformation recovery are measured up to values between 65 and 75% of the deformation recovery, corresponding with Figure 9, which marks the fundamental difference between the two types of LLDPEs. The LLDPE containing octene as a monomer gives a higher value of resilience than that with hexene as a monomer for the same value of deformation recovery, being the result of a higher concentration of interfibrillar tie molecules connecting neighbouring microfibrils.

The relation between resilience and deformation recovery changes for the highest values of deformation recovery. A 100% deformation recovery corresponds to 100% resilience, which is the result of the complex behaviour of the monofilaments under bending and the completely different mechanism of action for the two test methods. For dynamic bending, the maximum force for each cycle is meas-

ured, whereas for static bending the deformation and its recovery are measured.

■ Conclusions

The purpose of this study was to investigate the influence of process parameters on bending behaviour with two different methods: deformation recovery determined by static bending and resilience by dynamic bending. Monofilaments produced from LLDPEs of the same density and different cross-section areas were characterised by totally different bending behaviour in relation to the processing parameters, thickness and monomers.

By increasing the cold draw ratio (λ), the tensile properties increase with the parameter ($\lambda^2 - 1/\lambda$) for a nearly constant amount of the crystalline phase. The results indicate that the mechanical properties of the polyethylenes are influenced not only by the degree of crystallinity but also by connections between the crystallites by way of the intrafibrillar tie molecules; and their concentration depends on the molten state, the cooling of the monofilaments, and the monomer used.

The LLDPE with octene as a monomer has a higher concentration of intrafibrillar tie molecules in comparison to the one with a hexane monomer, which results from the resilience measurements and deformation recovery. By increasing the thickness, the number of microfibrillar tie molecules, calculated from the tensile properties of the monofilaments, is decreased as a result of the slower cooling of the monofilaments extruded.

The best results for the resilience and deformation recovery were obtained for the monofilaments without cold drawing, contrary to the mechanical properties such as the elastic modulus, which were in good correlation with the drawing ratio presented by the recalculated value ($\lambda^2 - 1/\lambda$). The increase in the final cross section of monofilaments based on the same LLDPE's results in a decrease in

the number of intrafibrillar tie molecules, due to a slow cooling. The use of octene instead of hexene as a monomer gives better results for the resilience due to the higher concentration of interfibrillar tie molecules for the same degree of DSC crystallinity of the tie LLDPE's.

During the dynamic bending of the monofilaments, the maximum force of the first cycle of bending (F_1) is in good correlation with the drawing ratio λ , and the elastic modulus measured. The maximum force of the last bending cycle (F_{300}) is practically non-dependent on the drawing ratio and is much lower in comparison with the maximum force of the first cycle (F_1). This is a result of the shearing deformation of the fibril structure and the increasing length of interfibrillar tie molecules due to the loosening of their connection with the other surfaces of the fibrils. Both test methods provide valuable information related to the influence of the processing parameters on the resilience. These two test methods are necessary in order to characterise the influence of the composition of the polyethylenes' and their processing into filaments.

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