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INFLUENCE OF HEAT TREATMENT ON THE BENDING BEHAVIOUR OF LLDPE MONOFILAMENTS

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Abstract:

It is known that artificial turf surfaces based on LLDPE monofilaments have the potential to replace natural turf surfaces used for several sport surfaces. Even though the production parameters have a strong influence on the behaviour of monofilaments and indirectly on the final product, the effect of heat treatment at different stages of the production lines is not studied in detail. Therefore, the influence of heat treatment during the production of monofilaments was investigated. This investigation includes a study of the mechanical properties such as tensile testing and bending behaviour and morphological analyses by employing DSC measurements. The results show that the applied heat treatment has a strong influence on the bending behaviour even though the classical studied morphology structures do not show significant changes. Heat treatment influences quite importantly the characteristics of the non-crystalline part of the monofilaments and results in better long-term properties, such as resilience, deformation recovery and fibrillation resistance.

Keywords:

LLDPE monofilaments, structure, DSC resilience

1. Introduction

The pile layer of artificial turf is one of the layers that directly influence the performance of the surface by affecting the quality of the game. As it is the top layer and as it is proven, it has a strong influence on the ball roll properties like ball roll distance, angel of the ball and the rebound of the ball. The former one depends only from the behaviour of the pile layer differently from the two other ones which are also affected by the infill layer and shock pad [1].

As described in the previous article [2], the pile layer is composed of monofilaments, which after their production are fixed on the backing of the carpet. The most used polymer for the monofilaments is Linear Low Density Polyethylene (LLDPE). These products are characterized by a very low abrasion, higher durability, skin friendly and better approximation to natural grass [3].

It is well known that the production parameters have a strong influence on the behaviour of the product. In the first article [2], the focus was mainly on the influence of the stretching ratio of the monofilaments and on their ability to recover imposed deformations (having good resilience). The ability of the monofilaments to recover seems to be crucial when the sport action (players and the ball move during the football game) is taking place.

To prevent the instability in the dimensions, physical and mechanical properties, heat setting or annealing is applied on the monofilaments. In addition, heat setting or annealing is a process known to eliminate the internal stresses generated during fabrication, i.e. stretching. The process itself will induce ductility, soften the material, relieve internal stress, refine the structure by making it more homogeneous and improve the properties of the stretched samples. The heat treatment fixes the material in a more relaxed state and thus avoids subsequent shrinkage as the internal stresses are relieved.

The mechanical properties are well described in several books and articles [4,5] but less is known about the influence of heat setting/ annealing on the bending behaviour.

The objective of this paper is to investigate the influence of heat setting on the bending behaviour of monofilaments at different production steps. The measurements of bending behaviour can be successfully obtained via dynamic bending mode [6] and static bending mode [2].

This paper describes and discusses the influence of heat treatment at different stages of the production on the bending behaviour of monofilaments. These influences are examined by morphology analysis. The structural/morphology analysis is performed by a combination of measurements resulting from DSC, Raman scattering and X-ray spectra. The transformed morphology supports the correlations between the structural parameters and the final properties of the product.

It is well known that most of the structural changes of oriented polymers occur in the temperature range nearby but below the melting temperature. Therefore, the investigations were performed at a temperature of 120°C. The heat treatment was performed with controlled shrinkage or with fixed ends of the monofilaments. Annealing was performed with fixed ends for 10 seconds at the temperature of 120°C.

2. Materials and methods

2.1. Materials

The polymer material used in this study was obtained from Dow Chemical Company. DOWLEX™ 2035G [7], linear low density polyethylene (LLDPE) with a density of 0.919 g/cm^3 and a melt index of 6 g/10 min.

2.2. The Line of Monofilament production

For a realistic approximation of the monofilaments, the production of monofilaments is performed on a pilot monofilament line from Oerlikon Barmag type 3E/24D installed at the Department of Textiles, Ghent University. A selection was made based on the results of the samples of previous article produced by a small extruder [2] The selected monofilaments are those with cold draw ratio (CDR) 7.2; 6.2; 5.5 and 3.3, with dTex of approximately 1980 [g/10 km]. These samples showed a significant difference on their behaviour based on the obtained results [2].

The extruder has a single screw diameter of 30 mm and a length of 24D. The temperature in the die was 220°C. The die has 24 diamond-shaped openings with a cross section of 70 mm^2 each. Monofilaments after the melt stage (section i in Figure 1) were pulled through a water bath and then passed through the oven, with air circulations at a temperature of 100°C (section I in Figure 1), this way finishing the first stage of the production line, cold drawing (CDR) of monofilaments.

After the first production stage of the monofilaments (section I in Figure 1), the controlled shrinkage is performed at a temperature of 120°C (section II in Figure 1). The shrinkage is controlled by changing the speeds of the rolls before and after the oven, reaching a value of 15%. After shrinkage, samples are annealed at controlled temperature 120°C for 10 seconds (section III in Figure 1).

Another series of samples are produced as presented in Figure 2, where the filaments after passing the second stretching go to heat setting at 120°C with fixed ends (the rolls on both sides have the same speed).

2.3. Test Methods

2.3.1. Mechanical properties and tensile testing

Tensile testing was performed on Instron 3369 tensile equipment at room temperature. The load cell was 500 N and the initial gauge length of 50 mm, with a test speed of 500 mm/min. The stress and strain obtained during the tensile deformations were the engineering stress and engineering strain measured directly between the clamps. Tensile strength and elasticity modulus were calculated from the obtained stress–strain curves.

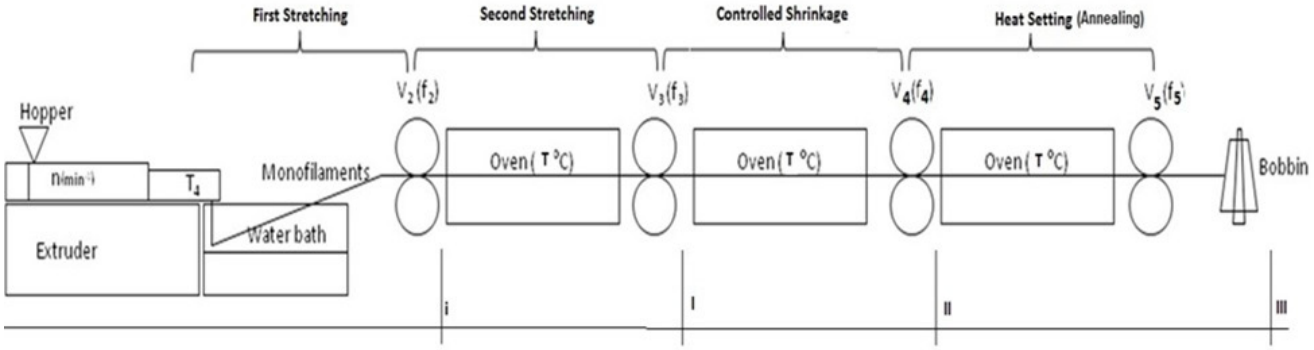


Figure 1. Schematic representation of the production of monofilaments in laboratory conditions (n, V_2, V_3, V_4, V_5 are the speeds of rolls for each step of production. f_2 ,f_3, f_4, f_5, are represent the cross section of monofilaments for each step.

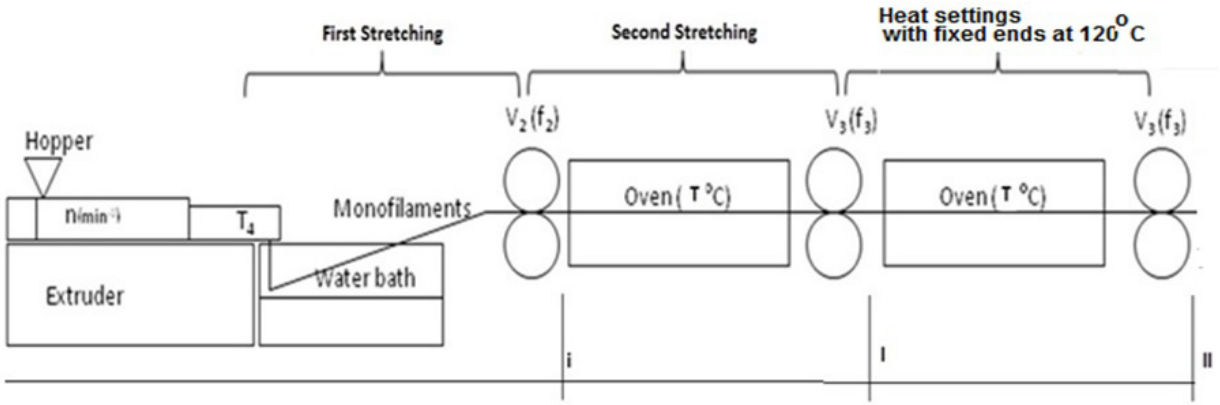


Figure 2. Schematic representation of the production of monofilaments with heat treatments with fixed ends at 120°C.

2.3.2. Bending behaviour, Resilience and Deformation Recovery

Bending behaviours of monofilaments were performed on dynamic [6] and static bending mode [2]. For dynamic bending is used Favimat R [6] (Tex Techno see Figure 3a) and the maximum bending force is monitored for 300 cycles. The preload force was 0.01 cN and the speed of bending 100 mm/min. The resilience of the monofilaments was calculated by using formula (1).

On static bending mode is monitored the deformation recovery of monofilaments after a certain time (40 minutes) of complete bending (see Figure 3b). The experiments are performed at ambient conditions (23±2°C).

Deformation recovery [2] is calculated by using formula (2). In both cases, the length of samples is 17.5 mm, which corresponds with the average free pile length in an artificial turf system.

$$R(\%) = \frac{F_{(300)}}{F_{(1)}} * 100 \quad (1)$$

where R is the resilience (%), F1 is the maximum force encountered during the first cycle (cN) andF300 is the maximum force encountered during the last cycle, the 300th cycle (cN).

$$\text{Deformation recovery } (\%) = \frac{Ø_{(tx)}}{90} * 100 \quad (2)$$

where the deformation recovery is expressed in percentage (%).

90° is the maximum angle, which corresponds with the perpendicular position of the filament at the beginning (t0), Ø (tx) is the measured value of the angle after 5 minutes relaxation time (tx).

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

2.4. 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 temperature and melting enthalpy was performed with an indium and tin sample. An enthalpy of 290 J/g for perfect crystalline polyethylene was used to calculate the percentage of crystallinity using the following equation:

$$\% \text{ CRYDSC} = (100 * \Delta H_{exp})/\Delta H° \quad (3)$$

where ΔH_{exp} is the experimentally determined heat of fusion and $\Delta H°$ is the heat of fusion of the perfect crystalline polyethylene.

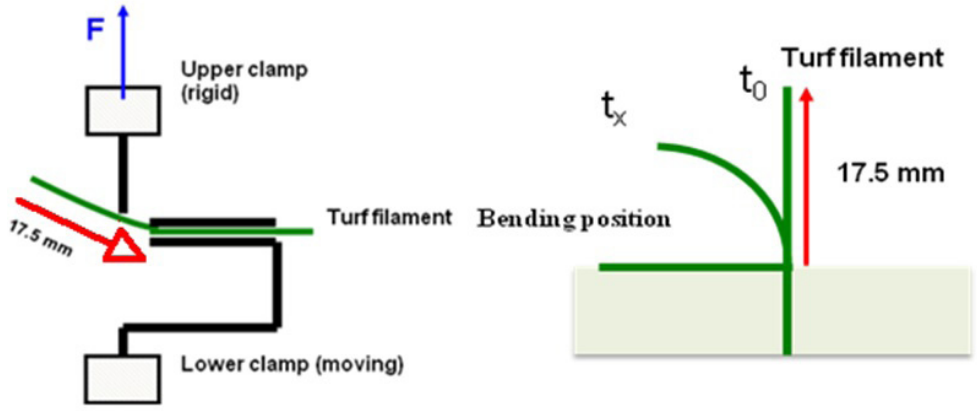
2.5. Shrinkage

The shrinkage experiment is performed according to the internal standard test method of the Department of Textiles of Ghent University [8]. It consists on performing the measurements of length of 1-m monofilaments under the weight of 5 and 505 g before and after treating them on the oven freely for 15 min at 75°C. After that, the percentage of shrinkage is calculated.

3. Results and discussions

3.1. Mechanical properties, E-Modulus and Maximum Load

The mechanical properties of the produced monofilaments are the main characteristics determining the structural changes of monofilaments induced during their processing and characterizing the performance of the final product. The measurements of the elasticity modulus deal with the initial slope between stress and strain, where the stress is proportional with the strain. The obtained results of the mechanical properties; elasticity modulus and bending properties, at different stages of the production line and treated at different conditions, are summarized in Tables 1 and 2, respectively.



a). b)

Figure 3. (a) Schematic representation of dynamic bending test experiment FavimatR; (b) schematic representation of the static bending experiment.

Table 1. Mechanical properties of samples at different stages of production and treated at different temperatures (CDR = imposed cold draw ratio before heatsetting).

CDR	Elasticity Modulus (MPa)			
	Original product	Fix ends at 120°C	15% shrinkage at 120°C	Annealed at 120 °C
7.2	216±3	219±3	122±17	139±7
6.2	177±4	171±3	90±7	120±5
5.5	159±4	122±7	71±6	91±4
3.3	63±4	63±2	45±3	53±2

Table 2. Bending behaviour of samples on dynamic (Resilience) and static bending mode at different stages of production and treated at different temperatures.

CDR	Resilience (%)			
	Original product	Fix ends at 120	15% shrinkage at 120°C	Annealed at 120°C
7.2	20.0±1.5	20.2±1.8	33.7±1.4	37.3±0.4
6.2	21.2±1.7	27.8±4.1	38.0±3.0	37.0±0.5
5.5	24.6±3.9	39.2±2.6	35.5±3.9	38.5±0.2
3.3	39.4±4.7	43.6±3.6	45.5±3.5	41.0±0.1
CDR	**F1 (cN)**			
	Original product	Fix ends at 120	15% shrinkage at 120°C	Annealed at 120 °C
7.2	2.9±1	2.7±0.4	1.8±0.2	2.2±0.6
6.2	2.1±0.4	2.2±0.8	1.6±0.6	1.7±0.5
5.5	1.7±1.3	1.8±0.4	1.5±0.9	1.4±0.3
3.3	0.9±0.4	0.8±0.3	0.9±0.5	1.2±0.3
CDR	**Deformation recovery (%)**			
	Original product	Fix ends at 120	15% shrinkage at 120°C	Annealed at 120 °C
7,2	51±6	79±9	55±5	76±2
6.2	63±6	84±3	68±7	76±3
5.5	66±6	82±5	75±6	76±2
3.3	74±5	85±5	77±6	81±3

The effective cold draw ratios is used in the different graphs, so for the samples with a shrinkage of 15% the effective cold draw ratio equals 85% of the starting cold draw ratio (CDR). With the stretching ratio defined as λ, equal to the length of the tested sample divided by the initial length, the measured mechanical properties are correlated with the first strain invariant I_1; $I_1 = \lambda^2-1/\lambda$. This is the same correlation as used in the theory of the rubber elasticity.

Figure 4 represents the relation of the elastic modulus of the produced samples at different stages in the production line versus the drawing ratio presented by using the formula (λ^2-1/λ). It is noteworthy that the values of the elastic modulus are increasing by increasing the draw ratio of the product. This relation remains the same for all the samples although they have undergone different heat treatment conditions.

When the original samples and those heat treated with fixed ends at 120°C are compared, the values of the elasticity modulus are found to have no significant difference. This could be explained with the fact that the percentage of crystallinty of these products does not show significant differences (Table 3). As the heat treatment is performed with fixed ends the blocks connected by the taut tie molecules (TTM) and hence the microfibrils are prevented from moving in such a direction that the end to end distance of the TTM would be changed [9].

In case of controlled shrinkages, of 15%, the values of the elastic modulus are decreased compared with the original product (Figure 4). The decrease of the elastic modulus after shrinkage is something expected, heat setting with free ends relaxes the TTM and decreases their end-to-end distance. Peterlin [9] described that the elastic values drop quite substantially for

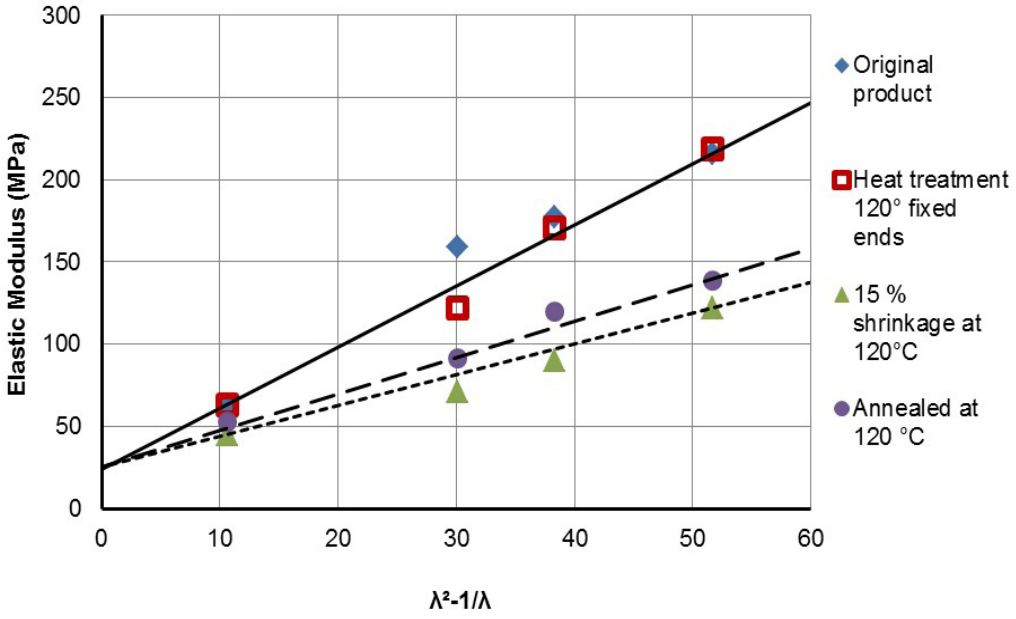


Figure 4. Comparison of the elasticity modulus of the different samples, upper line after cold drawing (stage I), middle line after annealing (stage III), lowest line after cold drawing and shrinkage (stage II).

Table 3. The amount of crystalline and non-crystalline parts calculated from DSC measurements for samples at different stages of the production line.

CDR	Original product		Fixed ends 120°C	
	Crystallinity (%)	Non Crystalline (%)	Crystallinity (%)	Non Crystalline (%)
7.2	51	49	51	49
6.2	48	52	49	51
5.5	47	53	47	53
3.2	43	57	44	56
CDR	**Controlled shrinkage:15% at 120°C**		**120°C for 10 seconds**	
	Crystallinity (%)	Non Crystalline (%)	Crystallinity (%)	Non Crystalline (%)
7.2	49	51	51	49
6.2	48	52	49	51
5.5	44	56	49	51
3.2	42	58	49	51

heat treated samples compared with the values of samples before the heat treatment. From the DSC measurements, there is no explanation as the values are not significantly changing.

Annealing at 120°C for 10 seconds shows improvement compared with the shrunk samples (Figure 4), and the values are approaching to the values of the original samples (Figure 4). This might be as a result of an increase of the enhanced crystallinity and the increased crystalline size of the annealed samples. In addition, the thickness of a crystal increases only with annealing temperatures near (but below) the melting temperature [10,11], whereas at lower annealing temperatures no changes are detected [9].

The temperature in the core of the product depends on the temperature in the oven and the time of staying in, the production speed and the type of the polymer. By knowing the temperature in the oven, the speed and the heat capacity of the product, it is possible to calculate the temperature in the core of the product by using the formula for heat transfer with convection:

$$\frac{T_f - T_0}{T_0 - T_{oven}} = \exp\left(-4 * \frac{h}{\rho C_p} * \frac{1}{dV_z} * y\right)$$

$$V_z = \frac{y}{t}$$

$$\frac{T_f - T_0}{T_0 - T_{oven}} = \exp\left(-4 * \frac{h}{\rho Cp} * \frac{1}{d} * t\right)$$

$$T_0 = 23°C$$

$$\rho C_p d = 12.5\ 10^2 \left[\frac{J}{m^2 K}\right] or \left[\frac{Ws}{m^2 K}\right]$$

$$h = 107^{\circ} \left[\frac{W}{m^2 K}\right]$$

$$\frac{T_f - T_0}{T_0 - T_{oven}} = \exp\left(-4 * \frac{107}{12.5\ 10^2} * t\right)$$

$$\frac{T_f - T_0}{T_0 - T_{oven}} = \exp(-0.34t)$$

for heat treatment at 120°C, the temperature in the core of monofilaments will be 92°C.

Where T_0 is the starting temperature of the monofilaments; T_f is the temperature of the monofilaments after heat transfer; T_{oven} is the temperature of the oven; H is the convection heat transfer coefficient; C_p is the specific heat for product; d is the thickness of the product; and V_z is the speed of the rolls in the production line of fibres.

A heat treatment at 120°C increases the temperature in the core of monofilaments up to 92°C. This temperature is sufficient to influence the molecules or lamellae of the product which melt at this temperature, and will have more possibilities to rearrange the structure of the product.

The crystalline bridges obtained after annealing with fixed ends are mainly formed by fully extended interfibrillar TTM increasing the elastic modulus. There is a difference between heat treatment with free ends (controlled shrinkage) and annealed (with fixed ends). Whereas in the former case, the loss of the high elasticity modulus is permanent, the loss is smaller and only short lived in the latter case. The elastic modulus recovers to a value higher than that obtained from previous heat treatments. Simultaneously, the density increases as a consequence of the slow partial recrystallization at room temperature, which brings the elasticity modulus almost back to its values before annealing. This is reported to reduce the flexibility of microfibrils composing the product, monofilament [9].

A better insight into the mechanical properties can be obtained by the correlation between the elasticity moduli and the degree of crystallinity. A good correlation seems to exist between the elastic moduli and the amount of the crystalline phase as measured by DSC-crystallinity and represented in Figure 5.

As a result of this correlation, the elastic modulus is very low up to a degree of crystallinity of 39 wt% and is increasing linearly afterwards with the degree of crystallinity. The extra degree of crystallinity above 39 wt% is linked by taut-tie molecules resulting in the increasing values of the elastic modulus. The first 39 wt% of crystallinity is dispersed in the non-crystalline phase of this LLDPE, without a link between these crystallites. As a result of this transformation, the elastic modulus is increased in relation to the first strain invariant.

For the cold-drawn samples and the monofilaments annealed with fixed ends, the elasticity modulus is increased to a value of 220 MPa with an increase of 10 wt% of crystallinity. After 15% shrinkage at 120°C, the values of the elasticity moduli are decreased to a value of 120 MPa for 10 wt% of crystallinity as a result of the decrease of the end-to-end distance of the taut tie molecules and a small increase to a value of 140 MPa is measured after the heat treatment at 120°C for 10 seconds. Shrinkage of 15% gives a decrease in the elasticity moduli by 45%. By using the value of elasticity modulus of taut-tie molecules in the all-trans configuration of 177 GPa, the elasticity modulus of 220 MPa is obtained by a concentration of 0.12% of taut-tie molecules connecting the 10 wt% of crystallinity.

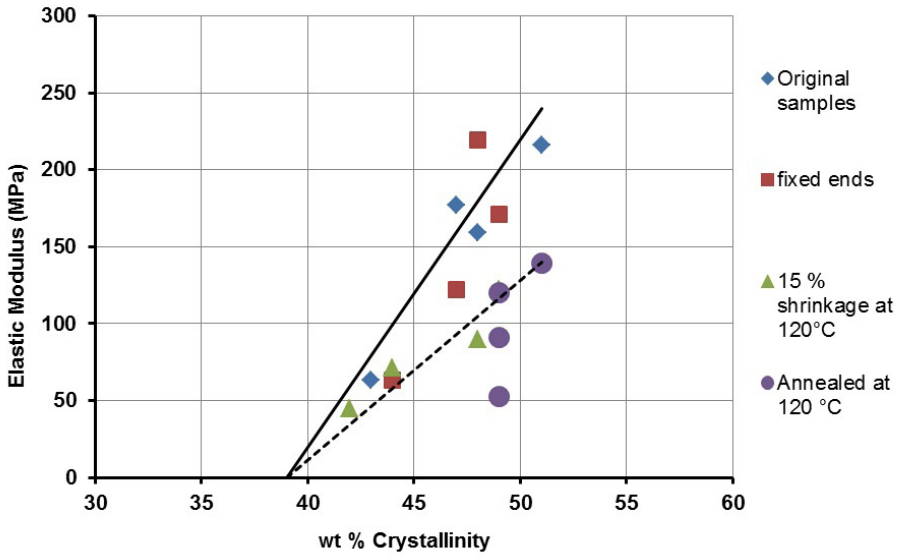


Figure 5. Elasticity modulus as a function of the degree of crystallinity (upper line = stretched monofilaments and the monofilaments annealed with fixed ends, lower line = shrinkage of 15% and annealed at 120°C for 10 s).

3.2. Resilience of monofilaments at different stages of the production line of monofilaments

The results obtained for resilience of the monofilaments at the dynamic bending mode are summarized in Table 2 and represented in Figures 6 and 7 vs. CDR presented by using the formula λ^2-1/λ. From the obtained result, it is obvious that the behaviour of the monofilaments after heat treatment is significantly improved compared with the original samples. This can be explained based on the morphological change which might take place. There are several factors affecting the morphological changes, such as the temperature and the annealing time. At elevated temperatures, the orientation of the crystallographic axes becomes random by influencing the behaviour of the product [10,12-14].

In addition, annealing at 110°C or below causes a morphological transformation accompanied by tilting the molecular chain around the b-axis [11]. Annealing above 110°C, single crystals assume a spherulitic structure with random orientation of the crystallographic axes and the increase of thickness of lamellae, which was explained by the melting of the thinner lamellae followed by recrystallization. According to literature and articles [15-17], the branches and connection between lamellae and molecules will be replaced by new connections.

By analysing step by step the obtained values of the resilience, the results are as follows: The relation between the resilience and the drawing ratio is confirmed as described in the previous article [2]. By increasing the drawing ratio, the resilience is decreasing significantly.

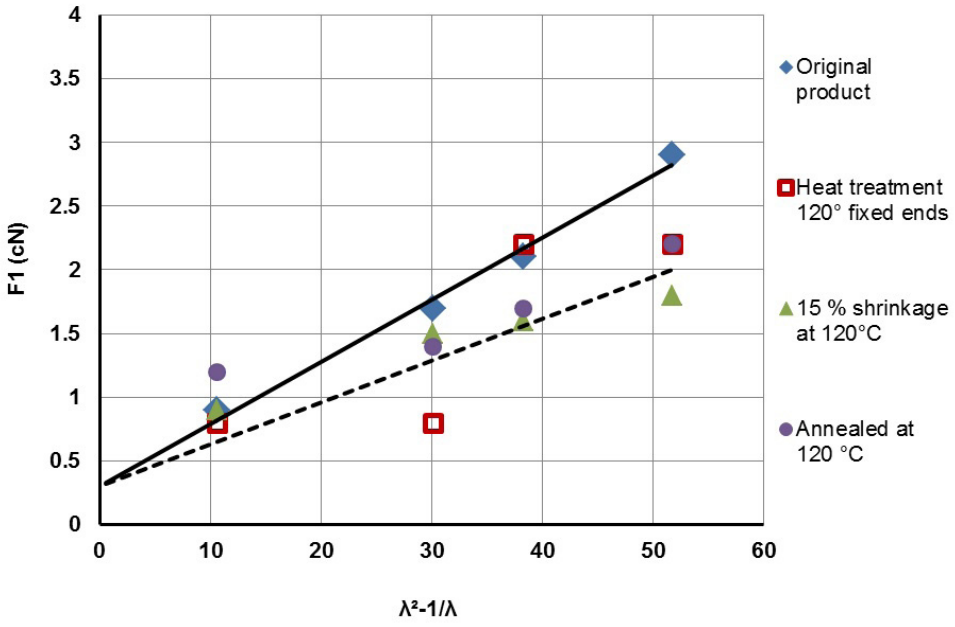


Figure 6. Variation of F1 in function of the drawing ratio for different stages of the production line and at different temperatures for all the samples.

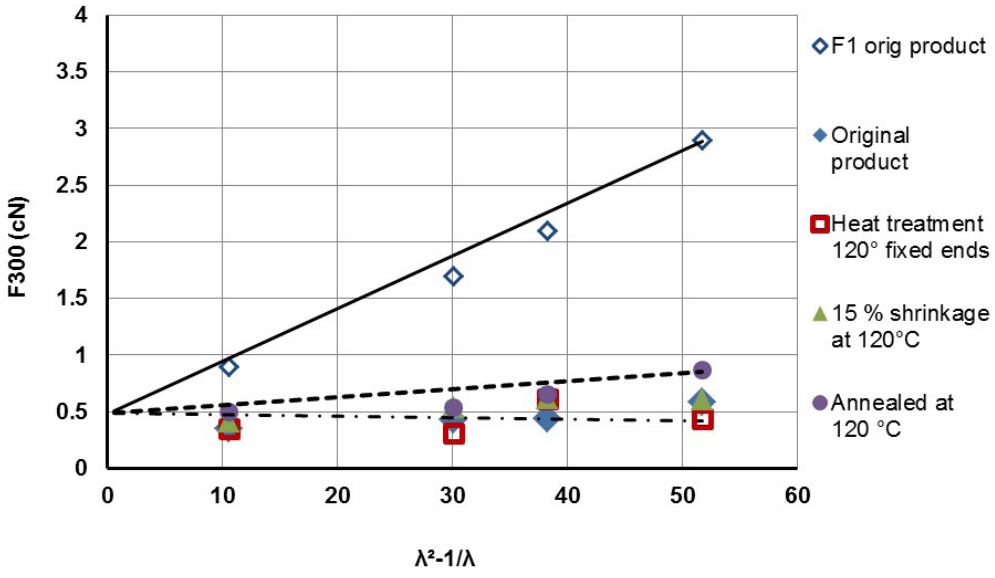


Figure 7. The measured forces F300 after 300 cycles on the dynamic bending test. The full line represents the results of F1.

The measured values of the bending force for the first cycle on the dynamic bending test (F_1) do not show a remarkable difference for the different stages of production (see Figure 6). Besides this, the correlation with the drawing ratio remains the same as for the elastic modulus, if the effective cold draw ratio is used. The decrease in the elastic modulus after shrinkage is compensated by the increase in the thickness, and the final results of F_1 are completely defined by the effective cold draw ratio.

The measured values of the bending force F_{300} after 300 cycles are shown in Figure 7. From this figure, it can be concluded that the obtained result of F_{300} can be split up into two lines: In the first line, the annealed samples at 120°C and the second line original samples, samples with 15% shrinkage at 120°C and, respectively, show the same correlation with the effective cold draw ratio, by showing a better behaviour compared with the first line. The samples in the second line, however, reach the temperature of the core of 92°C or up to 120°C and as a result the bending behaviour is improved.

These differences in behaviour are probably related to the more stable connections between the microfibrils for the monofilaments treated at temperatures above 92°C. This explains also the improvement of mechanical properties.

3.3. Deformation recovery of monofilaments at different production stages

The obtained results for the deformation recovery on static bending mode are summarized in Table 2. As expected, the deformation recovery shows the same relation, as previously stated vs. cold draw ratio. By increasing the cold draw ratio, the deformation recovery is decreasing.

The deformation recovery of samples after a heat treatment at 120°C with controlled shrinkage shows almost the same values as the values of the original product. But for samples with heat treatment at 120°C with fixed ends, the deformation recovery is significantly improved and values are almost the same as for annealed samples.

In Figure 8, the values of the deformation recovery are plotted vs. the drawing ratio at different production stages. The relation of the deformation recovery with the drawing ratio is very similar to the relation of the resilience with the draw ratio (Figure 7) although the values for the deformation recovery are much higher compared with those of resilience. This demonstrates the correlation between these two methods; however, referring to Figure 9, the correlation is not always strong (R^2=0.98÷0.92), as it was presented in the previous article [2].

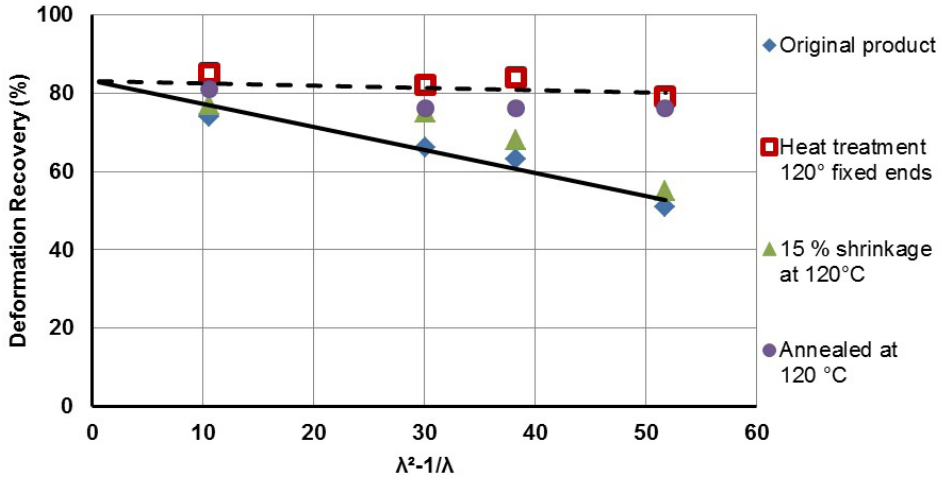


Figure 8. Deformation recovery of monofilaments at the static bending mode of monofilaments at different production stages in function of the drawing ratio presented by (l²-1/l).

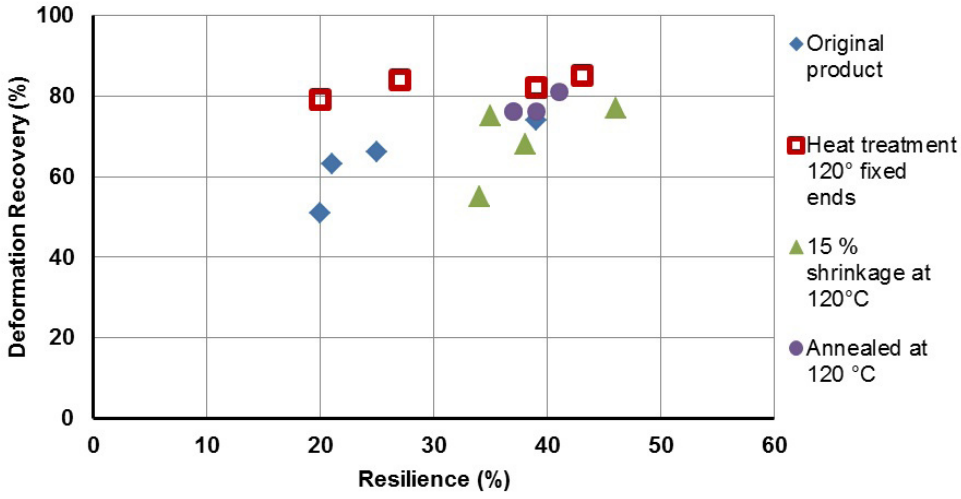


Figure 9. Resilience vs. deformation recovery of the monofilaments at different stages of the production line.

The good results of the commercial fibres are probably a result of the choice of the basic compositions. The industrial monofilaments are produced from a blend containing 85% LLDPE and 15% master-batch. The master batch contains the pigments, additional stabilizers and a polyethylene. This polyethylene is comparable with the LLDPE of the blend but is characterized by a MFI (Melt Flow Index) much higher than the other LLDPE. For example, the MFI of LLDPE is of the order of 4, the MFI of the masterbach is in some case equal to 19 and in other cases it is even higher than 59. This explains the differences in the behaviour of the monofilaments based on the pure and well-characterized LLDPE and the commercial ones based on a more complex composition of two different polyethylenes, different MFI and also differences in degrees of crystallinity.

Another important element shown by these results is the disappearance of the effect of stretching on solid stage (CDR) for samples after heat treatment with fixed ends and after annealing. The samples show almost the same values of deformation recovery, differently from resilience.

3.4. Resilience and deformation recovery as related to the degree of crystallinity

The measured values of the resilience and deformation recovery were analysed as function of the cold draw ratio and heat treatment afterwards. Some important changes of the values were already indicated in relation to the process conditions and more especially in relation to the heat treatment conditions. We have already explained that the elasticity modulus of the monofilaments can be directly related to the extra degree of crystallinity obtained during the cold drawing process. Therefore, it seems quite interesting to analyse the measured values of the resilience and deformation recovery in function of the degree of crystallinity or to the extra degree of crystallinity created during the stretching process. The measured values of the resilience and deformation recovery in function of the degree of crystallinity are represented on Figures 10 and 11.

From Figure 10, the values of the resilience of the monofilaments can be correlated with the degree of crystallinity and in such a

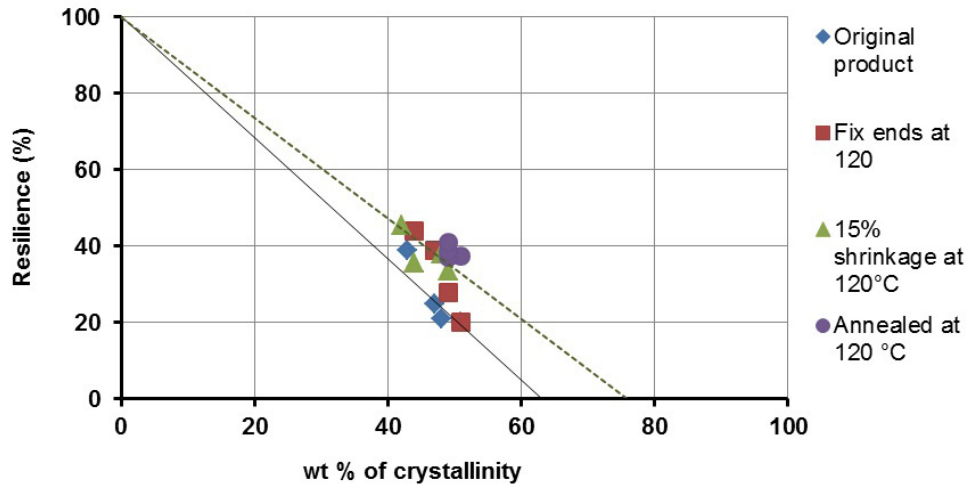


Figure 10. The resilience of the monofilaments as a function of the degree of crystallinity.

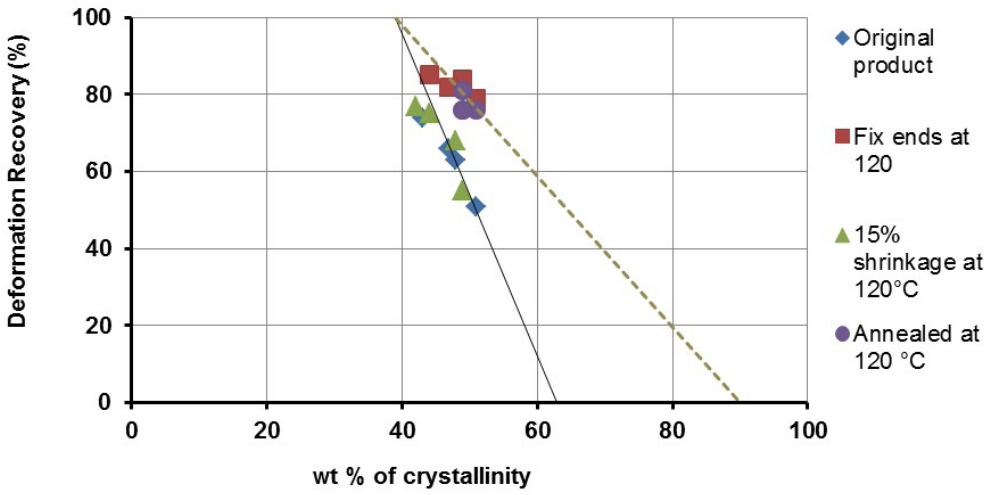


Figure 11. The deformation recovery of the monofilaments as a function of the degree of crystallinity.

way that the values of the resilience are equal to 100% for the complete amorphous phase and decreasing to a value of 50% for the product containing 39wt% of crystallinity and 61wt% of the no crystalline phase. The values of the resilience are decreasing afterwards by increasing the degree of crystallinity by the stretching process and going to zero for the structure containing 63wt% of crystallinity and 37wt% of non-crystalline phase (lower line in Figure 10). The limiting value of the resilience is increased to a value of 18% for the monofilaments with shrinkage of 15% at 120°C and the monofilaments with shrinkage of 15% at 120°C and annealed afterwards at 120°C during 10 seconds (upper line in Figure 10).

From Figure 11, a correlation exists between the deformation recovery of the monofilaments and the degree of crystallinity, but that this relationship is also a function of the processing parameters. The deformation recovery is 100% for the product containing 39wt% of crystallinity and 61wt% of the non-crystalline phase. This product reacts completely elastic for this bending deformation. The values of the deformation recovery are decreasing by increasing the degree of crystallinity, due to the stretching process, and obtaining a value of 50% for the highest cold draw ratio of the monofilaments and the ones with shrinkage of 15% at 120°C. This limiting value of the deformation recovery is increased to a value of 77% for the monofilaments with a draw ratio of 7.2 annealed at 120°C with fixed ends and for the monofilaments with a shrinkage of 15% and annealed at 120°C for 10 seconds. Annealing of the stretched monofilaments at 120° with fixed ends of with a shrinkage of 15% and further annealed at 120°C during 10 seconds are given the best results for the deformation recovery.

As a conclusion and by combining the results of the resilience and the deformation recovery, the best results were obtained for the stretched monofilaments with shrinkage of 15% at 120°C followed by an annealing at 120°C during 10 seconds. Is not important only the heatsettings temperature but also the time of heatsettings.

3.5. Effect of a heat treatment on the dimensional stability of monofilaments and shrinkage

As it was mentioned in the Introduction, another important aspect of the samples is the dimensional stability. This is important not only for aesthetic reasons but also because the loss in the length of the pile layer influences the properties of the ball roll [2]. In Table 4, the measured values of shrinkage are summarized for all the samples.

Original samples and samples with heat treatment with fixed ends do not show a significant difference; in both cases, the values of the shrinkage are relatively high. Better dimensional stability in the product is obtained for monofilaments after 15% shrinkage at 120°C and the monofilaments annealed at 120°C after shrinkage. Considering the shrinkage of the monofilaments after annealing at 120°C with fixed ends, it is obvious that the results of the shrinkage are not the same for the measurements under 505 or 5 g. This is the result of the deformed geometry of the monofilaments after annealing with fixed ends, the monofilaments are twisted around their symmetry axis and not completely straight along the length direction.

3.6. DSC measurements at different production stages

The DSC crystallinity values of samples are summarized in Table 3. As it was expected, the percentage crystalline phase is increased by increasing CDR, however, not enormously. But after performing heat treatment with fixed ends and also in case of controlled shrinkage and annealing at 120°C, the percentage of crystalline structure is almost constant. The possible changes in the morphology of the monofilaments, which could arise from heat treatment or annealing, were qualitatively investigated by the DSC curves. A close inspection of the DSC curves obtained for different annealing conditions, represented in Figure 12, shows that a weak and blurred peak appearing in the vicinity of 40°C for not annealed samples is

Table 4. Shrinkage of the monofilaments at different temperatures and measured on all the samples at different stages and with different CDR.

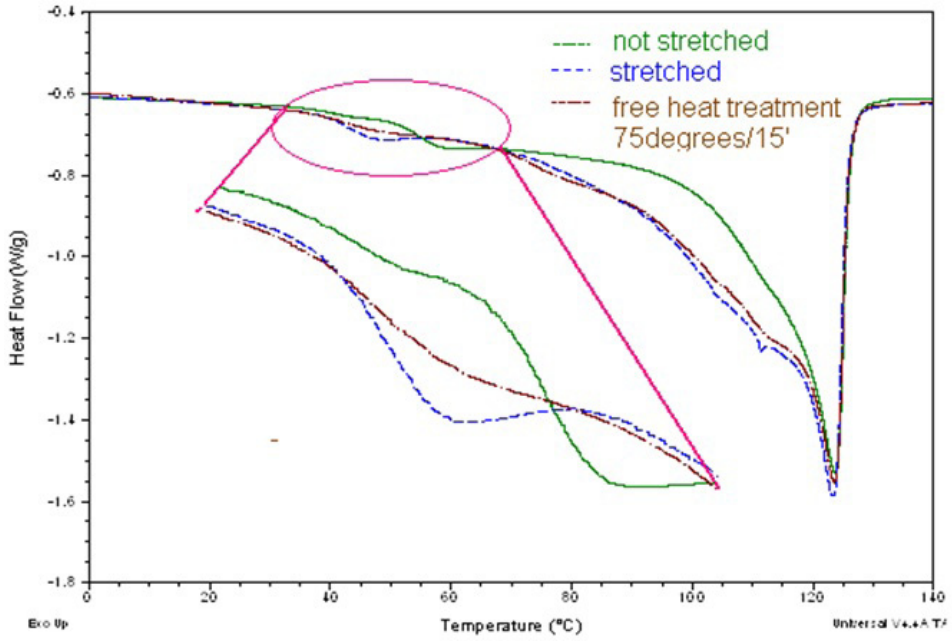
CDR	Original product		Fixed ends at 120°C	
	505 g	5 g	505 g	5 g
7.2	9.5±0.3	8.9±0.2	7.2	2.3±0.3
6.2	8.3±0.4	6.9±0.3	6.2	1.1±0.9
5.5	9.6±0.3	8.3±0.6	5.5	1.4±0.4
3.3	7.6±2.2	5.2±1.1	3.3	2.0±0.8
CDR	**15% Shrinkage at 120°C**		**Annealed at 120 °C**	
	505 g	5 g	505 g	5 g
7.2	2.3±0.3	1.6±0.7	1.6±0.5	1.1±0.9
6.2	1.1±0.9	0.8±0.6	2.0±0.3	0.7±0.6
5.5	1.4±0.4	1.4±0.1	1.6±0.2	0.6±0.3
3.3	2.0±0.8	1.4±0.1	1.0±0.9	0.0±0.2

changing for the annealed ones. This peak, characteristic of the LLDPE product, presumably reflects the melting of very small crystalline entities. Moreover, the shape and intensity of the melting peak centred in the vicinity of 120°C do not show a noticeable dependence on the annealing temperature.

Another difference in the DSC curves between original, heat treated and annealed samples is the change in the shape of the endothermal part. As a result of heat treatment, samples show broader melting features compared with the original samples. In addition, multiple melting peaks are characteristic for LLDPE materials, because of the presence of a broad distribution of crystal sizes and due to a highly heterogeneous structure [18]. Because of heat treatment, a disorientation of molecules is observed for both cases (see Figure 12), although not very visible. More visible is the difference in the endotherms between isotropic samples (not stretched) and heat treatment at 75°C (see Figure 12a). These results are in the same line as reported by Lagaron et al. [19].

In Table 3, the degree of crystallinity of the samples shows no difference compared with the original product, but the mechanical properties of annealed samples are improved compared with heat treatment samples under controlled shrinkage. This is in the same line with the publications [4,5]. It has been noted that annealing bulk polymer is a convenient method for raising its density and tensile modulus. Annealing is known to enhance the degree of crystallinity and molecular orientation of semicrystalline thermoplastic polymers, which in turn directly affect the physical and mechanical properties.

a) LLDPE DOWLEX 2035G.



b) LLDPE DOWLEX 2606G.

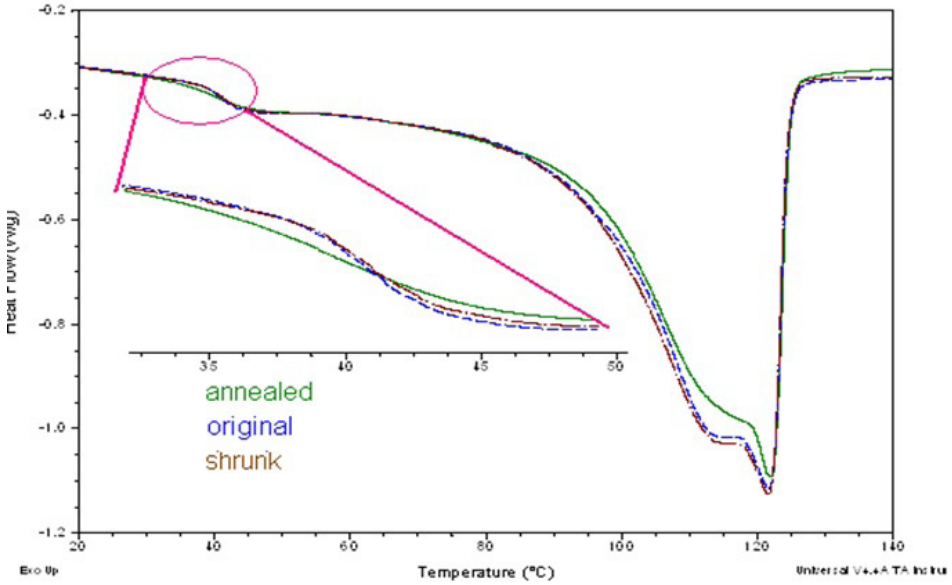


Figure 12. Influence of annealing in the DSC curves, more emphasis on the region at 40°C: (a) heat treatment at 75°C and (b) heat treatment at 120°C.

As it was reported [20], the increase in crystal perfection could reduce the number of TTM molecules which act as stress-transfer unit between the crystalline zones. Thus, a crystallinity threshold may exist and when it is overcome a decrease in toughness appears due to the lack of TTM molecules.

Taking into consideration the relation CDR and DSC crystallinity, for annealed samples, it is obvious that only the orientation of the product contributes to the mechanical properties, as the correlation between CDR and the elastic modulus (see Figure 12(a) and (b)) still remains but the values of DSC crystallinity (see Table 3) are almost constant for all the samples.

The crystal morphology changes occur during annealing at temperatures slightly above the original crystallization temperature of the crystals and far below their melting temperature. Annealing at 120°C, close to the melting temperature, could cause a recrystallization of the product, which might result in increases of the lamellae thickness and degree of crystallinity.

Compan et al. [21] suggested that the morphological changes occurring in films during annealing seem to favour the formation of molecular packing defects, and the changes that annealing may produce in the free volume are not important enough to affect the morphological change in a decisive way. Annealing processes may favour the formation of micro cavities (molecular packing defects) between the crystalline and amorphous face that can accommodate individual site molecules without disturbing the normal dissolution process in the rubbery region of the polymer matrix. According to this interpretation, annealing not only may cause crystallite thickening that hinders but also may provide packing defects between the crystalline and amorphous face [21]. In this case, the packing defect will be most probable as the melting temperature is not changing.

4. Conclusions

By employing tensile testing, it was found that heat treatment or annealing of polymeric materials causes changes in the properties of the materials. However, these changes are not directly detected by DSC measurements. Increasing annealing temperatures does not influence the melt temperatures. The effective degree of crystallinity can be obtained by combining the values of the elasticity modulus and DSC measurements. This correlation, combined with the degree of amorphous phase obtained from X-ray measurements, is the basis for the analysis of the bending properties of the monofilaments and their long-term properties.

The bending behaviour of the monofilaments in the static bending and in the dynamic bending mode is improved by the heat treatment process and more visible for samples with higher cold draw ratios. Samples with low cold draw ratios show less differences for the different processing stages. The result of the heat treatment is not always the same for the static bending behaviour or the dynamic bending test. The static bending test is a measurement of the reversible deformation of the monofilaments contrary to the dynamic test, which is the measurement of the stress response of the monofilaments in a rather small time scale.

Heat treatment (controlled shrinkage) and annealing (with fixed ends after passing the controlled shrinkage) was found to have a remarkable influence on the dimensional stability of the final product and on its properties. The controlled shrinkage stage seems to be very important as after this stage the product is stable along the length direction, without twisting around his symmetry axis.

Annealing and heat treatment carried out under proper conditions modify the complex structure of semicrystalline polymers, which in turn affect directly the physical and mechanical properties of the product and more especially the long-term properties.

By combining all these elements, mechanical properties, bending behaviour and dimensional stability, the optimal process parameters for monofilaments are the minimum cold draw ratio, just above the necking region, a controlled shrinkage at temperatures nearby the melting temperature followed by an annealing at the same temperature during a sufficient time period.

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