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Differential Scanning Calorimetry and Elasticity of Textured, Heat Set and Mechanical Strained Polylactide Multifilaments

Abstract
Industrially textured PLA multifilaments were heat set under different conditions at 110 ºC for 1 min and subjected to one cycle of deformation up to 20%. Thermal transitions of the original textured, heat set and cyclic strained filaments were measured using differential scanning calorimetry from 25 to 250 ºC. Cyclic deformation induces an endo-exo transition at peak temperatures between 55 - 60 ºC that is not observed in the original textured and heat set multifilaments. There is another endo-exo transition with peak temperatures between 67 and 72 ºC in all filaments, the intensity of which varies according to texturing conditions, heat setting and cycle strain. Texturing conditions, heat setting and cyclic strain play a role in thermal transitions, the strain at breaking and elastic properties of the filaments. The crystallinity and magnitude of the endo-exo thermal events detected by DSC are related to the strain at breaking and elasticity of polylactide textured multifilaments.

Key words: *polylactide, filaments, texturing, heat setting, cyclic strain, thermal transitions, mechanical properties, elasticity, differential scanning calorimetry.*

Introduction

The increasing demands on the consumption of renewable resources have led to a growing interest in fibres produced from nature derived products. As regards polyester, polylactide PLA multifilaments seem to be the best option to partially replace conventional PET filaments. Although producers of PLA speak of a developed product, experimental data yielded by industrial trials show some limitations regarding the relaxation phenomenon [1], dimensional stability [2], thermal transitions [3], mechanical characteristics [4] and stress relaxation [5].

Cyclic strain usually occurs during textile manufacturing. It is therefore interesting to evaluate the evolution of the stress, strain and elasticity of the filaments after cyclic deformation because of the high demands placed on the yarns by the weaving machines. A thorough understanding of the inter-relationships between the elasticity and processing factors is essential for elucidating the behaviour of these filaments during textile manufacturing [6]. Dimensional stability is one of the most important aspects to be considered from the point of view of technical applications and garment manufacture, although the positive effect of certain finishing processes on this property may prove to be detrimental to other desirable qualities [7]. The more rapidly and completely a fibre recovers from an imposed strain, the more elastic it is. Depending on the internal structure, elasticity can be improved after the first strain. This induces internal stresses that initiate a macromolecular bedding-in effect, resulting in a more compact and elastic structure. Texturing affects the fine structure of the filaments: 1) the higher the draw ratio, the higher the orientation of macromolecules and the longer the crystals formed during texturing; 2) the higher the temperature, the higher the crystallinity, the higher the size and perfection of the crystals formed and the higher the macromolecular package density in the filament [9]. Consequently, the intensity of texturing increases with an increase in both the pre-texturing draw ratio and temperature. The lower the values, the smaller the texturing effect on the filament.

The aims of this work were the following: 1) to study the effect of texturing conditions and post treatments on the mechanical properties and elasticity of PLA multifilaments; 2) to study the effect of texturing conditions and post treatments on the thermal transitions measured by differential scanning calorimetry DSC; and 3) to relate the mechanical properties and elasticity of the filaments with crystallinity as well as the other thermal events measured by DSC.

Materials and methods

Textured materials

A polylactide 167/68 dtex multifilament yarn produced and false-twist textured by ANTEX under different conditions of pre-texturing draw ratio and temperature, resulting in a variety of samples described in ***Table 1***.

Post treatments

1) Heat setting: The filaments of ***Table 1*** were heat set at 110 ºC for 1 min in an oven with forced air circulation to reproduce industrial heat setting conditions at lab scale. They were placed in a metallic frame to avoid thermal shrinkage during the treatment.
2) Cyclic strain: The heat set filaments were strained up to 20% at 60%/min and then left to recover at the same rate.

Methods

Tensile properties

Specimens with a gauge length of 100 mm were tested after conditioning in a standard atmosphere for 48 h. The specimens were subjected to tensile test-

Table 1. *Texturing conditions (draw ratio and temperature) of PLA 167 dtex/68 multifilament, sample reference, and yarn linear density of textured multifilaments; *Filament C3 was exhausted and therefore was not included in this study.*

Sample	Draw rat, v_1/v_0	Temp, ºC	Lin. density, dtex
A1	1.30	135	224.1
A2		150	221.1
A3		165	218.0
B1	1.35	135	216.3
B2		150	213.9
B3		165	213.6
C1	1.40	135	210.9
C2		150	206.9
C3*		165	205.4

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ing at 60%/min according to the ASTM D2101 standard. Using the Stress/strain curve (***Figure 1*** left), the stress σ_B in cN/tex and strain ε_B in % at breaking were determined.

Elasticity

The elasticity of the filaments was determined according to the ASTM D1774-79 standard with small modifications [7]. Specimens with a gauge length of 100 mm were subjected to cyclic deformation up to 20% at 60%/min according to the evolution shown in ***Figure 1*** (right). The pretension applied was 2.4 mN/tex (ASTM D2256 Standard). The samples were subjected to an initial deformation cycle of up to 20% and then left to retract to the original size, remaining there for 3 minutes. A second deformation cycle was performed under the same conditions and the following parameters in percentage were obtained:

- Immediate Elastic Recovery:
  IER = 100×AB/AD
- Delayed Elastic Recovery:
  DER = 100×BC/AD
- Permanent Deformation:
  PD = 100×CD/AD.

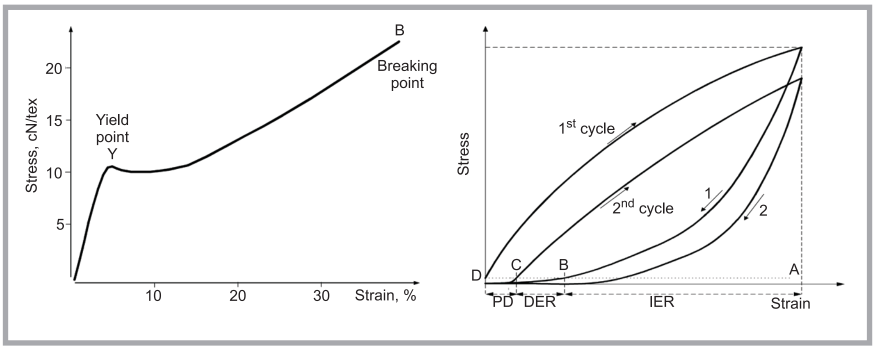

Figure 1. *Stress/strain (extension) curve of the PLA multifilaments, where the yield point and depletion (relaxation) after yield can be observed to determine the breaking parameters according to the ASTM D 2101 Standard (left). A cyclic strain of up to 20% was used to calculate the Immediate Elastic Recovery IER, the Delayed Elastic Recovery DER and the Permanent Deformation PD of the PLA multifilaments according to the ASTM D 1774-79 standard (right).*

Table 2. *Breaking stress in cN·tex^{-1} and strain in % of the original textured samples, heat set at 110 °C and cycle strained up to 20%.*

Sample	Original		Treatment:			
			Heat set at 110 ºC		Heat set and 20% strained	
	σ_B, cN·tex^{-1}	ε_B, %	σ_B, cN·tex^{-1}	ε_B, %	σ_B, cN·tex^{-1}	ε_B,%
A1	22.08	37.49	22.19	40.59	21.42	15.96
A2	23.29	38.00	26.06	39.44	23.10	15.11
A3	23.29	40.57	19.82	35.83	23.14	14.63
B1	23.41	34.54	23.35	38.70	23.63	15.32
B2	25.24	35.73	21.98	37.36	23.79	13.60
B3	24.17	36.22	22.13	36.20	23.39	13.42
C1	21.23	29.61	20.90	35.30	20.16	9.57
C2	23.75	32.77	22.09	35.03	24.10	13.61

Differential scanning calorimetry

Thermal events related to glass transition, relaxation, cold crystallisation and melting were determined by a differential scanning calorimeter - Mettler Toledo DSC-823. Filaments were cut into very short lengths and duplicated samples of approximately 6 mg were sealed in 40 µl aluminium punched pans to guarantee good contact of the sample with the DSC sensor. DSC curves were obtained under the following operating conditions: initial temperature 30 ºC, final temperature 250 ºC, heating rate 10 ºC/min and nitrogen purging gas 35 ml/min. Using the DSC curve (***Figure 2***), the areas below and above the base line enable us to measure the energy involved in the following thermal events:

- *ΔH_D in J/g*: Enthalpy of the endotherm with peak temperature close to 56 ºC.
- *ΔH_C in J/g*: Enthalpy of the exotherm with peak temperature close to 61 ºC. *$\Delta H_{B\ in}$ J/g*: Enthalpy of the endotherm with peak temperature close to 67 ºC.
- *$\Delta H_{A\ in}$ J/g*: Enthalpy of the exotherm with peak temperature close to 71 - 72 ºC.

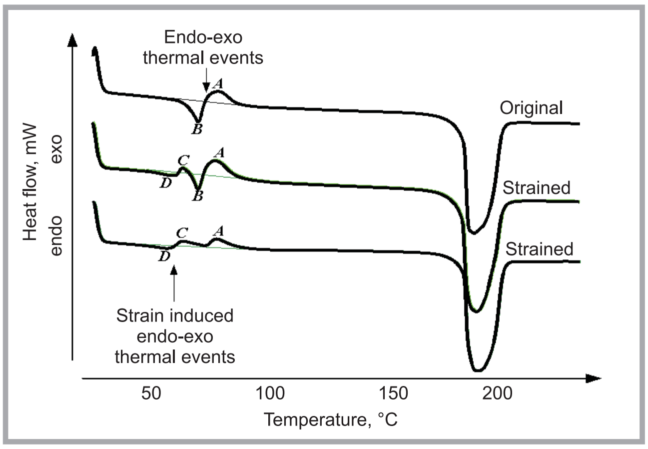

Figure 2. *Differential Scanning Calorimetry DSC plots of an original textured PLA multifilament, a slightly textured filament after cycle strain, and below a highly textured filament after cycle strain. The melting peak, the endo-exo AB event attributable to the amorphous phase and the endo-exo CD event caused by cycle straining of the filaments are shown.*

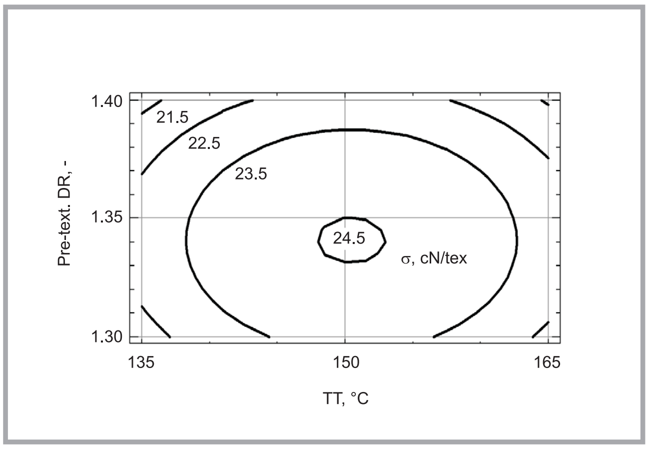

Figure 3. *Mean values of the stress at breaking of the original textured, heat set and cycle strained PLA multifilaments according to the initial texturing conditions; Pre-text DR - pre-texturing draw ratio, TT - texturing temperature in °C, σ - breaking strain in cN/tex.*

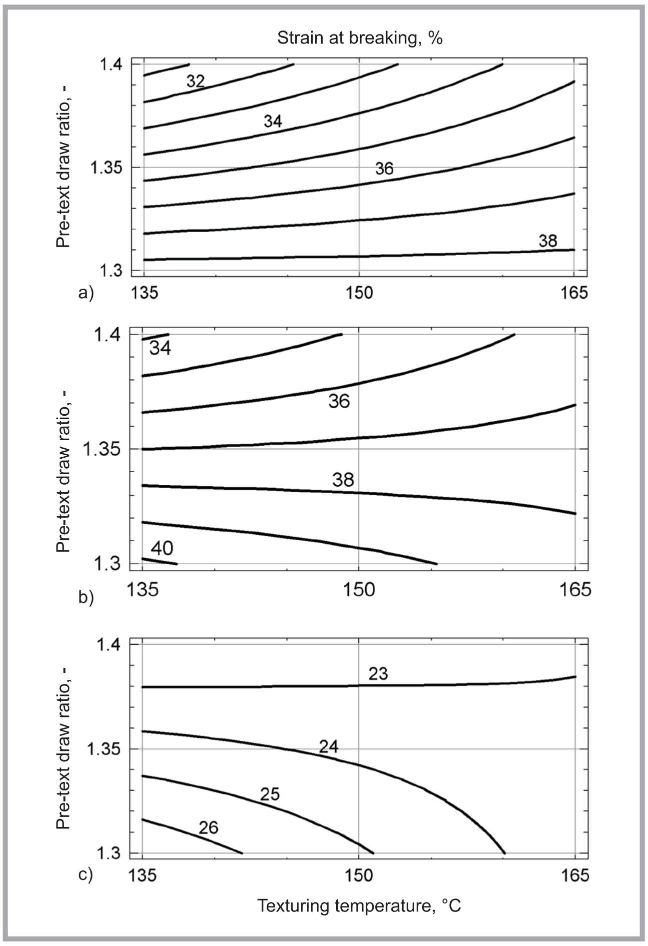

__Figure 4.__ Strain at breaking of the a) original textured PLA multifilaments, b) heat set filaments and c) cycle strained filaments.

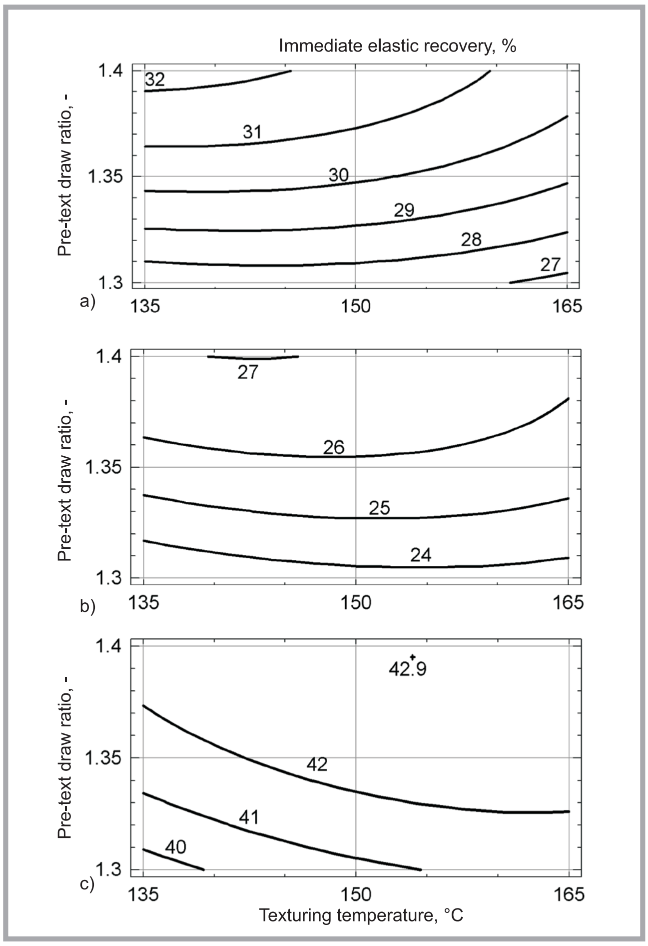

__Figure 5.__ Immediate elastic recovery IER of the original textured, heat set and cycle strained PLA multifilaments according to the texturing variables.

- *ΔH_m in J/g*: Melting enthalpy with onset temperature at approximately 159 ºC.

An estimation of the initial crystallinity X of the filaments in% can be calculated through the relationship $100\times(\Delta H_m + - \Delta H_A)/93.7$ [3]. The thermal energy of the endo-exo A B transition mainly attributable to the amorphous phase with peak temperatures between 67 and 72 ºC can be estimated from the amount $H_{AB} = \Delta H_A + \Delta H_B$. The cyclic strain gives rise to a second endo-exo C D transition with peak temperatures between 56 and 61 ºC, the thermal energy of which can be estimated through the amount $H_{CD} = \Delta H_C + \Delta H_D$.

Results and discussion

Tensile properties

Values of stress and strain at breaking are shown in ***Table 2***. As regards the stress at breaking, insignificant differences were observed between the original textured and post treated ones (heat set before and after being subjected to cyclic strain). As regards the stress and strain at yield, insignificant differences were observed between the original and post treated filaments, being the values of stress at yield between 50 and 55% of the stress at breaking and the strain at yield between 3.54 and 4.72% [4].

Using regression analysis, a second order polynomial function was fitted (10). The optimum value of stress at breaking was yielded by filaments produced at a pre-texturing draw ratio close to 1.35 and texturing temperature around 150 ºC, the central conditions of the experimental plan (***Figure 3***).

The strain at breaking was clearly influenced by the texturing conditions and treatments. The pre-texturing draw ratio that increases the internal alignment of macromolecules clearly decreases the breaking strain (***Figure 4***). The effect of the texturing temperature was rather contradictory owing to its effect on dif-

__Table 3.__ Immediate elastic recovery, delayed elastic recovery and permanent deformation of the original textured, heat set filaments and 20% cycle strained PLA multifilaments.

Sample	Original			Treatment: Heat set at 110 ºC			Treatment: Heat set and 20% strained		
	IER, %	DER, %	PD, %	IER, %	DER, %	PD, %	IER, %	DER, %	PD, %
A1	27.13	33.80	39.07	23.51	27.42	49.07	39.48	48.52	12.01
A2	27.45	33.42	39.14	23.37	27.64	48.99	40.54	47.25	12.22
A3	26.49	31.75	41.76	24.34	27.34	48.32	41.11	46.64	12.26
B1	30.63	35.16	34.21	25.13	27.34	47.54	41.65	46.18	12.17
B2	30.10	33.53	36.37	25.96	27.95	46.10	42.61	45.75	11.64
B3	28.96	32.00	39.04	25.37	27.39	47.24	42.27	45.40	12.33
C1	32.43	35.16	32.41	26.26	27.92	45.82	42.59	46.02	11.38
C2	31.90	33.59	34.51	27.05	27.94	45.01	42.84	45.22	11.93

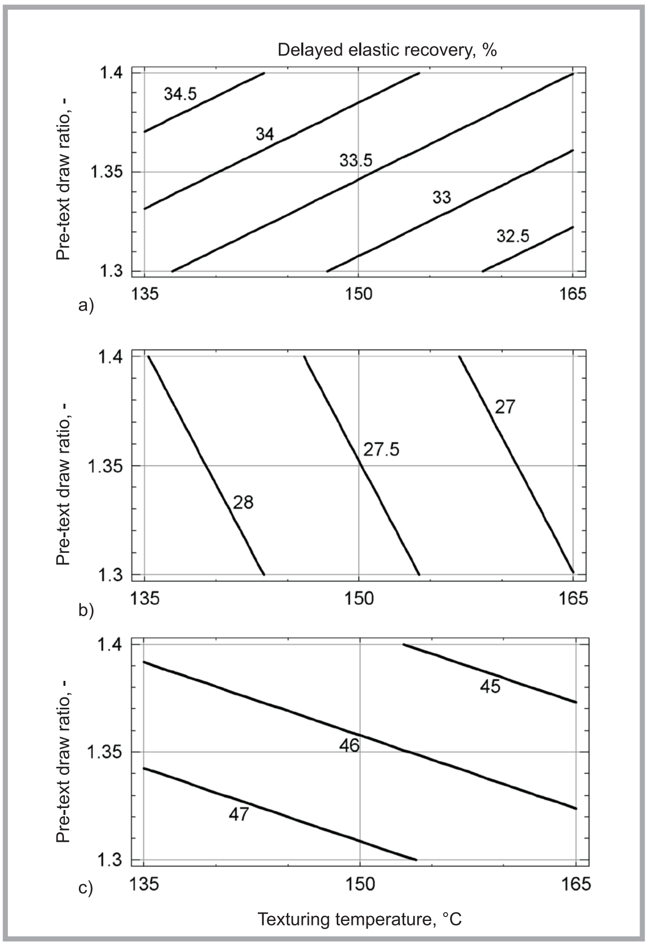

Figure 6. Delayed Elastic Recovery DER of the original textured, heat set and cycle strained PLA multifilaments according to the texturing variables.

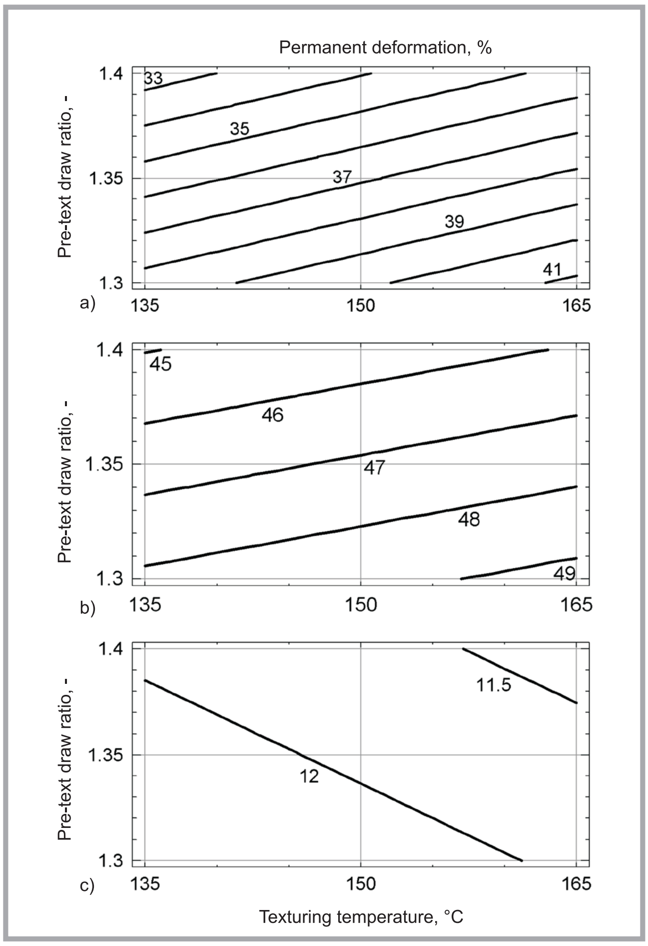

Figure 7. Permanent Deformation PD of the original textured, heat set and cycle strained PLA multifilaments according to the texturing variables.

ferently oriented macromolecules: When these were highly oriented (highest draw ratio), the temperature slightly increased the strain at breaking for textured and heat set filaments because of its contribution to the disorientation of the amorphous phase (***Figure 4.a*** and ***4.b***). By contrast, when the macromolecules were less oriented (lowest draw ratio), the temperature slightly decreased the strain at breaking for heat set and cycle strained filaments, facilitating chain folding, which led to an increase in crystal size (***Figure 4.b*** and ***4.c***). Although heat setting seems to increase the strain at breaking from 35.6% to 37.3%, the application of ANOVA shows this to be insignificant, whereas the decrease induced by cycle strain to 23.9% is highly significant.

Elasticity

Results are shown in ***Table 3***. By fitting a second order polynomial function to the experimental results [10], the immediate elastic recovery is clearly increased by the orientation (pre-texturing draw ratio) of macromolecules, with no effect of the texturing temperature on IER (***Figure 5***). Heat setting clearly decreases IER from 29.4% to 25.1%, and the cycle strain significantly increases IER up to 41.6%.

As regards delayed elastic recovery, no great differences could be attributed to the texturing conditions. The texturing temperature seems to show a slight negative influence on the DER of the original textured filaments, while the contrary occurs with the pre-texturing draw ratio. The same tendencies but with lower intensity can be observed in the heat set filaments. Heat setting significantly decreases DER from 33.6% to 27.6%, and after cycle strain increases DER up to 46.4%. After straining, the effect of texturing seems to be slightly negative on DER (***Figure 6***).

Figure 7 shows the evolution of the permanent deformation of the original textured, heat set and cycle strained PLA filaments according to the texturing conditions. As regards the original textured filaments, it is possible to observe the influence of the pre-texturing draw ratio and texturing temperature on PD: as the orientation decreases the permanent deformation, the temperature causes it to rise slightly. After heat setting, the effect of the texturing variables is the same but with less intensity, and, when subjected to cycle strain, the effect of the texturing variables on PD practically disappears. The heat setting increases PD from 37.1% to 47.3%, and after the cycle strain decreases to 12% as a result of the bedding-in effect on the macromolecules, causing the filaments to be more elastic.

Differential scanning calorimetry

Table 4 (see page 26) shows the results obtained by DSC of the samples. A first order transition corresponding to melting can be seen at a mean onset temperature of 158.5 ºC (***Figure 2***). An exo transition A with a mean peak temperature between 71 and 72 ºC, which can be attributed to cold crystallisation during the DSC scan, can be seen after exceeding endo peak B at 67 ºC [3]. This endo effect has been associated with the relaxation that occurs after the glass transition of the PLA.

The following two events: C (exo) and D (endo) only appear on samples that have been subjected to a 20% cycle strain. This means that the mechanical strain that causes macromolecules to be aligned along the filament axis gives rise to effects that are thermally detectable: exotherm C with a peak temperature of approximately 61 ºC appears after a slight endotherm D with a peak temperature of approximately 56 ºC, which can be attributed to a relaxation that probably occurs after a strain induced glass transition.

Figure 8 shows the evolution of relative crystallinity measured by DSC according to the texturing variables and treatments. It can be seen that the intensity of texturing increases crystallinity. The higher the draw ratio and temperature, the higher the crystallinity of the filaments. The effect of texturing is maintained after post treatments of heat setting and cycle strain. Heat setting increases the mean crystallinity from 34.2% to 47.5% J/g. The mean crystallinity of the cycle strained filaments shows a slight decrease of 0.6%, but the amount is not significant. The intensity of texturing decreases the total enthalpy of the endo-exo AB event, which means that this event can be attributed to the amorphous phase. The crystallinity increases at the expense of the amorphous phase as the intensity of texturing increases.

After heat setting, the effect of the texturing variables on the crystallinity and total enthalpy of the endo-exo AB event remains the same although the mean values show a significant increase in crystallinity and a significant decrease in the total enthalpy. In fact, the crystallinity and total enthalpy of the endo-exo AB event are highly correlated (r = -0.98). The heat setting and straining affect the amorphous phase of the filament. When considering the influence of the intensity of texturing on the total enthalpy of the endo-exo CD event induced after cycle straining, no significant relationship can be found between the texturing variables and total enthalpy CD, which is a measure of the internal reordering of the macromolecules induced by straining.

Table 4. *Energy of the thermal events measured on the DSC plots, according to Figure 2, of the original, heat set and 20% strained PLA textured multifilaments.*

Sample	Energy of the thermal events				
	ΔH_D/ J/g	ΔH_C/ J/g	ΔH_B/ J/g	ΔH_A/ J/g	ΔH_m/ J/g
Original:					
A1	-	-	7.740	14.350	43.290
A2	-	-	7.650	13.920	45.350
A3	-	-	5.430	10.290	44.210
B1	-	-	7.890	13.890	42.480
B2	-	-	6.510	11.550	44.560
B3	-	-	4.060	9.080	43.170
C1	-	-	5.810	11.680	44.230
C2	-	-	5.050	10.110	44.130
Heat set:					
A1	-	-	2.890	3.500	46.800
A2	-	-	4.950	7.725	46.960
A3	-	-	2.430	3.155	48.975
B1	-	-	2.725	2.415	47.090
B2	-	-	1.720	2.345	48.425
B3	-	-	1.790	2.670	47.905
C1	-	-	1.555	1.625	48.355
C2	-	-	2.350	2.240	47.140
20% Cycle Strained:					
A1	0.000	1.075	0.880	6.205	47.670
A2	0.000	1.970	0.000	4.275	48.055
A3	0.217	1.290	0.000	4.320	47.475
B1	0.360	1.265	0.375	4.420	48.045
B2	0.595	0.925	0.415	3.980	47.040
B3	0.850	1.080	0.000	2.525	48.010
C1	0.770	0.610	0.990	5.045	49.685
C2	0.590	1.640	0.000	2.785	49.335

Mechanical properties, elastic behaviour and thermal events detected by DSC

By applying multiple regression analysis [11], the relationships between mechanical properties, elasticity and thermal events detected by DSC (X - the relative crystallinity, H_{AB} - the total enthapy of the endo-exo AB thermal event and H_{CD} - the total enthalpy of the endo-exo CD event) were studied. There were no clear relationships between the stress at break

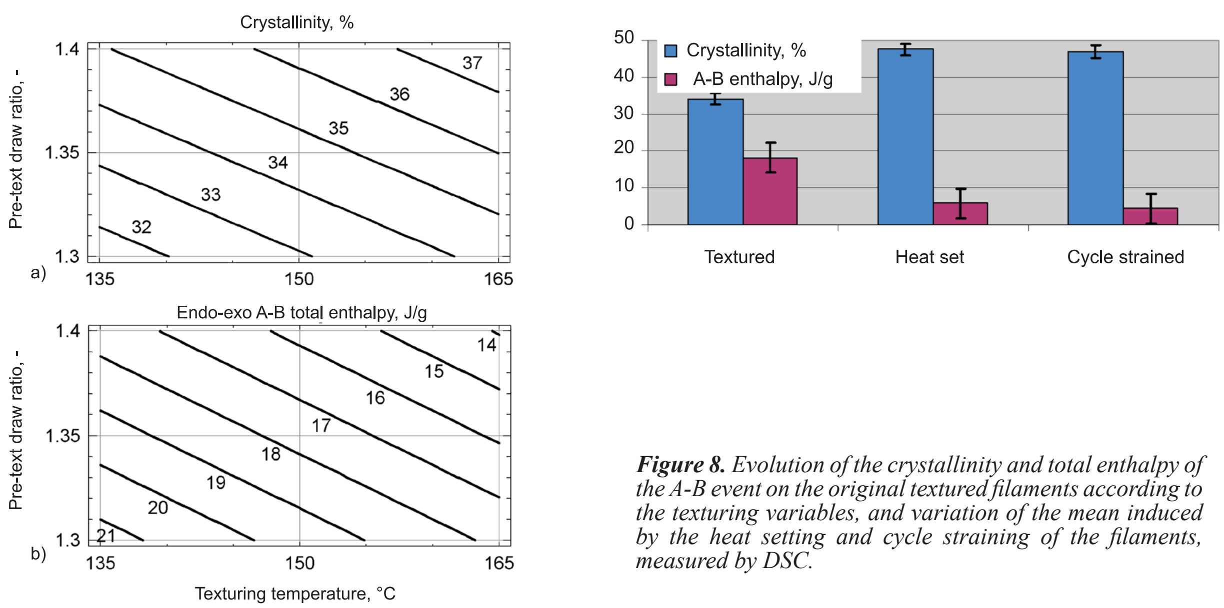

Figure 8. *Evolution of the crystallinity and total enthalpy of the A-B event on the original textured filaments according to the texturing variables, and variation of the mean induced by the heat setting and cycle straining of the filaments, measured by DSC.*

and variables X, H_{AB} and H_{CD}, but as regards the strain at break it was possible to observe the dominant effect of H_{CD} on this parameter. In fact, after straining, the heat set filaments decreased the strain at break, and H_{CD} accounts for more than 80% of the quadratic variation in the breaking strain. As for the elastic parameters, the following equations were fitted:

- $IER = 77.89 - 1.00X - 0.78H_{AB} + 8.54H_{CD}$ (Det. Coeff. $R^2 = 99.88\%$)
- $DER = 75.82 - 0.94X - 0.55H_{AB} + 10.16H_{CD}$ (Det. Coeff. $R^2 = 98.46\%$)
- $PD = -61.64 + 2.10X + 1.48H_{AB} - 18.73H_{CD}$ (Det. Coeff. $R^2 = 98.07\%$)

All thermally detectable events were significantly correlated with the elastic parameters of the filaments. The most important effect was that of the mechanically induced thermal event H_{CD}, which accounts for 52.9% of IER, 55.61% of DER and 51.39% of PD, favouring the elasticity and decreasing the plasticity of the strained filaments. The second contribution was related to the mobility of the amorphous fraction of filament H_{AB}, which accounts for 40.73% of IER, 41.81% of DER and 44.43% of PD. The higher the mobility of the amorphous phase, the higher the plasticity and the lower the elasticity of the filaments. Lastly, the crystallinity measured by DSC accounts for 6.37% of IER, 2.58% of DER and 4.18% of PD. Regarding the equations, it could be concluded that the smallest influence of crystallinity favours plasticity and decreases the elasticity of the yarns. The effect of crystallinity on the elastic parameters of the yarns can be explained by the highly negative correlation between the crystallinity and total enthalpy of the endo-exo AB event (r = -0.98), which predominates the elasticity. These two aspects enable us to conclude that an increase in yarn crystallinity promotes yarn elasticity and decreases yarn plasticity.

Conclusions

The following conclusions can be drawn concerning the mechanical and elastic properties of the filaments:

- Stress at breaking is not significantly influenced by the heat setting and cyclic strain of polylactide false-twist textured yarns.
- The strain at breaking is clearly decreased by the internal alignment of macromolecules induced by the pretexturing draw ratio. The texturing temperature slightly increases the strain at breaking when it is applied to highly oriented macromolecules, whereas the opposite occurs when it is applied to less oriented macromolecules. Heat setting slightly increases the strain at breaking, but after 20% cycle straining, the strain at breaking is reduced by 10%.
- Immediate elastic recovery is increased by the orientation of macromolecules, reduced by heat setting and greatly increased after cycle straining.
- Delayed elastic recovery is mainly influenced by the heat setting, which increases it, and by cycle straining, which reduces it.
- Permanent deformation is decreased by the orientation of macromolecules, slightly increased by the texturing temperature, increased by heat setting, and decreased by cycle straining.

The following conclusions may be drawn concerning the thermal events measured by differential scanning calorimetry:

- The higher the texturing effect, the higher the crystallinity of the filaments and the lower the intensity of the endo-exo AB event, which occurs at peak temperatures between 67 and 72 ºC. Heat setting increases crystallinity and reduces the intensity of the endo-exo AB event. Cycle straining does not affect crystallinity or the intensity of the AB event.
- Cycle straining induces an endo-exo CD event, which is thermally detectable at peak temperatures between 56 and 61 ºC approximately.
- The elastic behaviour of the filaments can be explained by the intensity of the thermal events detected by DSC. Of the three events, the most important is that related to cycle straining, followed by that related to the amorphous phase and crystallinity, where there is a high correlation between them.

Acknowledgments

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