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Influence of Drawing Parameters on the Properties of Melt Spun Poly(Lactic Acid) Fibres

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Abstract
The object of the investigation were fibres prepared from PLA type 6201D (NatureWorks LLC) in a classical two-step technological system comprising spinning at a speed below 1250 m/min and drawing. The model drawing processes were considered in which process parameters were changed such as the draw ratio, drawing speed and thermal conditions. The aim of this study was to define the impact of the drawing conditions on the mechanical properties of the PLA fibres: tenacity, elongation at break, initial modulus and temperature-induced shrinkage. Also, the crystallinity degree of the fibres was estimated by DSC measurements and an acoustic method was applied to define the fibre orientation. Testing the physical-mechanical properties was done according to the appropriate PN-EN ISO.

Key words: *poly(lactic acid) fibres, melt spinning, drawing conditions, mechanical properties, structure.*

Introduction

Substitution of synthetic crude oil-derived polymers with biodegradable materials obtained from renewable resources offers the opportunity to reduce petroleum consumption and to curtail the amount of durable waste, a threat to the environment. After packaging, textiles are another source of this burdensome waste. Most packaging materials and textiles are characterised by only one-way use.

Poly(lactic acid) (PLA) was first used as a raw material for medical use and is now gaining ground in commodity textiles [1 - 4]. In 1992, the Kanebo Co., Japan put the first PLA fibre on the market under the trade name Lactron made from the polymer Lacty provided by Shimadzu Co. Since that time, producers of PLA have been preparing special grades of the polymer designed for processing into fibrous products [5 - 7]. For the production of monofilaments, PLA grades are offered with a melt flow index (MFI) of 5 - 15 g/10 min, while for staple and continuous fibres, PLA is available with MFI = 15 - 30 g/10 min, and for spunbond nonwoven materials with MFI = 70 - 85 g/10 min. In addition to melt viscosity, the polymers differ in their content of isomer D which determines the melting temperature of PLA. Lactic acid is the raw material in the synthesis of PLA. It has two optical isomers, L(+) and D(-) lactic acid. PLA properties depend upon the stereochemical composition of the repeating units in the polymer chain. Homochiral PLA (L-PLA or D-PLA) is a stereo-regular, isotactic polymer, inclined to crystallisation, with a crystallisation degree of up to 60%. Its glass transition temperature (T_g) is 55 °C and melting temperature (T_m) is about 180 °C [8]. With an increased content of the D(-) isomer in proportion to the L(+) isomer in PLA, i.e. a deterioration in chemical purity, the ability of the polymer to crystallise decreases. With a D(-) isomer content of over 15%, the polymer is entirely amorphous. The higher the D(-) isomer content, the lower the melting temperature of PLA [9].

PLA with a D isomer content in the range of 1.4 - 2%, with a melting temperature of 160 - 170 °C, is a basic raw material in the manufacture of continuous and staple fibres. Polymers with a higher D isomer content (~10%) are used as low melting (120 - 130 °C) sheath material in bicomponent fibres, which play a role in binding fibres in nonwoven materials. PLA polymers with varied stereochemical composition may also be used in the preparation of bicomponent fibres of the side to side type that are capable of self-crimping as a result of the difference in shrinkage of the two components.

PLA fibres, like other synthetic fibres, may have utility in textile products for under- and outerwear, disposable sanitary and medical textiles, geotextiles, technical textiles, agriculture nonwoven, fishing nets and ropes [10, 11]. Depending on the intended application, the properties of the fibre are adjusted, including the mechanical and thermal properties and resistance to hydrolysis which is closely related to biodegradation ability. Fibre mechanical properties are influenced primarily by the parameters of formation which generate the internal structure of the fibre.

Many research results published in the last decade concern the estimation of the structural, mechanical and thermal properties and biodegradability of PLA fibres [12 - 21]. Fewer studies deal with assessments of the impact of formation conditions on the properties of the PLA fibre. Investigations have mostly been done in this field on the lab scale at low spinning speed or with a spinning speed in the range of 2000 - 5000 m/min [22 - 26].

The current study concerns the formation of PLA fibres in a classical, two-step process comprising spinning at a speed below 1250 m/min and drawing. The aim of the investigation was to define the impact of drawing conditions upon the main mechanical properties of PLA fibres: tenacity, elongation at break, initial modulus and temperature-induced shrinkage.

Materials and investigation methods

Polymer

Commercial poly(lactic acid) under the trade name NatureWorks PLA Polymer type 6201 D supplied by NatureWorks LLC (USA) was used in the formation of fibres. It is characterised by a D isomer content of 1.4% (as given by the manufacturer). The melt flow index $\mathrm{MFI}_{210^{o}\mathrm{C}}$ = 15.4 g/10 min was measured according to PN-EN ISO 1133:2002 on a LMI D4002 plastometer (Dynisco Co.). The glass transition temperature (T_g) and melting temperature (T_m) as determined by differential scanning calorimetry (DSC) during heating at a rate of 20 °C/min were 63 °C and 172.7 °C, respectively. The polymer was pre-dried to a moisture content below 50 ppm in a rotary vacuum dryer at 100 °C for 7 hours. The moisture content of the polymer was measured by the Karl Fischer colourmetric method using a DL39X apparatus (Mettler Toledo).

Fibre formation

The fibres were formed from a melt of the PLA 6201 D polymer in a two-step process comprising spinning and drawing. A multifilament fibre was spun on an experimental extruder spinning bank at a melt temperature of 240 °C with a capacity of 28.6 g/min and speed of 1000 m/min through a 24-hole spinneret. Spinning trials were also performed at speeds of 250, 500 and 1250 m/min. Lurol PT-L216, supplied by Goulston Technologies Inc. (USA), in a 5% solution, was used as the spinfinish. The multifilaments obtained were next drawn on a SZ-16 draw-twister (Barmag Co.). Variables in the course of drawing were: temperature of the godet in the range of 60 - 120 °C, temperature of the plate in the range of 80 - 120 °C, draw ratio in the range of 2.19 - 5.5 and drawing speed in the range of 230 - 750 m/min.

Test methods

Differential scanning calorimetry (DSC) measurements were made on a Diamond instrument (Perkin-Elmer Co.) in a nitrogen atmosphere. Samples of 7 - 10 mg in weight were analysed in the cycle: first heating → cooling → second heating in a temperature range of -60 °C to +190 °C and heating speed of 20 °C/min. The temperature and enthalpy of phase transitions were determined using the Pyris calculation program. The degree of crystallinity (X_c) was calculated by comparing the difference between the melting and crystallisation enthalpies with the melting enthalpy of a 100% crystalline PLA sample from the equation:

$$X_c\,(\%) = (\Delta H_m - \Delta H_{cc})/\Delta H^{\circ}_m \times 100$$

where:

ΔH_m – the melting enthalpy (first heating of the sample)
ΔH_{cc} – the enthalpy of cold crystallisation
ΔH°_m – the melting enthalpy of 100% crystalline PLA; H°_m = 93.1 J/g [27].

The molecular orientation index (f) of the fibre was determined by an acoustic method on the basis of measurements of sound propagation in the fibre [28, 29]. The testing was done on a Dynamic Module Tester made by Morgan Co. (USA) with the following parameters: sound frequency 10 Hz, paper shift 6.35 cm/min, shift of sender 6.35 cm/min, range 2×10^{-4} s.

The molecular orientation index was calculated by:

$$f = 1 - C_u^2 / C^2$$

Sound propagation speed C, km/s was calculated by:

$$C = \frac{\Delta L}{\Delta t}$$

where: *L* and *t* are readouts from the graph: distance covered by the sender and time interval, respectively.
C_u – speed of sound propagation in an amorphous fibre.

The physical-mechanical properties of the fibre were tested on an Instron 5540 tensile tester, typically used in textile metrology. The measurements were made according to Polish standards appropriate for continuous fibres: linear density (PN EN ISO 2060:1997, Way 1), breaking force (PN-EN ISO 2062:2010 Method A), tenacity (PN-EN ISO 2062:2010 Method A), elongation at break (PN-EN ISO 2062:2010 Method A) and initial modulus (PN-EN ISO 2062:2010 Method A). The values presented in Figures and Tables were obtained in 25 measurements performed.Shrinkage in hot water and hot air was tested according to PN-EN 14621:2007, the values were obtained in 5 measurements performed.

Results

Good mechanical properties of a fibre are attainable provided adequate process conditions employed in spinning, drawing and thermal processing of the fibre. A determination of the correlation between the conditions during the various phases of fibre formation is a prerequisite for the preparation of a technological process. Spinning conditions like take-up speed, extrusion rate, melt temperature and others have a profound influence on the process dynamics and creation of structure, and, as a consequence, on the physical and mechanical properties of the fibres obtained. The optimum melt temperature of 240 °C for the spinning of fibres from PLA 6201 D was defined in earlier works [30, 31].

Table 1 (see page 60) presents the basic structural parameters: crystallinity degree and molecular orientation index of PLA fibres spun at different speeds.

An increase in the spinning speed in the range of 250 - 1250 m/min resulted in a certain increase in fibre orientation. However, with spinning at low and medium take-up speed, under conditions of low molecular orientation, the crystallisation rate of PLA , compared with cooling rate of the polymer, reaches a level sufficiently low to obtain an amorphous fibre. The sound propagation speed in the fibre spun at a speed of 250 m/min was adopted as the C_u value for an amorphous fibre. The main focus of the investigation was the fibre spun at a speed of 1000 m/min.

***Table 1.** Basic structure parameters of PLA fibres spun at different speeds.*

Take-up speed, m/min	Crystallinity degree - X_c, %	Speed of sound propagation, km/s	Molecular orientation index, f
1250	9.0	1.476	0.244
1000	8.5	1.429	0.194
500	4.8	1.350	0.096
250	0.35	1.283	-

***Table 2.** Main physical-mechanical and structural properties of PLA fibres drawn at varying conditions; temperature of godet - 80 °C; X_c - the degree of crystallinity, f - molecular orientation index.*

Drawing	Draw ratio	Linear density, dtex	Tenacity, cN/tex	Elongation, %	Initial modulus, cN/tex	Shrinkage in 100 °C, H_2O, %	X_c, %	f
without stabilisation	2.19	132 ± 1	20.8 ± 0.4	83.5 ± 1.6	318 ± 10	71.2 ± 0.6	0.44	0.390
	2.80	104 ± 1	27.7 ± 0.5	48.1 ± 1	386 ± 14	74.1 ± 0.9	35.0	0.502
	3.39	86.3 ± 0.3	31.9 ± 0.6	29.5 ± 0.5	462 ± 14	61.8 ± 1.9	44.5	0.514
	4.00	73.3 ± 0.8	35.9 ± 0.9	24.7 ± 0.4	527 ± 18	38.9 ± 3.3	50.8	0.588
with stabilisation on plate; T of the plate = 120 °C	3.39	85.2 ± 0.6	35.5 ± 0.8	38.7 ± 0.8	467 ± 13	14.9 ± 0.8	49.2	0.544
	4.00	72,6 ± 0.7	45.0 ± 1.1	30.8 ± 0.4	536 ± 18	18.8 ± 0.9	51.6	0.588
	4.95	58.7 ± 0.2	45.3 ± 1.2	26.3 ± 0.3	600 ± 18	16.0 ± 0.7	53.5	0.624
	5.46	53.1 ± 0.7	42.3 ± 1.1	23.3 ± 0.9	640 ± 20	13.9 ± 0.7	54.7	0.641

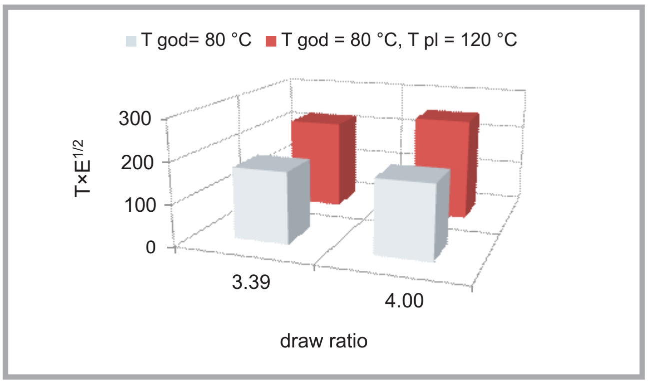

***Figure 1.** Comparison between the strength factors T×E½ of fibres drawn with and without stabilisation at different draw ratios.*

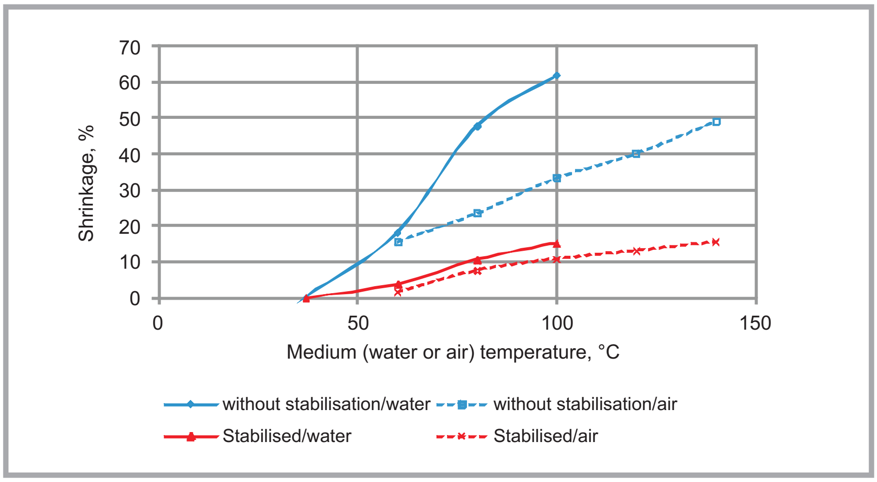

***Figure 2.** Shrinkage of PLA fibres drawn with and without stabilisation caused by the action of hot water and hot air.*

Table 2 shows the mechanical and structural parameters of PLA fibres drawn at a speed of 496 m/min at various draw ratios on a hot godet (80 °C) and drawn with stabilisation on a hot plate (120 °C).

It was found that it was not possible to draw the PLA fibres with stabilisation at a draw ratio below 3.39. Temperature and the draw ratio are two factors that influence the stress in the fibre in the drawing zone. When the fibre is drawn without stabilisation, the drawing point is situated below the godet where the fibre temperature is highest. In a drawing process combined with stabilisation on the plate, the drawing point moves to behind the plate. Fibre tension on the plate decreases, caused by fibre-to-plate friction. When the tension applied in the drawing zone is too low, it does not allow sufficient fibre stress between the godet and the plate, which leads to the fibre sticking to the hot plate of the drawing machine.

Figure 1 presents the comparison between the strength factors T x E½ of fibres drawn at draw ratios of 3.39 and 4 with and without stabilisation. The empirical index T×E½ describes the tenacity (T)-elongation (E) relationship for a large number of man-made fibre systems. The T×E½ factor is also useful in the development of fibre processes, where it can serve as an index of spinning/drawing process optimisation [32]. The higher the T×E½ index value, the better the mechanical properties of the fibre. Fibres that were stabilised at 120 °C on the heating plate during drawing showed better mechanical properties than those prepared without stabilisation.

Fibres drawn with stabilisation showed a higher degree of crystallinity in the range of 49.2 - 54.7% (***Table 2***). A sizable reduction in PLA fibre shrinkage occurred with stabilisation on a plate heated up to 120 °C. Shrinkage increased with an increasing draw ratio, up to a maximum of 18.8% and then decreased to 13.9%.

Drawing of the fibre causes an increase in the orientation, producing an arrangement of polymer chain segments that provides more favourable conditions for the formation of strong second-order bonds. Fibre shrinkage decreases along with the emergence of a more stable structure generated by a higher draw ratio.

Measurements of PLA fibre shrinkage (***Table 2***) were performed in water at 100 °C.

Figure 2 shows the dependence of the shrinkage of the PLA fibre, drawn with and without stabilisation at a draw ratio of 3.39 (position 3 and 5 in ***Table 2***), on the temperature of the medium in which the fibre was shrunk. The measurements of the temperature-induced change in fibre length were performed in water and air.

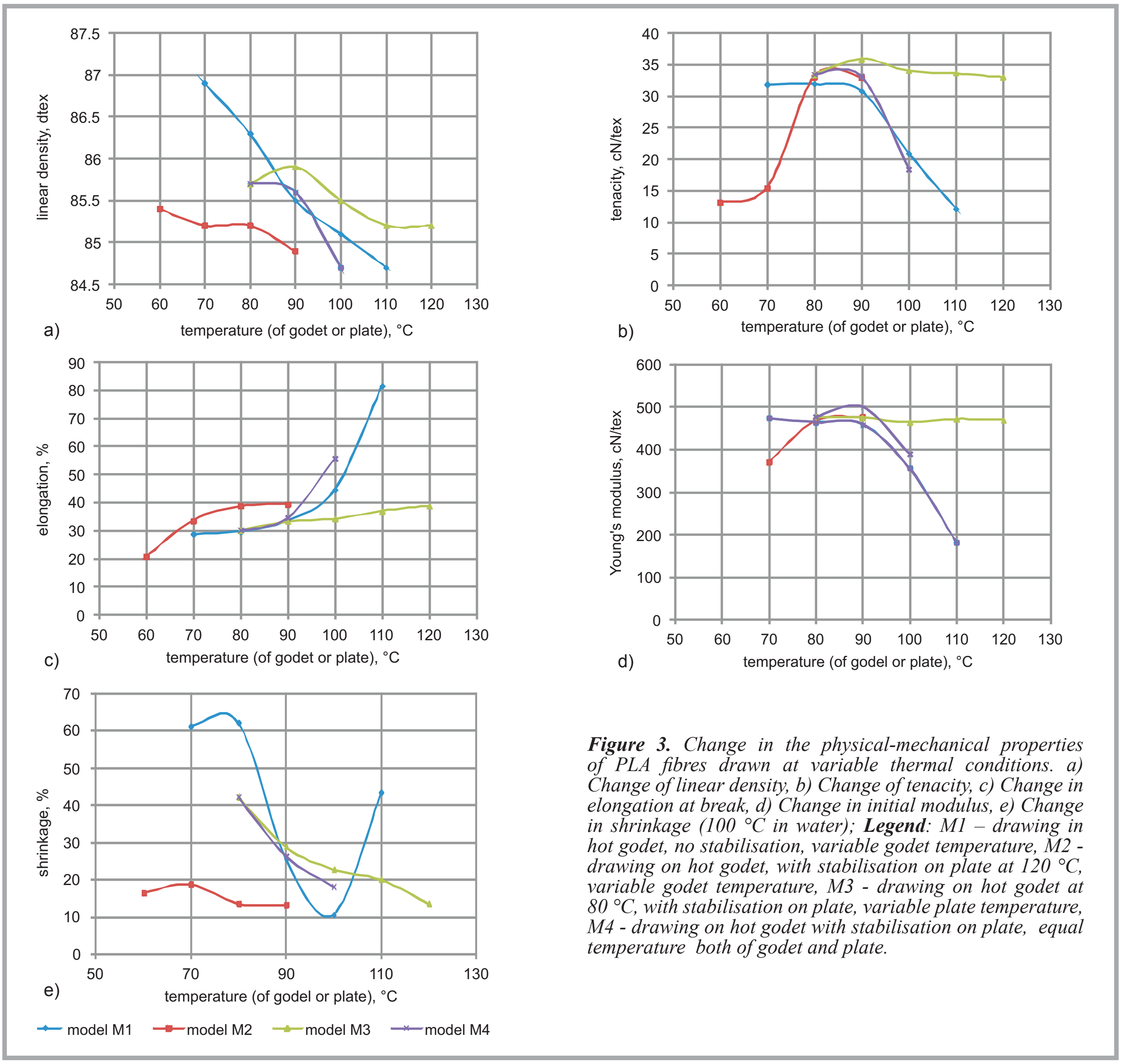

***Figure 3.** Change in the physical-mechanical properties of PLA fibres drawn at variable thermal conditions. a) Change of linear density, b) Change of tenacity, c) Change in elongation at break, d) Change in initial modulus, e) Change in shrinkage (100 °C in water); **Legend**: M1 – drawing in hot godet, no stabilisation, variable godet temperature, M2 - drawing on hot godet, with stabilisation on plate at 120 °C, variable godet temperature, M3 - drawing on hot godet at 80 °C, with stabilisation on plate, variable plate temperature, M4 - drawing on hot godet with stabilisation on plate, equal temperature both of godet and plate.*

The fibre shrinkage measured at 100 °C in water was 61.8% and 14.9% for the unstabilised and stabilised fibres, respectively. Measured at the same temperature in air, shrinkage was 33.3% and 10.7%, respectively. Water plays the role of a swelling agent that impairs molecular interaction in the fibre, thus facilitating the relaxation of internal stress. The higher the fibre heating temperature, the greater the fibre shrinkage.

The selection of a proper draw ratio to provide the optimal fibre properties depends on the destination of the prepared fibres. High tenacity, good dimensional stability and low elongation is expected in technical fibres. In textile fibres, adequate elongation comes to the forefront as it is essential both in processing and use. The optimal draw ratio for these fibres was selected in order to obtain an elongation at break of the fibre in the range of 35 ± 5%.

Model drawing processes (M1 - M4) of PLA fibres, linear density (count) 84 dtex/24f, were considered at a draw ratio of 3.39, speed of 496 m/min, and variable thermal conditions:

M1 - drawing on hot godet, no stabilisation, variable godet temperature
M2 - drawing on hot godet, with stabilisation on plate at 120 °C, variable godet temperature
M3 - drawing on hot godet at 80 °C, with stabilisation on plate, variable plate temperature
M4 - drawing on hot godet with stabilisation on plate, equal temperature of both godet and plate

Figure 3.a** – **3.e shows the relationship between fibre physical-mechanical properties and the thermal conditions of drawing.

The linear density of a drawn fibre is primarily governed by the draw ratio. The linear density of 288 dtex of the spun PLA fibres was selected to arrive at the ultimate 84 ± 1 dtex/24 f fibre. The calculated linear density of the fibre collected on the drawing machine at a draw ratio of 3.39 amounted to 85 dtex. The sizeable increase (up to 87 dtex, as seen in ***Figure 3.a***) of the linear density of fibres drawn without stabilisation and at a low

Table 3. *Structural properties of PLA fibres drawn at variable temperature conditions; draw ratio 3.39 and spinning speed 496 m/min; Xc -the degree of crystallinity, f - molecular orientation index.*

Model of drawing	Temperature of godet, °C	Temperature of plate , °C	X_c, %	f
M1	70	No plate	36.0	0.463
	80	No plate	44.5	0.514
	90	No plate	52.1	0.501
	100	No plate	46.5	0.463
	110	No plate	25.6	0.280
M2	60	120	34.5	0.526
	70	120	42.2	0.547
	80	120	49.2	0.544
	90	120	49.9	0.553
M3	80	80	45.1	0.540
	80	90	49.0	0.615
	80	100	52.0	0.575
	80	110	50.5	0.622
M4	80	80	45.1	0.540
	90	90	50.8	0.588
	100	100	37.7	0.398

Table 4. *Physical-mechanical and structural properties of PLA fibres drawn at variable conditions; draw ratio 3.39; godet temperature 80 °C; Xc - degree of crystallinity, f - molecular orientation index.*

Drawing	Draw speed, m/min	Linear density, dtex	Tenacity, cN/tex	Elongation at break, %	Shrinkage in 100 °C, H_2O, %	X_c, %	f
without stabilization	230	85.8 ± 0.6	33.4 ± 0.7	29.5 ± 0.7	55.5 ± 3.1	44.9	0.509
	753	86.4 ± 0.5	31.7 ± 0.5	30.3 ± 0.7	60.5 ± 5.7	49.5	0.497
with stabilization on plate; T of plate = 120 °C	230	85.4 ± 0.4	31.5 ± 0.9	41.0 ± 0.7	10.3 ± 0.4	50.2	0.602
	753	85.6 ± 0.4	32.2 ± 1.1	37.3 ± 1.3	14.0 ± 0.3	45.8	0.593

godet temperature was caused by the relaxation of the supermolecular structure of the fibre which underwent extensive deformation caused by low plasticity. The higher the godet temperature, the higher the plasticity of the fibre in the drawing zone. Heating of the fibre on the plate adds to the stability of its structure, thus influencing the relaxation degree which occurs in the time between the drawing and testing of the linear density; this limits the difference between the obtained and calculated linear density.

When fibres are drawn without stabilisation (M1), tenacity decreased along with godet temperature above 90 °C. Tenacity changed in the same way when drawing occurred with the godet and plate temperature maintained at the same level (M4, ***Figure 3.b***). Tenacity was promoted by crystallisation which supersedes the amorphous phase in which the polymer molecule chains are prone to rupture. The observed changes in tenacity were in line with the changes in the degree of crystallinity and molecular orientation index (***Table 3***).

The processes of recrystallisation and reorientation begin at a godet temperature above 90 °C; it is also accompanied by a decrease in the orientation index f and confirmed by a distinct increase in the elongation at break (***Figure 3.c***). In the case of PLA fibres drawn with stabilisation on a plate at 120 °C, tenacity increased along with an increase in godet temperature from 60 to 80 °C. The greatest tenacity was found for PLA fibres drawn on the godet at 80 °C and stabilised on a hot plate at 90 °C. A further increase in the plate temperature up to 120 °C did not further affect the tenacity. Previous studies have shown that tenacity decreases when PLA fibres are stabilised on the plate at a temperature above 120 °C [33].

Changes in the initial modulus (***Figure 3.d***) had exactly the same pattern as those of tenacity. Processes of reorientation were responsible for the distinct drop in tenacity and the modulus of the fibre along with increasing godet temperature in the drawing process without stabilisation. This was confirmed by the values of the orientation index f (***Table 3***).

An increase in the drawing temperature resulted in decreased shrinkage. The slight increase in shrinkage from 60.9 to 61.8% in the fibre drawn on the godet below 80 °C (model M1) reflected an increase in stress in the fibre before reaching an adequate temperature ($T_{fibre} < T_{g\,PLA}$). After exceeding a godet temperature of 100 °C, recrystallisation and reorientation of the PLA polymer proceeds in the fibre having the effect of shrinkage increase. It increased from 10.5 to 43.2% at a temperature of 110 °C (***Figure 3.e***). Shrinkage originates from internal stress. In the combined process of drawing with stabilisation, an increase in godet temperature had a minor influence on fibre shrinkage. Stabilisation of PLA fibres on a hot plate brings the fibre structure close to thermodynamic equilibrium thanks to the increased mobility of polymer macromolecules in the fibre, and leads to a shortened relaxation time.

Speed is an important parameter in any technological process and has an effect on the process output. Both spinning and drawing speed exert an impact on the fibre structure and, hence, on the physical-mechanical properties of the fibre.

Table 4 shows the structural parameters and physical-mechanical properties of the investigated PLA fibres (spun at 1000 m/min) drawn at variable speed with and without stabilisation. In both versions, fibres drawn at higher speeds have a lower orientation index. An increase in drawing speed from 230 to 753 m/min in a process with stabilisation caused the crystallinity degree of the PLA fibres to fall from 50.2 to 45.8%, while an increase from 44.9 to 49.5% occurred in the method without stabilisation. In both methods, fibres drawn at higher speeds showed greater shrinkage and inferior mechanical properties (***Figure 4***).

The adoption of a technological drawing speed is a compromise between the optimal mechanical properties and the output of the drawing process.

Summary

PLA fibres prepared in a classical two-step process comprising spinning at speeds below 1250 m/min and drawing were the subject of the present investigation. Model drawing processes were considered with variable parameters like the draw ratio, drawing speed and thermal conditions. PLA fibres with a linear density of 288 dtex spun through a 24-hole spinneret at a speed of 1000 m/min were drawn without stabilisation on a godet heated up to 60 - 110 °C, and with stabilisation on a plate heated up to 80 - 120 °C, with a draw ratio of 3.39 and a drawing speed of 496 m/min. Fibres prepared in this manner were characterised by the following physical-mechanical properties: linear density 84.6 - 86.7 dtex, tenacity 12.1 - 35.8 cN/tex, elongation at break 28.6 - 81.5%, initial modulus 181 - 475 cN/tex and shrinkage in 100 °C in water 10.5 - 61.8%.

Changes in the structure of PLA fibres gives rise to changes in the mechanical properties. The crystallinity degree of the fibres changed in the range of 8.5% for undrawn yarn to 51.2% for drawn yarn, and the orientation index from 0.192 to 0.622, respectively. By proper selection of the drawing process parameters, one can tailor the mechanical properties of PLA fibres by keeping in mind the intended application.

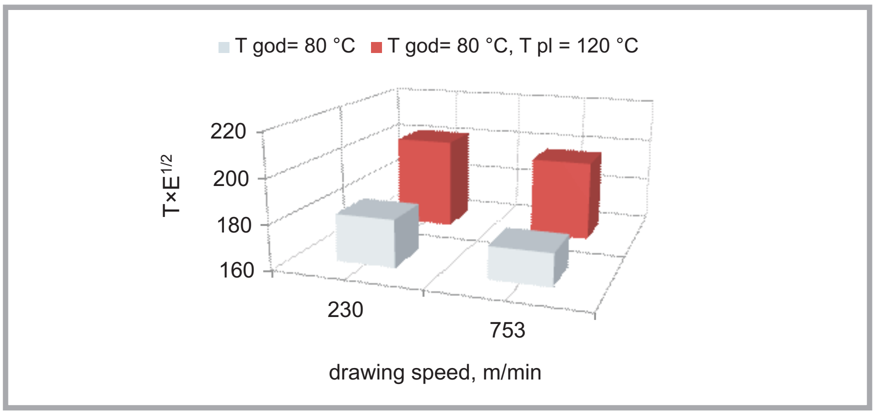

Figure 4. *Comparison of indices* $T \times E^{1/2}$ *of PLA fibre drawn without stabilisation and with stabilisation, at various speeds.*

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