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Characterization of the thermal properties of PLA fibers by modulated differential scanning calorimetry

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Abstract

Polylactide (PLA) has been melt spun to produce multifilament continuous yarns. The thermal characteristics of PLA filaments have been investigated using modulated differential scanning calorimetry (MDSC). With MDSC, it is possible to separate the different thermal events and to analyze them more precisely. The influence of hot drawing on thermal properties of PLA filaments has been studied. Hot drawing promotes an increase of glass transition temperature (T_g) and a decrease of heat capacity. The cold crystallization spreads on a larger range of temperature and the peak occurs at a lower temperature. The initial degrees of cristallinity of PLA filaments have been calculated thanks to the reversing and non reversing curves of MDSC. Tensile properties of PLA filaments are also investigated.

Keywords: Modulated differential scanning calorimetry (MDSC); Fibers; PLA

1. Introduction

For a long time, polylactide (PLA), a hydrolysable aliphatic polyester, has been mainly used in surgical and biomedical applications [1–3] because of the high cost of PLA. Nowadays, new applications are investigated in order to use PLA as a common polymer since recent ways to synthesize PLA provide an economically viable biodegradable commodity polymer [4–6]. Moreover PLA has interesting mechanical properties in comparison with standard polymers. Another major advantage of PLA is that it is produced from lactic acid, which can be obtained from 100% renewable resources such as corn or sugar beets. So, PLA can be used to produce injection stretch-blown molded bottles, films, extrusion-thermoformed containers and fibers [7]. A lot of studies have been carried out to produce PLA fibers with different kinds of spinning processes [8]. Solution spinning of PLA can be realized, but in this case, solvents such as chloroform and toluene are necessary [1,9] and the production speed is rather low. The melt spinning process allows to make PLA fibers without solvent at higher speeds and with more evenness. The PLA filaments can be spun at high-speed take up velocities [10–13]. In this case, PLA is melt-extruded through a die and the filaments are directly collected by the means of winder up to 5000 m/min. Another method is spin drawing [10,14–17] which is a two-stage process. Here the PLA is melt-extruded through a die in a first stage, and then the as-spun filaments are hot drawn between two rolls and collected on a winder.

Most papers about PLA fibers discuss about the thermal properties analysed by conventional DSC. If multiple transitions occur in the same range of temperature or if different thermal events overlap, the interpretation can be problematic. This is particularly the case for PLA. A peak related to the relaxation of macromolecules occurs indeed in the same temperature range as the glass transition. So, the determination of glass transition temperature cannot be very precise. Furthermore, calculating the initial degree of cristallinity with conventional DSC is generally wrong for strongly oriented polymers such as fibers because it is difficult to set exactly the limits of integration of crystallization and melting peaks. This kind of error can be particularly important when different thermal transitions overlap. Using MDSC allows to avoid a certain number of these drawbacks [18]. In order to separate the different thermal events, the method consists in superimposing a faster sinusoidal heating rate onto a slower underlying linear heating rate [19]. In addition to the linear temperature ramp, the amplitude and the period of the sinusoidal temperature ramp have to be chosen in MDSC in comparison with conventional DSC. The signal obtained is

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a modulated heat flow. The deconvolution of this signal allows to determine the total heat flow (the same as in conventional DSC) which is separated in two components: on one hand, the reversing heat flow, on the other hand, a nonreversing heat flow. Glass transition is a typical reversing event, while enthalpy of relaxation and crystallization are nonreversing ones. Melting is a reversing phenomenon, even if nonreversing signals can be observed if the experimental conditions are not convenient. To measure the initial degree of cristallinity of oriented polymers, it is necessary to find the conditions for which it will be possible to distinguish the melting endotherm as a reversing event and the phenomenon of recrystallization during the melting as a nonreversing one. If the convenient parameters are used, the measure of the initial degree of cristallinity can be made by the calculation of the difference between the areas under the reversing and nonreversing heat flows.

The aim of this paper is to precisely understand the different thermal properties of PLA fibers such as glass transition, cold crystallization, melting, and initial degree of cristallinity. MDSC was first used to distinguish the glass transition from the associated relaxation peak. It allowed us to determine more precisely the glass transition temperature, and to understand the influence of hot drawing on T_g. Moreover, MDSC was used to show the phenomenon of recrystallization during melting and to calculate the initial degree of cristallinity of PLA fibers drawn at different draw ratios.

Some measurements of the tensile properties have also been done to show the influence of drawing on the mechanical properties of PLA filaments.

2. Experimental

2.1. Spin-drawing of PLA

PLA was supplied by Galactic (Belgium). Spin-drawing of PLA is realised with the spinning device Spinboy I from Busschaert Engineering. PLA pellets are first melted in a single screw extruder from 220 to 225 °C. Then, melted PLA passes through two dies consisting of 40 circular channels with a diameter of 400 μm to produce a multifilament yarn which is coated with Filapan CTC, a spin-finish supplied by Boehme. At last, the multifilament yarn is hot drawn between two rolls at different speeds and temperatures. The speed of the first roll is fixed at 150 or 200 m/min. The draw ratio (DR), which is the ratio of the speeds of the first and second roll, varies between one (the as-spun filament) and four. The different spin drawing conditions of the PLA filaments and their dimensional characteristics are summarised in Table 1.

2.2. Characterization of the thermal properties of PLA fibers

The thermal properties of PLA fibers are investigated using a TA Instruments DSC 2920 with the modulation option. Two series of parameters (underlying rate, modulation and period) are used to study the glass transition and relaxation enthalpy on one hand, and the phenomena of crystallization and melting on the other hand. For all experiments, the purge gas is helium (25 ml/min). Temperature and heat of fusion are calibrated with indium, the heat capacity being calibrated with a sapphire sample. Different underlying rates, modulations and periods have been tried. The most suitable parameters have been chosen and are described in the next paragraphs.

2.2.1. Study of the glass transition and enthalpy of relaxation of PLA fibers by MDSC

In order to separate the glass transition and the relaxation phenomenon, the underlying rate used is 1 °C/min, with an amplitude of 1 °C and a period of 60 s. These parameters allow to observe the glass transition in the reversing curve, and the relaxation phenomenon in the nonreversing one.

2.2.2. Study of cold crystallization, recrystallization and melting of PLA fibers by MDSC

To observe cold crystallization, recrystallization during melting or melting itself, the underlying rate used is 5 °C/min,

Table 1
Conditions of spinning of PLA and results of MDSC

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Draw ratio between rolls	2	3	2	3	4
Speed roll 1	200	200	150	150	150
Speed roll 2	400	600	300	450	600
T roll 1 (°C)	70	70	70	70	70
T roll 2 (°C)	60	60	60	60	60
Diameter of filaments (μm)	52.09	45.50	56.40	52.50	46.40
T_g (°C)	61.26	61.70	61.12	65.15	66.85
C_p (J/g/°C)	0.43	0.39	0.55	0.46	0.27
T relaxation peak (°C)	61.10	62.65	61.14	65.94	67.03
H relaxation (J/g)	4.73	10.20	2.74	9.89	1.49
T_c (°C)	96.23	73.16	95.97	99.95	/
$H_{crys+recrys}$ (J/g)	46.70	29.51	30.03	45.23	26.47
T_m (°C)	152.59	144.83	151.58	147.07	146.07
H_m (J/g)	56.74	44.71	38.17	61.31	64.50
Degree of cristallinty (%)	10.73	16.24	8.70	17.18	40.63

T, temperature; ΔC_p, variation of heat capacity; ΔH, enthalpy; T_c, temperature of cold crystallisation; T_m, melting temperature; ΔH_m, melting enthalpy.

with an amplitude of 0.7 °C and a period of 60 s. These parameters allow to separate the cold crystallisation/recrystallization in the nonreversing curve and the melting endotherm in the reversing curve.

2.3. Tensile properties of PLA filaments

2.3.1. Fineness of filaments

Before measuring the tensile properties, the fineness of each filament is measured with a Vibroskop from Zweigle (following the standard NF G 07-306). The Vibroskop measures the linear density (g/km) of the filaments. So with the density of PLA, it is possible to calculate the diameter of the filaments. All the diameters represent an average value of 50 tests.

2.3.2. Measure of the tensile properties

The measurement of the tensile properties of PLA filaments has been carried out following the standard NF EN ISO 5079 on a tensile testing machine of Zwick (1456); the cell force used is 10 N. All the tests have been made at standard atmosphere (the temperature is 20±2 °C and the relative humidity is 65±5%). The length of the sample is 20 mm. Samples are properly placed to be sure that filaments break between the two clips. All the results represent an average value of fifty tests.

3. Results and discussion

3.1. Characterization of the thermal properties of PLA fibers

3.1.1. Study of the glass transition of PLA fibers

When PLA is spun, an increase of T_g up to 66.85 °C is observed when DR increased (Fig. 1). The same trend has been observed for fibers and microfibers of PET [18]. This phenomenon is linked to the degree of cristallinity. The higher the DR, the more important the degree of cristallinity and so the more restricted is the molecular mobility. The value of T_g is directly related to the macromolecular movements in the polymer. Therefore, the higher the cristallinity, the higher the energy necessary to move the chains in the amorphous phase. As a consequence, the temperature to pass from a glassy state to a rubbery state will be higher. The increase of T_g can be interpreted as a decrease of the content of amorphous phase, it can also be seen as the decrease of ΔC_p when DR increases (from 0.55 J/g/°C for sample 3 to 0.27 J/g/°C for sample 5).

3.1.2. Study of the relaxation enthalpy of PLA fibers

Glass transition of PLA fibers is always immediately followed by a broad endothermic peak which is related to the relaxation of macromolecules. This peak can be considered as the relaxation of macromolecules, which are blocked at the glassy state in a non stable conformation. So, just after the glass transition, the macromolecules have enough mobility to move and settle back to a more stable conformation. It is for an intermediate DR (DR=3) that the relaxation enthalpy is the most important (9.89 J/g, Table 1). For a higher DR (DR=4), relaxation enthalpy falls down to 1.49 J/g. So, the macromolecules seem to be highly blocked for an intermediate DR. For a lower DR, the macromolecules are stabilized in a state which scarcely evolves after the glass transition: the strains during the drawing are weak, so the molecules are not blocked in a non stable conformation. In opposition, for the highest DR, the strains are so important that the macromolecules are blocked and will not evolve much even if the temperature exceeds T_g.

The relaxation peak being just after the glass transition, its temperature follows the same trend as T_g when DR increases (Table 1). T_g increasing with DR, the consequence is an increase of the relaxation temperature.

For the samples with DR=3 or 4, there is a peak immediately after the relaxation peak which corresponds to the cold crystallisation peak (Fig. 2).

3.1.3. Cold crystallisation of PLA fibers during the DSC scans

For PLA fibers with low degree of cristallinity (sample 1 or 3), the cold crystallization peak is clear and sharp at 96 °C (Fig. 3). When DR increases, the cold crystallisation spreads on a wider temperature range (Fig. 4). The cold crystallization occurs just after the relaxation phenomenon, except for sample 4 where the maximum is at 100.1 °C. In comparison with sample 2, which undergoes the same hot drawing, the same cold crystallisation is not observed. The difference between the two products is the speed of the first roll before the hot-drawing. Actually, there is a pre-drawing between the dies and

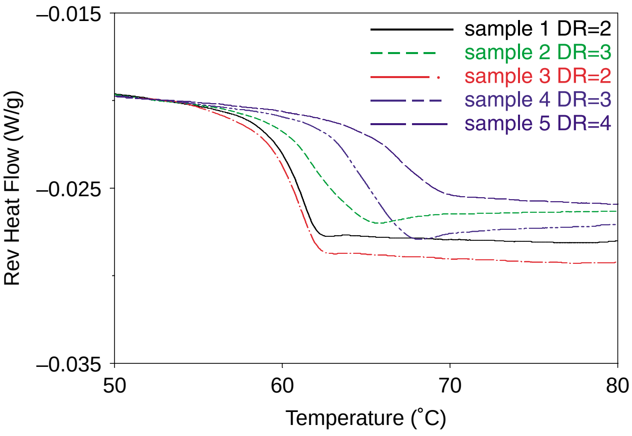

Fig. 1. Glass transition PLA fibers (reversing curves).

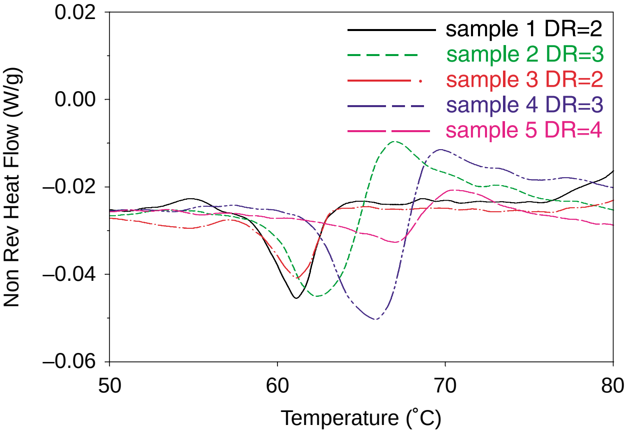

Fig. 2. Relaxation peak of PLA fibers (nonreversing curves).

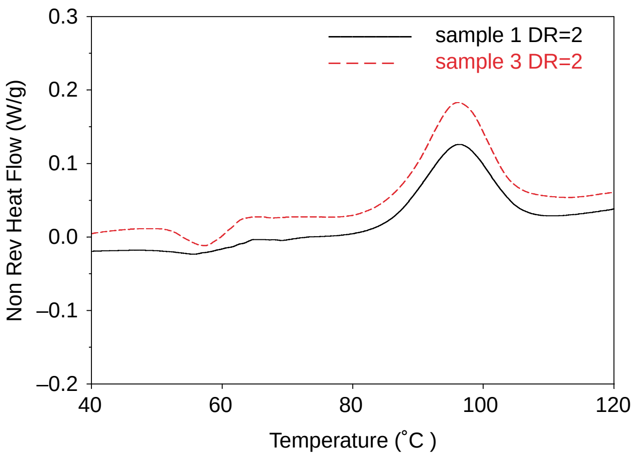

Fig. 3. Cold crystallisation of PLA fibers with low DR (nonreversing curves).

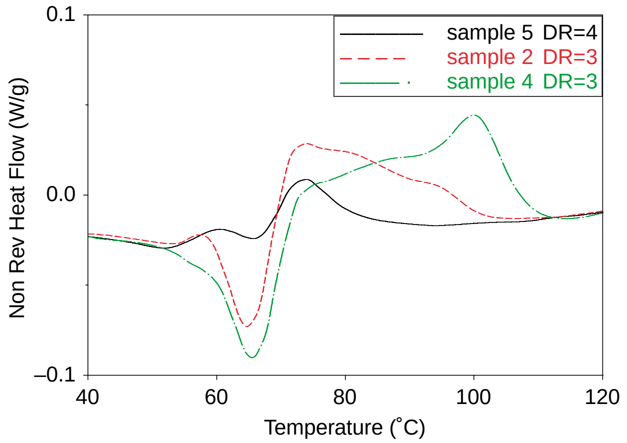

Fig. 4. Cold crystallisation of PLA fibers with high DR (nonreversing curves).

the first roll. So, the higher the first roll speed, the more important the pre-drawing.

So the higher the DR, the higher the decrease in the cold crystallization temperature and the lower the cold crystallization enthalpy. The drawing leads to an orientation of the PLA chains, which increases the degree of cristallinity. So PLA fibers which have undergone a high hot-drawing have a less important cold crystallization during the DSC scan.

3.1.4. Recrystallization and melting of PLA fibers

The study of the melting of PLA [20] showed the double-melting behaviour of poly(L-lactic acid). In general, the first endotherm is attributed to the melting of the original crystals, the second endotherm being attributed to the crystals formed or perfected during the DSC scan [21]. MDSC allows to see that some recrystallization phenomena occur as soon as PLA begins to melt. The Figs. 5–7 present the MDSC curves of sample 1, 4 and 5, respectively. For each sample, the beginning of melting can be observed just after the cold crystallisation peak on the reversing curves. At the same time, on nonreversing curves, a recrystallization that occurs during the melting can also be observed. So in order to calculate the initial degree of cristallinity, it is necessary to measure the area under the melting endotherm on the reversing curve and the area under the different exotherms of crystallization and recrystallization. The following equation gives the initial degree of cristallinity: $\chi = \Delta H_{\mathrm{m}} - \Delta H_{\mathrm{crys+recrys}}/93.6$, where χ is the degree of cristallinity, ΔH_{m} the melting enthalpy, $\Delta H_{\mathrm{crys+recrys}}$ the crystallisation enthalpy and 93.6 the melting enthalpy in J/g of 100% crystalline PLA [22]. This method is more precise, because with conventional DSC, the limits of integration are not always really precise because of the overlapping of the different phenomena. By separating the thermal events on a reversing curve and a non reversing curve, it becomes easier to determine the initial degree of cristallinity (Table 1). As expected, the degree of cristallinity increases with the DR up to 40.63% for sample 5, which undergoes the highest hot-draw rate. For sample drawn at low DR, the degree of cristallinity is low, which explains why glass transition and peak of cold crystallization appear more clearly than for fibers which have undergone higher drawing.

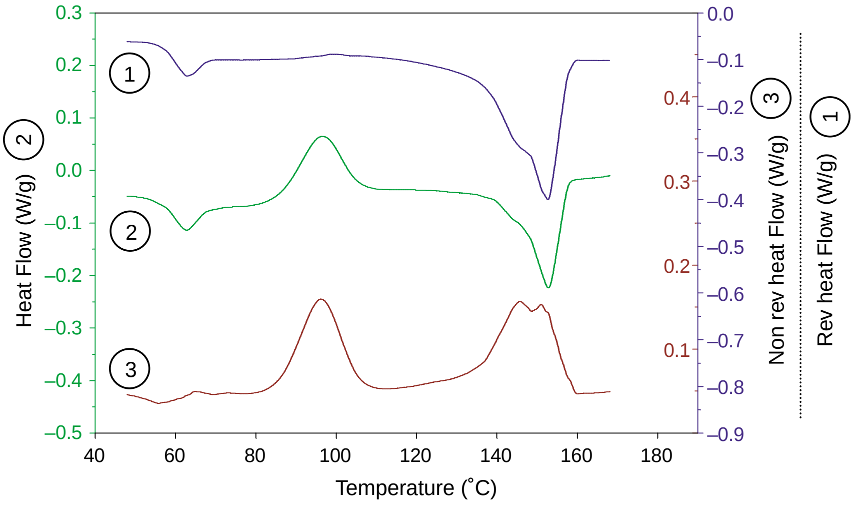

Fig. 5. MDSC curves of sample 1 (DR = 2).

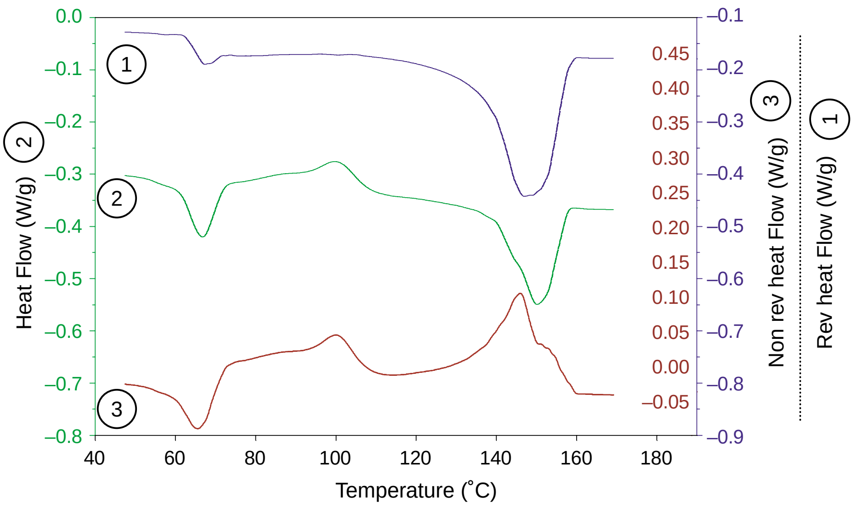

Fig. 6. MDSC curves of sample 4 (DR=3).

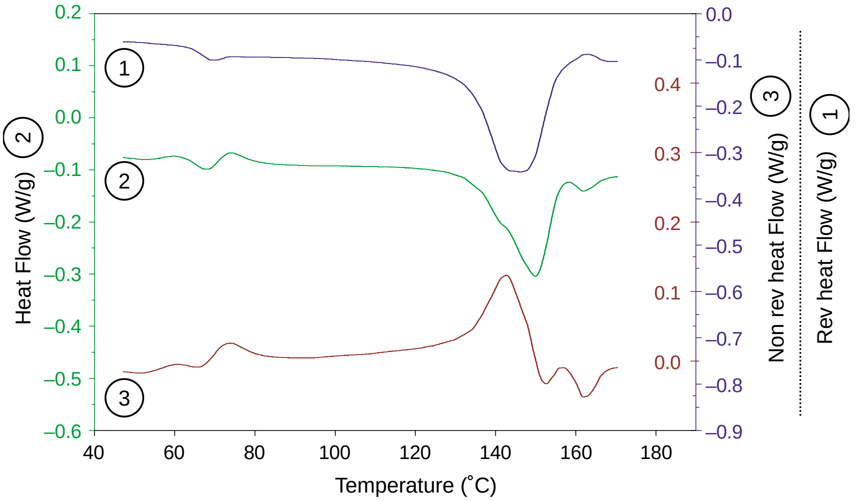

Fig. 7. MDSC curves of sample 5 (DR=4).

3.2. *Tensile properties of PLA fibers*

The drawing applied to filaments is known to improve the tensile properties of polymer. The drawing of the PLA filaments allows an alignment of the macromolecules in the drawing direction which provokes an increase of the Young's modulus and tensile strength. The sample 3, 4 and 5 (Table 2) shows this improvement. For a low DR (DR=2), the mechanical properties are low. The Young's modulus is 4.2 GPa and the tensile strength is only 280 MPa. For a higher DR, the Young's modulus is 5.7 GPa (i.e. an increase of 28.5%) and the tensile strength reaches 414 MPa (i.e. an increase of 47.8%). At the same time, the elongation at break decreases strongly when the DR increases. At low DR, the elongation at break is 138.3% for sample 3 and falls down to 53.3%.

The orientation of the PLA macromolecules have been demonstrated with the MDSC: an increase of the degree of cristallinity is observed with the DR, so it is consistent with the observed improvement of the mechanical properties of the PLA filaments.

Table 2
Tensile properties of PLA filaments

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Draw ratio between rolls	2	3	2	3	4
Speed roll 1	200	200	150	150	150
Speed roll 2	400	600	300	450	600
Diameter of filaments (μm)	52.09	45.5	56.4	52.5	46.4
Modulus (GPa)	4.7	5.3	4.2	4.7	5.7
Tensile strength (MPa)	258	350	280	319	414
Elongation at break (%)	117.1	56.4	138.3	75.9	53.3

4. Conclusion

Modulated differential scanning calorimetry is a very powerful tool to analyse the thermal events of strongly oriented polymer. For the first time, as far as we know, thermal characteristics of PLA filaments have been studied with this technique. It allows to determine more precisely the influence of hot drawing on glass transition, relaxation, crystallization and melting by analysing the reversing and non reversing curves. First, the separation of glass transition and relaxation allows to measure more easily the glass transition temperature, T_g being an important parameter which must be well known if the fibres are to be dyed. Then, the determination of the initial degree of cristallinity has been made easier since the crystallization and melting phenomena have been separated. So, the study of the different thermal events shows the strong influence of hot drawing. T_g increased with drawing ratio, while ΔC_p and temperature of cold crystallisation decreased, as a consequence of the increasing crystallinity rate. At the same time, the tensile measurements show an increase of the mechanical properties with DR, which can be explained by the molecular orientation of macromolecules.

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