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An insight on the process-properties relationships of melt spun PLA fibers

Abstract

Polylactic acid (PLA) fibers are receiving growing interest as one of the recent innovative materials being developed for various applications. The inherent biodegradability of PLA makes it highly attractive for biomedical and health care sectors. PLA fibers need to be partially and/or highly oriented to allow high performance and readiness for a wide range of manufacturability. In this study, the structure and properties of PLA fibers, manufactured at different spinning speeds, were studied. Laser diffractometer, polarized light microscopy, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were used to determine diameter, birefringence, molecular orientation, enthalpy and degree of crystallinity of as spun and drawn PLA fibers. The results of DSC and XRD exhibited that the degree of crystallinity of the PLA fibers is significantly improved for the drawn PLA fibers compared to the as spun fibers and leveled off in the case of changing the take up speeds of drawn fibers.

Key words: Biodegradable, Crystallinity, Orientation, PLA, Fibers

Introduction

Biodegradable materials have been given increasing attention in the last few decades. The biodegradable polymers degradation feature offers attractive advantage in contrast with the low recycle ratio of most plastics, such as polyethylene (PE) or polypropylene

(PP). Also, the obtained products from biodegradable polymers fit in the natural recycling processes [1, 2].

PLA is the first feasible thermoplastic fibers that can be produced from a plant-based renewable resources, such as corn and sugar cane, and extruded by conventional melt-spinning processing technologies. PLA successfully bridges the gap between synthetic and natural fibers, thereby expanding its application range, from medical and pharmaceutical to environmentally benign films and fibers for packaging, houseware, and clothing. PLA fibers have particularly attracted attention in commercial textiles due to its various advantages, such as ease of melt processing, unique property spectrum, renewable source origin, and ease of composting and recycling at the end of its useful life [3-4]. PLA has been intensively studied due to its biocompatibilty, sustainabilty, and environmentally-friendly characteristics, as well as its desirable physical and mechanical properties [5].

PLA is a biodegradable polymer with excellent mechanical properties, easy processability, and reasonable price. Many products such as shopping bags, mulch films, cutleries, office utensils, flower pots, yoghurt cans, and toothbrush handles can be made from PLA, which may also be used in medical and engineering applications [4, 6].

The building block of PLA is lactic acid that exist as optically active D- or L-enantiomers [7]. The decomposition of PLA occurs by hydrolysis, followed by biodegradation via bacteria [8], therefore PLA as nontoxic material can be absorbed by the human body. The mechanical and thermal properties of such fibers are strongly dependent on drawing speed and drawing temperature [9].

The birefringence measurement is a rapid and powerful tool for the study of morphological characteristics of deformed semi crystalline polymers and consequently the physical structure can be investigated accurately [10-12]. In particular the birefringence is mainly used to measure the degree of the molecular alignment in uniaxial oriented fibers that utilized in several structure techniques (Hamza, 2005). The optical properties include the birefringence of as spun isotactic polypropylene fibers with different draw-down ratios (DDR) were measured at different take-up speeds ranging from 200 m/min to 1000 m/min using different techniques such as WXRD, DSC, microinterferometry [13, 14].

The degree of crystallinity of polymer is a temperature-dependent physical property. Various analytical techniques can be used to measure the crystallinity, such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and nuclear magnetic resonance (NMR) measurement [15]. DSC is probably the most widely used techniques for measuring crystallinity of thermally treated polymers [16, 17].

In this work, PLA fibers are extruded at different spinning parameters, in particular take up and drawing speeds. The structural properties including birefringence of as spun and drawn PLA fibers were investigated using different techniques, such as polarized light microscopy, DSC and XRD.

Materials and methods

Melt spinning of fibers

In this work, a semicrystalline PLA polymer was used in this work. The polymer grade is 4032 and its molecular weight was $17.19X10^4$. The fibers melt spinning process was

carried out using a single Busschart extruder of diameter 35 mm with a spinneret of L/D ratio of 35:1. Extruder different zones temperature was 200°C and the die temperature was 210°C. A multifilament bundle spun by melt extrusion passed through a vertical air quenching system. Cooling of the filament was optimized by passing the multifilament through a distance of 6 m at a take-up speed of 1000 m/min. Figure 1 gives the schematic diagram of the fiber spinning. By changing the speed of the first roller set (R_1) different degrees of melt drawing were obtained. Drawing of fibers was achieved by varying the speed between R_1, the roller set (R_2) and roller set (R_3). The different roller sets are kept at room temperature T =25 ^oC except roller set 3 was kept at T= 70 ^oC to avoid the shrinkage of fiber induced. The drawing process under consideration is cold drawn process.

The as spun fibers are collected at the bottom of (R_1) without any drawing process by allowing filaments to go directly to the winder. The fibers after drawn were made when filaments were forced to pass through the godet station (R_1–R_5) and then to the winder. In this work, four samples were considered for investigation; as spun (reference) and three drawn fibers coded as D200, D400 and D600 formed at different speeds of take-up (200, 400 and 600 m/min) at R_1. The take-up speed ratio between the roller sets (R_5 : R_1) was (2 : 1) to allow further drawing.

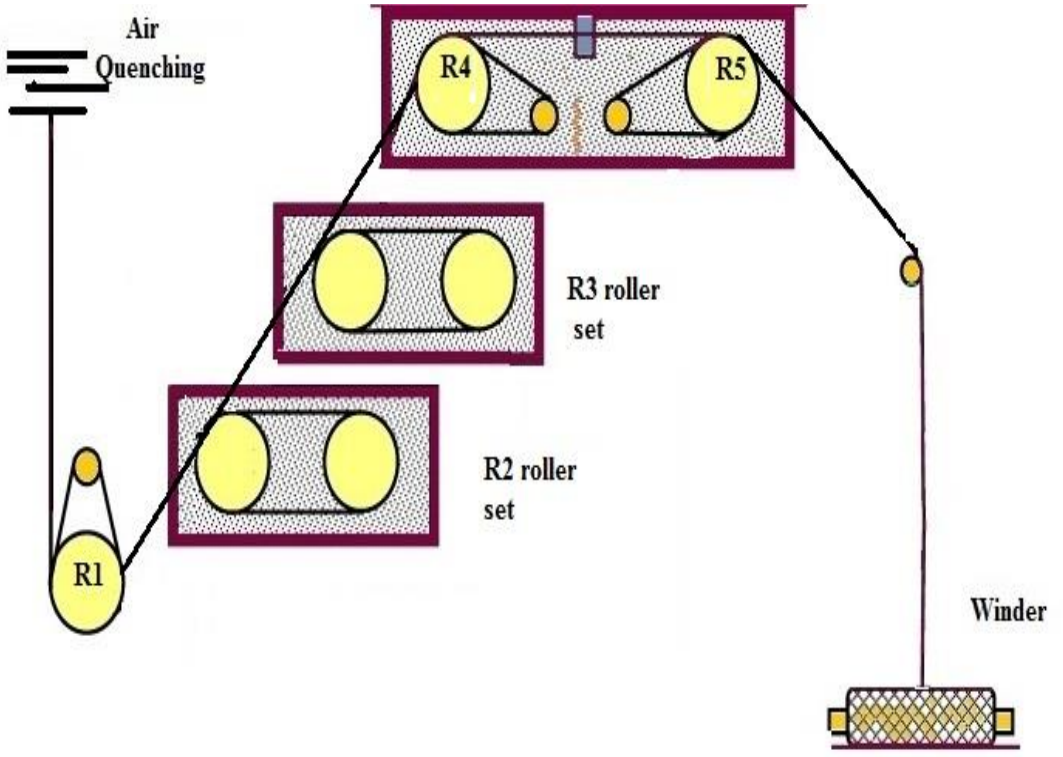


Figure 1**:** A schematic diagram showing the melt spinning set up used to manufacture PLA fibers**.**

Differential scanning calorimetry

The DSC (Differential scanning calorimetry) is a thermosanalytical technique in which measures the heat flow into or from a sample as it is either heated, cooled or under isothermal conditions. A Perkin- Elmer Diamond -1 DSC apparatus was used to determine the DSC thermograms of PLA samples. Samples of PLA fibers with weights 10-14 mg were analyzed using cycling heat and cool within the temperature range 40

ºC to 200 ºC at a heating rate of 10 °C/min. The measurements were collected under a nitrogen atmosphere. The degree of crystallinity was measured using the obtained enthalpy of fusion and the heat fusion of complete crystallization of PLA fibers using the following equation [18]:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0} \text{ x } 100 \qquad (1)$$

Where χ_c is the weight fraction crystallinity, ΔH_f is the enthalpy of fusion, and ΔH_f^0 is the heat fusion of complete crystallization of material at equilibrium melting temperature for PLA it was 93.7 J/g. [18].

X-Ray Diffraction technique

The microstructural properties of the PLA samples were measured using X-ray diffraction (XRD). A Brucke D8 diffractometer with (CuKα source, λ = 0.154 nm) radiation monochromatized with a graphite diffracted beam monochromator was used. The diffractograms for the PLA samples were recorded over a 2θ range of 10°– 60°. The total intensity of diffraction is the sum of crystalline and amorphous intensities regions, therefore the crystallinity of PLA fibers can be calculated using the following equation (6) [19].

$$\chi = \frac{\mathrm{A_{cry}}}{\mathrm{A_{cry}+A_{amp}}} \qquad (2)$$

Where A_{cry} the area enclosed under the crystalline peak. A_{amp} is the enclosed area under the amorphous peaks.

Results and discussion

Diameter measurements of PLA fibers

Laser diffraction phenomenon and set up (Figure 2) was used to determine the fiber diameter of the tested samples. The diameter of tested fiber (d) is determined using the following equation and figure 2:[20]

$$d = \frac{\lambda l}{a} \qquad (3)$$

where L is the distance between the fiber and the screen, a is the distance from the center of the first maximum of the diffraction pattern to the first minimum, and λ is the wavelength of the He–Ne laser beam used 632.8 nm. Figure 3(a-d) shows a selection of the obtained diffraction patterns of the tested PLA samples. According to the spinneret configuration, the extruded fibers exhibited circular transverse cross sections. Using the laser diffraction technique, the fiber diameter was measured at different orientation angles. The obtained transverse sectional shape of the samples under investigation were given in figure 3 (b). It is clear that the sectional area of the samples under investigation were circular sections.

The measured diameters of PLA samples are shown in Table 1. As expected the take up speed and drawing has a significant effect on the fiber diameter and its cross sectional area as the fiber diameter has been knocked down for example by ~ 90% in the case of D600 sample.

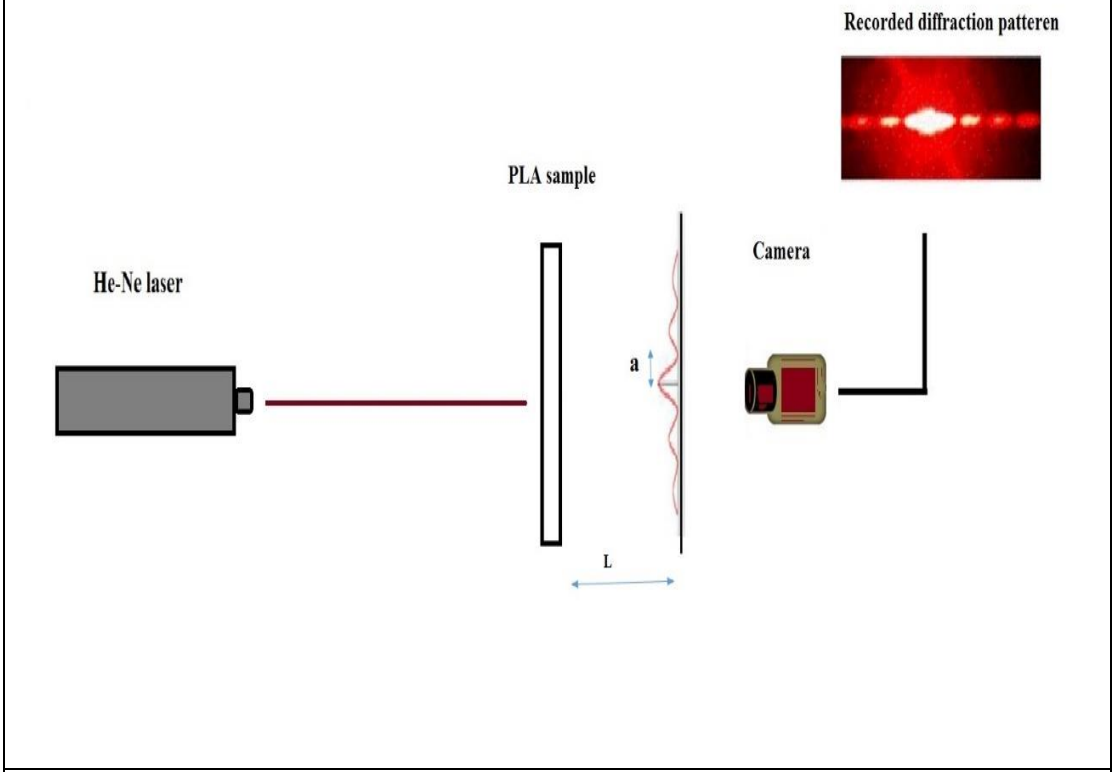
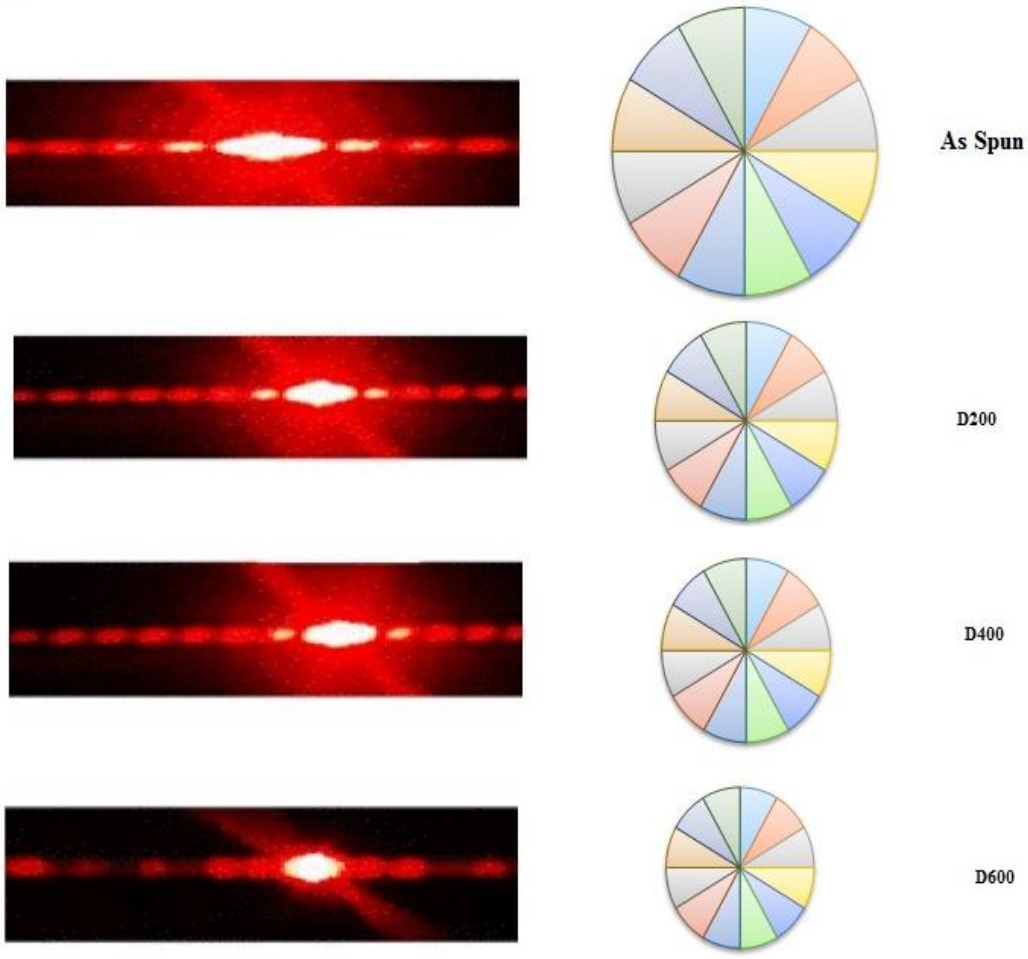


Figure 2**:** Show the experimental setup of laser beam diffraction pattern**.**



(a) (b)

Figure 3: shows a selection of the obtained diffraction patterns of PLA samples

Table 1: Measured diameter, linear density and shrinkage ratio of PLA fibers extruded.

Sample code	As spun	D200	D400	D600
Fiber diameter (µm)	340 ± 11.2	54 ±1.5	41.2 ±1.1	32.5 ±0.9
Linear density (dTex)	110.55 ±1.2	72.32±0.6	63.56±0.7	51.62±0.2
Shrinkage ratio (%)	5.34	13.90	14.60	15.40

The shrinkage ratio

The shrinkage of the sample under investigation can be measured using the following equation [21]:

$$S = \frac{(l_0 - l_1)}{l_0} x\ 100 \qquad (4)$$

Where l_0 is the sample length under tension, l_1 is the length after removing the tension. Table 1 gives the calculated data of the shrinkage ratio for the different samples, it is found that as the shrinkage ratio increases when the fiber becomes finer up on the increase of take up speed and the drawing impact. If these drawn fibers are allowed to shrink freely for a certain time, two processes occur. The first one is orientation of noncrystalline chains which decrease, the second process is the decrease in the crystallites thicken [Ref please].

Determination of the birefringence and molecular orientation of PLA fibers

Birefringence is a fundamental optical parameter. Measuring the birefringence of fibers can be consider as an indicator to the molecular orientation of the samples under consideration. To measure the birefringence of the tested sample polarized light microscope was used. Polarized light microscopes have a high degree of sensitivity to be used for quantitative and qualitative studies. The birefringence of PLA fibers was

measured using a polarized microscope called Axioskp 40 Pol/40 A Pol, Ziess. Birefringence can be assess using the Michel-Levy chart and the measured diameter of the sample under study. The Michel-Lévy chart is a rapid way of determining birefringence from the thickness and the maximum interference color it is displaying. Using Michel-Levy chart as produced by Zeiss the birefringence can be measured using the following equation [22].

$$\Delta n = \frac{R_r}{1000d} \quad (5)$$

Where R_r is the phase retardation and d is the fiber diameter. A sample was fixed on a glass slide with using a suitable adhesion material then transferred to the microscope stage. Adjusting the microscope until obtaining the colors. Using the calculated values of the fiber diameter given in Table 1 and the obtained color pattern formed, a diagonal line in the chart will be chosen according this data and its slope is $1/\Delta n$. When the fiber experienced further drawing during the melt spinning, the polymer chains including molecules will be rearranged and get orientated along the fiber axis, consequently the optical anisotropy or the birefringence will be improved. As shown in Figure 4 there is a significant difference between the birefringence of as spun and the drawn PLA fibers. Quantitatively, it is found that the birefringence of D600 sample improved by 26% compared to the as spun fiber. The difference between the birefringence values of drawn PLA fibers (D200, D400, and D600) is minimal owning to the highly molecular orientation achieved during the drawing of PLA fibers

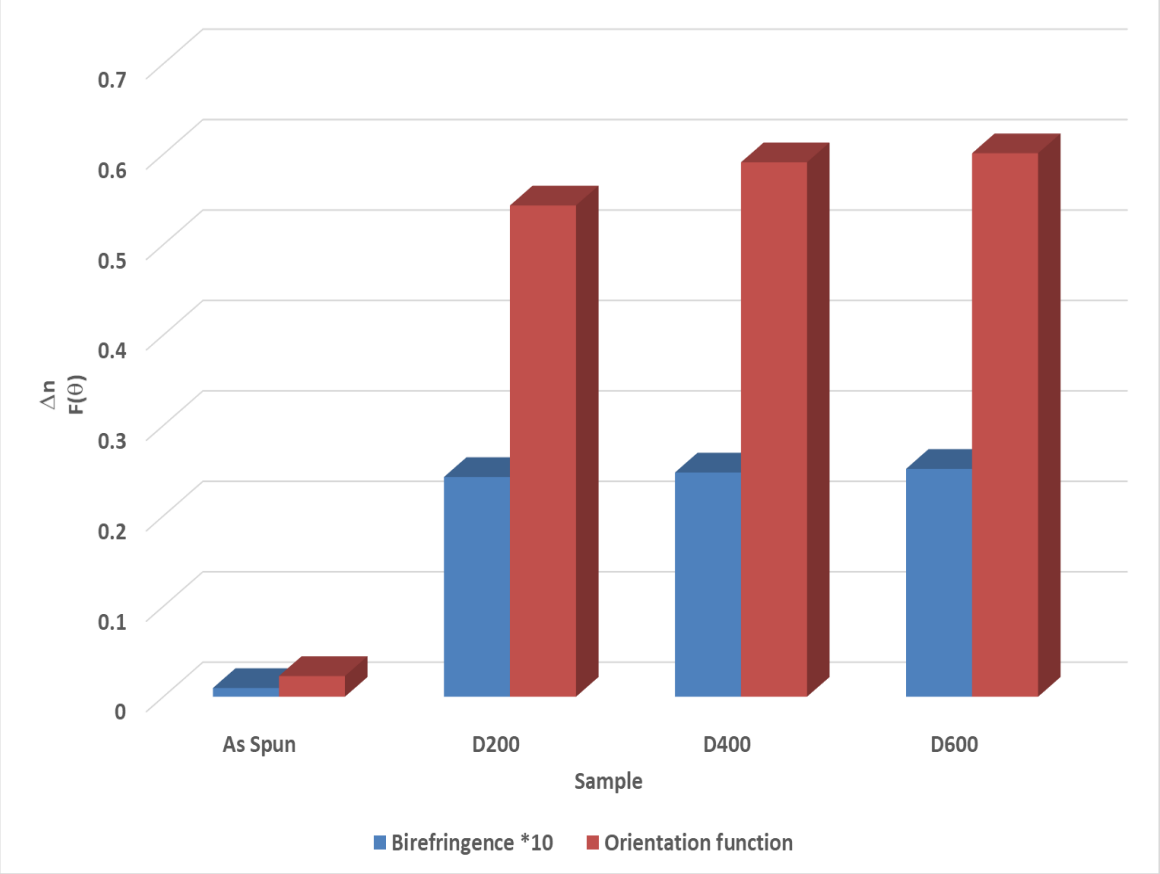


Figure 4: The measured birefringence and orientation function of PLA samples

The degree of molecular orientation of polymers mainly depends on the Herman's orientation factor that relates the oriented birefringence with the maximum intrinsic birefringence. The maximum intrinsic birefringence is defined as the maximum observable birefringence at complete orientation of the fiber [23], for PLA fibers the $\Delta n_{max} = 0.04196$ [24]. The molecular orientation of PLA samples under investigation were calculated using the following equation:

$$F(\theta) = \Delta n / \Delta n_{max} \quad (6)$$

As shown in Figure 4, the molecular orientation of PLA exhibited the same trend of the birefringence of PLA fibers drawn at different speeds.

The crystallinity measurements of PLA fibers

The heat flow thermograms obtained using DSC for different PLA fibers are presented in Figure 5. For as spun fiber, a glass transition shoulder and an endotherm of chain relaxation occurred at 62 °C. The melting crystallization exothermic and melting endothermic patterns obtained for the tested PLA is similar to virgin PLA studied by [25]. The melting crystallization temperature during melt drawing was decreased, and thereby the orientation of the polymer chains facilitated the crystallization for that kind of treatment. For drawn D600 no melting crystallization isotherm was detected. Thus, there was no more free amorphous chains to be crystallized during heating process. As shown in in Table 2, the glass transition temperature Tg increased slightly after drawing process, and there was no endotherm of chain relaxation for the other drawn samples (D200 and D400). The melting temperature showed no considerable variation with increasing the take up speed. Rahbar and Mojtahedi claimed that this might be due to the existence of crystals with lower perfection, size, and stability [26] . The heat of fusion is the energy required to overcome van der Waals' force to transform the disorder in a semicrystalline polymer when heated [27]. The heat of fusion can be considered as a measure of the fiber crystallinity [28]. It is clear that the take up speed did not show any variation in the heat of fusion.

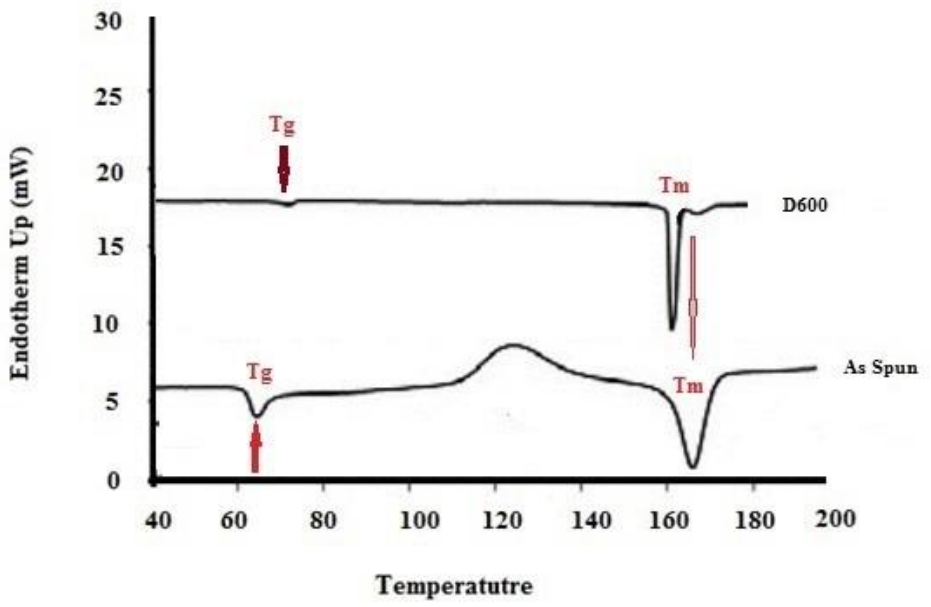


Figure 5: DSC thermograms of as spun PLA fibers and example of drawn PLA fibers: D600 sample

Table 2. DSC and XRD parameters of PLA fibers produced at different take up speeds

Sample code	Tg (°C)	T_m (°C)	ΔH_f (J/g)	X_{DSC} (%)	X_{XRD} (%)
As spun	62.6	165.3	33.5	25.75	14.5
D200	64.2	163.5	45.9	48.98	52.4
D400	65.6	161.3	44.4	47.38	53.21
D600	65.4	160.0	45.1	48.13	53.9

One of the most important features of semicrystalline plastics is the polymer's crystallinity degree. This refers to the overall level of crystalline component in relation to its amorphous component. The percent of crystallinity are related to many of the properties of semicrystalline polymer like: brittleness, toughness, modulus, optical clarity or creep. The calculated values of the crystallinity of PLA fibers samples with the aid of equation 1 are given in Table 2. As shown in Figure 6, the degree of crystallinity changed significantly due to the drawing and compared to the as spun PLA fibers. Thus, the drawing process enhanced the structural properties of PLA fibers. But the change in the measured crystallinity of drawn fibers D200, D400 and D600 at different take up speeds was insignificant. The DSC results showed that the spinning speed has insignificant effect on the fiber crystallinity in the case of drawn PLA fibers; D200, D400 and D600.

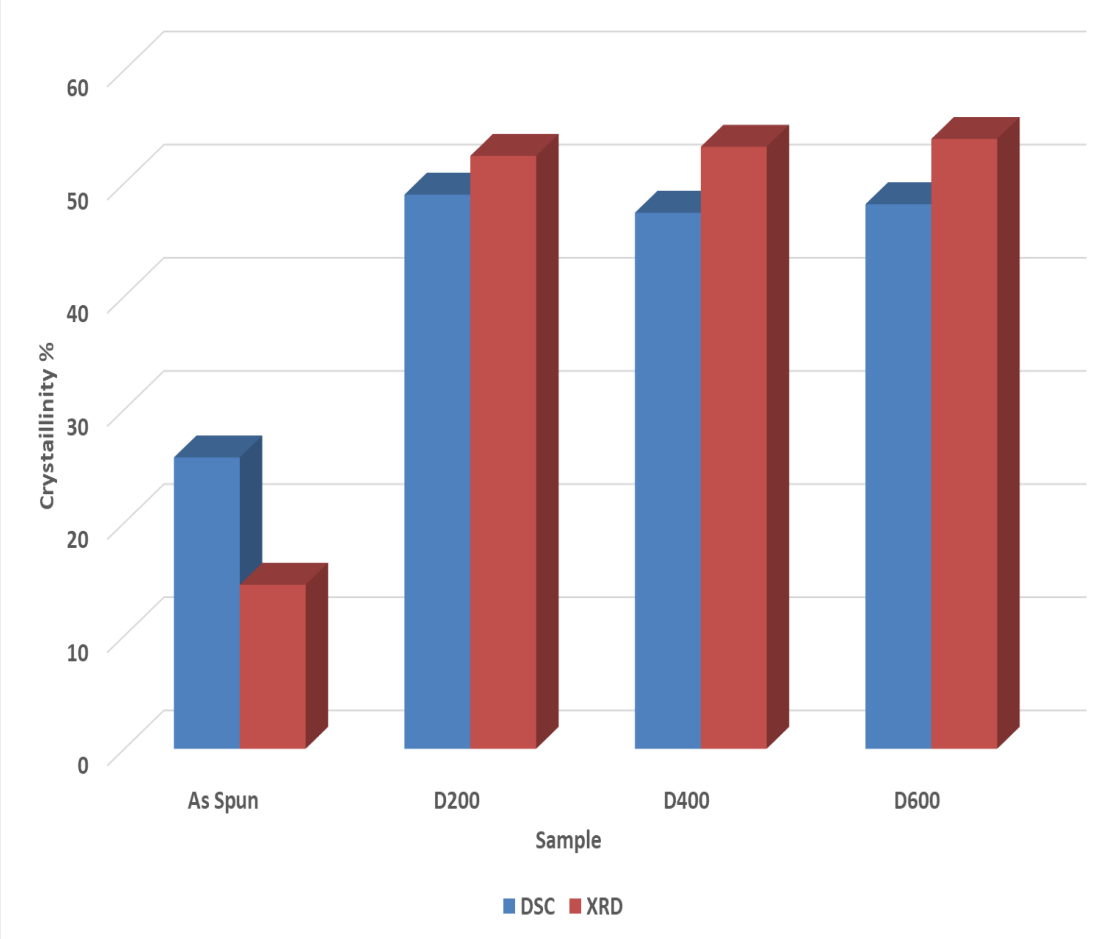


Figure 6: The obtained crystallinity values measured using DSC and XRD techniques.

The values of the crystallinity calculated using XRD technique with the aid of equation 2 was given in table 2. It is clear that the PLA fiber samples have the same diffraction patterns which mean that same crystal structure has been achieved in spite of the effect of take up speed. It is clear that the crystals with peaks positions of (020) and (110) were formed due to the drawing process applied to PLA samples. Similar to the DSC crystallinity results, the XRD measured crystallinity values showed that the drawing

process has significant effect on the structural properties of the tested PLA samples compared to the as spun samples. In case of drawn fibers. It is clear from the obtained structural properties that the take up speed has insignificant effect in this range of selected take up speeds. When the samples of PLA fiber under consideration are drawn at different take up speeds two processes take place. The first process is the non-crystalline chains become oriented. The second process is occurrence of crystallization.

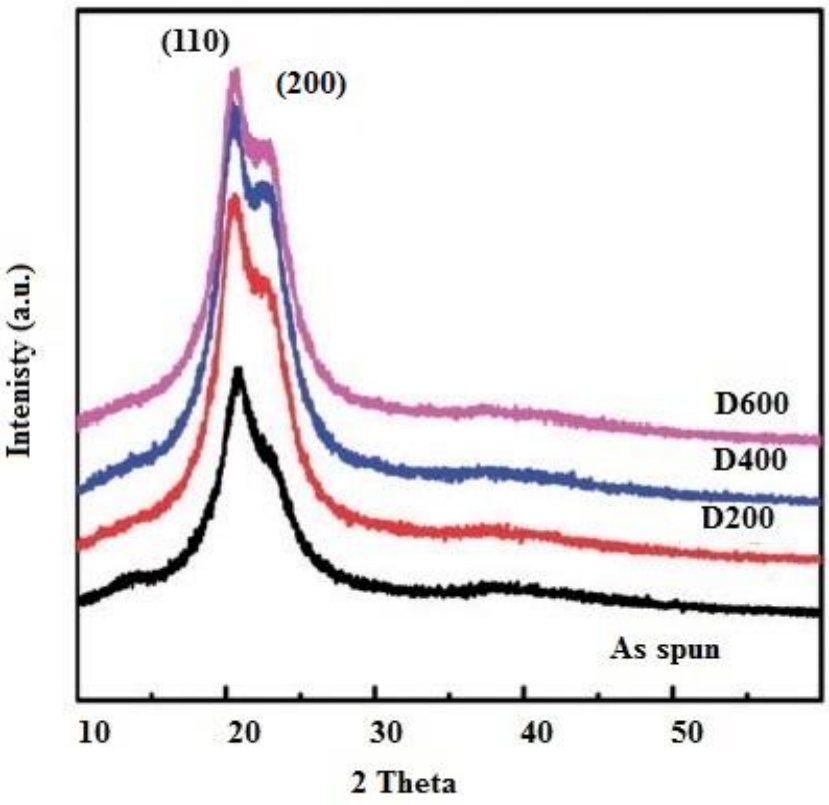


Figure 7: XRD diffraction patterns of obtained for as spun and drawn PLA fibers.

Conclusion

Melt spinning process was successfully used to extrude a set PLA fibers, as-spun and cold-drawn fibers at low take up speeds 200 m/min, 400 m/min and 600 m/min. The low spinning speeds were considered in this study to produce partially oriented PLA fiber which can me post drawn for further investigations. Polarized microscopy, DSC and XRD were successfully used to determine the physical properties of PLA fibers. The following remarks are concluded:

- The drawing has significant effect of the PLA fibers' characteristics.
- The diameter of drawn PLA fiber has significantly decreased by ~ 90% in the case of D600 sample compared to the as spun sample.
- The shrinkage ratio of PLA fibers increased when the take up speed increased.
- The birefringence, molecular orientation and the degree of crystallinity of PLA fibers are improved by the cold drawing.
- During the cold drawing, the take up speed has minimal effect on the properties of PLA fibers; D200, D400 and D600.

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Figure & Table captions

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Table 2. DSC properties of PLA fibers produced at different take up speeds

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