Biodegradable Fibers of Poly(L-lactide) Produced by High-Speed Melt Spinning and Spin Drawing

G. SCHMACK,[1] B. TÄNDLER,[1] R. VOGEL,[1] R. BEYREUTHER,[1] S. JACOBSEN,[2] H.-G. FRITZ[2]

[1] Institut fuer Polymer Forschung (IPF) Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany

[2] Institut fuer Kunststofftechnologie (IKT), University of Stuttgart, Böblinger Strasse 70, 70199 Stuttgart, Germany

ABSTRACT: A polylactide (PLA type LA 0200 K) was spun in high-speed melt spinning and spin drawing processes. The fibers were characterized with regard to the degree of crystallinity, the orientation, and the textile physical properties. The polymer was produced by a reactive extrusion polymerization process, and its hydrolytic degradation during the processes of drying and spinning and its thermal and rheological properties were characterized. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2785–2797, 1999

Key words: biodegradable polymer; polylactide; polylactide fibers; high-speed melt spinning process; spin drawing process

INTRODUCTION

Biodegradable polymers represent a new class of materials. Recently, they have gained more and more importance, even outside of biomedical applications.

One of the most promising biodegradable polymers is polylactide (PLA), an aliphatic polyester. PLA is of great interest from the viewpoint of environmental protection due to its mechanical property profile, its thermoplastic processability, and its biodegradability. More and more companies [e.g., Shimadzu Corp. (Lacty[R]),[1] Mitsui Chemicals (Lacea[R]),[2] Cargill Dow Polymers LLC (EcoPLA[R])[3]] are marketing PLA in addition to the established PLA of pharmaceutical quality.

PLA is produced using conventional chemical synthesis. The synthesis is basically possible in two ways, the polycondensation of lactic acid and the ring-opening polymerization of lactide. A higher molar mass can be reached by the polymerization concept. Lactic acid is in both cases the starting monomer. It is produced by means of bacterial fermentation from renewable resources. Pure L-lactic acid can be dimerized into L-lactide.

At the Institut fuer Kunststofftechnologie, University of Stuttgart, a novel polymerization process for the generation of PLA was developed in cooperation with the CERM University of Liège. This process allows the polymerization by means of reactive extrusion, starting from a catalytically initiated ring-opening procedure of lactide instead of the discontinuous batch process.[4]

In many potential textile technological applications (e.g., for nonwoven materials) the fiber forming process is of general importance. However, a more effective polymer synthesis also requires a more effective spinning process to reduce the cost that is still higher than common polymers.

In the last decade the morphology, thermal and mechanical properties, and degradation kinetics of PLA fibers have been studied intensively. Fambri et al.[5] compiled a list of present literature data of PLA fibers that were spun at quite different technological conditions (dry spinning, melt spin-

Table I Average Values of Molecular Parameter M_N, M_w, and M_Z, Molar Mass Distribution M_w/M_N, and Degradation Index from SEC Measurements

Samples	M_N (g/mol)	M_w (g/mol)	M_Z (g/mol)	M_w/M_N	DI
Virgin material	76,000	164,000	288,000	2.2	0.35
Fibers	56,000	113,000	186,000	2.0	

ning, spin drawing). In addition, the fibers partly showed a considerably large fiber diameter (up to 500 μm) that indicates the use of unconventional spinning devices (capillary rheometer), too. They assessed their quite low spinning and drawing rates of only a few meters per minute to be very critical, because that limits a possible extension for industrial application. Apart from technological differences, the reached levels of tensile strengths are also a function of the different mo-

lecular weights and the different chain compositions of the PLA polymers used.

It is well known[3] that the melting temperature and the degree of crystallinity of PLA polymerized from L-lactide can be controlled by the thermoplastic processing and by the insertion of D-lactic acid units and other monomer units[6] in the chain.

The broad range of the processing possibilities (extrusion, thermoforming, injection molding, in-

Figure 1 Dependence of the complex melt viscosity on the shear frequency of the dried and undried material and the as-spun fibers.

Figure 2 The time dependence of the viscosity function of the dried and undried material and the as-spun fibers.

jection blow molding, melt spinning, blowing film, extrusion coating, cast film) also requires a broad spectrum of different PLA provenances to realize the structure–property relations according to the relevant processing and thus their intended application.

The present study was carried out to investigate the PLA type LA 0200 K in the high-speed melt spinning and spin drawing process.

EXPERIMENTAL

Characterization of Polymer

The pelletized polymer (PLA type LA 0200 K, provided by IKT Stuttgart) was characterized with regard to its hydrolytic degradation during the process of drying and spinning and its ther-

mal and rheological properties to derive suitable parameters for the high-speed spinning and spin drawing processes.

The PLA type LA 0200 K is a copolymer of L-lactide (92 wt %) and *meso*-lactide (8 wt %).

Determination of Water Content

The water content of the pellets was determined by Coulometric titration at 120°C according to Karl Fischer. The samples were heated in an oven and the water was transported to the titration vessel. The water content of the undried PLA polymer was 0.255%. It was too high for a spinning grade. The water content for poly(ethylene terephthalate) (PET) is about 0.005% and it was also used for PLA in the drying process.

Figure 3 Cole–Cole plot of the material and the as-spun fibers.

Drying Conditions

The pellets were dried in a drum dryer at a temperature of 120°C under a vacuum for 16 h and afterward filled and kept under a nitrogen atmosphere.

Viscosity of PLA Solutions

The PLA was dissolved in chloroform and appropriate concentration series were produced. The relative viscosities of the solutions were measured at 20°C in an Ubbelohde capillary viscosimeter. The intrinsic viscosities 1.01 dL/g for the virgin material and 0.91 dL/g for the as-spun fibers were calculated from the relative viscosities according to an empirical relationship of Huggins. By means of the relationship[7]

$$\eta_{\text{int}} = 1.04 \cdot 10^{-4} M_v^{0.75}$$

the molecular weight M_v was estimated. The comparison between the estimated molecular weights of the dried PLA material and those of the as-spun fibers showed that in spite of the low water content of 0.005%, a polymer degradation takes places during the spinning process from the dried polymer (M_v = 207,000 g/mol) to the as-spun fibers (M_v = 180,000 g/mol), which is within the usual limits.[8,9]

Size-Exclusion Chromatography (SEC)

For the SEC the samples (pellets and as-spun fibers) were dissolved in chloroform. A Zorbax PSM Trimodal–S column was used for the separation. The detection was carried out by means of a differential refractometer (Detector RI/LS) at room temperature. Chloroform was used for elution, and a flow rate of 1 mL/min was applied. Because a product-specific calibration for the

Figure 4 The temperature dependence of the viscosity function of the dried and undried material and the as-spun fibers.

samples was not available, the number-average molar mass (M_N), the weight-average molar mass (M_W), the Z-average molar mass (M_Z), and the molar mass distribution (M_W/M_N) were calculated using calibrations with polystyrene molecular weight standards. For that reason the values have only relative character.

Table I gives the average values of the molecular parameter, the molar mass distribution M_W/M_N, and the degradation index (DI) = (M_{No}/M_N)$^{-1}$ resulting from the SEC measurements. The degradation index[9] is equal to the average number of chain scissions per number average of the initial macromolecules during the spinning process. The values illustrate the influence of the spinning process on the change of the molar mass, the molar mass distribution, and the extent of degradation. In spite of all the above-mentioned

Figure 5 DSC scan of the basic polymer: first heating to 200°C.

Figure 6 DSC scans of the basic polymer: first heating, first cooling, and second heating.

Figure 7 DSC scans of the high-speed spun fibers.

limitations concerning the relative character of the values, it can be derived that the virgin polymer has a relatively small molar mass distribution and the degradation during the spinning process is related mainly to the higher molecular proportions, which are characterized by the M_Z values. These data confirm the changes of the molecular weights determined using the viscosity measurements.

Dynamic Rheological Measurements

The oscillating measurements with polymer melts were carried out with dried and undried PLA polymers and as-spun fibers by means of a rotational rheometer (ARES, Rheometric Scientific, Inc.). The geometry chosen for these measurements was a plate/plate arrangement (plate diameter 25 mm, gap width 2 mm). The measurements were carried out under a nitrogen atmosphere at 170°C in a shear frequency range of 10^{-1} to 10^{+2} rad/s. In addition, the stability of the viscosity was determined by means of a time sweep over 15 min at 170 °C and 1 rad/s and a temperature sweep was recorded at a mean shear frequency of 1 rad/s and at a cooling rate of 5 K/min. The complex melt viscosity η^*, the storage modulus G', and the loss modulus G'' were determined.

Figure 1 shows the dependence of the melt viscosity η^* as a function of the frequency of the dried and undried material and the as-spun fibers. The measurements were carried out from the higher to the lower shear frequencies to determine the thermal degradation occurring during the measured time. The degradation of the polymers resulting in a viscosity decrease is over-

lapped by the decreases of the complex viscosity function as a result of the structure-viscous behavior. The decrease of the melt viscosity of the undried material (0.255% water content) at lower shear frequencies indicates a substantial degradation during the measurement. The dried polymer (0.005% water content) and the as-spun fibers show a zero shear viscosity. The zero shear viscosities were about 2270 Pa s for dried pellets and about 1070 Pa s for as-spun fibers.

The time dependence of the viscosity function (Fig. 2) confirms this different degradation behavior. It shows the strong degradation of the undried polymer (water content of 0.255%) and the moderate degradation and thus the relative stability of the dried PLA (water content 0.005%) and the as-spun fibers.

The storage and the loss moduli of the samples are shown in the so-called modified Cole–Cole presentation (Fig. 3), which is a correlation between

Figure 8 DSC scans of the spin-drawn fibers.

Figure 9   Crystallinity as a function of the take-up velocity and the draw ratio.

the storage and the loss modulus that complies with a different frequency in each point. It is independent of temperature and molecular weight. In the area of the high moduli the values of the dried polymers and the as-spun fibers coincide. In the logarithmic scale the function shows the usual linear slope of 0.5; in the range of lower moduli (i.e., in the terminal flow region) the deviation from the linearity increases because of the degradation, which is even more evident for the as-spun fibers.

Figure 4 shows the temperature sweep of the viscosity at an average shear frequency of 1 rad/s, which has been aborted in the glass-transition area. Besides the already discussed differences in the viscosity between the dried and undried materials and the as-spun fibers, in this figure the different step heights in the glass-transition area concerning the melt of the polymers and the as-spun fibers are characteristic. This suggests a postcrystallization in the as-spun fibers. Furthermore, the glass-transition area of the undried polymer is shifted downward by about 5 K.

Thermal Analysis by Differential Scanning Calorimetry (DSC)

The DSC measurements were carried out for the pellets and the fibers in a temperature range of −50 to +180°C and +40 to +180°C, respectively, with a heating rate of 20 K/min under nitrogen flow. The glass-transition area, the melt area, and the crystallinity were characterized.

Figure 5 shows the DSC scan of the virgin material in the range of 50–200°C. Apart from a small endothermic peak with a maximum at 64°C and an enthalpy of 3 J/g directly above the glass-transition area ($T_g = 57°C$), no melting area can be detected. This means that the basic polymer [a copolymer of L-lactide (92 wt %) and *meso*-lactide (8 wt %)] is amorphous and the strong crystallization tendency characteristic for poly(L-lactide) has been inhibited by the chosen kind of modification.

In order to determine the peak at 64 °C, the polymer was exposed to a defined first heating and cooling process and a subsequent second heating process in the range from −40 to +90°C. Figure 6 shows the corresponding scans. It can be clearly recognized that this peak manifests itself only in the first heating scan. The second heating scan above the glass-transition range only shows the usual relaxation peak. This means that the first peak results from a minor sublimation as is proved by the weight loss of the sample (1%).

Figure 10   Birefringence as a function of the take-up velocity and the draw ratio.

Spinning Experiments

High-Speed Spinning

The fibers were spun using a spinning device at the Institut fuer Polymer Forschung Dresden. The equipment consists of an extruder (18-mm screw diameter) with a spinning pump, and a spin-pack, three heated godets, and two winders for take-up velocities up to 2000 m/min and for the range of 2000–6000 m/min. To investigate the influence of the take-up velocity on the properties of the filaments, the mass throughput of the spinning pump was kept constant at 16.2 g/min to reach a homogeneous melt treatment up to the spinneret independent of the take-up velocity. The geometry of the extruder screw was chosen in the usual way for PET and the conditions of extrusion (temperature profile) were adapted according to the lower melting temperature of PLA type LA 0200K of 185°C. The spin pack contained two double filter screens. A 12-hole spinneret was used and yarns with 12 filaments were spun. The diameter of a single spinneret hole was 0.3 mm

and its length 0.6 mm. The filaments were moistened with a nonaqueous preparation (Silastol). The filaments were taken up by means of two winders in the ranges of 1000–2000 and 2000–5000 m/min.

Spin Drawing

The spin drawing was carried out using the same equipment. The filaments were taken up at about 200 m/min and were drawn between the first and the second heated godets. The temperatures of the godets were chosen in a way that the temperature of the first godet was above the glass-transition area (65°C) and the temperature of the second godet was in the range of the crystallization (110°C). The draw ratios were varied in a range of 4–6, which means that the velocities of the second godet were between 800 and 1200 m/min. Because of the crystallization, the length of the filaments varied so that a tension between the second godet and winder was necessary during spinning.

Figure 11 Elongation at break as a function of the take-up velocity and the draw ratio.

Characterization of Fibers

From the fibers produced using the different technologies the stress–strain curves and DSC scans were picked up and the birefringence was measured to show the correlation between the textile physical values, the degree of crystallization, and the orientation of the fibers.

Birefringence. The measurements of birefringence were carried out using a polarizing microscope and an Ehringhaus twin compensator.

Stress–Strain Measurements. The mechanical properties were measured by means of an Instron stress–strain universal tester (TF-CM) according to DIN 53834. Young's modulus, the physical break stress, and the elongation at break were calculated.

DISCUSSION

Figures 7–15 show the DSC scans of the high-

speed spun and the spin-drawn fibers the degree of crystallinity of the filaments calculated from the values of the melting enthalpy ΔH ($\Delta H = 93.6$ J/g for 100% crystalline PLA[10]), the birefringence Δn, the stress–strain curves, the elongation at break ε, the physical break stress σ, and the Young's modulus E in dependence on the spinning velocity v and the draw ratio DR, respectively. These values can be found in Table II.

Melting Enthalpy

The DSC scans of the high-speed spun and spin-drawn filaments are shown in Figures 7 and 8. The scans of the high-speed spun filaments show a range of glass transition between 52 and 54°C, a cold crystallization, and a melting peak. At spinning speeds of 1000 m/min we do not get a crystalline fiber within the spinning process. The crystallization only takes place during the heating process in the DSC. The difference between the cold crystallization and the melting peak is zero. With increasing spinning velocity, especially

Figure 12 Physical break stress as a function of the take-up velocity and the draw ratio.

in the range above 2500 m/min, a crystalline part of the fiber is being generated already during the spinning process, whereas the part resulting from the cold crystallization in the DSC is reduced and the beginning of the cold crystallization also shifts toward lower temperatures. At rising spinning speeds the degree of crystallinity increases. The increase of the degree of crystallization observed in the range between 3000 and 5000 m/min may be due to the orientation-initiated crystallization resulting from the higher spinning stress that is known from the usual spinning polymers.[11] Further investigation is needed to determinate this behavior in detail. Mezghani and Spruiell[8] found out in spinning experiments with PLA that there is a slight decline in the degree of crystallinity above 3000 m/min. This difference might be due to the use of different PLA provenances and spinning conditions.

The scans of the spin-drawn fibers (Fig. 8) show nearly no cold crystallization during the heating process in the DSC above the glass-transition range. The crystalline part in the fibers is being increased by the process of drawing and simultaneous thermal fixation, avoiding a cold

crystallization during the heating process in the DSC. The differences in correlation between the degree of crystallinity and the spinning speed and the drawing ratio, respectively, very clearly show the structural differences between the two types of fibers (Fig. 9).

Birefringence

The values of the birefringence (Fig. 10) of the high-speed spun PLA fibers are relatively low compared with polyamide (PA) and PET fibers. The function shows a slight increase at rising spinning speeds. In the range above 3500 m/min, again a decline of the values can be found; but due to the relatively low degree of crystallinity, it is not very pronounced.

The spin-drawn filaments have higher values of birefringence, because they have a higher degree of crystallinity in contrast to the high-speed spun PLA fibers.

Elongation at Break

The reached values for the elongation at break (Fig. 11) that are dependent on the spinning

Figure 13   Young's modulus as a function of the take-up velocity and the draw ratio.

speed are, in principle, lower compared to the PA, and at spinning speeds of about 5000 m/min they already reach values of 30%. The influence of the draw ratio on the elongation at break can be neglected.

Physical Break Stress

The physical break stress (Fig. 12) of the high-speed spun fibers changes only slightly at the given experimental conditions at a spinning

Figure 14   Stress–strain curves of the high-speed spun fibers.

Figure 15   Stress–strain curves of the spin-drawn fibers.

Table II   Physical Properties of High-Speed Spun Fibers and Spin-Drawn Fibers

v (m/min)	ε (%)	σ (MPa)	E (GPa)	Δn	ΔH (%)
1000	161.4	284	3.2	0.00332	0
1500	115.4	276	3.1	0.00467	0
2000	83.0	289	3.7	0.00582	0
2500	68.4	328	4.2	0.00661	1
3000	56.1	304	4.1	0.00812	6
3500	47.3	291	3.8	0.00940	10
4000	35.7	317	4.0	0.00899	1
4500	33.4	198	3.8	0.00818	4
5000	31.4	205	3.6	0.00835	11
DR					
4.0	33.7	211	4.3	0.01804	19
4.5	32.9	271	4.8	0.01950	20
5.0	28.3	343	5.4	0.02110	22
5.5	25.6	430	6.1	0.02312	21
6.0	19.7	460	6.3	0.02612	24

speed of 1000–4000 m/min. Above 4000 m/min it decreases. This can be correlated with the orientation behavior and the change of the crystallinity that is dependent on the spinning speed.

In contrast to this, the change of the draw ratio has a much stronger influence on the level of the physical break stress of the spin-drawn fibers. At a draw ratio of 6 a satisfying level of strength could be reached. The reason for the differences in the level of physical break stress of the high-speed spun and spin-drawn fibers is the different degree of crystallinity and the varying levels of orientation.

Young's Modulus

From the stress–strain curves of the fibers (Figs. 14, 15) it follows that in the range of small deformations the spin-drawn fibers are relatively rigid whereas the high-speed spun PLA fibers are quite soft. The high-speed spun fibers show a relatively broad drawing range that is characteristic for partly crystalline polymer fibers. In comparison to the usual fiber-forming polymers (PA 6, E = 2.7–3.6 GPa; PET, E = 10–13 GPa),[1] an average value for the Young's modulus can be stated. The course of the Young's modulus (Fig. 13) also represents the different structural levels concerning the orientation and degree of crystallinity between the high-speed spun and spin-drawn fibers.

SUMMARY

It was shown that the PLA type LA 0200 K, polymerized by means of reactive extrusion, can be spun both in a high-speed spinning process with a take-up velocity of up to 5000 m/min and in a spin drawing process up to a draw ratio of 6. The values for tensile strength, elongation at break, and Young's moduli reached in the spin drawing process confirm the values given in the literature[1,8] for PLA, although the melting temperatures and the degree of crystallinity of the PLA fibers used in our experiments were notably lower.

The results show that by reactive extrusion polymerization of PLA a degradable thermoplastic polymer can be provided in larger amounts. This polymer can be processed by more effective spinning technologies to fibers having attractive properties. This means that the polymer can be produced less expensively because its properties do not show the pharmaceutical quality of established PLA products.

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