High-Speed Melt Spinning of Various Grades of Polylactides

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ABSTRACT: Five kinds of polylactides (PLAs), with different D-lactide contents and tacticities, were subjected to high-speed melt-spinning experiments. In addition to stereochemical purity, the PLA types differed in molecular mass and molecular mass distribution. The properties of the different PLA materials were characterized by thermogravimetry, differential scanning calorimetry, dynamic mechanical analysis, size exclusion chromatography, and ^{1}H-NMR and ^{13}C-NMR spectroscopy. The material was spun with a high-speed spinning process within the range 2000–5000 m/min. The physical and tensile properties of the fibers were determined. The maximum tensile properties of the fibers were a 300 MPa tenacity at an elongation at break of 30% and a tensile modulus of 6.8 GPa. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 800–806, 2004

Key words: biodegradable; fibers; structure–property relations

INTRODUCTION

In the past decade, much attention has been paid to polylactide (PLA). This increasing commercial interest in PLA has resulted from the unique combination of biodegradability, thermoplastic processability, and the ecological advantage of the use of raw material from renewable resources. Consequently, PLA is one prominent alternative for the replacement of conventional petroleum-derived polymers with those from renewable materials. PLA offers great opportunities in a wide range of commodity applications such as packaging, disposable articles, and agricultural applications. However, the number of articles on melt spinning[1–7] and especially on the high-speed melt spinning[8–14] of PLA is limited.

This study was carried out to investigate the spinnability of different PLA types by a high-speed melt-spinning process because the fiber-forming process is of general importance for other potential textile technological processes, especially for the spunbonding nonwoven process. Five kinds of PLA with different D-lactide contents (*D*s) and different tacticities were investigated, and the following question was answered: which tolerances in molecular mass distribution (M_w/M_n, where M_w is the weight-average molecular weight and M_n is the number-average molecular weight) in correlation with low-molecular-mass contents could be accepted in a high-speed spinning process? The effects of different PLA grades and melt-spinning conditions on the development of the morphology of the fibers and on the orientation and the crystallinity in the filaments were determined. The achieved physical fiber properties were correlated with the polymer material and processing conditions.

EXPERIMENTAL

Characterization of PLA pellets

Poly(L-lactides) (PLAs) with different molecular masses and M_w/M_n values and different *D* values were studied. The different polymers, called PLA 1, PLA 2, PLA 3, PLA 4, and PLA 5, were characterized with regard to their thermal, rheological, and molecular properties to derive suitable parameters for the high-speed melt-spinning process. The PLA polymers were synthesized by ring-opening polymerization, and polymerization by means of reactive extrusion.

Thermogravimetry

The thermal stabilities of the dried polymers were investigated with a PerkinElmer (Überlingen, Germany) thermogravimetric system (TGS 7) under a nitrogen atmosphere at a heating rate of 10 K/min in the temperature range 30–700°C.

Dedicated to Prof. Dr. Habil R. Beyreuther on the occasion of his 65th birthday.

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TABLE I
Physical Properties of the PLAs

Polymer	D (%)	iii (%)	T_d (°C)	T_g (°C)	T_m (°C)	α (%)	η_0 (Pa s)	E_A (kJ/mol)	η_{int} (dl/g)	M_v (g/mol)	M_w/M_n
PLA 1	8	76	313	57	—	0	601	100	1.01	205000	2.2
PLA 2	3	97	156	52	162	0	1415	169	1.55	365000	7.7
PLA 3	3	88	254	61	161	40	777	97	1.35	305000	5.3
PLA 4	5	84	313	62	153	35	2604	61	1.69	410000	2.6
PLA 5	1	94	313	67	170	42	2167	63	1.67	405000	2.4

E_A = activation energy; η_{int} = intrinsic viscosity.
[a] Determined by SEC.

Differential scanning calorimetry (DSC)

The thermal analysis was carried out by means of DSC with a PerkinElmer DSC 7 calorimeter. The first heating scans of the PLA pellets were performed in the temperature range −60 to 250°C at a heating rate of 20 K/min under a nitrogen flow. (The first heating scans of the PLA fibers were performed in the temperature range 40–190°C under the same conditions.)

Dynamic mechanical measurements

The oscillating measurements on the melts were carried out with dried samples with a rotational rheometer (ARES, Rheometric Scientific, Inc., Piscataway, NJ). The geometry chosen for these measurements was a plate/plate arrangement. The measurements were carried out under a nitrogen atmosphere at 190 and 210°C in a shear frequency range of 10^{-1} to 10^{+2} rad/s.

Drying conditions

Before melt processing, the pellets were dried in a drum dryer at a temperature of 100°C under a vacuum for 16 h. The water content of the pellets was determined by coulometric titration. The water content of the dried pellets was about 0.005%.

The measurements of the viscosity of the solutions and size exclusion chromatography were carried out as described elsewhere.[11] Table I gives the average values of molecular mass determined by solution viscosity (M_v's) and the molar mass distributions.

^{1}H-NMR and ^{13}C-NMR

^{1}H-NMR and ^{13}C-NMR analyses were carried out with a DRX 500 NMR spectrometer (Bruker, Reinstetten, Germany) operating at 500.13 MHz for ^{1}H-NMR and at 125.75 MHz for ^{13}C-NMR. $CDCl_3$ was used as solvent, lock substance, and internal standard [δ (^{1}H) = 7.26 ppm and δ (^{13}C) = 77.0 ppm]. The spectra were measured at 303 K with sample tubes with outer diameters of 5 mm. The quantitative ^{13}C-NMR spectra were obtained with inverse gated decoupling, 30° pulses, and a pulse delay of 8 s.

High-speed spinning process

The fibers were spun with a spinning device at the Institut für Polymerforschung Dresden as described elsewhere.[11,12] The equipment consisted of an extruder with a spinning pump and a spin-pack, hopper, and winder. The mass throughput of the spinning pump was varied in correlation to the take-up velocity to reach a uniform filament diameter. Yarns with 12 filaments were spun. The filaments were taken up with a winder in the range 2000–5000 m/min.

Characterization of PLA fibers

DSC scans, birefringence, and stress–strain curves were performed to show the influence of the molecular characteristics on the resultant fiber structure, degree of crystallinity (α), orientation, and tensile properties.

The measurements of birefringence and the stress–strain measurements were carried out as described elsewhere.[11]

RESULTS AND DISCUSSION

Characterization of PLA pellets

Thermal stability

Figure 1 shows the dependence of the mass loss of the different PLA types on the temperature. The thermogravimetric studies demonstrated different thermal stabilities of the dried PLA types. The temperatures at which a mass loss of 1% occurred, the so-called degradation temperatures (T_d's), are presented in Table I. PLA 1, 4, and 5 exhibited thermal stability up to a temperature of 310°C, whereas PLA 2 had already started to degrade at 150°C. PLA 3 was stable up to a temperature of 250°C.

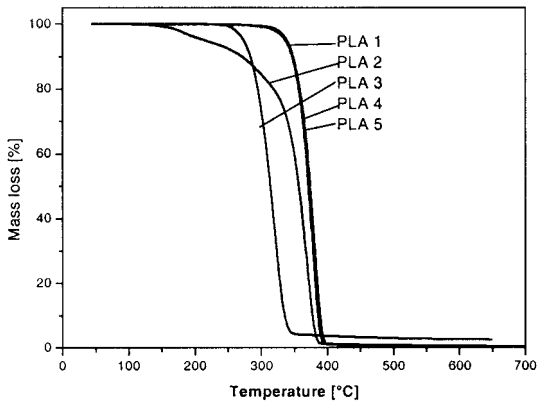


Figure 1 Mass loss (%) of the different PLA types versus temperature.

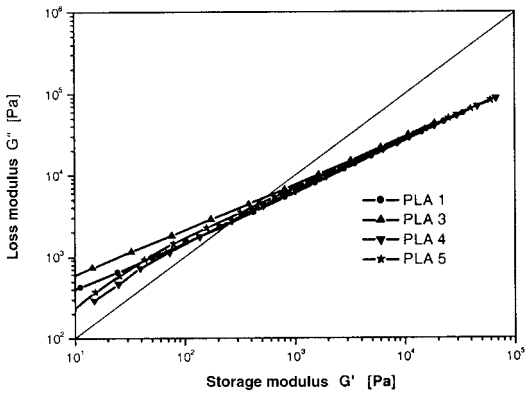


Figure 3 Modified Cole–Cole plot.

DSC

The stereochemical compositions of the PLAs, *D* values, and tacticities had an explicit effect on the melting temperature (T_m), rate of crystallization, and crystallinity.

Figure 2 shows the first heating scans of the PLA pellets. All of the DSC scans exhibited a glass-transition region. The glass-transition region for PLA 1 and 2 passed over to a sublimation peak, which indicated low-molecular-mass contents in the basic polymer and an incompletely finished chemical reaction. For PLA 1, no melting peak was detected. That means that pellets of PLA 1 were amorphous, and the strong crystallization tendency characteristic for PLA was inhibited by the high *D* of 8% used in the polymer synthesis. The pellets of PLA 2 were also amorphous. The cold crystallization took place only during the heating process in the DSC after the sublimation of lactide. The exothermic and endothermic peak areas were equal. The different T_m's and different α's of PLA 3, 4, and 5 were the result of the variable *D*s in the polymers and of the different M_w/M_n values. The glass-transition temperatures (T_g's) and T_m's and the crystallinity of the investigated PLA types are compiled in Table I. The α was calculated from the values of the enthalpies. The melting enthalpy of an infinitely large crystal was assumed to be 93.6 J/g.[15]

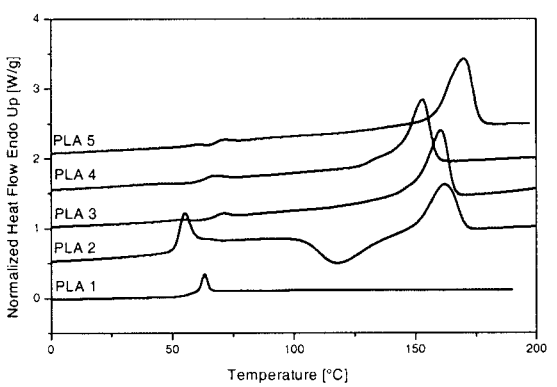


Figure 2 DSC scans of the first heating of the different PLA basic materials (in each case, the scans were shifted 0.5 units within the heat flow scale).

Rheological characterization

Each thermoforming process influences the structure and the properties of the obtained polymer samples in a different way. This is particularly pronounced for high-speed melt spinning because this process puts extremely high demands on the deformation ability of the melts at high deformation speeds. The tensile stress within the fiber formation zone is a very important factor for reaching a high orientation and crystallinity. It acts against the rheological force, which consists of elastic and viscous parts of strain, equivalent to the storage (G') and loss (G'') moduli, respectively. This ratio may be seen as one important factor for the spinnability of polymers. For commercially used spinnable polymers, the ratio is about 10.[16] The master curves of G'' versus G' of the single PLA types are shown in the so-called modified Cole–Cole plot (Fig. 3). A straight line was marked, corresponding to $G''/G' = 10$. The master curves of the single PLA types were only in the high modulus range below this straight line.

As shown in Figure 4, the complex viscosity functions were represented at 190°C. For a good spinnability, the melting viscosity in the die should be in the range of about 100–450 Pa s. For PLA 2, this viscosity was achieved at about 200°C, considerably above its T_d. The spinning temperatures at the aforementioned spinning viscosities were calculated with the Arrhenius equation. The activation energies (see Table I) were determined from the temperature dependence of the viscosities.

The zero-shear viscosities (η_0's) are compiled in Table I. They were calculated from the complex viscosity functions as threshold value by a zero-shear fre-

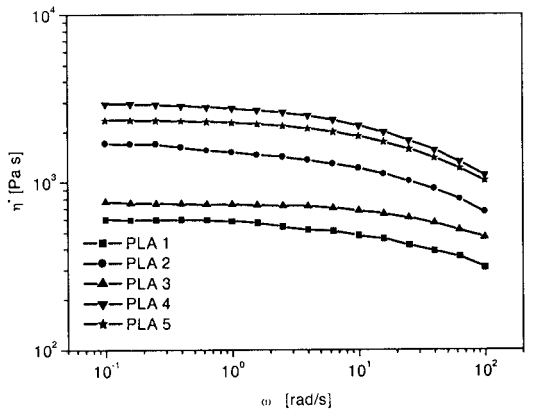


Figure 4 Dependence of the complex melt viscosities (η^*) on the shear frequency (ω) of the different PLA basic materials.

quency. The complex viscosity functions and the η_0's showed considerable differences between the individual PLA types 1–5, which essentially correlated with the obtained molecular masses (see Table I).

NMR spectroscopy

The structure of the PLA types, their tacticity, and the low molecular mass impurities were investigated by NMR spectroscopy before and after the spinning process.

These spectra were recorded for clarification of the great differences in the polymer properties between PLA 2 and the other PLA types. The following question had to be answered: which tolerances in M_w/M_n in correlation with low molecular mass contents could be accepted in the high-speed spinning process? The NMR spectra of PLA 3, 4, and 5 did not show large differences. Hence, a comparison of these spectra is not shown. For example, two regions from the ^{1}H-NMR and ^{13}C-NMR spectra, the spectra of PLA 5 and PLA 2, are presented in Figure 5(a–d). All five PLA types were predominantly isotactic. The polymer tacticity was characterized by the content of tetrads (*iii*) determined from integration of the region of the carbonyl carbons in the ^{13}C-NMR spectra, according to the assignments given by Bero et al.[17] [Fig. 5(c,d)]. The order of *iii* (Table I) corresponded well with the D-isomer content determined by DSC, except for that of PLA 2.

Oligomers proved by NMR spectroscopy for PLA 2 [Fig. 5(a)] caused a lowered T_m so that the correlation between T_m and D was no longer valid. The oligomer content in PLA 2 was the reason for the great differences in polymer properties between PLA 2 and the other PLA types.

During the high-speed spinning process, different chemical reactions, for example, transesterification or postpolymerization, may result in changed material properties. No structural changes were observed within the accuracy of the NMR measurements, except for in PLA 2. Here, the oligomer content was slightly reduced, possibly by postpolymerization reactions or sublimation during the spinning process.

Characterization of PLA fibers

Spinnability

High-speed melt spinning was possible for the PLA 1, 3, 4, and 5 in the range of about 2000–5000 m/min. The spinnability of PLA 2 was extremely restricted. The effects of different PLA types and melt-spinning conditions on the development of the morphology of the fibers, the orientation, and the crystallinity in the filaments were determined and the following results were received.

Crystallinity

The DSC scans of the high-speed-spun PLA filaments are shown in Figure 6(a–e). All of the scans showed a range of glass transition at about 52–67°C, a cold crystallization, and a melting range. The cold crystallization took place only during the heating process in the DSC. With increasing spinning velocity, the beginning of the cold crystallization was shifted toward lower temperatures, the cold crystallization range decreased, and the α increased. That indicated a higher orientation in the fibers and, thus, a higher degree of orientation-initiated crystallization.

The dependence of α of the high-speed spun PLA filaments on the take-up velocity is shown in Figure 7.

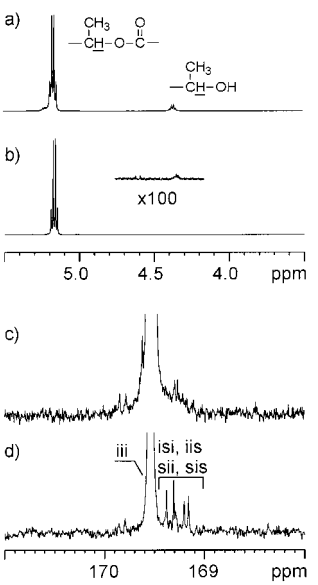
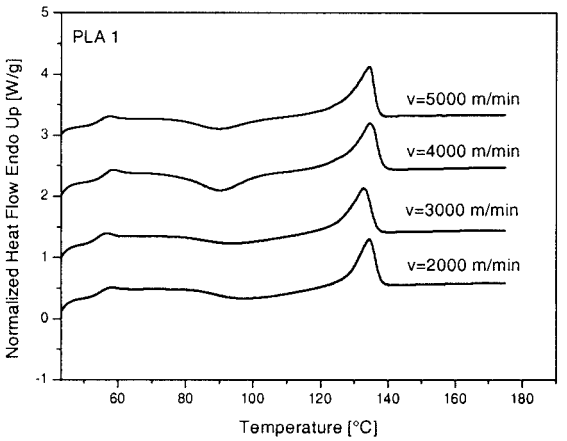
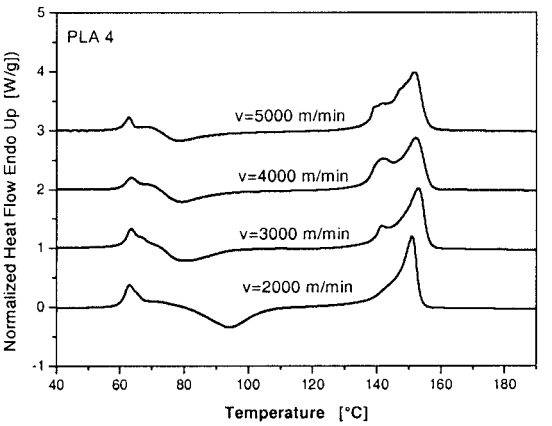


Figure 5 ^{1}H-NMR spectra (CH region) and ^{13}C-NMR spectra (carbonyl carbon of PLA) of (a, c) PLA 2 and (b, d) PLA 5.



(a)



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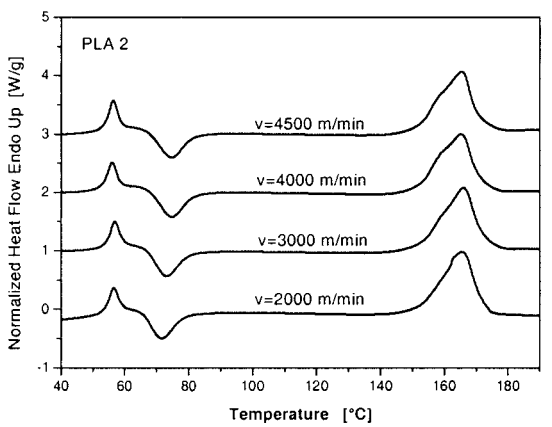
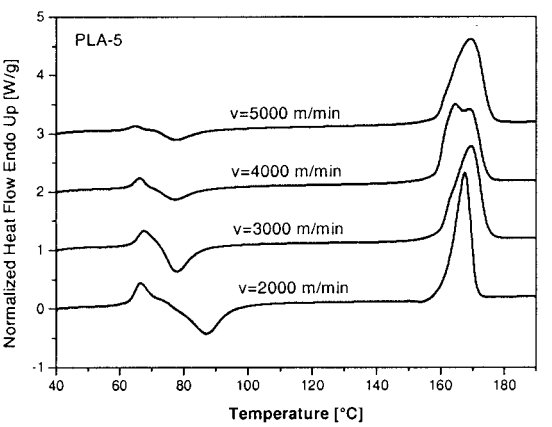
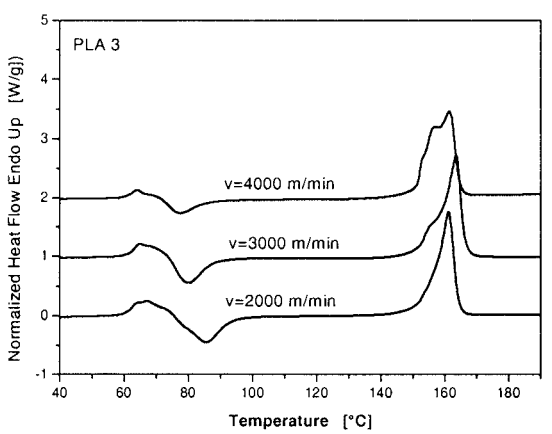


(b)



(e)



(c)

Figure 6 DSC scans of the PLA fibers spun at different speeds (in each case, the scans were shifted 1 unit within the heat flow scale).

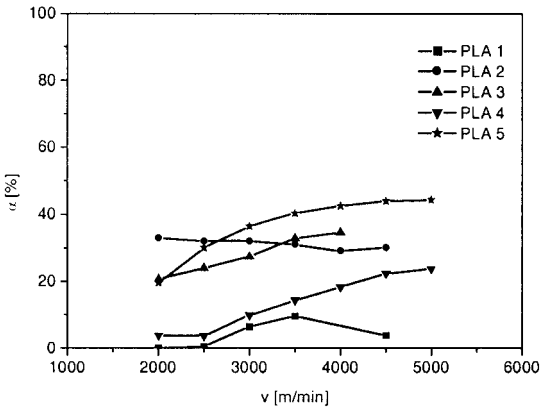


Figure 7 Dependence of degree of crystallinity (α) on the take-up velocity (v) of the different PLA fibers.

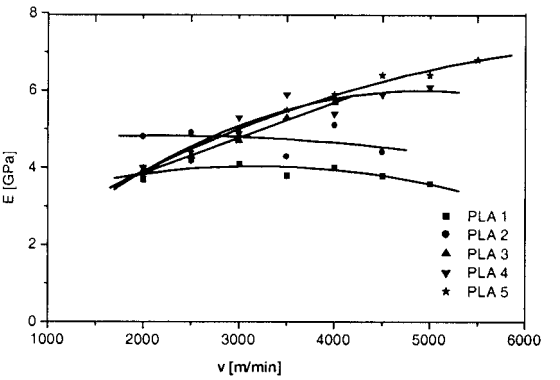


Figure 9 Dependence of tensile moduli (E) on the take-up velocity (v) of the different PLA fibers.

First, there was a correlation between α and Ds of the different PLA fiber types. Second, the crystallinity of the PLA fibers was influenced by the take-up velocity. The increase in α observed in the range 2500–5000 m/min was a result of orientation-initiated crystallization. This phenomenon is known to take place at higher spinning stresses for other commonly used spinning polymers.[18]

In spinning experiments with PLA, Mezghani and Spruiell[9] found a slight decline in α above a spinning speed of 3000 m/min. The difference in our results might have been due to the use of different PLAs, the different titer, and other spinning conditions (an air drag device). In contrast to our experimental setup, the fibers could freely relax in the setup of Mezghani and Spruiell.[9]

Birefringence

The birefringence of the different PLA fibers are shown as function of take-up velocity in Figure 8. The curves of PLA 1, 3, 4, and 5 showed a slight increase at rising spinning speeds. The variation of birefringence with the spinning speed was similar to that of the crystallinity of the different PLA fibers. For PLA 1, a decline in the values was found in the range above 3500 m/min; which was not very pronounced because of the relatively low α. The birefringence of PLA 2 fibers was independent of the take-up velocity.

Tensile properties

The dependence of the tensile properties, tensile modulus, elongation at break, and tenacity, on the take-up velocity is shown in Figures 9–11. Correlations were seen between the structural and molecular properties of the pellets and the tensile properties of the fibers. PLA fibers 4 and 5, with a higher molecular mass and a narrower M_w/M_n, reached the highest tensile moduli and tenacities. The high D in combination with a low molecular mass caused the low textile physical values of PLA 1. However, a broad M_w/M_n combined with unreacted low molecular mass contents extremely hindered the spinnability, as proven in the case of PLA 2.

The values for the elongation at break (Fig. 10) changed in the range of spinning velocities of 2000–5000 m/min from about 80 to 30%. The elongation values of the different PLA fiber types were almost

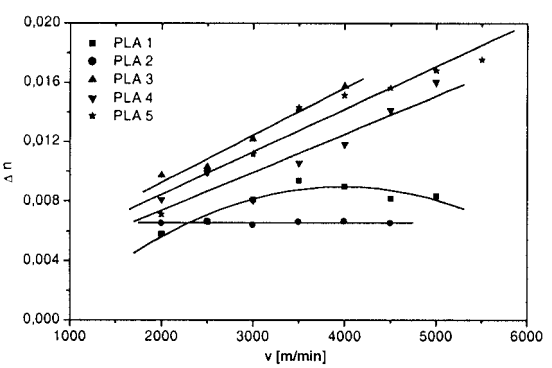


Figure 8 Dependence of birefringence (Δn) on the take-up velocity (v) of the different PLA fibers.

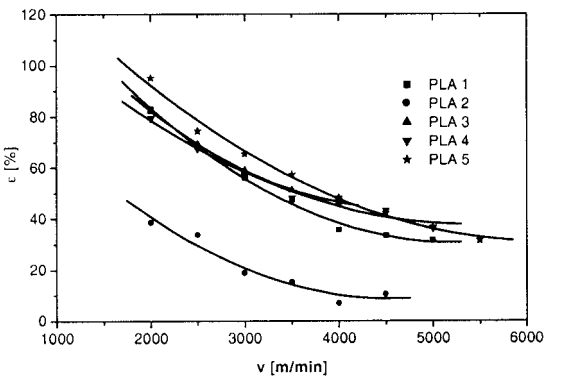


Figure 10 Dependence of elongation (ε) on the take-up velocity (v) of the different PLA fibers.

identical, except for PLA 2, an indication for a similar orientation.

Figure 12 shows the distinct dependence of the tenacity of the fibers spun by a take-up velocity of 4000 m/min on the molecular mass for PLA types 1, 3, 4, and 5. The deviation of the fibers made from PLA 2 were attributed to the extremely broad M_w/M_n.

CONCLUSIONS

Five types of PLAs with different *D*s and different tacticities were subjected to high-speed melt-spinning experiments. The PLA types differed in stereochemical purity, molecular mass, and M_w/M_n. The effects of polymer properties and melt-spinning conditions on the development of the morphology, orientation, and crystallinity of the filaments were determined. The textile physical fiber properties achieved were correlated with the polymer materials' properties and the spinning conditions.

The decisive factors regarding spinnability were the molecular mass and the M_w/M_n of the PLA types. The spinnability was realized for the investigated PLA 1, 3, 4, and 5 in the range 2000–5000 m/min. The spinnability of PLA 2 was extremely restricted because of the broad M_w/M_n in correlation to unreacted low molecular mass contents.

α, which was influenced by *D* and the extent of orientation-initiated crystallization, had a decisive influence on the tensile properties of the investigated PLA fibers.

The tensile moduli of PLA 3, 4, and 5 were relatively high so that the fibers were relatively rigid, whereas the tensile moduli of PLA 1 was low, resulting in softer fibers. The values of tenacity and elongation at break of PLA 1, 3, 4, and 5 were in the range of textile fiber applications, for example, by a spunbonding nonwoven process.

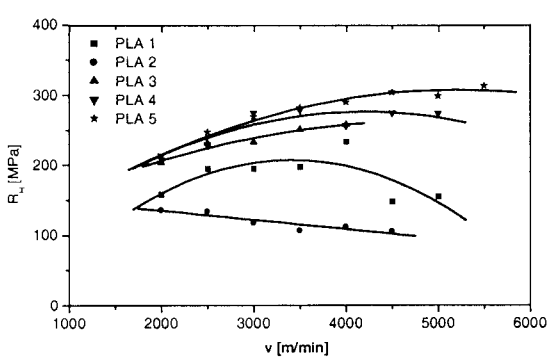


Figure 11 Dependence of tenacity (R_H) on the take-up velocity (v) of the different PLA fibers.

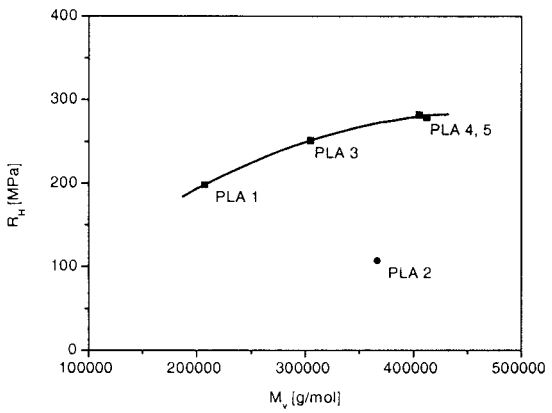


Figure 12 Dependence of tenacity (R_H) on the molecular mass (M_v).

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