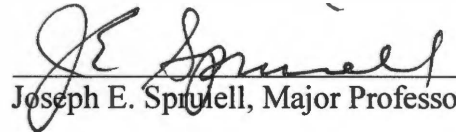
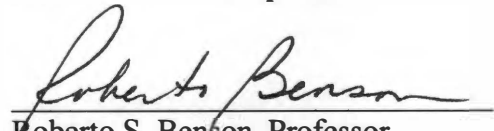


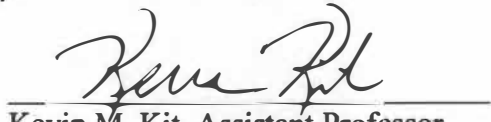
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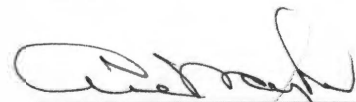

Joseph E. Spirell, Major Professor

We have read this thesis and
recommend its acceptance:


Roberto S. Benson, Professor


Kevin M. Kit, Assistant Professor

Acceptance for the Council:


Vice Provost and Dean of
Graduate Studies

**ON THE FINE STRUCTURE
OF POLY(L-LACTIC ACID) FILAMENTS**

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee, Knoxville

Xiaoyun Ling

August 2003

Thesis
2003
.L56

DEDICATION

This thesis is dedicated to my dear parents, Guoqing Ling and Yayuan Jiang, for their encouragement and support, and also to my dear husband, Kenneth M. Keilman, for always seeing my potential, believing in me and being there for me during the difficult times.

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ABSTRACT

Poly(lactic acid) (PLA) is finding many new applications beyond its early use in bioabsorbable sutures. Consequently, there is considerable worldwide interest in understanding the relationship between processing, structure and properties for PLA. There is relatively little discussion in the literature about the best methods to determine such important characteristics as degree of crystallinity and the amount of molecular orientation present in processed PLA materials. And many physical constants for this polymer are either not available, or they exhibit a considerable variability among the various groups that have attempted to measure them. It is with this in mind that the present study was undertaken.

The context for the study was the need to characterize the fine structure of PLA fibers. But in view of the current state of understanding of the characteristics and the methods of characterizing PLA, the study became a much broader one which involved finding appropriate means to measure the important structural characteristics (including an understanding of associated errors) and to measure some of the necessary parameters needed in future studies of PLA. Attempts were made to establish the following quantities for PLA: (1) amorphous density, (2) 100% crystalline density, (3) the intrinsic transverse moduli of the amorphous and crystalline phases, and (4) amorphous and crystalline intrinsic birefringences.

The amorphous density was determined by directly measuring the density of an amorphous fiber that was prepared by melt spinning with no drawdown force other than gravity. This gave $\rho_a = 1.2503 \pm 0.002 \text{ g/cm}^3$ for the amorphous density.

The crystalline density was calculated from the mass and volume in the unit cell of PLA. An X-ray diffraction pattern of a highly oriented PLA rod was indexed as the orthorhombic α -phase with lattice constants: $a = 10.57 \pm 0.084 \text{ \AA}$, $b = 6.13 \pm 0.007 \text{ \AA}$, $c = 28.91 \pm 0.017 \text{ \AA}$. This cell contains 20 monomer units, which gives the 100% crystalline density $\rho_c = 1.2762 \pm 0.0013 \text{ g/cm}^3$. This value is near the mean of previous values published in the literature.

The intrinsic transverse elastic moduli of the crystalline and amorphous phases were obtained from measurements on a series of unoriented (random) samples that contained a range of degrees of crystallinity. The values obtained were $E_{t,am}^o = 2.72 \times 10^{10} \text{ dynes/cm}^2$ and $E_{t,c}^o = 4.12 \times 10^{10} \text{ dynes/cm}^2$.

These values were used in characterizing the structure of melt spun fibers in both the as-spun condition and after annealing. Two PLA samples having similar molecular weight but slight difference in the D-isomer content (0.8% versus 1.3%) were melt spun at high speeds. One sample called PLLA1 (0.8%D) was spun at 223°C while the second sample called PLLA2 (1.3%D) was spun at 208°C. The crystallinity and orientation development of the as-spun and annealed fibers were then studied by means of differential scanning calorimetry (DSC), density gradient column (DGC), optical birefringence, wide angle x-ray diffraction (WAXD) and sonic modulus.

X-ray pattern analysis of both as-spun and annealed fibers suggests that all of them are α phase PLLA, which is commonly observed in melt spun PLA fibers.

The higher extrusion temperature of processing PLLA1 compared to PLLA2 leads to lower spinline stress and stress-induced crystallization due to lower viscosity

at the upper part of the spinline. Moreover, higher extrusion temperature results in larger extent of thermal degradation of PLLA1 than PLLA2 and the resulting lower molecular weight was expected to further lower the spinline stress during preparation of PLLA1 fibers. Due to the higher stress in the spinline of PLLA2 compared to PLLA1, the crystallinity and molecular orientation rise more rapidly with spinning speed.

Percentage crystallinity values from both DSC and DGC methods bear the same tendency: as take-up velocity increases, so does the crystallinity, with DGC values closer to reality for as-spun fibers having low values of crystallinity. This conclusion is based on a comparison of x-ray patterns and x-ray crystallinity measurements with the DSC and DGC measurements. Percentage crystallinity improved after annealing and tends to level off at higher annealing temperature. Even though the basic trends observed are mostly the same, the absolute values exhibit large discrepancies. Although WAXS values were in better agreement with DGC values for as-spun fibers, the DSC and WAXD values are in better agreement for the annealed fibers. From such observation, we believe that at low crystallinity level (especially those fibers that show “cold crystallization” peaks), the DGC values were more accurate than DSC values because the fibers crystallize during the heating procedure and it is difficult to correct for this effect. This problem is not as significant for the annealed samples since there is little or no additional crystallization during heating in the DSC. Therefore, DSC values would be more reliable, while DGC encounters a common problem of trapping air on the fine fibers, which makes accurate measurements difficult. Since an accurate method of separating the scattering from

the amorphous and crystalline phases of x-ray patterns is still unavailable, WAXD crystallinity of PLLAs serves more as a qualitative than quantitative method.

A method for determining crystalline orientation was developed that uses the (0010) reflection to measure the c-axis orientation factor and the (200) reflection to measure the a-axis orientation factor. The crystalline orientation factor reached $f_{c,z} \sim 0.9$, $f_{b,z} \sim -0.4$ and $f_{a,z} \sim -0.5$ for both PLLAs, but PLLA2 developed the high orientation at much earlier stage of spinning due to the higher stress it experienced. Compared with the development of crystalline orientation factor, the amorphous orientation factor developed much more slowly. Percentage crystallinity improved after annealing and tends to level off at higher annealing temperature. Crystalline orientation factor substantially improved for fibers spun under lower take-up velocities and slightly improved for those spun under higher take-up velocities.

The trend of birefringence was in qualitative agreement with the measured crystalline and amorphous orientation factors. Birefringence values increased gradually with take-up velocity in PLLA1 fibers, but reached a maximum in PLLA2 before it slightly decreases. This decrease is believed to result from the radial temperature distribution caused by rapid cooling during high-speed spinning process. The outer skin of fiber cools faster, leading to higher viscosity on the fiber surface, when combined with the spinning stress, it crystallized first, which allows the inner part of the fiber to relax. Thus, the inner part actually experiences less stress-induced crystallization.

Using the measured birefringences, crystallinities and orientation factors of the fibers, an attempt was made to determine the intrinsic birefringences of the amorphous

and crystalline phases of PLA. The value for the crystalline phase was in reasonable agreement with rough estimates calculated from bond polarizabilities, but this was not the case for the amorphous phase. The latter result may well be due to the accumulated errors associated with its determination, especially the errors in the amorphous orientation factors.

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Chapter 1 . INTRODUCTION

First introduced in 1932 by Carothers, who developed a process involving the direct condensation polymerization of lactic acid in solvents under high vacuum, PLA, Poly(lactic acid), a hydrolysable aliphatic polyester, has been used mainly in biomedical applications for decades. Medical sutures based on Poly(L-lactic acid) (PLLA) are commercially available, and the fixation of bone fractures by means of bars, rods or pins made of PLLA has been evaluated by many research groups. Amorphous and transparent poly(D,L-lactic acid)s are of interest as matrices for drug-delivery systems and as films or foils for wound treatment and other applications in medicine and agriculture. Though PLAs are expensive replacements for conventional thermoplastics, they're getting more and more attention due to the growing awareness of environmental protection. Unlike conventional thermoplastics, which are petroleum-based polymers, PLA is a bio-based polymer from renewable natural sources such as corns, dairy wastes and potato skins. It is biodegradable under hydrolysis, thermal mechanism or biotic environment and converts back to lactic acid, which is non-toxic, and nutrients for growth of new plants and crops and for further conversion to PLA. Thus, it is called the "green plastic". For example, PLLA has recently been accepted for use as a future packaging material ¹, not only because of its good mechanical properties that are comparable to today's standard packaging materials made of polystyrene and polypropylene, but also because of its environmental suitability. In addition, its better dyeability over PET and Nylon, its good UV resistance and resilience are all very promising for PLAs' future applications

in the forms of fibers, fabrics, nonwovens and films. **Table 1.1** lists some examples of PLA applications as thermoplastics, as given on Cargill Dow LLC website.²

The propose of this thesis is to study the fine structure of high-speed melt spun fibers and annealed fibers in order to understand the structure-process relationship of PLLA fibers. Major goals of this research is to get a better understanding of what would be the proper methods to determine important characteristics of PLLA fine fibers such as the degree of crystallinity and the amount of molecular orientation, and to measure important physical constants so as to benefit further researches to enhance the existing biomedical applications of PLLA as well as to explore more promising applications of PLLA as thermoplastic to substitute PET, Nylon, PP, PE in the near future.

Table 1.1 Examples of PLA Application as Thermoplastics²

	End-Use Examples	Benefits
PLA-Based Apparel	• Performance Activewear • Fashion Activewear • High-end Fashionwear • Casual Blends	• Excellent hand and drape • Moisture management and wicking • Easy care(resists wrinkling) • Natural-based fiber
PLA-Based Fabrics	• Carpet Tile • Industrial Wall Panels • Upholstery and Interior Furnishings • Automotive • Outdoor Fabrics, Awnings	• Sustainability • Resiliency • Reduced flammability, smoke generation and toxicity • Good soiling resistance and stain removal compared with Nylon 6 and 6.6 • UV resistance
PLA-Based Nonvovens	• Ag and geotextiles • Wipes • Diaper/ADL • Binder Fiber	• Degradability • Enhanced wicking • Low linting • Resilience • Controllable thermal bonding • Enhanced wet strength • Natural-based fiber

Chapter 2 . LITERATURE REVIEW

2.1 PLA Synthesis

There are two major routes to produce PLA from the lactic acid monomer, which is derived from fermentation of agricultural raw materials such as, sugar and corn. **Figure 2.1** illustrates the polymerization processes.

Poly(lactic acid) is generated using a polycondensation reaction starting from lactic acid. It involves removal of water of condensation by solvent under high vacuum and temperatures. The main drawback is that the reaction results in low to intermediate molecular weight polymer. It also requires long reaction times and cruel reaction conditions. This polymer can be used as is, or coupled using isocyanates, epoxides or peroxide to produce a range of molecular weights.³

Poly(lactide) is produced from an alternative method, which is to remove water under milder conditions and without solvent, producing a cyclic intermediate dimer, referred to as lactide. This monomer is readily purified under vacuum distillation. Ring-opening polymerization of the cyclic dimer is accomplished under heat, again without the need for solvent. Usually the polymerization is catalyzed by organo-metallic compounds, which are classified into anionic or cationic initiators.⁴ **Figure 2.2** includes most popular catalysts. This method generates high molecular weight polymers and by controlling the purity of the dimer it is possible to produce a wide range of molecular weights.⁵ The disadvantage of this method is due to the fact that the process needs the additional step of dimerization, which increases the overall cost of the polymerization.

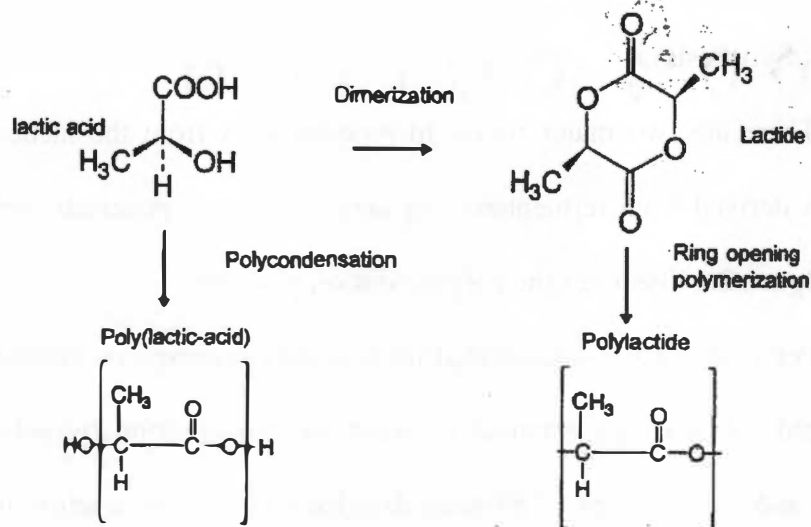


Figure 2.1 Comparison of Polymerization of Poly(lactide) and Poly(lactic acid) ⁵

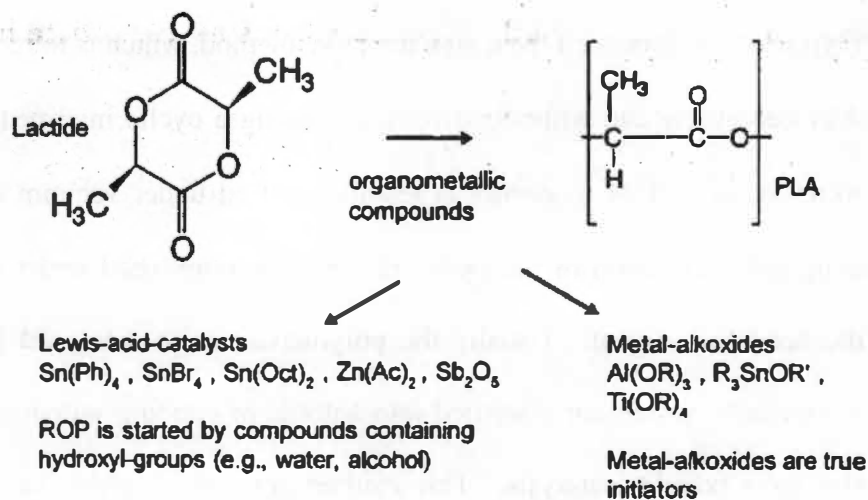


Figure 2.2 Catalysts of Ring-Opening Polymerization ⁵

Recently, some progress has been achieved and high molecular weight PLLA was obtained by sequential melt/solid polycondensation.^{6 7 8} A high quality poly(L-lactic acid) was obtained in high yield in a relatively short reaction time and its molecular weight exceeded 500,000, which has never been obtained by the simple melt-polymerization and is comparable with that of the poly(L-lactide) obtained by the ring-opening polymerization.

Aiming at lowering the cost of PLA production, thus enhancing its potential applications other than biomedical devices; a novel polymerization process was introduced.⁵ The innovative approach uses reactive extrusion techniques in a closely intermeshing co-rotating twin-screw extruder. The residence time is only about five minutes. The conversion reached was 0.97 and PLA of $M_n = 91,000$ with a polydispersity of 1.58 was obtained. **Figure 2.3** shows the comparison between the traditional process and this new method.⁵

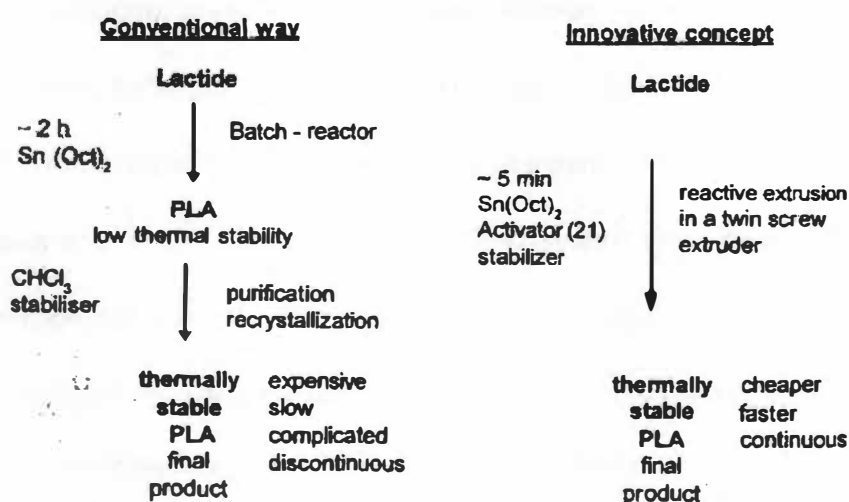


Figure 2.3 Poly(lactide) Synthesis – Conventional Way vs. Innovative Concept⁵

It is worth noting that both lactic acid and lactide are chiral. There are two acid enantiomers and four different lactides. Indeed, the lactide cycle bears two identical asymmetric carbon atoms in L-lactide, D-lactide, and D,L-lactide, which is a 50/50 mixture of L- and D- lactides, or two different ones in meso-lactide. Consequently, by maneuvering the process conditions, it is possible to produce PLAs with different compositions and chiralities to meet the requirements of various applications.

2.2 Crystal Structure and Morphology of PLLA

There are three PLLA crystal structures reported so far. In 1968, De Santis and Kovacs⁹ first determined the α crystal structure as pseudo-orthorhombic with the chains in a left-handed 10/3 helical conformation and two molecules passing through the unit cell packed in an anti-parallel fashion. The lattice constants are $a = 10.7\text{\AA}$, $b = 6.45\text{\AA}$, and $c = 27.8\text{\AA}$ and the cell contains 20 monomer units. In 1982, Eling et al.¹⁰ reported for the first time the existence of another structure of PLLA, which was then called the β structure. The structure was found in fibers of high molecular weight PLLA spun from semi-dilute solutions of PLLA in toluene, when drawn at high hot draw ratio. This process re-melted in a partial modification of the α -form to stable β -form. So the drawn fibers contained this β -form, but considerable α -form as well. No unit cell dimension was proposed at the time. Recently, a γ -form has been obtained by epitaxial crystallization in hexamethylbenzene (HMB) at a T_c in the neighborhood of 140°C .¹¹ The crystal structure of this new form was established by electron

diffraction and packing energy analysis. Two anti-parallel helices are packed in an orthorhombic unit cell whose parameters are $a = 9.95\text{\AA}$, $b = 6.25\text{\AA}$, and $c = 8.8\text{\AA}$.¹¹

W. Hoogsteen et al.¹² found both α and β crystal structures for solution-spun (chloroform and toluene) poly(L-lactide) depending on the spinning and drawing conditions. The pseudo-orthorhombic α structure ($a = 10.6\text{\AA}$, $b = 6.1\text{\AA}$, and $c = 28.8\text{\AA}$) contains two chains in the unit cell and is found at relatively low drawing temperatures and/or low hot-draw ratios. At higher drawing temperatures and/or higher hot-draw ratios the β structure appeared. For β structure an orthorhombic unit cell is proposed ($a = 10.31\text{\AA}$, $b = 18.21\text{\AA}$, and $c = 9.00\text{\AA}$) containing six chains. The chain conformations of the α and β structure are left-handed $10/3$ and $3/1$ helices, respectively. Meridional small-angle X-ray scattering experiments revealed that the α -form exists as a lamellar-folded-chain morphology, while β structure corresponds to fibrillar morphology. DSC scans of unconstrained fibers shows that the β structure melts at lower temperature than the α structure (175°C vs. 185°C), suggesting that the α -form is more stable than the β -form. They also noticed that annealing actually causes irreversible transformation into α -form.

Merega et al.¹³ confirmed that α -form of PLLA has a pseudo-orthorhombic unit cell containing 2 $10/3$ polymeric helices. They found slightly different lattice constants ($a = 10.7\text{\AA}$, $b = 6.126\text{\AA}$, and $c = 28.939\text{\AA}$).

Kobayashi et al.¹⁴ used their newly-developed optical method named HAUP (high accuracy universal polarimeter) to confirm that the α -form molecular residues were arranged on a nonintegral $10/3$ helix as De Santis and Kovacs⁹ reported and

validated the atomic positions in a monomeric unit, which were proposed by Hoogsteen et al.¹² However, they found the previous reports concerning X-ray diffraction intensities conflict significantly with their results and the positions of the two helical chains was in error. They proposed an orthorhombic crystal structure with lattice constants as $a = 10.5\text{\AA}$, $b = 6.1\text{\AA}$, and $c = 28.8\text{\AA}$, which is very close to what Hoogsteen et al.¹² got.

Tadakazu Miyata and Toru Masuko¹⁵ prepared solution-grown PLLA lozenge-shaped α - crystals from 0.01% (w/w) or 0.08% (w/w) acetonitrile solution by an isothermal crystallization method. They found orthorhombic unit cell with parameters as $a = 10.78\text{\AA}$, $b = 6.04\text{\AA}$, and $c = 28.7\text{\AA}$ (chain axis) and this unit cell of the PLLA solution-grown crystals contains 20 monomeric units/ two molecular chains in terms of density measurements. They proposed that the two molecular chains locate at the center and also at each corner of the unit cell.

Brizzolara et al.¹⁶ examined the packing mode of enantiomeric PLA chains using energetic computer simulation method, simulated the crystal structure of α - and β - PLLA on the basis of molecular simulations. **Figure 2.4** shows the simulated

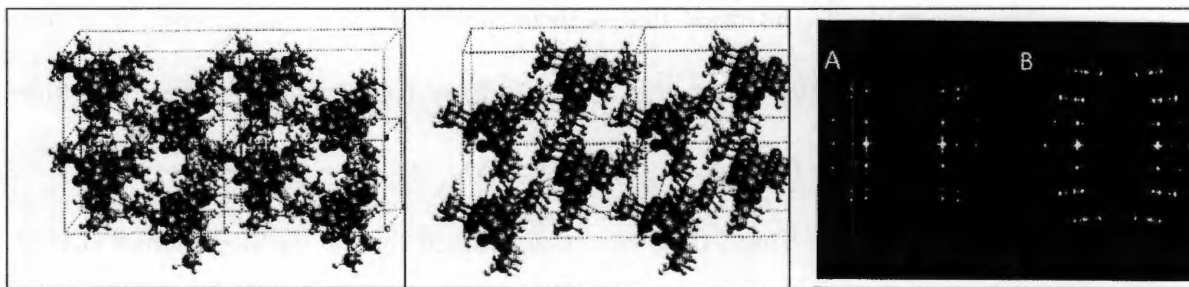


Figure 2.4 Simulated Crystal α -PLLA, β -PLLA and Fiber Pattern of α - and β -PLLA. (from left to right)¹⁶

crystal structures and x-ray fiber patterns. Their unit cell dimensions calculated for orthorhombic α -form strongly differed from other published value ($a = 7.10\text{\AA}$, $b = 9.40\text{\AA}$, and $c = 29.86\text{\AA}$). Possible orthorhombic β -form parameters are $a = 10.60\text{\AA}$, $b = 6.05\text{\AA}$, and $c = 9.40\text{\AA}$. Also, they found lamellar stereocomplex crystals exhibit an uncommon triangular shape, i.e. a distorted 3/1 helix α -form other than the α and β forms and suggested that the instability of the pure 3/1 helix is caused by the packing and that it leads to the distortion along the chain axis, without transformation into a 10/3 helix. The unit cell parameter for this distorted form might be $a = 11.70\text{\AA}$, $b = 6.10\text{\AA}$, and $c = 31.40\text{\AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 97^\circ$.

Cartier et al.¹⁷ also observed the triangular single crystal of PLA stereocomplex and believed that the triangular crystals are a morphological marker of the frustrated character of the packing in the unit cell. J. Puiggali et al.¹⁸ continued on to study the frustrated structure of poly(L-lactide) and calculated a trigonal unit-cell of parameters $a = b = 10.52\text{\AA}$, $c = 8.8\text{\AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, with frustrated packing of three three-fold helices. **Table 2.1** lists all the lattice constants in above reports. It is clear from the quoted results that there is reasonable agreement for the structure of the α -form, but the structure of β - and γ -form are not well established.

Conventionally, X-ray diffraction is the method to study crystal structure. A few groups used NMR to study crystallinity and morphology of PLLA. Thakur et al. investigated highly crystalline, partially crystalline, and amorphous PLLA by solid state ^{13}C CP-MAS NMR.¹⁹ Espartero et al.²⁰ took time to investigate the low molecular weight PLAs, which are intermediate byproducts during the hydrolytic

Table 2.1 Summary of Lattice Constants of PLLA Structures

Crystal Structure	a (Å)	b(Å)	c(Å)	Crystal System	Authors
α	10.7	6.45	27.8	pseudo-orthorhombic	De Santis and Kovac
	10.6	6.1	28.8	pseudo-orthorhombic	Hoogsteen et al
	10.7	6.126	28.939	pseudo-orthorhombic	Merega et al
	10.5	6.1	28.8	orthorhombic	Kobayashi et al
	10.78	6.04	28.7	orthorhombic	Miyata and Masuko
	7.10	9.40	29.86	orthorhombic	Brizzolara et al
β	10.31	18.21	9.00	Orthorhombic (Six 3/1 helices)	Hoogsten et al
	10.60	6.05	9.40	Orthorhombic (Two <i>parallel</i> 3/1 helices)	Brizzolara et al
frustrated	10.52	10.52	8.8	Trigonal (Three 3/1 helices frustrated crystal structure)	Cartier et al Puiggali et al
γ	9.95	6.25	8.8	Orthorhombic (Two <i>antiparallel</i> 3/1 helices)	Cartier et al

degradation of high molecular weight homo- and copolymers. Ito et al.²¹ investigated the structure of uniaxially oriented PLLA with different draw ratios in the solid state using ¹³C NMR spectroscopy and confirmed the existence of both α and β forms with 10/3 and 3/1 helices. Other groups used vibrational analysis (IR and Raman) to analyze the morphology, conformation, configuration, and chain mobility of poly(lactic acid)s.²²⁻²⁴ Lee et al.²⁵ used FT-IR to study the structure and orientation of uniaxially stretched PLLA samples according to the fact that IR spectra contain two types of absorption bands. One type is sensitive to structure as well as orientation, the

other is sensitive only to the orientation. They found that the orientation in uniaxially stretched PLLA was determined by the drawing rate, drawing temperature and draw ratio. For the amorphous sample, a higher orientation was obtained at a lower drawing temperature due to the slower chain relaxation. On the other hand, a higher orientation was achieved for the pre-crystallized samples at a higher drawing temperature due to the larger deformation of spherulites.

Finally, Hideto Tsuji and Yoshito Ikada²⁶ explored the effects of annealing conditions on thermal properties, mechanical properties and morphologies of poly(L-lactide) films by DSC, PM and tensile testing. PLLA films prepared by solution casting were annealed by three different processes: process A, direct annealing of the as-cast film; process B, melting and annealing, and process C, melting, quenching and annealing. In the case of process B, the morphology depended strongly on the annealing temperature, while it depended only slightly on the annealing temperature in the case of processes A and C. In process C, nucleation occurred upon quenching or in the process of temperature rise after quenching, and its nucleation a shorter time than in process B, and the radius of the spherulites formed was much smaller compared with that of the spherulites formed by process B. The crystallinity and melting temperature increased with increasing annealing temperature and time of processes B and C, whereas in process A the annealing conditions only slightly affected those values. Tensile strength showed similar behavior to Young's modulus, but decreased when large crystallites or spherulites were formed. In the case of processes A and B, elongation at break decreased with increasing crystallinity.

2.3 Crystallization Kinetics

2.3.1 Basic Concepts

The study of crystallization is very important to understanding polymer processing. Crystallization is a process of phase transformation, where an ordered structure is generated from a disordered phase such as a melt or dilute solution obeying the laws of thermodynamics. Crystallization consists of the primary nucleation and subsequent growth of a new phase within an existing phase. There are two types of primary nucleation, homogenous and heterogeneous. In the latter, a nucleus forms at the interface with a second phase, which may be impurities or nucleating agents, while homogeneous nucleation is the random formation of nuclei throughout the melt without the presence of a second phase. Crystal growth follows the primary nucleation, where crystalline or ordered cells form as more molecules are added to crystals. Whether crystallization takes place, and its speed, is determined by the kinetics of the process and the way the kinetics interacts with externally imposed variables.

Two most important variables to crystallization are temperature and cooling rate. Crystallization rate varies with temperatures. The growth slows down by increasing viscosity at temperature close to glass transition temperature T_g and by diminishing thermodynamic driving force as the melting point T_m is approached. Cooling rate also play a very active role in the mechanism of phase transformation under non-isothermal conditions. At higher cooling rates the activation of nuclei occurs at lower temperatures, the reduced molecular mobility enhances the nucleation rate as compared to the crystal growth rate, leading to the formation of a large number

of smaller crystals. When the samples are cooled at lower scanning rates, crystallization occurs at higher temperatures. In polymer processing, the control of the temperature profile during cooling, in the final stage of a process, determines the development of a specific morphology, which influences the final properties of the material. Cooling rate can be adjusted to modify the level of crystallinity and the crystal morphology of a polymer. Thus, by controlling the degree of supercooling, a great variety of morphologies can be obtained during the crystallization process of flexible chain polymers.

Generally, studies of crystallization are performed under isothermal or non-isothermal conditions. An isothermal crystallization is carried out by rapidly cooling a polymer liquid from above its melting temperature to the crystallization temperature, T_c , and holding it at that temperature until crystallization is completed, while non-isothermal crystallization is usually carried out under continuous cooling conditions.

Analysis of the overall crystallization rate under isothermal conditions is generally accomplished with the use of the Avrami equation that permits one to calculate the crystallinity fraction, $X(t)$, as a function of the elapsed time. A general form of Avrami equation is:

$$X(t) = 1 - \exp(-Kt^n) \quad (2.1)$$

where $X(t)$ is the crystalline fraction in the sample at time t . K and n are constants typical of a given morphology and type of nucleation. K is the overall crystallization rate constant containing nucleation and growth rates and is temperature dependent; n is the Avrami index, and contains information on nucleation and growth geometry. In practice, Avrami index n decreases as crystallization proceeds. A plot of

$\ln[-\ln(1 - X(t))]$ versus $\ln(t)$, often referred to as an Avrami plot, should be theoretically linear with n being the slope and $\ln(k)$ the intercept.

Isothermal crystallization is limited to idealized conditions, in which external conditions are assumed to be constant. The theoretical analysis is relatively easy. However, in the real world, the external conditions change continuously so that the understanding of non-isothermal crystallization becomes important to industrial processes. Nakamura et al.^{27, 28}, Ziabicki²⁹, Harnisch and Muschik³⁰ and Ozawa³¹ are a few examples of the research groups who have devoted efforts to the study of non-isothermal crystallization. However, their treatments are still far from being without fault and none are suitable for all polymers.

Depending on the rate that the chains deposited on the crystal surface, there are three regimes of crystallization kinetics from the melt. Regime I occurs when one surface nucleus causes the completion of the entire substrate of length L . Regime II takes place when multiple surface nuclei deposits on the same crystallizing surface. When the niche separation characteristic of the substrate in regime II approaches the fold thickness of the lamellae, it enters regime III. Regime III is very important to rapid cooling systems.³² The overall crystallization kinetics based on Lauritzen-Hoffman³³ theory defined the linear growth rate G of a chain-folded polymer crystal as:

$$G = G_o \exp\left(\frac{-u^*}{R(T - T_\infty)}\right) \exp\left(\frac{-K_g}{T\Delta T f(T)}\right) \quad (2.2)$$

where R is the gas constant, u^* is the activation barrier to transport molecules from the melt to the crystal surface, $\Delta T = T_m^0 - T$ is the supercooling, $f(T)$ is a function that is an approximate correction factor for the heat of fusion change during the supercooling.

$$f(T) = \frac{2T}{T_m^0 + T} \quad (2.3)$$

And $K_g = \frac{\beta b_0 \sigma \sigma_e T_m^0}{k_B \Delta h_f}$, is called secondary nucleation constant. Here b_0 is the layer thickness, σ is the crystal growth face surface energy, σ_e is the crystal fold surface energy, Δh_f is the heat of fusion per unit volume, k_B is the Boltzmann constant. β can be 4 if the growth rate is in regime I or III, or 2 if the growth rate is in regime II.

2.3.2 Crystallization Kinetics of PLAs

Fischer et al.³⁴ carried out a detailed study of the crystallization of lactide stereo copolymers in order to investigate the structure of solution grown crystals and obtain information on the crystallization behavior of these copolymers with different contents of non-crystallizable D,L-lactide units. Single crystals were obtained by isothermal crystallization from 0.1% solutions of xylene using different crystallization temperatures T_c . They found that at constant supercooling, only small variations of long spacing were observed, while the thickness of the crystalline layer decreases systematically with increasing D- content. On the other hand, at constant crystallization temperature, they observed increasing in long spacing, but constant crystalline thickness.

Kalb and Pennings³⁵ studied the general crystallization behavior of PLLA. They found that PLLA could crystallize either from the melt or from solution. Spherulites grown from the melt were negatively birefringent. The equilibrium melting point and the glass transition temperature were found to be about 215°C and 55°C, respectively. Crystallization from dilute toluene or xylene solution yielded large lozenge-shaped lamellar single crystals about 10 nm thick. Electron diffraction revealed a hexagonal unit cell with dimensions smaller than reported earlier possibly due to the difference in specimen morphology (i.e. fiber and single crystal).

Vasanthakumrai and Pennings³⁶ investigated the isothermal crystallization kinetics of PLLA crystals from the melt as a function of supercooling and the molecular weight using hot stage microscopy. In the crystallization temperature range studied, it is clear that the growth rate increases with decrease of molecular weight as shown in **Figure 2.5**. While higher molecular weight samples crystallized in regime II, they observed the transition from regime I to regime II above 163°C for the sample (D) with lowest molecular weight when applying LH theory (**Figure 2.6**) and the morphology changes corresponding to the regime transition, i.e. regime I behavior corresponding to axialite formation above 163°C and regime II corresponding to spherulitic morphology below 163°C. However, no information was available at temperature below 114°C due to high nucleation density, which makes a clear measurement of the crystal growth rate difficult.

Iannace and Nicolos³⁷ studied isothermal crystallization of PLLA in the temperature range of 90°C to 135°C by means of DSC. They observed a maximum in

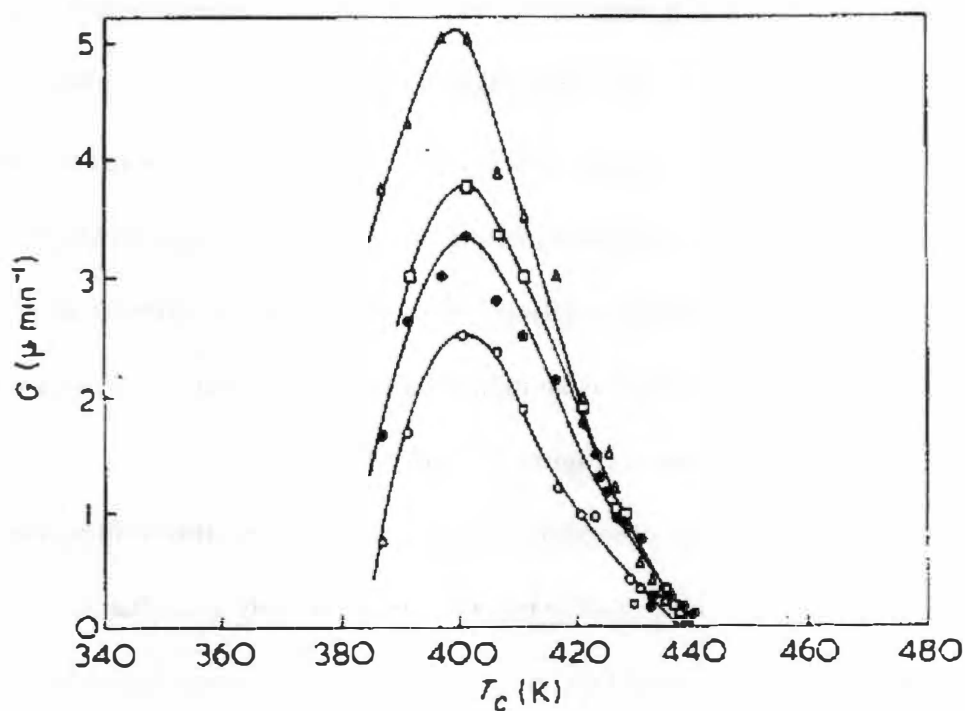


Figure 2.5 Radius Growth Rate G as a Function of Crystallization Temperature T_c for Different Molecular Weight Samples of PLLA. ($\circ$ - A $M_v=6.9 \cdot 10^5$, $\bullet$ - B $M_v=3.5 \cdot 10^5$, $\square$ - C $M_v=2.6 \cdot 10^5$, Δ - D $M_v=1.5 \cdot 10^5$)³⁶

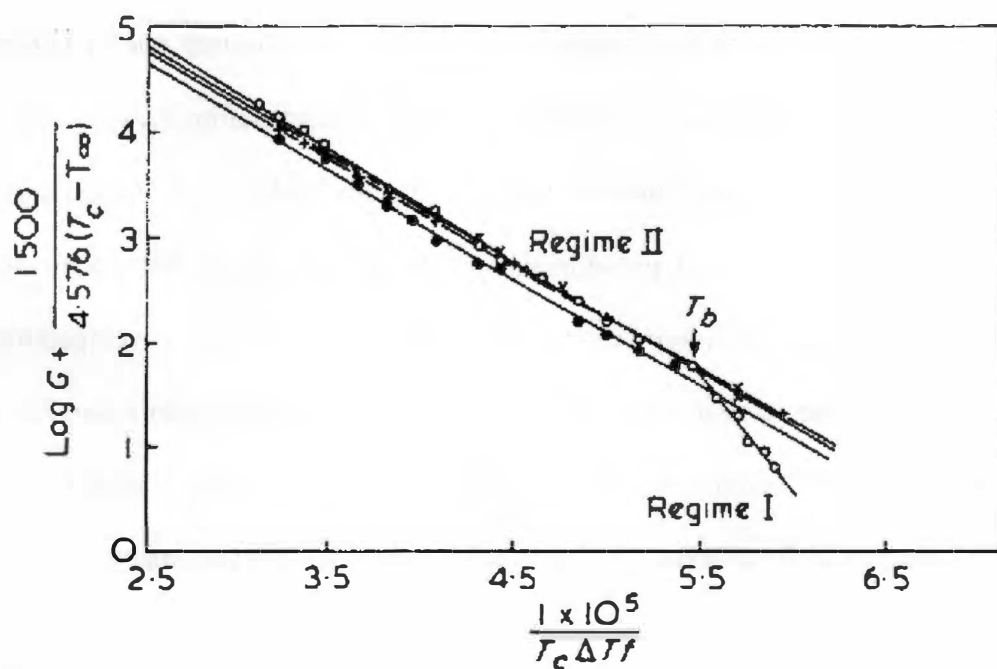


Figure 2.6 Crystallization Growth Rate Regime of PLLAs ($\bullet$ -A, $\circ$ -B, $\square$ -C, Δ -D)³⁶

crystallization kinetics was around 105°C and a transition from regime II to regime III is present around 115°C. At crystallization temperature below 105°C, further crystallization occurs upon heating (cold crystallization); this behavior is not detected for T_c above 110°C. The equilibrium melting point was found to be about 206.2°C by extrapolation of Hoffman-Weeks analysis. They also found the Avrami index $n = 3$, for all the T_c investigated, which is an indication that the growing of crystals is three-dimensional and heterogeneous. (Figure 2.7 and 2.8)

Mazzullo et al.³⁸ also observed the regime II to regime III transition, but it was around 140°C with 67°C supercooling rate in isothermal analysis of PLLA.

Urbanovici et al.³⁹ used DSC to investigate the isothermal melt crystallization kinetics of poly(L-lactic acid) at 110, 115, 120, 125 and 130°C. At temperatures above 130°C, the crystallization process is slow and incomplete, while at temperatures below 110°C the crystallization is fast and it is difficult to obtain, with appropriate accuracy, the initial part of the isothermal DSC curve. At a heating rate of 10K/min, the glass transition temperature T_g and the melting peak temperature T_m were found to be 63°C and 185°C. They believe that the Avrami index = 3 corresponds to homogeneous nucleation and two-dimensional linear growth of the nuclei during crystallization, using both Avrami model and the new kinetics model developed by the group. Based on the Avrami model, they introduced a third parameter r into the new “generalized Avrami” model, where r satisfies $r > 0$. The new kinetic model offers a better description of the experimental data than the classical Avrami kinetic model.

$$1 - X(t) = [1 + (r - 1)(kt)^n]^{1/r} \quad (2.4)$$

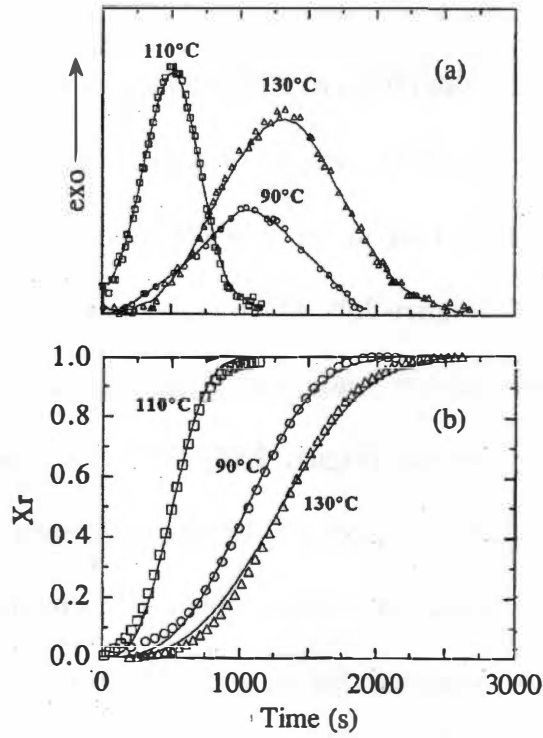


Figure 2.7 Isothermal Melt Crystallization at T_c (a) Heat Flow (b) Crystallinity vs. Crystallization Time³⁷

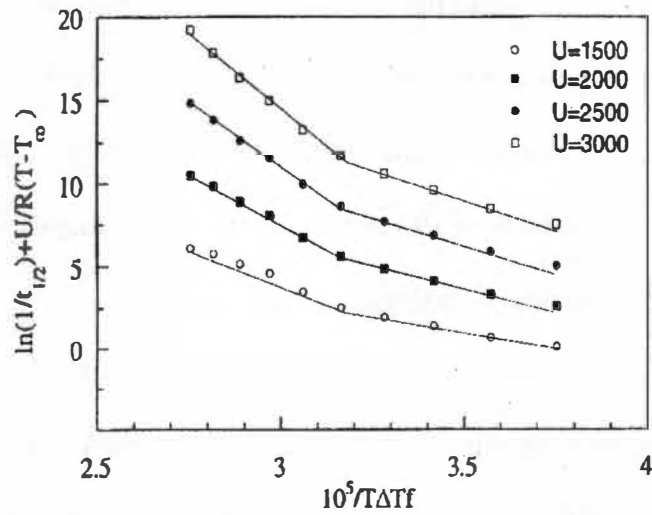


Figure 2.8 Regime Analyses for PLLA. Transition from Regime II to Regime III³⁷

Miyata and Masuko ⁴⁰ studied both isothermal and non-isothermal crystallization of poly(L-lactide) films of different molecular weight by DSC, OM and a depolarized-light intensity (DLI) method. Overall isothermal crystallization rate of the polymer determined by DLI in the range from 90°C to 140°C indicated the maximum value at 105°C (**Figure 2.9**), which is the same as reported by Iannace and Nicolos ³⁷. This temperature is lower than that (120°C) at which the maximum spherulite growth rate is observed (**Figure 2.10**). They found that the PLLA polymer exhibited an average Avrami exponent $n = 4$ in the isothermal DLI experiments over the whole temperature range examined, which is different from other groups mentioned above. They suggested that the PLLA spherulites growth mode is three-dimensional and homogeneous. Furthermore, they believe that the n value gradually became 3 over longer time, since larger spherulites sandwiched between two glass plates have grown into a disc-like shape. In addition, the overall isothermal crystallization rate increases with decreasing molecular weight of PLLA, which is consistent with Vasanthakumrai and Pennings' ³⁶ finding. In non-isothermal crystallization, the crystallinity of PLLA films increase remarkably with a decrease in the cooling rate, accompanied by a kind of annealing effect.

Recently, Maria Laura Di Lorenzo ⁴¹ used both isothermal and non-isothermal to measure the spherulite growth rates G of PLLA. Combined with the self-nucleation procedure, they were able to approach a much larger temperature range within a single experiment. Analysis of experimental G data with Hoffman and Lauritzen theory detected a regime II-III transition at 120°C.

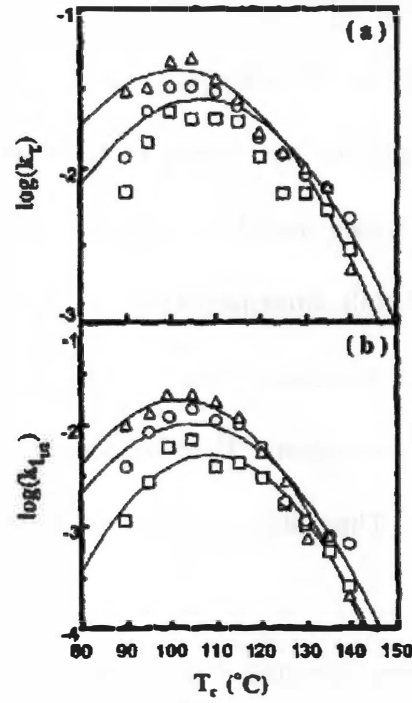


Figure 2.9 Isothermal Overall Crystallization Rate as a Function of Crystallization Temperature T_c for PLLA films. ($\square$ - $M_w=2.0 \cdot 10^5$, $\circ$ - $1.0 \cdot 10^5$, Δ - $5.0 \cdot 10^4$)⁴⁰

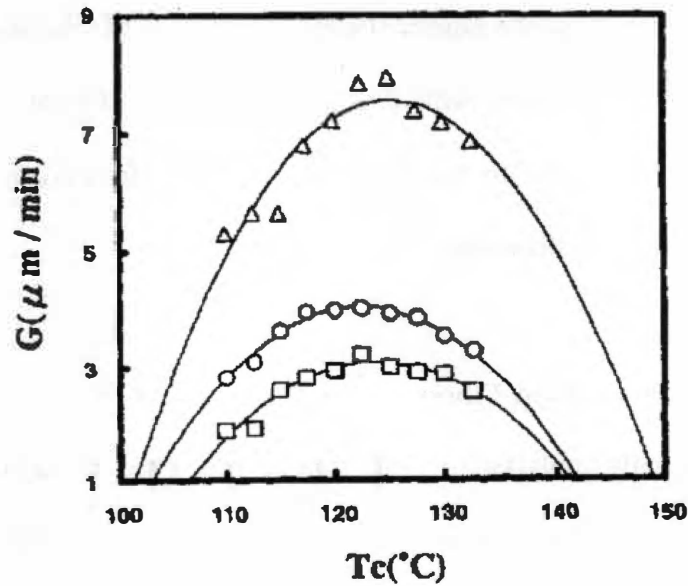


Figure 2.10 Crystallization Growth Rate as a Function of Isothermal Crystallization Temperature T_c for PLLA films. ($\square$ - $M_w=2.0 \cdot 10^5$, $\circ$ - $1.0 \cdot 10^5$, Δ - $5.0 \cdot 10^4$)⁴⁰

In order to analyze the effect of cooling rate on the development of crystalline morphology and the mobility of the amorphous phase, non-isothermal crystallization experiments were also carried out by Iannace et al.⁴² in the range between 0.5 and 7°C/min. Crystallinity decreased from 0.56 to 0.061 with an increase of cooling rate from 0.5 to 5°C/min. Crystallization performed at lower cooling rate (2°C/min) is accompanied by a change of kinetics around 115°C. They suggested that it could be related to the transition from regime II to regime III occurring during the non-isothermal crystal growth. They also provided CCT plot from the non-isothermal DSC data. (Figure 2.11)

Aside from the groups reported either regime I-II or regime II-III transition, Huang et al.⁴³ didn't observe the transition in the LH plots of poly(L-lactide-co-meso-lactide). It means that the crystallization of this copolymer was completed in one regime within the temperature ranges studied. Figure 2.12 Shows the LH plots of poly(L-lactide-co-meso-lactide) with different copolymer content. They ruled out regime I crystallization due to the high supercooling and were not certain if it's definitely regime II crystallization.

2.4 Spinning Process of PLA Fibers

Conventionally, poly(lactic acid) can be processed through thermoforming, paper-coating, biaxial film fabrication, fiber spinning, blow molding and injection molding.³ PLA fibers can be prepared by several techniques such as: melt spinning, solution spinning (dry spinning) or hot drawing depending on the application requirements of the final product. For biomedical application, solution spinning is

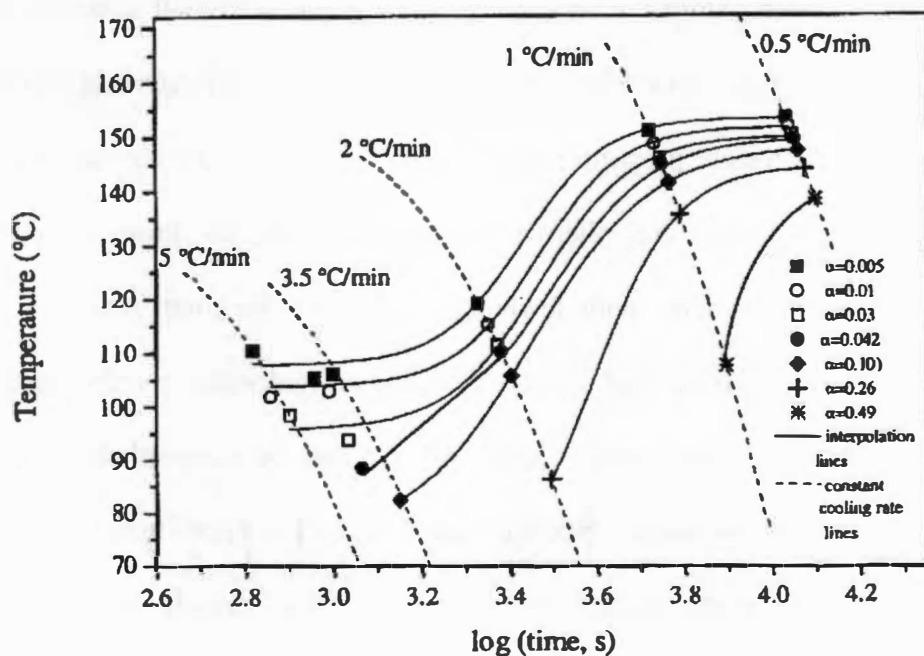


Figure 2.11 Continuous Cooling Transformation (CCT) Plot Obtained from Non-isothermal DSC Data (α : crystallinity)

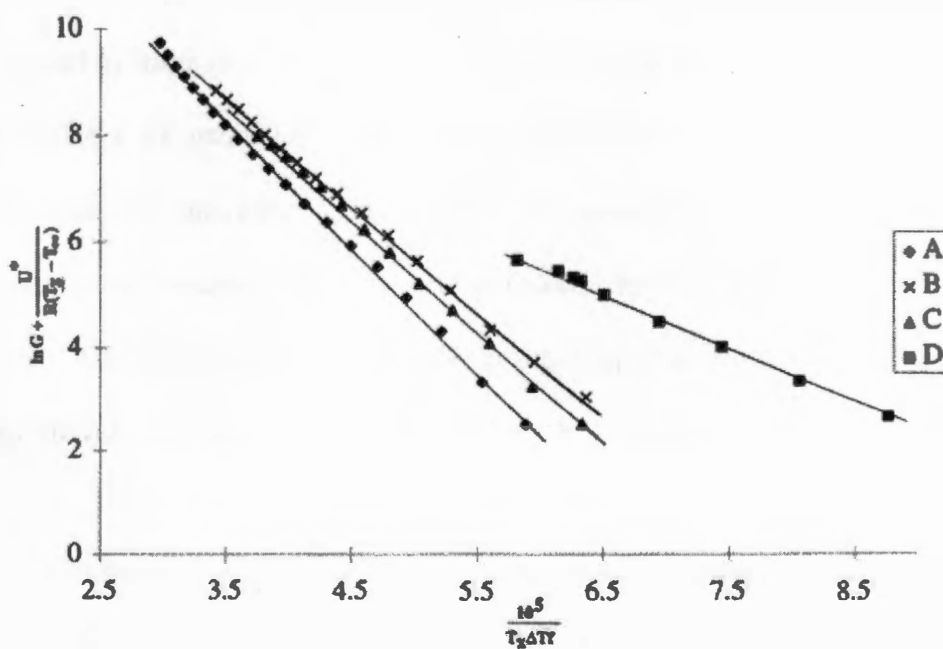


Figure 2.12 LH plots of poly(L-lactide-co-meso-lactide) with different copolymer content. (meso%: A-0%, B-3%, C-6%, D-12%)⁴³

avoided due to its toxicity from the solvent, though compared to melt-spinning, the preparation of PLLA fibers from semi-dilute solutions using a dry-spinning process often yields improved tensile properties due to (1) the reduction in the number of entanglements and (2) the less thermal degradation due to lower spinning temperatures. Molecular chains with fewer entanglements are more ready to get oriented during the processing and fibers with higher molecular weight usually provide higher mechanical properties. Melt spinning can be accomplished under either very high speed or low speed. Fibers collected under low speed may further go through a hot-drawing stage to get preferred orientation, which favors some applications.

PLA is well suited for melt spinning into fibers. The processing temperature is more typical of polyolefin's (approximately 220°C) but its properties are more like those of polyesters. Similar to PET, drying is crucial to PLA in terms of the properties of final products. Due to the hydrolytic degradation mechanism, PLA pellets need to be vacuum dried before processing; the proper drying temperature is controlled by the stereo-regularity of the material. Basically, the more the L-isomer content, the higher the temperature. **Figure 2.13** provides drying curves for PLA pellets as function of initial morphology and drying temperature according to the equilibrium moisture level.²

In order to optimize mechanical properties of fibers, high-speed melt spinning and drawing are two usual ways to increase the chain extension in the fiber, thereby reaching higher strength and stiffness⁴⁴. The melt-spinning/hot drawing⁴⁵, solution-spinning/hot-drawing¹⁰, and high speed melt-spinning⁴⁶ methods have been applied

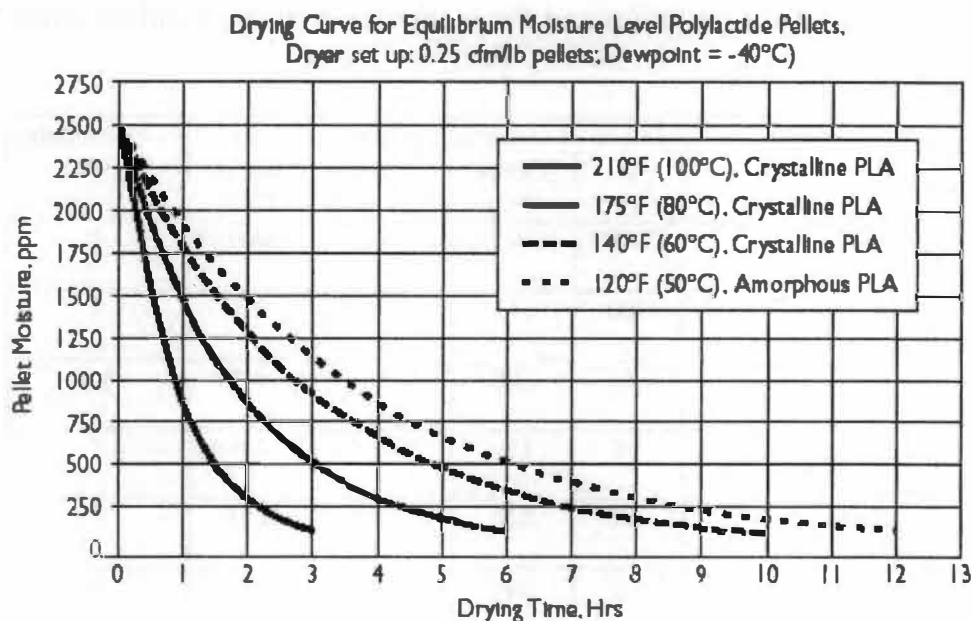


Figure 2.13 Drying Curve for Amorphous and Crystalline PLA Pellets ²

in order to enhance the mechanical properties of PLLA, mainly of high molecular weight. Zone-drawing method was applied by Okuzake *et al.* ⁴⁷ to improve the mechanical properties of low molecular weight PLLA. The values of Young's modulus and ultimate stress from different groups are listed in **Table 2.2** ⁴⁸.

2.4.1 Solution-spinning/hot drawing ¹⁰

In regular spin-draw procedure, the solution spinning speed was generally low, of order 0.5-20 m/min. Preferred mechanical properties were developed through hot drawing. PLLA fibers can be drawn more easily from solution-spun filaments than melt-spun filaments. The resulting morphology is essentially free of entanglement, which leads to better tensile properties of solution-spun fibers than melt-spun fibers.

Table 2.2 List of Conditions and Properties for melt spun and hot drawn PLLA fibers (*fiber not drawn) ⁴⁸

Author	Initial M_v ($\times 10^{-3}$)	Extrusion Temp. (°C)	Collection Speed (m min ⁻¹)	Fiber Strength (GPa)	Fiber Modulus (GPa)
Schneider	19-182	160-190	*	0.48-0.69	7
Eling et al.	300	185	0.25-0.35	0.5	7
Hyon et al.	360	200	*	0.7	8.5
Dauner et al.	98	190	*	0.4	*
Pennings et al.	280	210	1	0.53	9
Fambri et al.	330	240	(2) 5-20	0.87	9
Schmack et al.	207	185	200	0.46	6.3
*Mezghani & Spruiell	$M_w = 212.5$	233	(4500) 160-4500	0.39	6
*Schmack et al.	207 ($M_w = 164$)	185	1000-5000	0.33	4

Eling *et al.* ¹⁰ obtained the stress-strain curve of drawn PLLA samples made by solution spinning. It can be seen in **Figure 2.14** that the initial modulus is the same for all draw ratios. With increasing draw ratio, the tensile stress increases and the initiation of yielding increases accordingly. **Figure 2.15** shows the relationship between ultimate tensile stress and draw ratio λ for two PLLA polymers of different MW. For the low MW sample B, the ultimate mechanical properties are achieved at draw ratios between 18 and 25, reflected by the plateau on the curve. It also indicates that the maximum number of molecular entanglements and crystalline defects have been removed at this level.

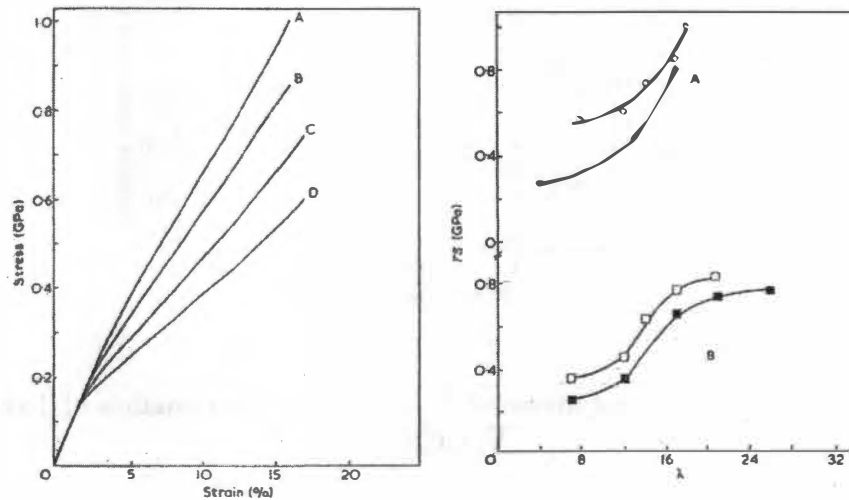


Figure 2.14 (left) Stress-Strain Curve for Fibers of Various Draw Ratio, A(18)B(17)C(14)D(8) ¹⁰

Figure 2.15 (right) Tensile Stress vs. Draw Ratio A-high MW (○200.5°C,●196.5°C) B-low MW(□180°C,■190°C) ¹⁰

Similarly, no plateau observed on high MW samples A tells us that the optimal drawing conditions, which would lead to the ultimate mechanical properties, were not attained.

2.4.2 Melt-spinning/hot drawing ⁴⁵

Fambri et al. ⁴⁵ produced PLLA fibers using the melt-spinning/hot drawing two-stage method. At very low take-up velocity, they found that the Young's modulus increases steeply at first from 2.8 to 4.1 GPa, reaching almost constant at take-up velocity above 10m/min, whereas yield stress and ultimate tensile strength increases linearly with the take-up velocity to 128 and 209 MPa, respectively in the range of take-up velocities studied. (Figure 2.16)

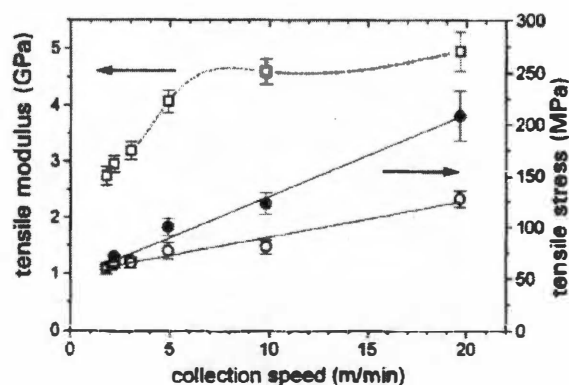


Figure 2.16 Modulus and Stress of As-spun Fiber as Function of Take-up Velocity⁴⁵

They also collected dynamic modulus data of PLLA. (Figure 2.17) The storage modulus, E' , at room temperature was 1.8, 2.8 and 3.5 GPa for fibers collected at 1.8, 10 and 20 m/min, respectively. $\tan\delta$ is a parameter very sensitive to the degree of molecular motion, whose value decreases when molecular orientation or characteristic ratio C_∞ increases⁴⁹. It ranges from 1.4 for fiber collected at 1.8 m/min to about 0.6 for fibers collected 10 and 20 m/min. We can see that crystallinity of as-spun fibers does not increase linearly with take-up velocity as in Figure 2.18. (The overall draw ratio of 4.3, 27.7 and 57.6 corresponds to collection speed of 1.8, 10 and 20 m/min.) Based on the information of $\tan\delta$, it seems that sample a in Figure 2.17 is lower crystallinity and lower orientation, b higher crystallinity and higher orientation and c lower crystallinity and higher orientation even the storage modulus increased. The increase in orientation of the amorphous phase affects and to some extent improves the fiber mechanical properties.

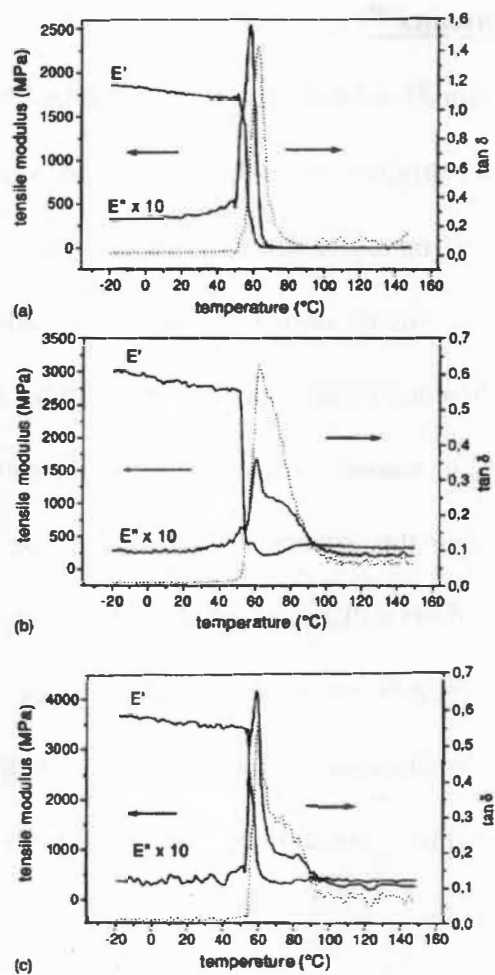


Figure 2.17 DMA Thermogram of as-spun Fibers, a(1.82m/min), b(10m/min), c(20m/min) ⁴⁵

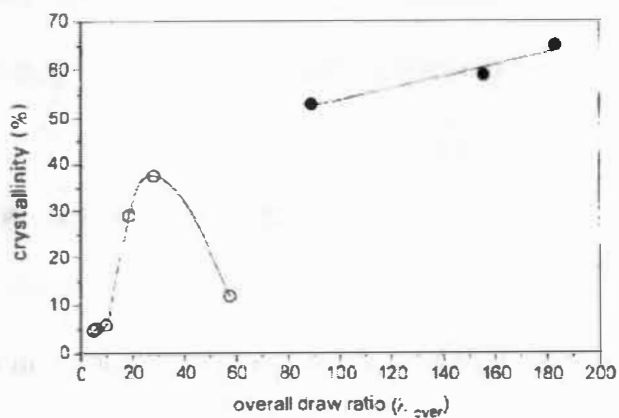


Figure 2.18 Crystallinity as Function of Total Draw Ratio, as-spun (white), hot-drawn (black) ⁴⁵

2.4.3 High-speed melt spinning⁴⁶

The spin-draw methods are too slow for commercialization. High-speed melt spinning is favorable for productivity. In high-speed spinning, fibers enter the ambient air and are taken up by a draw down device. The radial temperature distribution is such that the outside skin is cooler which leads to greater viscosity on the surface. Thus, at sufficient spinning speeds, the spinning stress becomes larger on the outer diameter, which causes polymer coil deformation thereby increasing molecular orientation. When this occurs, crystallization rates dramatically increase. At this point stress-induced crystallization occurs, beginning with the outer diameter of the fiber. The partial crystallization of the outer surface limits deformation with respect to the deformable inner region. This causes a shear deformation to take place between the non-deformable crystallized outer region and the deformable uncrystallized inner region⁵⁰.

Mezghani and Spruiell⁴⁶ conducted high-speed melt spinning of PLLA with take-up velocity from 100 to 5000 m/min. **Figure 2.19** shows typical stress-strain curves for as-spun PLLA filaments as a function of take-up velocity. **Figure 2.20** shows an expended view of the early portion of these curves. It seems that at very low take-up velocity 100m/min, the polymer is very brittle and it only shows the elastic deformation. This is due to the lack of orientation of the molecule so that the crystallization kinetics is so slow that polymer is easily quenched to amorphous state upon air contact. As take-up velocity increases, the Young's modulus and ultimate stress develop substantially. As in **Figure 2.21** and **Figure 2.22**, which represents the average value of six samples, the Young's modulus and ultimate stress climb to a

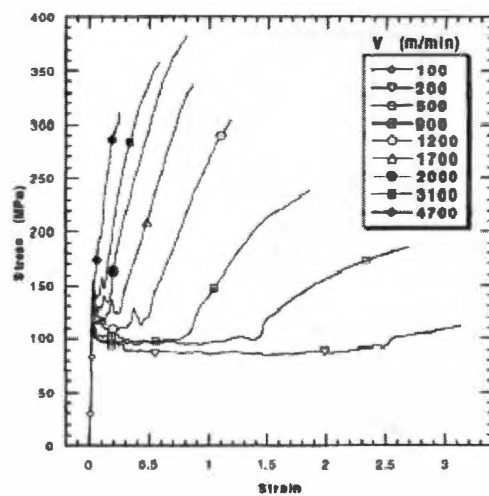


Figure 2.19 Stress-Strain Curve of As-spun PLLA filaments⁴⁶

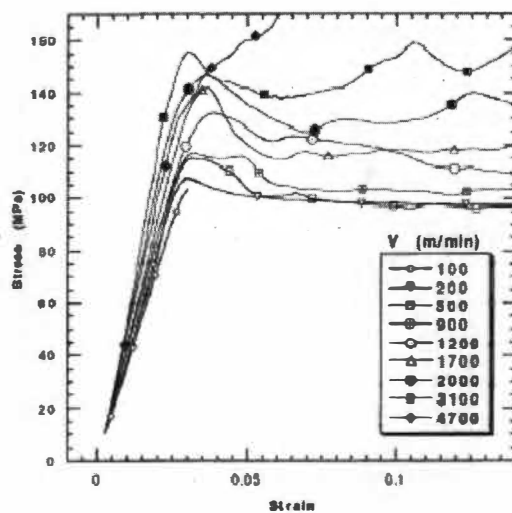


Figure 2.20 Enlargement of the initial portion of Figure 2.18⁴⁶

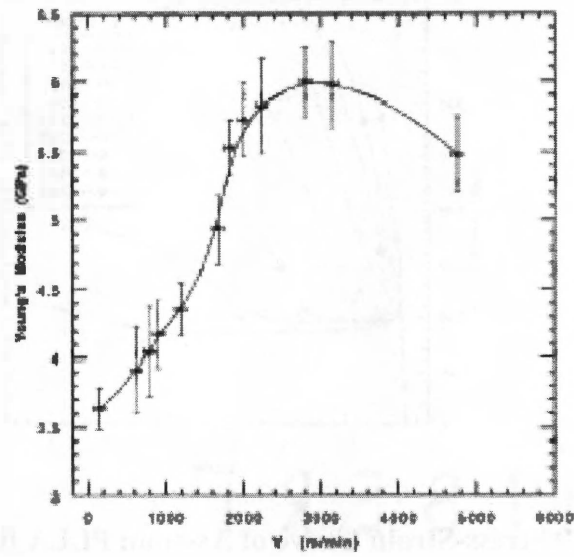


Figure 2.21 Young's Modulus vs. Take-up Velocity of As-spun Filaments⁴⁶

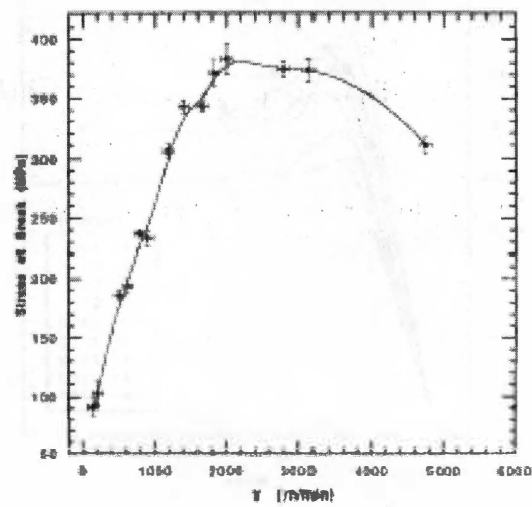


Figure 2.22 Tensile Strength vs. Take-up Velocity of As-spun Filaments⁴⁶

maximum then decrease with increasing take-up velocity. It is known that modulus is a function of both crystallinity and molecular orientation and ultimate stress is determined by the degree of chain extension and the degree of molecular orientation relative to the fiber axis. By examining **Figure 2.23**, the crystallinity and overall orientation characterized by birefringence both reach a maximum in the neighborhood of 3000 m/min, just like the curve of Young's modulus and ultimate stress. With increased take-up velocity and spinline stress, molecular orientation is developed in the spinline and the crystallization kinetics increases. The increase in the crystallization is such that it is sufficient to overwhelm the increasing cooling rate due to the high speed spinning. The decrease in crystallinity, birefringence, Young's modulus and ultimate stress around 3000m/min is associated with saturation of the crystallization rates accompanied with an increased cooling rate, coupled with relaxation of the inner core of the filament after the beginning of stress-induced crystallization near the surface. This effect is largely a result of thermal gradients across of filament.

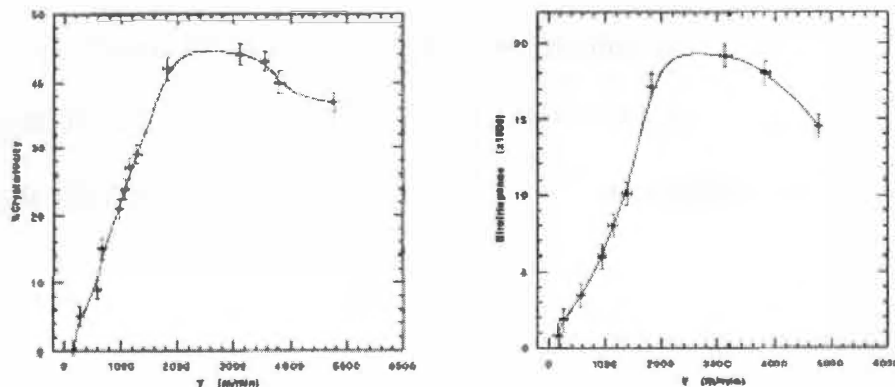


Figure 2.23 Crystallinity and Birefringence vs. Take-up Velocity of As-spun PLLA filaments⁴⁶

2.4.4 Melt spinning/zone drawing⁴⁷

Zone drawing is a technique developed in Hidenori et al.'s laboratory⁴⁷. It was performed using a tensile tester with a narrow band heater mounted on its crosshead, where the heater temperature was held constant over the experimental period by thermo-regulator. And this method is designated to investigate and improve the tensile and dynamic mechanical properties of low MW PLLA.

The optimum conditions of zone-drawing and tensile properties are summarized in **Table 2.3 and 2.4**. Notice that the attained Young's modulus for ZD-3 is 9.1GPa. This value is close to Penning's⁵¹ 9GPa and Fambri's⁴⁵ 9.2GPa, regardless of its Mv one order smaller than those authors' samples. This result confirmed that the tensile properties are improved with the processes, though a low MW polymer has numerous structural defects.

The temperature dependence of the storage and loss modulus of this low MW PLLA shows in **Figure 2.24 and 2.25**. E' increases as Young's modulus increases and for ZD-3, it reaches a maximum value of 10.4 GPa at room temperature, which is about four times the original value. E'' peaks at 75°C and increases in height with process. Because E'' peak indicates the energy dissipation of frictional heat during one cycle of a sinusoidal deformation, the increase of peak height implies that the intermolecular friction between adjacent chains increases and the modulus increases.

2.4.5 Others

The final properties of fibers depend on spinning variables such as molecular weight, molecular weight distribution, solvent quality and solvent composition⁵²,

Table 2.3 Optimum Conditions for Zone-Drawing⁴⁷

Fiber	Drawing Temperature (°C)	Applied Tension (MPa)	Heater Speed (mm min ⁻¹)
ZD-1	60	7.5	50
ZD-2	70	36.4	50
ZD-3	90	28.5	50

Table 2.4 Tensile Properties of Various Fibers⁴⁷

Fiber	Young's Modulus (GPa)	Strength at Break (MPa)	Elongation at Break (%)
Original	1.8 ± 0.2	16 ± 4	1.9 ± 0.3
ZD-1	6.3 ± 0.2	231 ± 18	33.7 ± 2.6
ZD-2	7.9 ± 0.2	250 ± 10	18.9 ± 2.7
ZD-3	9.1 ± 0.3	275 ± 11	28.0 ± 4.4

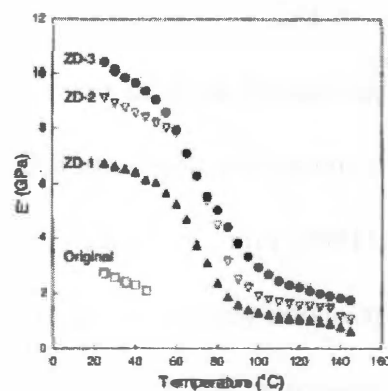


Figure 2.24 Storage Modulus E' vs. Temperature of ZD fibers. 110 Hz, 2°C/min⁴⁷

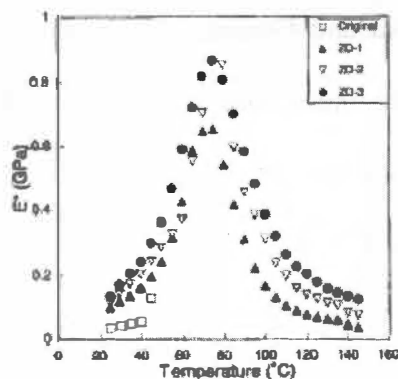


Figure 2.25 Loss Modulus E'' vs. Temperature of ZD fibers. 110 Hz, 2°C/min⁴⁷

ambient temperature⁵³, spinning speed, spinline draw ratio, and die geometry⁵⁴. The same holds for the hot-draw variables such as drawing temperature and deformation rate⁵⁵.

2.5 Degradation of PLA

There are three possible mechanisms when PLAs undergo degradation, namely, thermal, hydrolytic and biological degradation.

2.5.1 Thermal degradation

The thermal stability of PLLA is poor at elevated temperatures. Bigg⁵⁶ mentioned that poly(lactic acid) quickly loses its thermal stability when heated above its melting point. Significant molecular degradation detected when PLA was held 10°C above its melting point (160°C) for a prolonged period of time. Migliaresi et al.⁵⁷ had shown that thermal degradation was not due to hydrolysis, but chain splintering. They concluded that large molecular weight reductions (greater than 50%) were unavoidable. Oxidation of PLA wasn't obvious enough to be measured during thermal degradation. Gupta and Deshmukh⁵⁸ proposed that the carbonyl carbon-oxygen linkage is the most likely bond to split by isothermal heating. The same groups also studied the kinetics for the thermal degradation of poly(lactide) and suggested it to be first order⁵⁹.

Reactions involved in the thermal degradation of PLAs can be thermohydrolysis⁶⁰, zipper-like depolymerization^{61,62}, thermooxidative degradation^{61,63}, and transesterification reactions^{62,64}.

Some studies proved that the thermal degradation of poly(L-lactide) is accelerated by the increasing moisture content of the polymer and pre-dry could reduce the effect. Other studies, on the other hand, have reported the difference of the extent of thermal degradation between carefully dried and undried PLLA was not observed ^{61, 62}. Zipper-like depolymerization of the polymer is a significant mechanism of PLA degradation. Zhang et al. ⁶⁵ proposed a mechanism for this backbiting depolymerization in the presence of tin(II) 2-ethylhexanoate. McNeill and Leiper ⁶³ as well as Gupta and Deshmukh ⁵⁸ suggested thermooxidative random main-chain scission as the contributing mechanism to the thermal degradation of poly(lactide). Inter- and intra- molecular transesterifications are typical interchange reactions for condensation polymers above or near their melting points ⁶⁶.

2.5.2 Hydrolytic degradation

Hydrolysis of polymers leads to molecular fragmentation, which can be regarded as a reverse polycondensation reaction. Various factors such as chemical structure, molecular weight and its distribution, purity, morphology, shape of the specimen and the history of the polymer, as well as the conditions under which the hydrolysis is conducted can affect this process ⁶⁷.

The amorphous parts of the polyesters were believed to undergo hydrolysis before the crystalline regions because of a higher rate of water penetration into the disordered phase. So the initial degree of crystallinity of the polyesters can affect the rate of hydrolytic degradation as the higher crystal content leads to reduction of water permeation in the system. After molecules fragment in amorphous regions at the first

stage of hydrolytic degradation, the restraint that was tying the crystal blocks together by entanglement is removed by the hydrolysis and the remaining crystal chain segments therefore acquire more mobility. This leads to rearrangement of the polymer chains and an increased crystallinity ³⁴. The degradation rate depends on the temperature during the hydrolysis. It is due not only to the increased hydrolysis rate at elevated temperatures ⁶⁸, but also to the increased flexibility of the polymer above the glass transition temperature. The number average molecular weight has significantly decreased before any weight loss can be detected ⁶⁹. In the second stage, the hydrolytic degradation of the crystalline regions of the polyester occurs, leading to an increased rate of mass loss and eventually complete degradation. In addition, the degradation of poly(lactide) in aqueous medium was reported by Li et al. to proceed more rapidly in the center of a specimen ⁷⁰.

2.5.3 Biodegradation

Biodegradation is initiated and maintained by enzymes or microorganisms, which also result in a fragmentation of the molecules. This subject is getting more and more interest among researchers. Karjomaa et al. ⁷¹ studied the effect of molecular weight of PLLA on the biodegradation and found that degradation was decreased with increasing chain length. McCarthy et al. ⁷² investigated the effects of physical aging and morphology on the enzymatic degradation of PLLA. They concluded that morphological changes due to the aging affect degradation rate due to reduction of chain mobility, which was reflected in a lower degradation rate.

2.6 Intrinsic Birefringence

Intrinsic birefringence is the birefringence of a perfectly oriented polymer sample. Both Δ_c^o and Δ_a^o are very important in correlations of the mechanical properties with the structure. It can be theoretically calculated from bond polarizabilities providing the conformation of the polymer is already known. Or it can be derived from experimental data from the following equation with values of birefringence Δ_T , crystallinity X_c and both crystalline orientation factor f_c and amorphous orientation factor f_a achieved from other measurements.

$$\Delta_T = X_c \Delta_c^o f_c + (1 - X_c) \Delta_a^o f_a \quad (2.6)$$

If we focus the works on polyesters, we noticed that various attempts have been made to decide the intrinsic birefringence of poly(ethylene terephthalate) (PET). Dumbleton⁷³ reported $\Delta_c^o = 0.220$ and $\Delta_a^o = 0.275$ which was based on Samuels⁷⁴ two-phase model and used by lots of authors to calculate the amorphous orientation factor. Okajima et al.⁷⁵ arrived $\Delta_c^o = 0.216-0.220$ and $\Delta_a^o = 0.213-0.216$, while Konda et al.⁷⁶ used $\Delta_c^o = \Delta_a^o = 0.212$.

Stein⁷⁷ has shown that $\Delta_c^o = K \Delta_a^o$, where K is a constant equal or greater than unity, i.e. Δ_a^o is equal or greater than Δ_c^o , due to internal field effects. However, some groups found results that disagree Steins theory. Among them, Gupta et al.⁷⁸ found $\Delta_c^o = 0.29$ and $\Delta_a^o = 0.22$ for PET providing Samuel's two phase theory is applicable to PET. In **Figure 2.26**, 20 samples were used to conduct the least squares analysis and a straight line was fitted to estimate the intrinsic birefringence values. They also

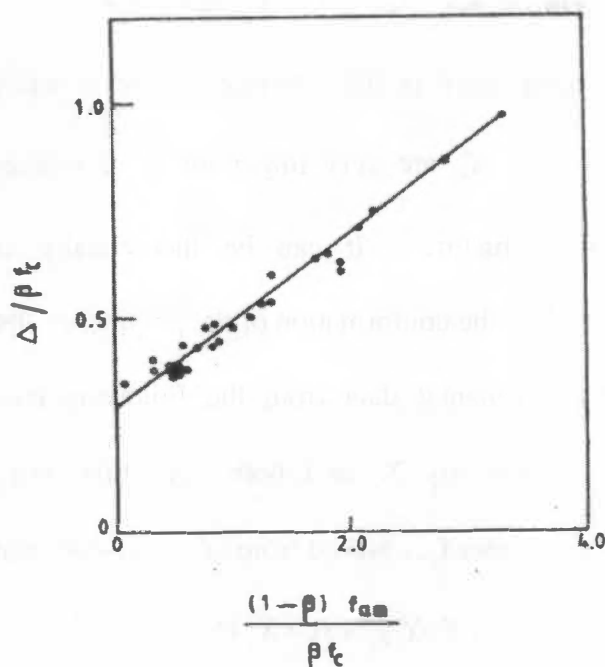


Figure 2.26 Data for Calculation of Intrinsic Birefringence of the Crystalline and Amorphous Phase⁷⁸

examined Dumbleton's data, which was based on four samples with different draw ratios. A linear fit of the first three data of Dumbleton's data (**Figure 2.27**) gave $\Delta_c^\circ = 0.30$ and $\Delta_a^\circ = 0.24$, which is very close to what Gupta et al. got. Devries et al.⁷⁹ obtained $\Delta_c^\circ = 0.22$ and $\Delta_a^\circ = 0.20$, Kugugi et al.⁸⁰ $\Delta_c^\circ = 0.24$ and $\Delta_a^\circ = 0.22$ and Garg⁸¹ $\Delta_c^\circ = 0.22$ and $\Delta_a^\circ = 0.19$. The same phenomenon was observed in other polymers such as nylon 6 by Matsumoto et al.⁸².

Chuah⁸³ found highly oriented poly(trimethylene terephthalate) (PTT) fiber has a low birefringence. The intrinsic birefringence Δ_c° of PTT crystal was calculated from its bond polarizabilities to be 0.029, which is almost an order of magnitude

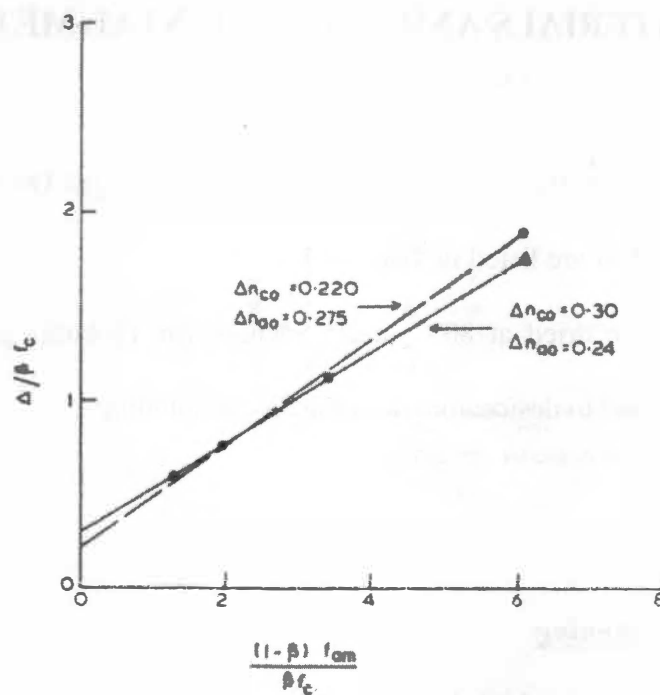


Figure 2.27 Dumbleton's Plot (---) Taken from ⁷³. The Solid Line Gives Different Values of Intrinsic Birefringence ⁷⁸

smaller than poly(ethylene terephthalate)'s value at 0.22 ⁷³ as well as poly(butalene terephthalate)'s value at 0.153-0.168 ⁸⁴. The author claimed the small Δ_c^o is due to the arrangement of PTT's methylene groups in gauche conformations, causing the chain-repeating unite to be tilted $\sim 53^\circ$ away from the c axis toward the basal plane.

Chapter 3 . MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials

The polymers used in this research were provided by Cargill Dow LLC. The molecular weight parameters are listed in **Table 3.1**.

PLLA pellets were dried at 80°C under vacuum for 12 hours prior to melt spinning. Then transferred to desiccators until the day of spinning.

3.2 Processing

3.2.1 High-speed Melt Spinning

Melt spinning was conducted using a screw extruder supplied by Forne Associates of West Germany equipped with a constant displacement melt pump that provided a constant extrusion rate. It is a four-heating-zone extruder with a 13mm diameter screw. Constant mass throughput was maintained by a Zenith constant displacement gear pump. The spin-pack was assembled with filter screens and a single-hole spinneret with diameter of 1mm. The L/D ratio of the spinneret capillaries was 5.

Pre-dried polymer pellets were put into a hopper purged with dry nitrogen gas to help protect them from hydrolytic degradation. For take-up velocity 1000m/min

Table 3.1 PLLA Material Identification, Molecular Weights, % D Composition and Polydispersity

ID	Mn	Mw	PDI	D%
PLLA1	91.6k	202.0k	2.21	0.8%
PLLA2	93.1k	211.9k	2.28	1.3%

and up, a 6.25 inch diameter godet was positioned 350cm below the spinneret exit, establishing a cooling path in room temperature. The achieved maximum take-up velocity was 4500m/min for PLLA1 and 3500m/min for PLLA2. The spinning conditions are summarized in **Table 3.2**.

3.2.2 Post-extrusion Annealing

Annealing was conducted using Napco oven under controlled temperatures with fluctuation about $\pm 2^\circ\text{C}$. Selected as-spun fibers were annealed under tension at 60, 80, 100, 125, and 150°C for 30mins.

3.3 Characterization Techniques

3.3.1 Phase Analysis

Phase identification and determination of lattice constants was made possible by using the Philips X'Pert Pro materials diffractometer. A 2-axes measurement, namely the azimuthal ψ and 2θ axes, was programmed to scan the well-aligned fiber samples in a transmission mode with a point source. Standard powder of lanthanum hexaboride (LaB_6) was smear on the sample by means of a little alcohol solution in order to calibrate and to eliminate systematic errors in the measurement.

Peaks identified with both 2θ and ψ positions by X'Pert Epitaxy software were

Table 3.2 Spinning Conditions for PLLA1 and PLLA2

ID	Extrusion Temperature	Mass Throughput	Take-up Velocity
PLLA1	223°C	5.2 g/min	1000-4500m/min
PLLA2	208°C	5.1 g/min	1000-3500m/min

used to match the literature values to determine the possible phases presented in the samples. The angle ψ is the angle we must tilt the sample from the vertical in order to get diffraction from a given set of planes assuming that the fiber is highly oriented and that a particular direction, such as c-axis, is parallel to the fiber axis. This is equivalent to the problem of finding the angle between two planes in a single crystal. For this latter problem, it is well known that the concept of the reciprocal lattice can be used. Since the reciprocal lattice vector, r_{hkl}^* , is perpendicular to the (hkl) planes, the angle φ between planes with indices (hkl) and planes with indices (h'k'l') is given, for the orthorhombic crystal system, by

$$\cos \varphi = \frac{r_{hkl}^* \cdot r_{h'k'l'}^*}{|r_{hkl}^*| |r_{h'k'l'}^*|} = \frac{(ha^* + kb^* + lc^*) \cdot (h'a^* + k'b^* + l'c^*)}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2} \left(\frac{h'^2}{a^2} + \frac{k'^2}{b^2} + \frac{l'^2}{c^2}\right)^{1/2}}$$

(3.1)

$$\begin{aligned} &= \frac{hh'a^*a^* + kk'b^*b^* + ll'c^*c^*}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2} \left(\frac{h'^2}{a^2} + \frac{k'^2}{b^2} + \frac{l'^2}{c^2}\right)^{1/2}} \\ &= \frac{\frac{hh'}{a^2} + \frac{kk'}{b^2} + \frac{ll'}{c^2}}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2} \left(\frac{h'^2}{a^2} + \frac{k'^2}{b^2} + \frac{l'^2}{c^2}\right)^{1/2}} \end{aligned}$$

As illustration in **Figure 3.1**, diffraction from planes that are 90 degree from the (00l) plane would occur on the equator (or hk0) at $\psi = 0$ if the fiber axis (c axis or [00l]) is placed vertically. Then by tilting an angle ψ , which is equal to $\psi = 90 - \varphi$, diffraction from a given plane (hkl) could also be observed at projected direction,

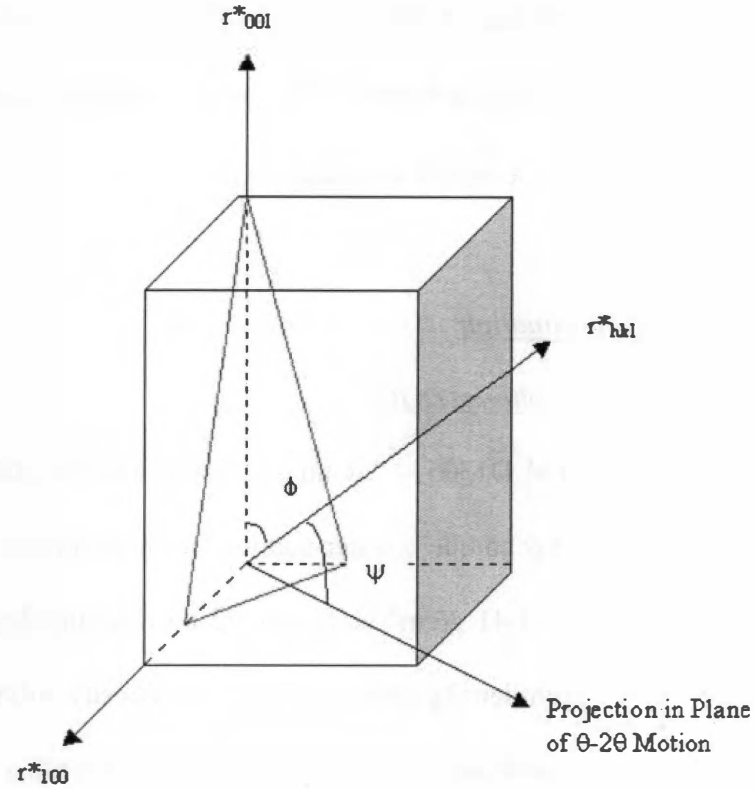


Figure 3.1 Schematic Illustration of the Calculation of Angle ψ

where ϕ is the angle between r_{001}^* and r_{hkl}^* . For the case that the c-axis tends to be parallel to the fiber axis in a highly oriented fiber, the above equations can be simplified to calculate the tilting angle ψ for any arbitrary (hkl) plane,

$$\cos \phi = \frac{r_{hkl}^* \cdot r_{001}^*}{|r_{hkl}^*| |r_{001}^*|} = \frac{(ha^* + kb^* + lc^*) \cdot (c^*)}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2} \left(\frac{1}{c^2}\right)^{1/2}} = \frac{l/c}{\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)^{1/2}} \quad (3.2)$$

$$\psi = 90 - \phi \quad (3.3)$$

Thus, the corresponding ψ values of any (hkl) planes are easily computed, provided the lattice parameters are known. The combination of 2θ and ψ information greatly helps narrow down the search to locate the (hkl) planes.

3.3.2 Crystallinity Determination

3.3.2.1 Density Gradient Column (DGC)

According to ASTM D1505 – “Standard Test Method for Density of Plastics by the Density Gradient Technique”, water-sodium bromide liquid systems targeting density range from 1.00 – 1.41 g/cm³ was selected because the density of PLLA is around 1.25 g/cm³. A high-density solution and a low-density solution of water and sodium bromide was prepared according to the desired testing range, which is 1.22 – 1.28 g/cm³ in this case. A density column with smooth gradient was made by pouring and mixing these two solutions gradually. A Haake N3-R constant-temperature circulator was connected to the column, maintaining it at $23 \pm 0.1^\circ\text{C}$. Four standard glass beads of density of 1.245, 1.255, 1.265, 1.275 g/cm³ were placed into the column for calibration. The equilibrium position was recorded after 24 hours and a linear calibration plot of height versus density was generated. Then samples were wetted in the low-density solution first before put into the density gradient column. Height positions of samples were read off the scale of the column after 24 hours equilibrium and the density value was converted from height measurements according to the calibration plot.

The crystallinity of the samples can be calculated from the equation:

$$X_c = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \times 100\% \quad (3.4)$$

where ρ is the average density of three specimens, ρ_a and ρ_c are the density of 100% amorphous and crystalline samples. The value of ρ_a can be derived by measuring the density of a totally amorphous sample. The value of ρ_c can be theoretically calculated from the lattice constants of the sample. The most commonly used value for PLA are $\rho_a = 1.248 \text{ g/cm}^3$ and $\rho_c = 1.290 \text{ g/cm}^3$.³⁴ In this thesis, $\rho_a = 1.2503 \text{ g/cm}^3$ and $\rho_c = 1.2762 \text{ g/cm}^3$ were used based on measurements made in the course of the research.

3.3.2.2 Thermal Analysis – (DSC)

The thermal analysis was performed using a Mettler DSC-821 differential scanning calorimeter (DSC). Calibration of the equipment was achieved by using an indium standard ($\Delta H = 28.45 \text{ J/g}$; T_m (onset) = 156.61°C). The scans were carried out in the range from 30°C to 200°C with heating rate at 10°C/min .

All fiber samples were chopped into small pieces of about 5mm long and placed into aluminum pans, which were then crimped. The samples weighed about 5 mg.

Thermal transitions were determined by peak positions. The degree of crystallinity was calculated according to the following equation, assuming the heat of fusion of the 100% crystalline poly(lactic acid) is 93 J/g .³⁴

$$X_c \% = \frac{||\Delta H_m| - |\Delta H_c||}{93} \times 100\% \quad (3.5)$$

where ΔH_c is the enthalpy of crystallization and ΔH_m is the enthalpy of melting.

3.3.2.3 Wide Angle X-ray Diffraction (WAXD)

A Phillips X'Pert Pro materials diffractometer with CuK α radiation at $\lambda = 1.5418 \text{ \AA}$, which operates at 45 kV and 40 mA, was used to make equatorial 2θ scans of the randomly distributed samples, which was made by chopping the fibers into very small pieces and stack into the window of an aluminum holder. Not only the peak positions and intensities were shown, but also we can use the graph to determine the crystallinity of the fiber samples. To do so, a scan of an amorphous sample under the same condition was performed to get a general idea where the amorphous peak locates and what its FWHM is. With the aid of the Profit software, the separation of the crystalline peaks and amorphous peak was achieved and each integrated intensity value was given. The crystallinity of the sample then can be calculated using the following simple equation:

$$X_c = \frac{I_c}{I_c + I_a} \times 100\% \quad (3.6)$$

where I_c is the total integrated intensity of all the crystalline peaks and I_a is the integrated intensity of the amorphous peak.

3.3.3 Molecular Orientation

3.3.3.1 Optical Birefringence: Determination of the Overall Molecular Orientation

Birefringence is a measure of the total molecular orientation of a system. It is defined as the difference in the principle refractive index parallel $n_{\parallel}$ and perpendicular $n_{\perp}$ to the stretch direction for a uniaxially oriented specimen.⁷⁴

Birefringence measurements were carried out on an Olympus BH-2 Polarizing microscope with Berek compensators. The birefringence value is calculated by:

$$\Delta_r = \frac{\Gamma}{d} \quad (3.7)$$

where Γ is the retardation and d is the diameter of the fiber. The retardation was determined by reading off Berek compensator scales the values of black lines observance in two directions. The sum of the two values was used to decide the retardation according to the tables provided by the compensator vendor. Fiber diameter was measured on a television screen, which is attached to the microscope by a Sony CCD video camera. The calibration was done using a graduated slide with 0.01 mm increment. Each birefringence value recorded represents the average from 12 specimens.

For a uniaxially oriented polymer, assuming two-phase system, the measured birefringence is defined as:

$$\Delta_r = X_c \Delta_c^o f_c + (1 - X_c) \Delta_{am}^o f_{am} + \Delta_f \quad (3.8)$$

where X_c is the crystallinity, Δ_c^o and Δ_{am}^o are the intrinsic birefringence of the perfectly oriented crystal and amorphous region, f_c and f_{am} are the crystalline and amorphous orientation factors of the sample. Δ_f is the form birefringence, which relates to the effect of the shape of the crystallite in the medium and is negligible in most cases. Hence when the birefringence, the crystallinity, the crystalline orientation factors and the intrinsic birefringence are known for a polymer, the amorphous orientation factor f_{am} can be calculated from above equation. Or if f_c , f_{am} , X_c and Δ_r

are obtained from different experimental techniques, the intrinsic birefringence of the crystalline and amorphous phase can be calculated.

3.3.3.2 Wide-Angle X-ray Diffraction: Determination of the Crystalline Orientation

Crystalline orientation factors of PLLA were derived from azimuthal x-ray scans using a Phillips X'Pert Pro materials diffractometer generating CuK α radiation at $\lambda = 1.5418 \text{ \AA}$. It was operated at 45 kV and 40 mA. Regular 2θ scans were performed first to decide the peak positions and determine relative background. At selected peak positions, azimuthal scans were run from $\psi = -90^\circ$ to $\psi = 90^\circ$.

Based on Herman's earlier work, Stein proposed descriptions of degree of orientation of a particular crystalline axis to a reference direction (Z) as follows.

$$f_{a,z} = \frac{1}{2}(3 \langle \cos^2 \varphi_{a,z} \rangle - 1) \quad (3.9)$$

$$f_{b,z} = \frac{1}{2}(3 \langle \cos^2 \varphi_{b,z} \rangle - 1) \quad (3.10)$$

$$f_{c,z} = \frac{1}{2}(3 \langle \cos^2 \varphi_{c,z} \rangle - 1) \quad (3.11)$$

where ϕ is the angle between reference direction Z and a specified crystallographic direction; the **a**, **b**, **c** are the unit cell vectors that describe the sign and shape of the unit cell; and $\langle \cos^2 \varphi_{c,z} \rangle$ is the mean squared cosine averaged over all crystallites of the angle ϕ between c crystalline axis and Z

When the value of the crystalline orientation factor equals 1, the specified crystal axis is at perfect alignment with Z. Likewise, a value of 0 indicates totally

random orientation and a value of -0.5 means that the specified crystal axis is perpendicular to Z. For an orthorhombic unit cell, the following relationships exist due to the system symmetry.

$$\langle \cos^2 \phi_{a,z} + \cos^2 \phi_{b,z} + \cos^2 \phi_{c,z} \rangle = 1 \quad (3.12)$$

$$f_{a,z} + f_{b,z} + f_{c,z} = 0 \quad (3.13)$$

The mean squared cosine of the angle ϕ over all crystallites between any (h k l) plane normal (N) and the fiber axis was defined as:

$$\text{Second-order moment: } \langle \cos^2 \phi_{hkl,z} \rangle = \frac{\int_0^\pi I(\phi) \sin \phi \cos^2 \phi d\phi}{\int_0^\pi I(\phi) \sin \phi d\phi} \quad (3.14)$$

For example, as to (0 0 l) plane normal, $\langle \cos^2 \phi_{hkl,z} \rangle = \langle \cos^2 \phi_{00l,z} \rangle = \langle \cos^2 \phi_{c,z} \rangle$ and the corresponding crystalline orientation factor: $f_{c,z} = \frac{1}{2}(3 \langle \cos^2 \phi_{c,z} \rangle - 1)$. In the present case, we measured $f_{c,z}$ from the azimuthal intensity distribution of the (0 0 10) reflection. Similarly the (2 0 0) reflection was used to compute the value of $f_{a,z}$. The value of $f_{b,z}$ was then obtained from **Equation 3.13**.

The peak intensities of the targeted reflections were corrected by measuring background intensities, which were scanned azimuthally under the same condition as the peak scans. The background intensities were subtracted from the peak intensities before further treatment of peaks and the calculation of orientation function were applied.

3.3.3.3. Sonic Modulus: Determination of the Amorphous Orientation

Sonic modulus technique was used to determine the amorphous orientation factor. The fibers were tested on the dynamic modulus tester PPM-5R from Lawson-Hemphill, Inc. The results were based on the measurements of 5 specimens of each sample and the average was taken.

Assuming two-phase system and bulk compressibility, the sonic modulus of oriented and unoriented fibers can be determined by the following equations.⁷⁴

$$\frac{1}{E_{or}} = \left(\frac{X_c}{E_{t,c}^o} \right) (1 - \langle \cos^2 \theta_c \rangle) + \left(\frac{1 - X_c}{E_{t,am}^o} \right) (1 - \langle \cos^2 \theta_a \rangle) \text{ Oriented Fibers} \quad (3.15)$$

since $\langle \cos^2 \theta_c \rangle = 1/3$ for unoriented samples,

$$\frac{3}{2E_u} = \left(\frac{X_c}{E_{t,c}^o} \right) + \left(\frac{1 - X_c}{E_{t,am}^o} \right) \text{ Unoriented Fibers} \quad (3.16)$$

Once the intrinsic transverse moduli of the crystalline $E_{t,c}^o$ and amorphous $E_{t,am}^o$ regions have been determined from the measurements on unoriented samples, the amorphous orientation factor f_a of any oriented sample can be determined from experimental values of the sonic modulus E_{or} , the crystallinity X_c , and the crystal orientation factor f_c , according to the transformation of **Equation 3.15**:

$$\frac{3}{2E_{or}} = \left(\frac{X_c}{E_{t,c}^o} \right) (1 - f_c) + \left(\frac{1 - X_c}{E_{t,am}^o} \right) (1 - f_{am}) \quad (3.17)$$

In the sonic modulus experiment, the fibers were mounted between the transmit transducer and the receive transducer, with a small load just enough to hold the fiber taut. When the transmit transducer was moved towards the receive transducer in one centimeter increments, the transition time in microseconds was

recorded along with the distance between the transducers. When plotted the transit time and distance, the sonic velocity through the fibers can be determined. As $E = \rho C^2$, where E is the sonic modulus, ρ is the density and C is the sonic velocity, if the density is known, the sonic modulus can be calculated.

First all of, a series of the unoriented samples of different density was prepared. Unoriented fiber filaments were collected under no drawdown force other than the gravity and annealed at different temperatures to obtain different crystallinity.

Thus, **Equation 3.16** can be written as $\frac{1}{E_u} = \frac{2}{3} \left(\frac{1}{E_{t,c}^o} - \frac{1}{E_{am}^o} \right) X_c + \frac{2}{3} \left(\frac{1}{E_{t,am}^o} \right)$. Plot $1/E_u$ vs. X_c , $E_{t,am}^o$ can be calculated from the intercept and $E_{t,c}^o$ can be calculated from the slope. Then we can use these two parameters to calculate f_{am} with measured E_{or} and known X_c and f_c using **Equation 3.17**:

Once f_{am} is calculated from the experimental data, along with the f_c got from X-ray diffraction, the birefringence and the crystallinity value, the intrinsic birefringence of both crystalline and amorphous phase can be estimated and compared to the values derived from theoretical calculation based on bond polarizability, if available.

$\Delta_T = X_c \Delta_c^o f_c + (1 - X_c) \Delta_a^o f_{am}$ can be written as: $\frac{\Delta_T}{X_c f_c} = \Delta_c^o + \frac{(1 - X_c)}{X_c} \frac{f_{am}}{f_c} \Delta_a^o$

simply plot $\frac{\Delta_T}{X_c f_c}$ vs. $\frac{(1 - X_c)}{X_c} \frac{f_{am}}{f_c}$, the slope should be the intrinsic birefringence of amorphous phase and the intercept should be the intrinsic birefringence of crystalline phase.

Chapter 4 . RESULTS AND DISCUSSIONS

4.1 Measurement of Amorphous and Crystalline Density

Although there is literature that gives the values of the amorphous and crystalline densities of PLLA, there is considerable variability in the values. Since these densities are critically important to a proper determination of many of the quantities measured in this research, we decided to make our own measurements of them.

An amorphous sample was acquired by extruding fibers without any other external force than the gravity. The corresponding amorphous density was then determined from the equilibrium resting height of the sample in the density gradient column according to the calibration equation. The resulting value is $\rho_a = 1.2503 \pm 0.0002 \text{ g/cm}^3$. The error quoted is based on the resolution of the density gradient column. It does not include all potential sources of error. In the literature, $\rho_a = 1.248 \text{ g/cm}^3$ was found in a completely amorphous DL-poly lactide by Fischer³⁴, which is 0.0023 smaller than our value. This is a difference of less than 0.2%. The difference could be due to the use of different D- content polymer, and there are also some obvious sources of error in any such measurements. Among them are the accuracy of the density gradient column, the amount of water absorbed in the sample, the form of the sample and the reading from the column. Based on the potential sources of error, we believe that our value and that of Fischer's are virtually equivalent.

The crystalline phase commonly observed in PLLA melt spun fiber is the α phase. The crystalline density is commonly determined from the lattice parameters of the PLLA unit cell using the following equation:

$$\rho_c = \frac{n * M}{V * N_A} \quad (4.1)$$

where n is the number of monomers in the unit cell, M is the molecular weight of the monomer, V is the volume of the unit cell and N_A is Avogadro's number, 6.02×10^{23} . In order to calculate the crystalline density, the information of lattice constants has to be obtained first for the α phase. Here we used a 2-axes x-ray scan to measure the location of the diffraction peaks (2θ and ψ) for PLLA. This type of pattern is equivalent to a "fiber pattern" and gives an additional quantity, ψ , for each diffraction peak, that helps considerably in the indexing of the pattern, especially when there are many diffraction peaks, as is the case for a well crystallized PLLA.

In order to best index PLLA and determine its crystalline density, a PLLA rod of diameter 2mm made by a former graduate student of our group was used. It was known to have very strong orientation according to its flat film pattern (**Figure 4.1**)⁸⁵, showing lots of strong reflection spots and consisting of the α phase. The fabrication of this rod was achieved by pulling ~200 filaments of PLLA fibers through a pultrusion die at 175°C under proper tension. The 2-axes scan of the PLLA rod provided a nice 2-D pattern, shown in **Figure 4.2**. By use of the semi-automatic search function of the software, 34 peak positions, identified by both 2θ and ψ , were located.

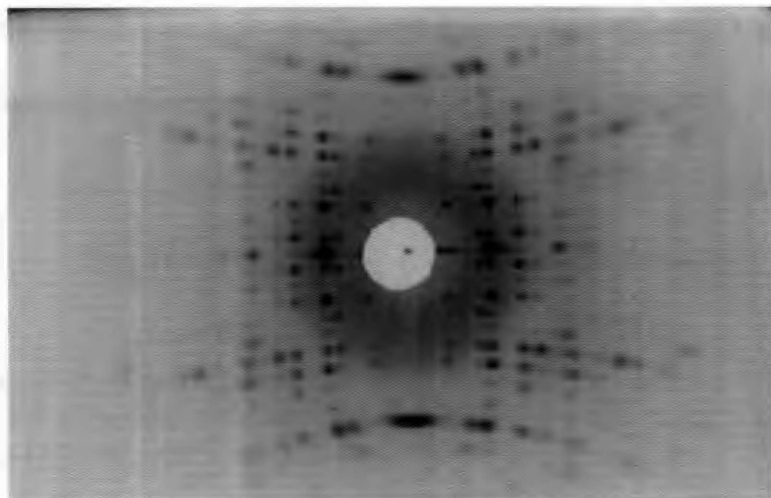


Figure 4.1 Flat Film Pattern of Highly Oriented PLLA Rod (d = 2mm)

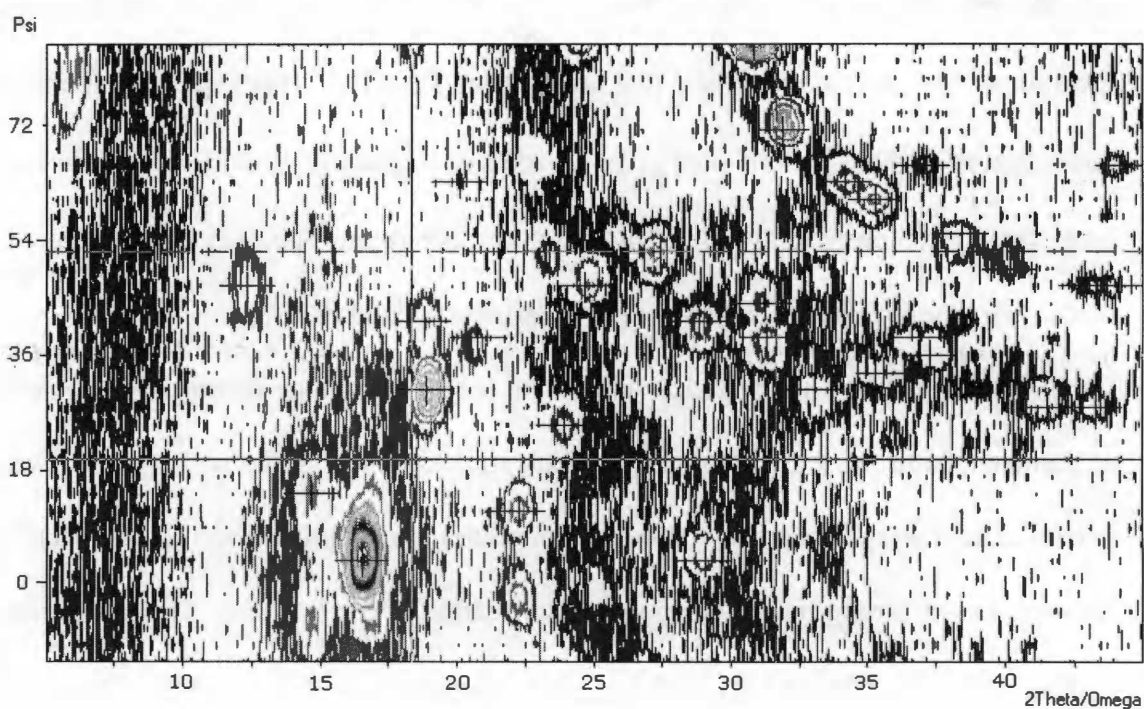


Figure 4.2 2-axes Scan Pattern of Highly Oriented PLLA Rod (d = 2mm)

In order to index the pattern, Kobayashi et al.'s¹⁴ lattice constants ($a = 10.5\text{\AA}$, $b = 6.1\text{\AA}$, $c = 28.8\text{\AA}$, $\rho_c = 1.2967\text{ g/cm}^3$) for the α phase were used to calculate the 2θ and ψ values for each corresponding (hkl) plane. Both the 2θ and ψ positions were matched between the experimentally observed values and the calculated values, and the possible indices for each observed peak are listed in **Table 4.1**. Also listed are the difference of observed and calculated values, $\Delta 2\theta$ and $\Delta\psi$.

$\Delta\psi$ values range from 0 to 3. Since the step size of the azimuthal scan is 3, the ψ values are in reasonable agreement with the literature in regard to picking the correct (hkl) indices. Some of the 2θ positions could be two possible planes superimposed on each other because they share the same ψ value and the 2θ values are very close to each other.

In order to calibrate the 2θ scale and eliminate systematic errors, lanthanum hexaboride (LaB_6) powders purchased from National Bureau of Standards (NBS) were used. This was especially important because of the specific configuration (transmission mode) used to execute the 2-axes scans. Powders of LaB_6 were dispersed in alcohol first, and then painted on PLLA fibers. A 2θ scan along the equator was performed and all the LaB_6 peak positions identified (**Figure 4.3**). The calibration of $\Delta 2\theta$ versus 2θ is plotted in **Figure 4.4**. 2θ values of the observed scan were then corrected using the calibration equation. The random error is more prominent than what we usually observe in standard powder data, which is performed on a flat sample under reflection scan mode. The deposition of LaB_6 on the fiber in our experiment is not physically as flat as standard powder samples. This evidently

Table 4.1 Indices of Highly Oriented PLLA Rod

Peak No.	Observed 2 θ (°)	Observed ψ (°)	Calculated 2 θ (°)	Calculated ψ (°)	(h k l)	$\Delta 2\theta$ (°)	$\Delta \psi$ (°)
1	12.36	48	12.483	48	(1 0 3)	0.123	0
2	14.70	12	14.833	12	(0 1 1)	0.133	0
3	16.54	0	16.795	0	(1 1 0)	0.255	0
			16.874		(2 0 0)	0.334	
4	18.34	90	18.469	90	(0 0 6)	0.129	0
5	18.84	42	19.053	40	(0 1 4)	0.213	2
6	18.90	30	19.184	29	(1 1 3)	0.284	1
			19.253		(2 0 3)	0.353	
7	20.14	66	20.326	66	(1 0 6)	0.186	0
8	20.76	39	20.860	36	(1 1 4)	0.100	3
			20.924		(2 0 4)	0.164	
9	22.30	9	22.538	8	(2 1 1)	0.238	1
10	23.40	54	23.565	52	(0 1 6)	0.165	2
11	23.90	24	24.192	23	(2 1 3)	0.292	1
12	24.58	90	24.710	90	(0 0 8)	0.130	0
13	24.70	48	25.063	48	(1 1 6)	0.363	0
			25.117		(2 0 6)	0.417	
14	27.40	54	27.471	52	(1 1 7)	0.071	2
			27.521		(2 0 7)	0.121	
15	28.82	42	29.126	40	(2 1 6)	0.306	2
16	29.08	0	29.257	0	(0 2 0)	0.177	0
			29.397		(3 1 0)	0.317	
17	30.82	90	31.026	90	(0 0 10)	0.206	0
18	31.22	45	31.246	44	(2 1 7)	0.026	1
19	31.28	39	31.611	36	(3 0 6)	0.331	3
20	31.90	75	32.203	75	(1 0 10)	0.303	0
21	33.02	30	33.210	28	(0 2 5)	0.190	2
			33.335		(3 1 5)	0.315	
22	34.18	66	34.407	65	(0 1 10)	0.227	1
23	35.28	63	35.484	61	(1 1 10)	0.204	2
			35.523		(2 0 10)	0.243	
24	35.56	33	35.888	31	(1 2 6)	0.328	2
25	36.90	39	36.647	37	(0 2 7)	-0.253	2
			36.761		(3 1 7)	-0.139	
26	37.00	69	37.345	67	(0 1 11)	0.345	2
27	37.24	36	37.668	36	(1 2 7)	0.428	0
28	38.44	57	38.557	54	(2 1 10)	0.117	3
29	40.16	51	40.530	51	(3 0 10)	0.370	0
30	41.52	27	41.893	27	(4 1 6)	0.373	0
31	42.96	48	43.167	47	(0 2 10)	0.207	1
			43.267		(3 1 10)	0.307	
32	43.28	27	43.609	26	(3 2 6)	0.329	1
33	44.16	48	44.061	46	(1 2 10)	-0.099	2
34	44.28	69	44.311	67	(1 1 13)	0.031	2
			44.344			0.064	

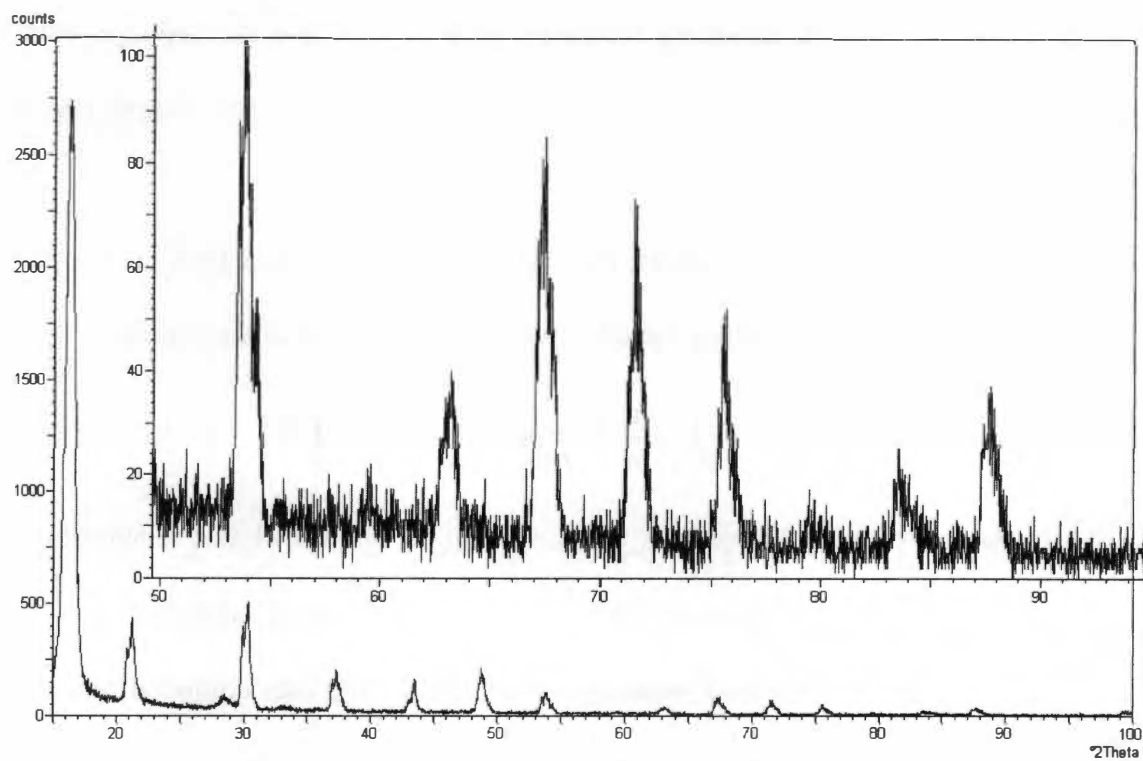


Figure 4.3 Equator 2θ Scan of LaB₆ Powder Embedded in PLLA Fibers

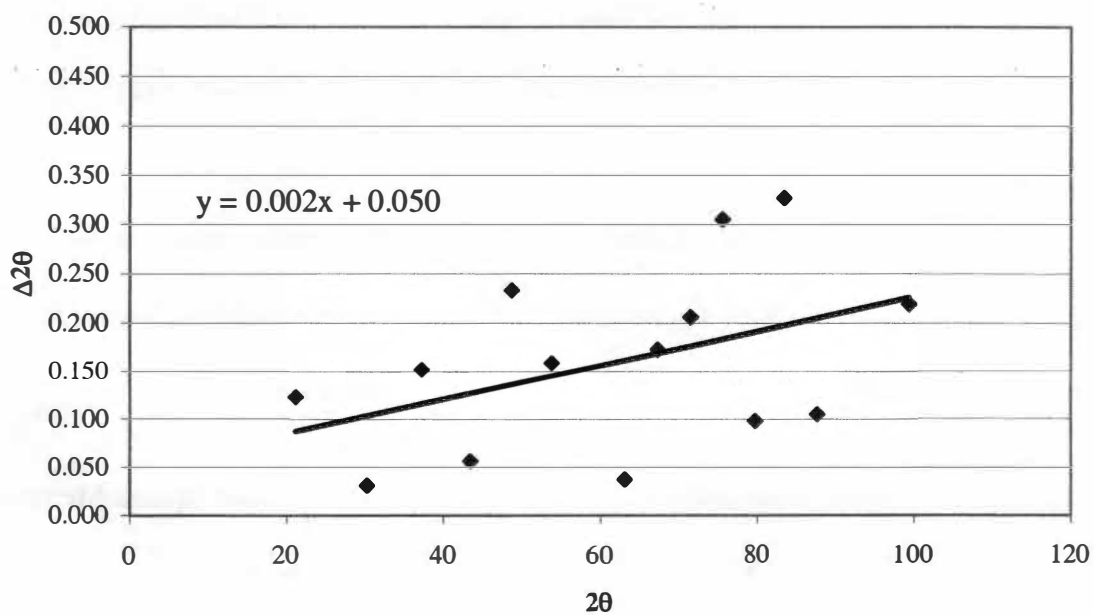


Figure 4.4 Δ2θ vs. 2θ Calibration Plot of LaB₆

led to the scattering of data points. Another reason could be that the step size of 0.02, which is consistent to the 2-axes scan, is larger than when we usually run the standards.

For the orthorhombic system, the value of d-spacing of any (hkl) crystal plane can be found from the following equation, where a, b and c are lattice constants.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (4.2)$$

Knowing (hkl), 2θ position, the wavelength λ and the classic relationship of $\lambda = 2d \sin \theta$, a series of equations can be written to solve for the lattice constants a, b and c. A simple Fortran least square program (NBS_LSQ.exe) compiled especially for this calculation purpose was used to generate the best set of a, b and c. The approximate lattice constants, the crystal system, 2θ values and the indices were required as input. The results are listed in Table 4.2. The program also computes the volume of the unit cell and the standard errors in the lattice constants and the unit cell volume.

These values of lattice constants give the unit cell volume equal to $1874.39 \pm 1.9 \text{ \AA}^3$ according to the least square fitting program. This amounts to a potential error in the unit cell of only 0.10%.

Table 4.2 Lattice Constants of Orthorhombic PLLA by Least Square Method

	a (Å)	b (Å)	c (Å)	V (Å ³)
Present Value	10.57 ± 0.084	6.13 ± 0.007	28.91 ± 0.017	1874.39 ± 1.9

Once the lattice constants were decided, it was then applied to calculate a new set of 2θ values, which can be compared with the observed 2θ values. Such a plot is shown in **Figure 4.5** based on the 2θ values corrected for systematic errors. It shows a reasonable agreement with the measured values.

Because we can calculate the 100% crystalline density from the lattice constant, it is very important to get reliable sets of data, thus ensure the reliability of the data calculated based on the crystalline density value, such as the crystallinity value based on DGC, or the calculation of intrinsic birefringence, etc. Due to its high importance, we looked back at the lattice constants different groups had proposed and calculated the crystalline density for comparison in **Table 4.3**. Excluding Brizzolara et al.'s results on the basis that the crystalline density is obviously too low, our value is near the mean of the other values. Obviously, crystalline density is very sensitive to small changes in the lattice parameters, the literature values ranging from 1.2467 – 1.2967 g/cm³, while the *a* value ranges from 10.5Å to 10.78Å, *b* from 6.04Å – 6.45Å and *c* from 27.8Å – 28.939Å. For example, if *a*, *b* and *c* values each change 0.1%, the change in density value is substantial, as in **Table 4.4**. In the following section, we use the density value we found, i.e. 1.2762 ± 0.0013 g/cm³ to perform the other analyses. Note that the quoted error is due only to the estimated error in the volume of the unit cell as given in **Table 4.2**.

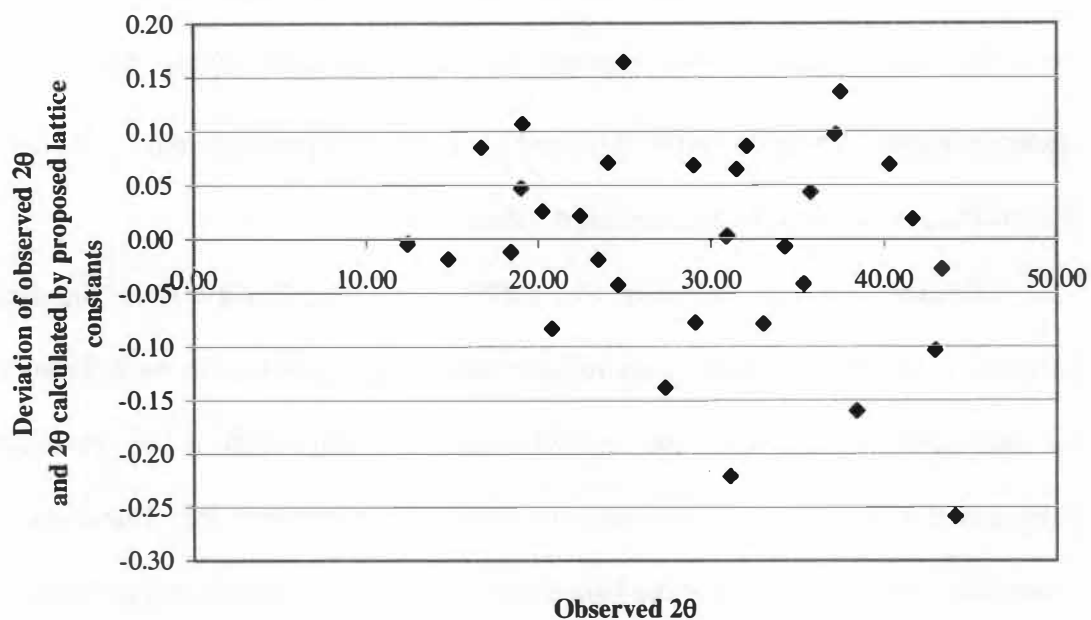


Figure 4.5 Deviation of 2 θ vs. Observed 2 θ of Highly Oriented PLLA Rod with Lattice Constants of $a = 10.57\text{\AA}$, $b = 6.13\text{\AA}$ and $c = 28.91\text{\AA}$

Table 4.3 Crystalline Density of Proposed Lattice Constants by Different Groups

a (Å)	b(Å)	c(Å)	Crystal System	Authors	Density (g/cm ³)
10.7	6.45	27.8	pseudo-orthorhombic	De Santis and Kovac	1.2467
10.6	6.1	28.8	pseudo-orthorhombic	Hoogsteen et al	1.2845
10.7	6.126	28.939	pseudo-orthorhombic	Merega et al	1.2610
10.5	6.1	28.8	orthorhombic	Kobayashi et al	1.2967
10.78	6.04	28.7	orthorhombic	Miyata and Masuko	1.2801
7.10	9.40	29.86	orthorhombic	Brizzolara et al	1.2003
10.57	6.13	28.91	orthorhombic	Present Value	1.2762 $\pm$ 0.0013

Table 4.4 Resultant Density Change of 0.1% Lattice Parameters Change

	a (Å)	b(Å)	c(Å)	Density (g/cm ³)
	10.4895	6.0939	28.7712	1.3006
Kobayashi et al.	10.5	6.1	28.8	1.2967
	10.5105	6.1061	28.8288	1.2929

4.2 The Structure of As-spun Filaments

4.2.1 X-ray Diffraction Data and Phase Present

2-axes x-ray patterns of selected as-spun fibers are shown in **Figure 4.6**. The most obvious features of these patterns is that they all indicate much lower crystallinity and orientation than the pattern of the rod sample shown in **Figure 4.1-2**. In these patterns, many of the reflections are too weak to be observed. In spite of this fact, the reflections that are observed are consistent with the crystal form being α phase. Annealed fibers also exhibited patterns that are consistent with α phase, as discussed in section 4.3.

4.2.2 Thermal Properties

All the DSC thermographs of as-spun fibers show a distinctive exothermic “cold crystallization” peak, which is a clear indication of restrained crystallization during the high-speed fiber spinning process and re-crystallization during the heating of DSC scans. **Figure 4.7** shows the combined thermograph of PLLA1 fibers spun under different take-up velocities. It seems that the melting temperature (T_m) of each sample is in close neighborhood of 170°C, while the crystallization temperature (T_c) decreases with increasing take-up velocity. This suggests that higher take-up velocities result in a higher crystallization rate during the heating procedure.⁸⁶ For fibers spun at 4500m/min, we observed an obscure bimodal melting peak, which could be the melting of smaller stress-induced crystals formed during the high-speed spinning preceding the melting of the larger crystals formed during the heating of the

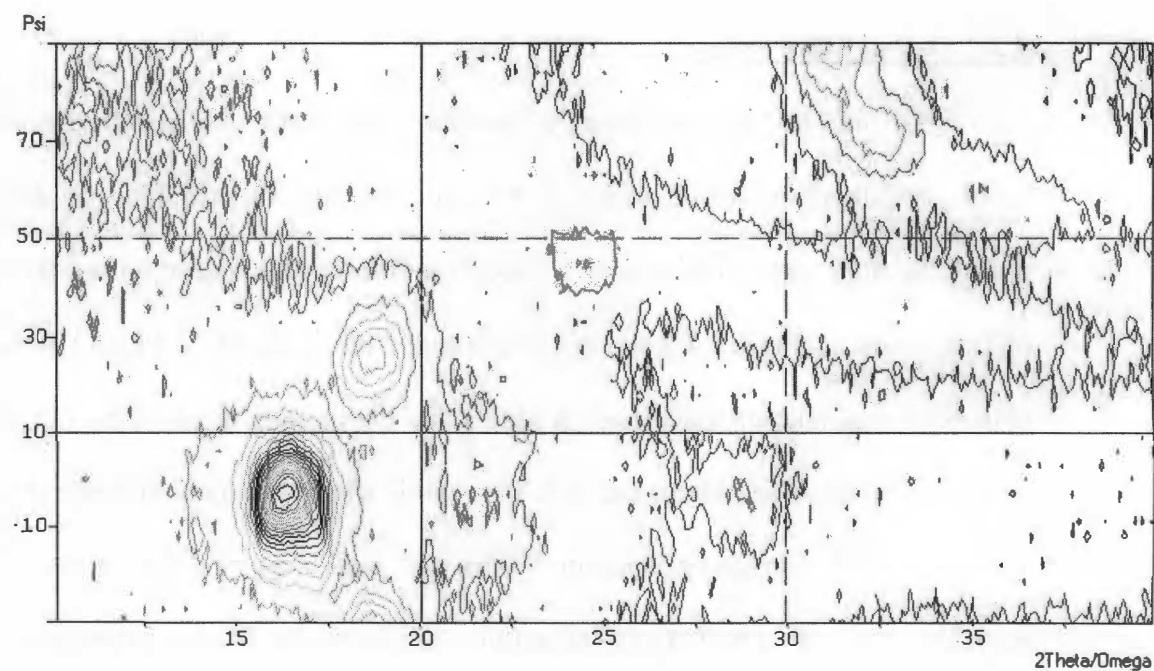
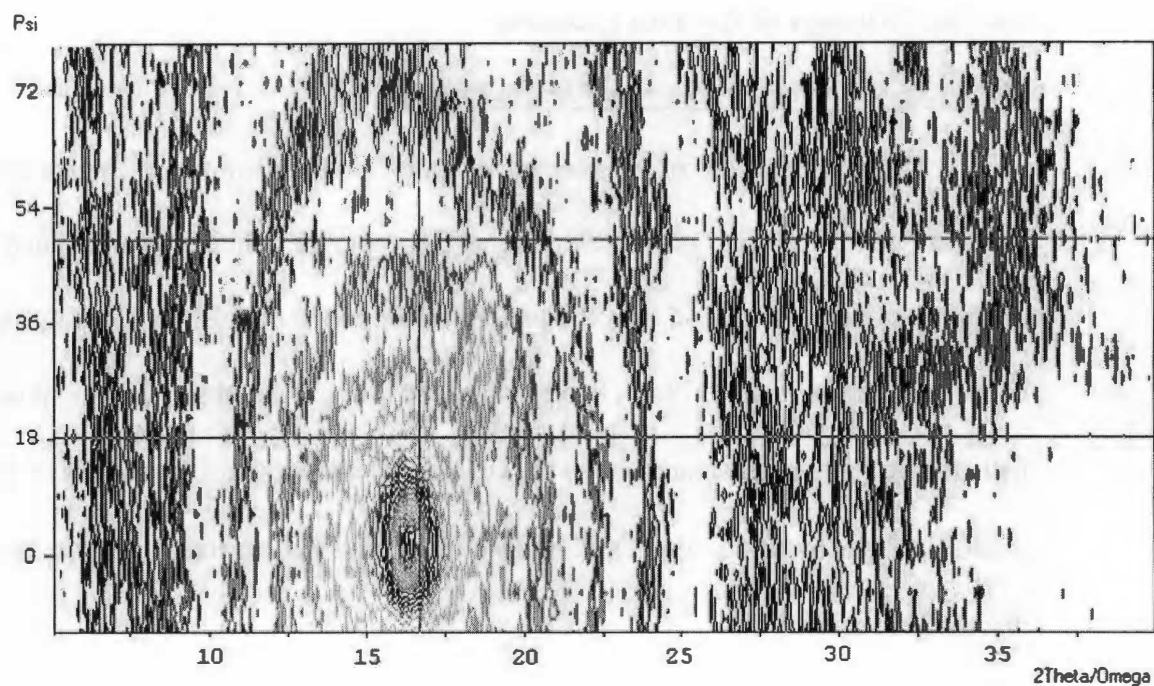


Figure 4.6 2-axes Scan Pattern of As-spun PLLA Fibers: PLLA1-4500 (upper), PLLA2-3000 (lower)

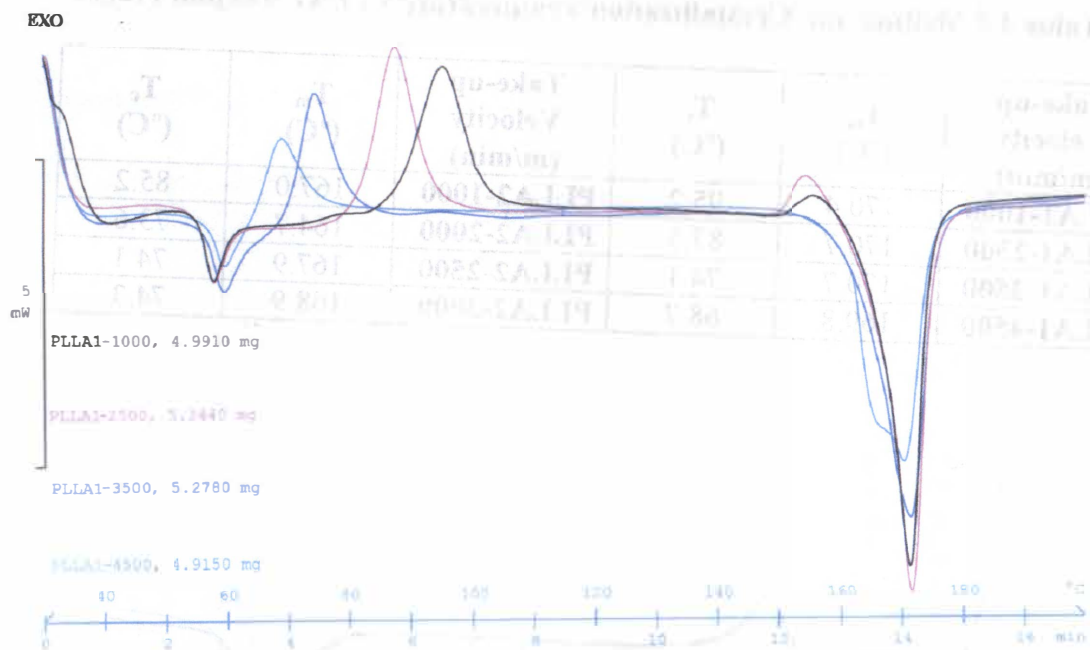


Figure 4.7 DSC Thermograph of As-spun PLLA1 Fibers of Different Take-up Velocities

DSC scan. **Table 4.5** lists the melting and cold crystallization temperature of both PLLAs.

In **Figure 4.8**, except for PLLA2-1000, which crystallizes at 85.2°C, the “cold crystallization” peak position of other PLLA2 as-spun samples are around 74°C. This is different from what we observed in PLLA1, which showed a descending trend in crystallization temperature corresponding to increasing take-up velocity. This could be due to saturation of the effect of stress in the spinline of PLLA2 fibers above 2000m/min. The melting temperature of PLLA2 is slightly lower than that of PLLA1 due to the higher D-content of PLLA2 vs. PLLA1 (1.3% vs. 0.8%), which was concluded in M. Williams in her thesis.⁸⁷ Huang et. al.⁴³ proposed that only long L lactide sequences are capable of crystallization and the attachment of D lactide units interfered with the growth of L-lactide crystals. Recently, Schmack et. al.⁸⁸ claimed

Table 4.5 Melting and Crystallization Temperature PLLA1 As-spun Fibers

Take-up Velocity (m/min)	T _m (°C)	T _c (°C)	Take-up Velocity (m/min)	T _m (°C)	T _c (°C)
PLLA1-1000	170.4	95.2	PLLA2-1000	167.0	85.2
PLLA1-2500	170.7	87.5	PLLA2-2000	164.7	73.6
PLLA1-3500	170.7	74.1	PLLA2-2500	167.9	74.1
PLLA1-4500	169.8	68.7	PLLA2-3000	168.9	74.3

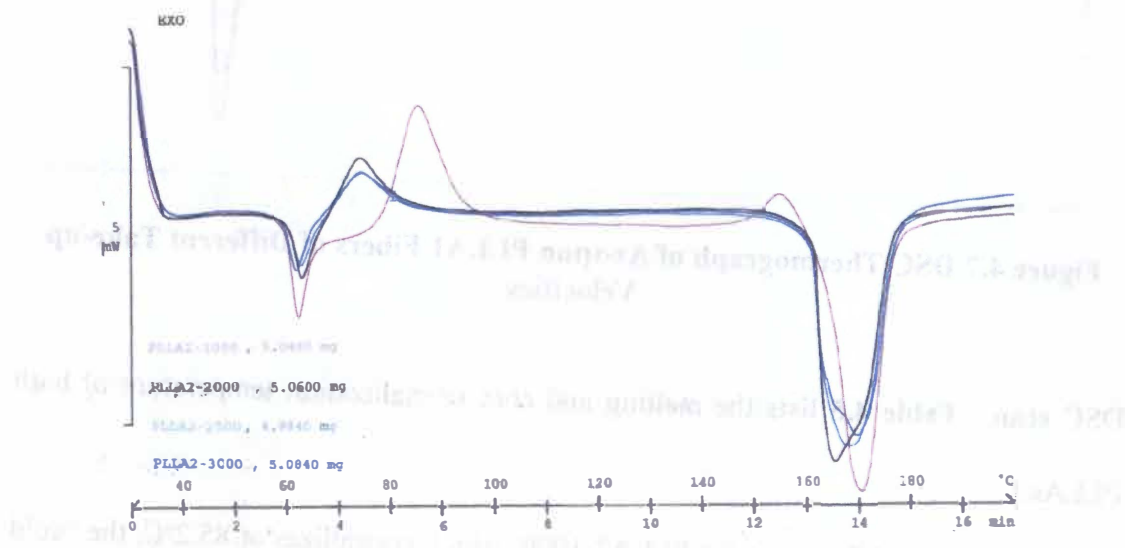


Figure 4.8 DSC Thermograph of As-spun PLLA2 Fibers of Different Take-up Velocities

that the correlation between T_m and D lactide content is not valid. Based on their NMR spectroscopy results, they believed that the amount of oligomers in PLA samples plays a major role in lowering melting temperature. Their conclusion was derived from DSC scans of a series of PLA pellets of different D lactide content. It is likely that both D content and the presence of oligomers have an effect on the melting temperature. This would be expected based on the Flory-Huggins Equation.

The shape of the melting peaks of PLLA2 is broader than that of PLLA1. It could be an indication of broader distribution of the size of crystallites within PLLA2 fiber. The endothermic melting peaks of PLLA2 as-spun fibers spun under take-up velocity of 2000m/min or higher are bimodal. The software detected melting temperature of PLLA2-2000 is 164.7°C, which could be the first melting peak of the bimodal, and the second melting peak would be around 169°C from the thermograph.

4.2.3 Crystallinity

The crystallinity calculated from both DSC and DGC measurements is listed in **Table 4.6**. Clearly the values obtained from DSC are consistently larger than those obtained from DGC. DGC measures the density of fibers as it is; it does not involve heating like DSC does, thus DGC introduces less artificial factor into the results. But density measurements on fine fibers can be difficult. The air trapped between the fibers possibly lowered the resting height reading from the column and thus the density values. The calculation of crystallinity from DGC requires the known density value of 100% crystalline and amorphous materials. As for PLLA, most groups have used Fischer's value of $\rho_a = 1.248 \text{ g/cm}^3$ and $\rho_c = 1.290 \text{ g/cm}^3$.³⁴ We have used $\rho_a = 1.2503 \text{ g/cm}^3$ and $\rho_c = 1.2762 \text{ g/cm}^3$ based on our own findings as presented earlier. Because it is not certain which method gives the more accurate results, we have chosen to give both DSC and DGC values. Meanwhile, WAXD was performed on randomized samples to qualitatively and semi-quantitatively get an idea which data is more or less reliable, DSC or DGC. Scans obtained from different as-spun samples were normalized first, and then plotted as **Figure 4.9**. It is quite obvious that as-spun

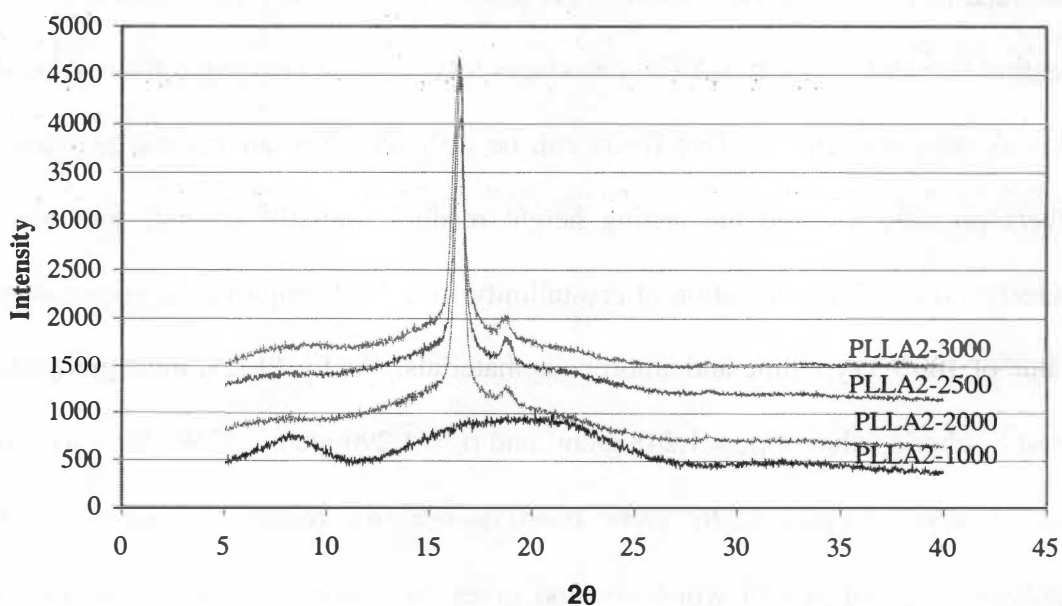
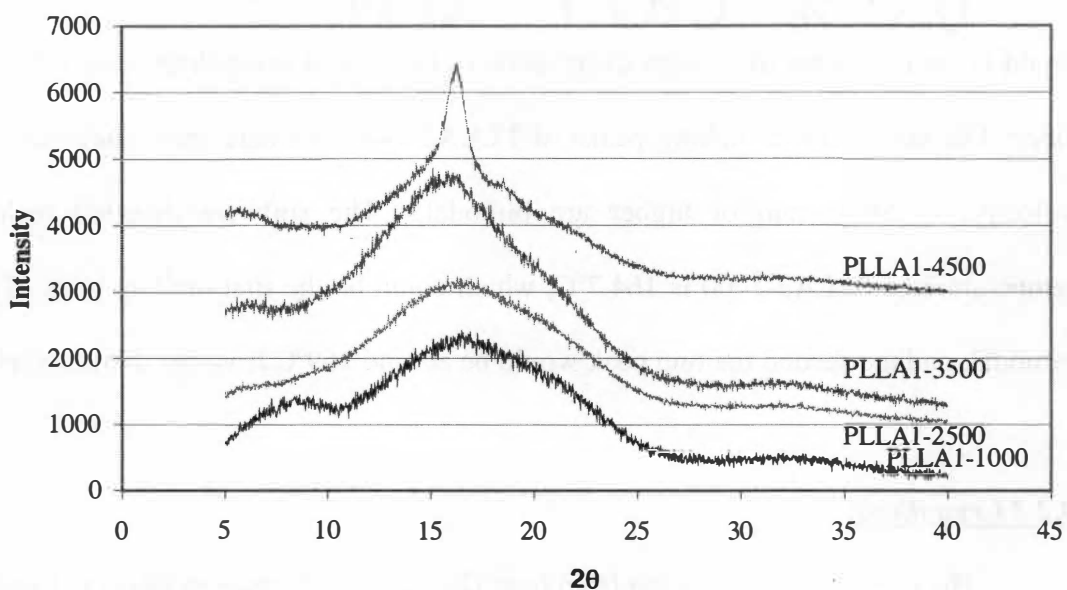


Figure 4.9 Normalized X-ray 2θ Scans of As-spun PLLA1 (upper) and PLLA2 (lower) (scans have been shifted vertically so that they are more readily observed)

Table 4.6 Crystallinity of As-spun PLLA Fibers by DSC and DGC

Take-up Velocity (m/min)	Xc-DSC (%)	Xc-DGC (%)	Xc-X-ray (%)	Take-up Velocity (m/min)	Xc-DSC (%)	Xc-DGC (%)	Xc-X-ray (%)
PLLA1-1000	14.5%	3.1%	3.4%	PLLA2-1000	11.7%	10.0%	13.2%
PLLA1-2500	12.9%	6.0%	4.2%	PLLA2-2000	40.5%	24.9%	18.6%
PLLA1-3500	35.7%	15.4%	6.4%	PLLA2-2500	42.4%	26.9%	23.5%
PLLA1-4500	45.1%	26.2%	11.8%	PLLA2-3000	41.7%	29.4%	24.6%

PLLA1-1000, PLLA1-2500, PLLA1-3500 and PLLA2-1000 fibers do not contain much crystallinity, as the peaks appeared to be a broad amorphous lump. PLLA1-4500 fiber starts to show substantial crystallinity as crystal peaks are readily observed. Crystallinity develops much earlier in the PLLA2 samples. PLLA2-2000, PLLA2-2500 and PLLA2-3000 developed quite an amount of crystallinity, presenting quite sharp crystal peaks. Judging from the appearance of the x-ray peaks, we believe that the crystallinity value acquired from DGC technique is probably more accurate for the as-spun fibers since it seems to be substantiated by the x-ray results, which is also listed in **Table 4.6**. It is clear that the PLLA1-1000 is close to amorphous from the x-ray pattern (3.4% by Profit), while the DSC gives a crystallinity value of 14.5% and DGC gives 3.1%. The rest of the density data supports that as well.

Figure 4.10 shows the crystallinity vs. take-up velocity relationship by means of DSC and DGC. It almost seems like there is more discrepancy at higher take-up velocity than lower take-up velocity. Even though the absolute crystallinity values were different from these two methods, the trend observed was in surprising agreement. Crystallinity increases with the take-up velocity for both PLLAs. It seems that PLLA2 as-spun fibers developed higher crystallinity than PLLA1 during the

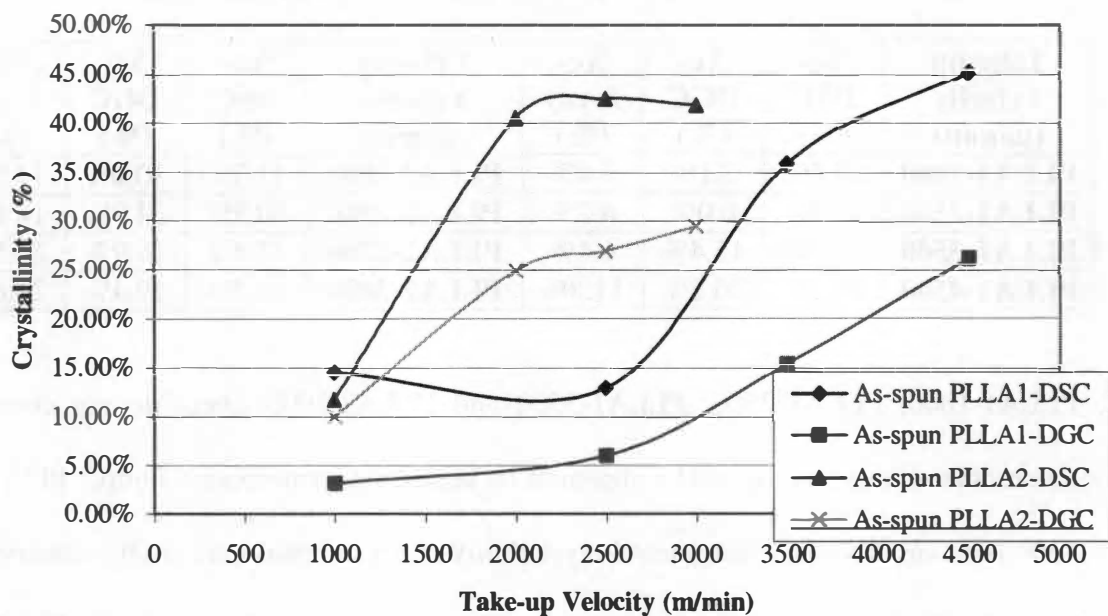


Figure 4.10 Relationship between the Crystallinity and Take-up Velocity of As-spun PLLAs by DSC and DGC

spinning process, especially at lower take-up velocities. There are several reasons that can cause the difference in crystallinity during spinning, all involve the stress in the spinline, which is directly related to the stress-induced crystallization in high-speed fiber spinning: (1) higher molecular weight would increase the stress in the spinline, which enhanced the stress-induced crystallization; (2) lower mass throughput would increase the cooling rate in the spinline, thus increase the spinline stress and stress-induced crystallization; (3) higher extrusion temperature leads to higher cooling rate, but lower spinline stress and stress induced crystallization due to lower viscosity in upper part of the spinline and (4) lower D-content samples are more capable of crystallization when there is less D-units to interfere with the growth front of long L-

units sequence, thus experiencing stress at an earlier stage. Being of almost the same molecular weight ($M_w = 91.6k$ vs. $M_w = 93.1k$) and processed at similar mass throughput (5.1g vs. 5.2g), the most influential factor of crystallinity difference was the difference in extrusion temperature profiles (223°C vs. 208°C). Also the higher temperature profile may have led to higher degree of thermal degradation, which results in lower molecular weight in PLLA1 than PLLA2. Both higher extrusion temperature and lower molecular weight creates lower spinline stresses, thus lower stress-induced crystallinity. The difference in D-content between the two samples likely has some effect as well. But, since PLLA1 has lower D-content we would expect it to crystallize more readily on the basis of D-content. Since the opposite was observed, the lower extrusion temperature of PLLA2 must be the explanation for the observed differences between the two series of as-spun fibers. The effect of D-content could possibly be overshadowed by the above two stronger ones, which are dominant in the as-spun fiber spinning process.

4.2.4 Crystalline Orientation Factor

The orientation factor was calculated from X-ray azimuthal scans of the (2 0 0) and (0 0 10) reflections. (0 0 10) azimuthal scan shows two (2 0 7) reflections on both side and is about 46° in ψ away from (0 0 10) peak. Program Origin 6.1 was used to remove the effect of (2 0 7) planes by proper fitting procedure. An example of a typical fitting is shown in **Figure 4.11**.

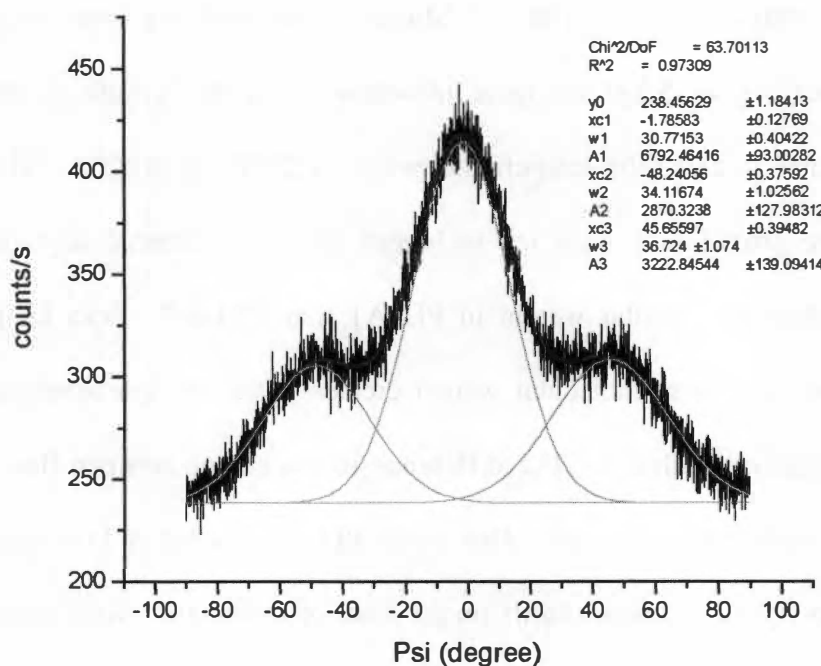


Figure 4.11 Example of Origin 6.1 Peak Fitting in Calculation of Crystalline Orientation Factors of (0 0 10) Reflection

The crystalline orientation factors of PLLA1, as shown in Figure 4.12, shows that at low take-up velocity, the molecular chains were almost random. As the take-up velocity increases, the c-axis orientation function gradually increases with it, indicating that the molecular chains gradually became more aligned with the fiber axis. At the same time, the a-axis and b-axis orientation function decreases, with $f_{a,z}$ at a faster decline than $f_{b,z}$. The decrease of both $f_{a,z}$ and $f_{b,z}$ indicate that the a and b unit cell vectors are becoming perpendicular to the fiber axis.

For PLLA2, as in Figure 4.13, the initial state is almost the same as PLLA1 as-spun fibers, i.e. the c axes and, hence, the molecular chains were nearly random. As take-up velocity increased to 2000 m/min, the molecular chains (c-axis) became

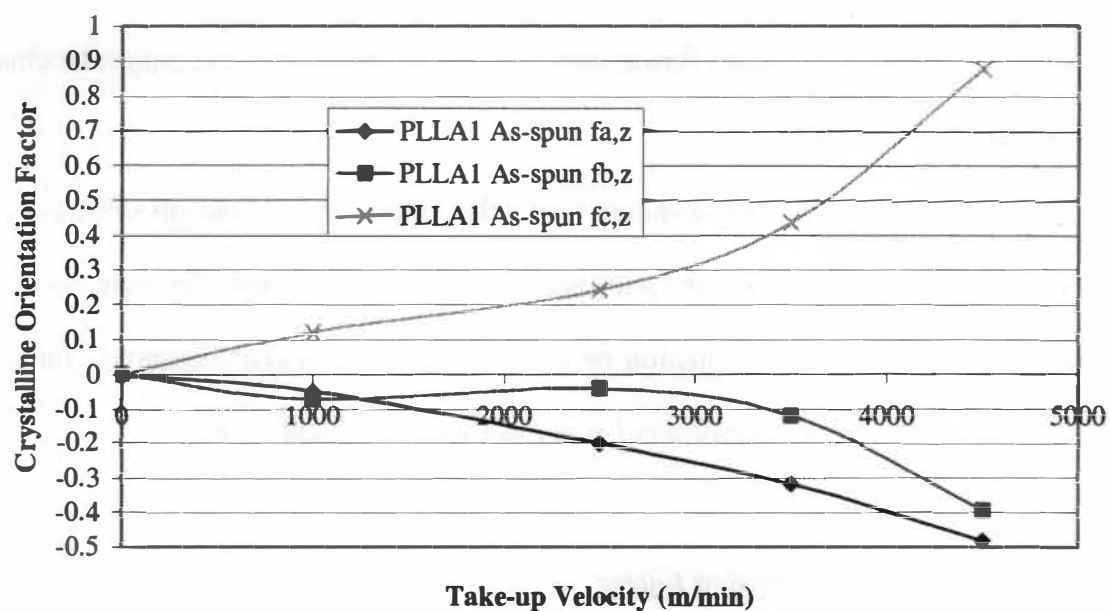


Figure 4.12 Crystalline Orientation Factor vs. Take-up Velocity of As-spun PLLA1

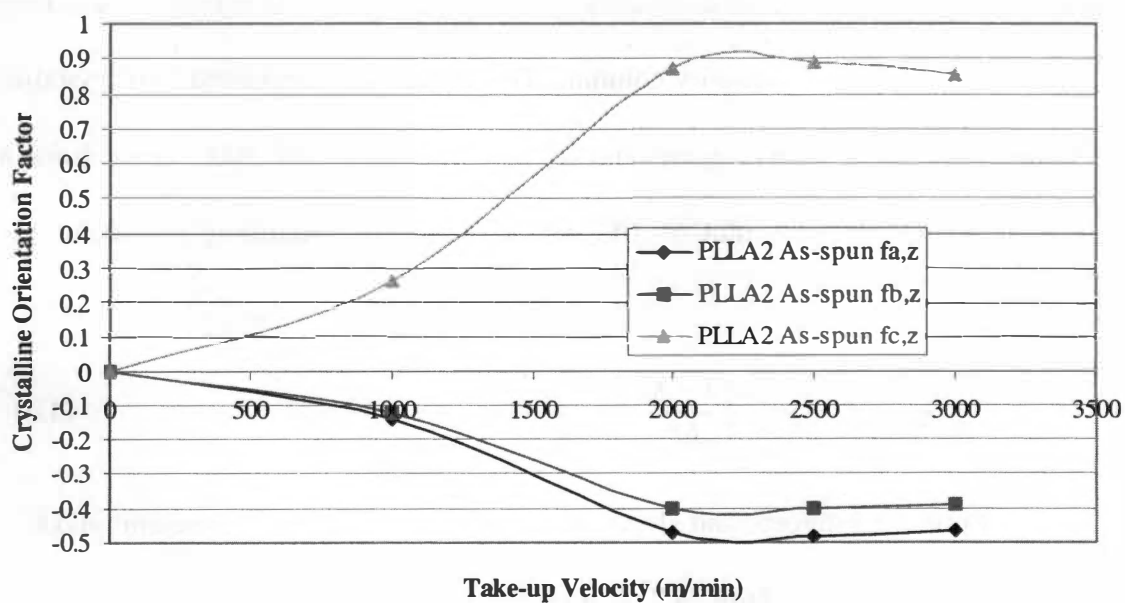


Figure 4.13 Crystalline Orientation Factor vs. Take-up Velocity of As-spun PLLA2

almost parallel to the fiber axis. The a- and b- axes became perpendicular to the fiber axis. As the take-up velocity further increased, the orientation of the molecular chains remains almost the same.

In both PLLAs, the c-axes are randomly oriented at low take-up velocities and become more and more oriented with the fiber axis as take-up velocity increases. The highest c-axis orientation function reached is ~ 0.9 , the b-axis orientation function decreased to ~ -0.4 and a-axis orientation function approached ~ -0.5 .

4.2.5 Amorphous Orientation Factor

The determination of amorphous orientation factor f_{am} was made possible by means of sonic modulus measurements.

Unoriented fibers collected from the spinning line at no external force other than gravity were annealed under different temperatures for 30 minutes. Density data were obtained from the density column. These data were converted into crystallinity values using $\rho_a = 1.2503 \text{ g/cm}^3$ and $\rho_c = 1.2762 \text{ g/cm}^3$ for 100% amorphous and crystalline samples. A plot of $1/E_u$ vs. X_c was made according to the following equation.

$$\frac{3}{2E_u} = \left(\frac{X_c}{E_{t,c}^o} \right) + \left(\frac{1-X_c}{E_{t,am}^o} \right) = \frac{1}{E_{t,am}^o} + \left(\frac{1}{E_{t,c}^o} - \frac{1}{E_{t,am}^o} \right) X_c \quad (4.3)$$

From the intercept and slope, we got $E_{t,am}^o = 2.72 \times 10^{10} \text{ dyne/cm}^2$ and $E_{t,c}^o = 4.12 \times 10^{10} \text{ dyne/cm}^2$. (Table 4.7, Figure 4.14)

Table 4.7 Data of Unoriented PLLA Samples for Calculation of $E_{t,am}^0$ and $E_{t,c}^0$

	Sonic Speed C (km/sec)	ρ (g/cm ³)	X_c (%)	$Eu \times 10^{-10}$ (dyne/cm ²)	$1/Eu \times 10^{10}$
Unannealed	1.802	1.2503	0.02%	4.060	0.246
Annealed at 75°C	1.806	1.2520	6.7%	4.084	0.245
Annealed at 90°C	1.855	1.2544	15.9%	4.316	0.232
Annealed at 105°C	1.956	1.2581	30.7%	4.814	0.208
Annealed at 120°C	1.990	1.2654	58.7%	5.011	0.200
Annealed at 135°C	2.028	1.2666	63.6%	5.207	0.192
Annealed at 150°C	2.044	1.2683	70.1%	5.299	0.189

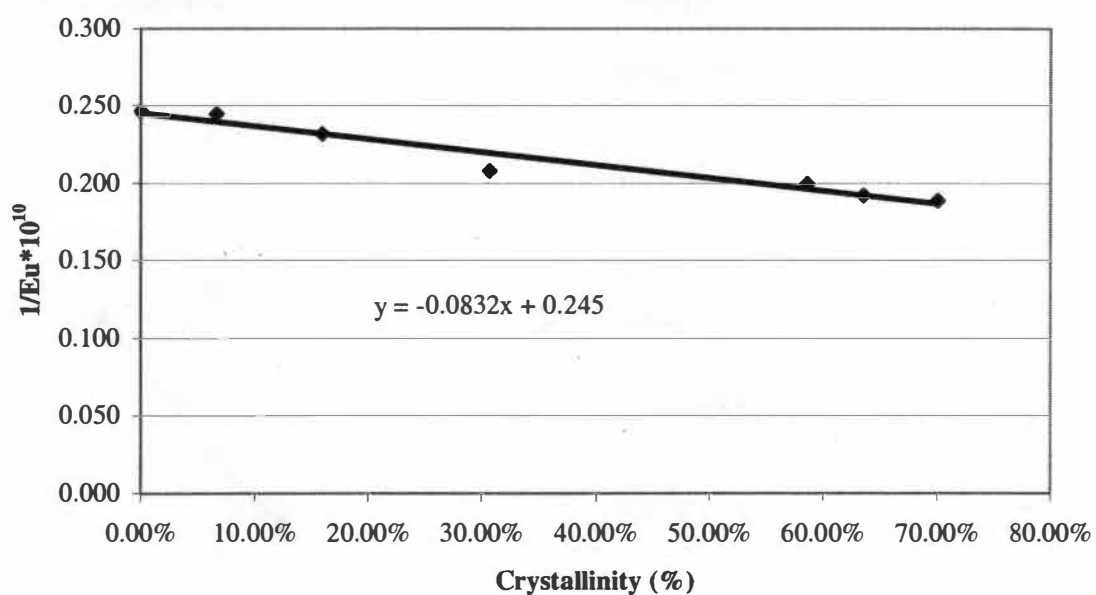


Figure 4.14 Plot of $1/Eu$ vs. Degree of Crystallinity X_c of Unoriented PLLA Fibers

Once $E_{t,am}^o$ and $E_{t,c}^o$ are determined, f_{am} of oriented fibers can be determined from experimental values of the sonic modulus E , the crystallinity X_c , and the crystal orientation factor f_c based on the following equation.

$$\frac{3}{2E_{or}} = \left(\frac{X_c}{E_{t,c}^o} \right) (1 - f_c) + \left(\frac{1 - X_c}{E_{t,am}^o} \right) (1 - f_{am}) \quad (4.4)$$

The results for as-spun PLLA fibers are plotted in **Figure 4.15** along with the crystalline orientation factor f_c .

It seems that f_{am} increases very slowly with take-up velocities, while f_c increases sharply and reached as high as ~ 0.9 .

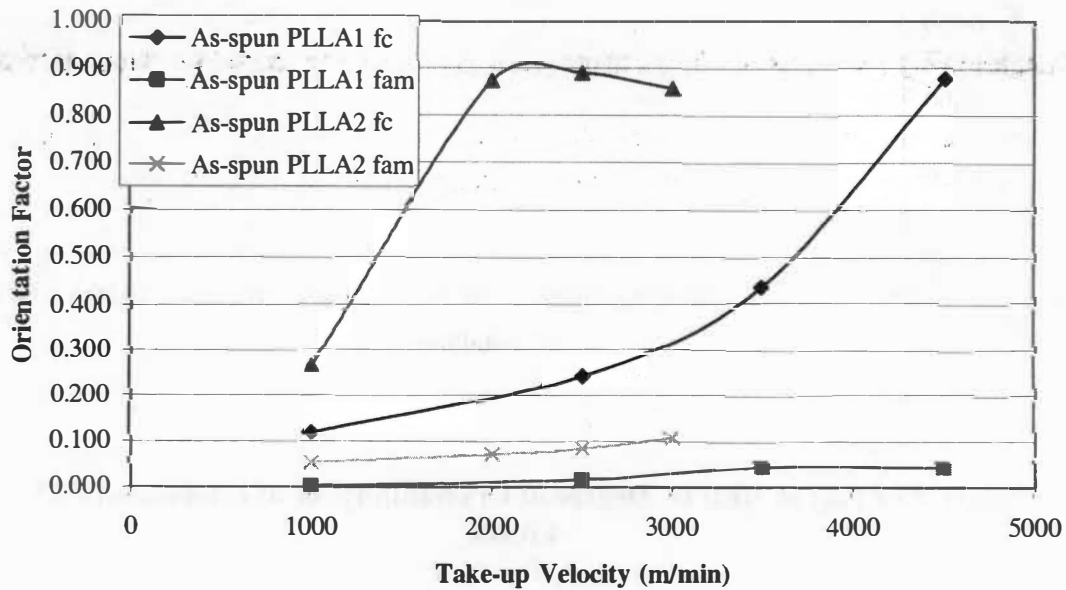


Figure 4.15 Crystalline and Amorphous Orientation of As-spun PLLAs

4.2.6 Optical Birefringence

The birefringence as a function of take-up velocity is shown in **Figure 4.16**. Overall molecular orientation increased for PLLA1 as take-up velocity increases. PLLA1 showed lower level of orientation than PLLA2 largely due to the same reason that cause the change of crystallinity, i.e. the lower stress introduced to the spinline under higher extrusion temperature and even less stress from lower molecular weight due to the possible thermal degradation caused by higher extrusion temperature. Birefringence of PLLA2 increased first and then reached a maximum and decreased slightly with increasing spinning speed. This phenomenon was observed before in the research of our group.^{87,46} We proposed that it is likely as a result of radial variation in the fiber. At the higher take-up velocities, the outer part of the fiber crystallized first, allowing the material in the inner part of the fiber to relax, which causes it to cool down without experiencing as much stress-induced crystallization.⁸⁹

4.3 The Effect of Annealing on the Structure of PLLA Fibers

4.3.1 X-ray Diffraction Data and Phase Present

Fibers spun under different take-up velocities were subjected to annealing under fixed length at 125°C for 30 minutes. Fibers spun under 3500m/min (PLLA1) and 2000m/min (PLLA2) were subjected to annealing at different temperatures for 30 minutes. A 2-axes x-ray pattern of PLLA2 spun at 3000 m/min and annealed at 125°C for 30 minutes is shown in **Figure 4.17**. After annealing, only a few more reflections were observed compared with as-spun fibers. It still exhibited α phase pattern.

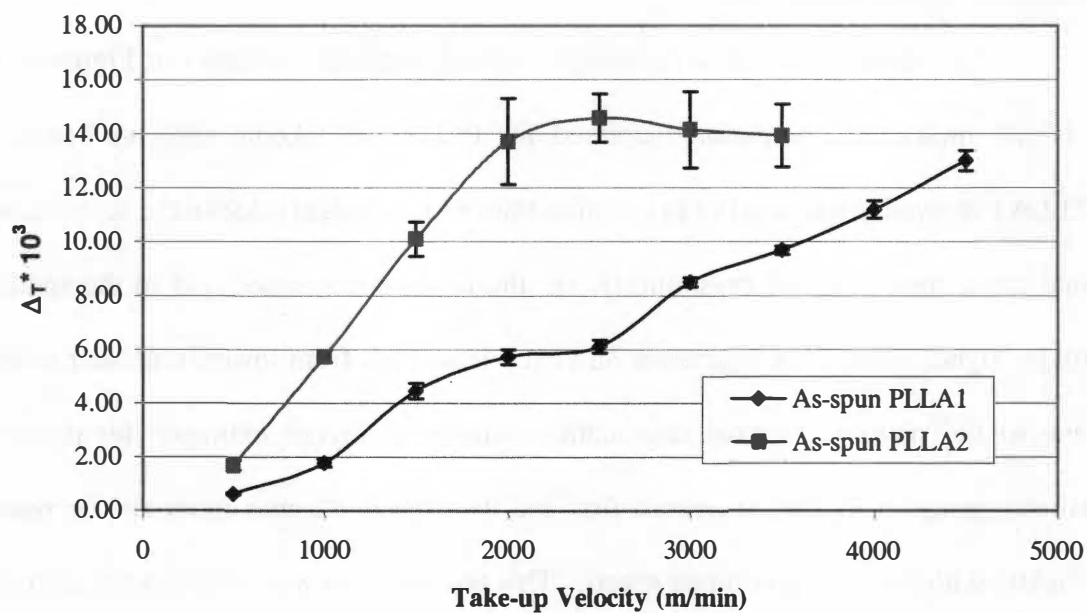


Figure 4.16 Birefringence of As-spun PLLAs vs. Take-up Velocity

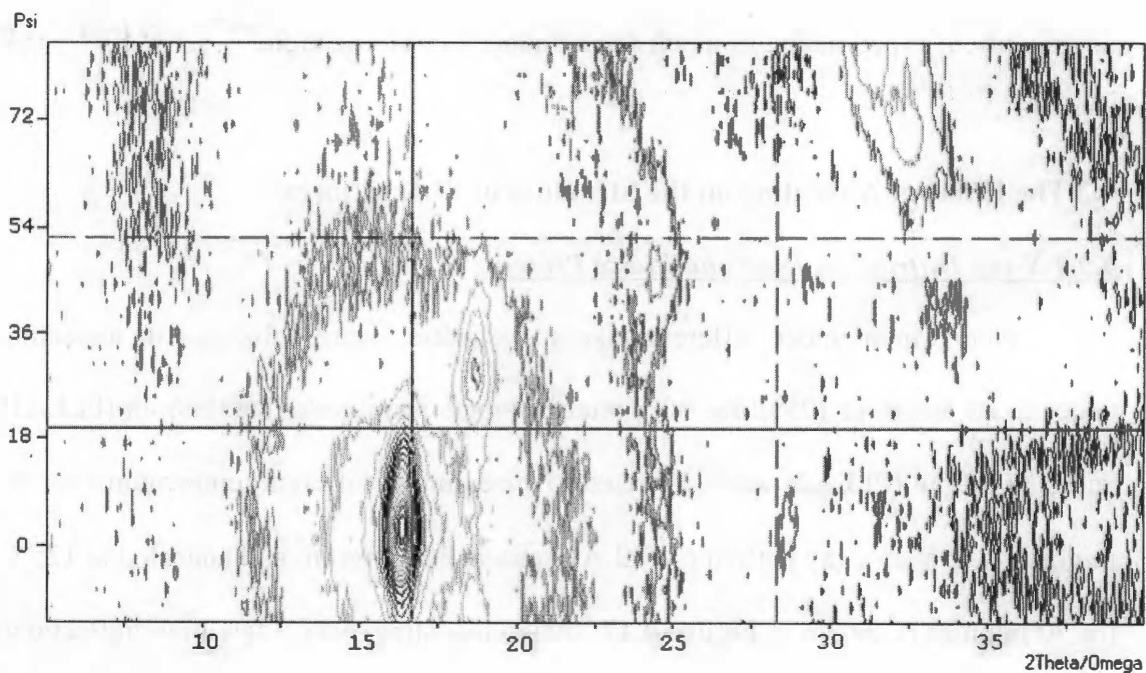


Figure 4.17 2-axes Scan Pattern of Annealed PLLA Fiber (PLLA2-3000-125)

4.3.2 Thermal Properties

The “cold crystallization” peak disappeared due to the crystallization during annealing, except for the fibers annealed under 60°C, which as expected, still shows a “cold crystallization” peak at 70.8°C and 73.8°C for PLLA1-3500 and PLLA2-2000, respectively. As we observed in as-spun fibers, the crystallization temperature of PLLA1-3500 is 74.1°C and that of PLLA2-2000 is 73.6°C. 60°C is just not a high enough temperature to initiate and complete the crystallization within the time allowed at the annealing temperature. The melting temperatures of annealed PLLAs remain almost the same as the as-spun counterpart. The data are listed in **Table 4.8**.

The difference in melting temperature between the annealed PLLA1 and annealed PLLA2 samples is likely due to differences in lamellae thickness. The greater D-content of PLLA2 may restrict the lamellae thickness somewhat compared to that of PLLA1. This is consistent with the higher crystallinity of PLLA1 after annealing as described in the next section.

Table 4.8 Melting Temperature of Annealed PLLA1 and PLLA2 Fibers

Sample ID	T _m (°C)	Sample ID	T _m (°C)
PLLA1-1000-125	170.7	PLLA2-1000-125	168.6
PLLA1-2500-125	169.6	PLLA2-2000-125	164.8
PLLA1-3500-125	169.9	PLLA2-2500-125	165.2
PLLA1-4500-125	169.4	PLLA2-3000-125	165.4
PLLA1-3500	170.7	PLLA2-2000	164.7
PLLA1-3500-60	169.9	PLLA2-2000-60	165.2
PLLA1-3500-80	169.5	PLLA2-2000-80	164.8
PLLA1-3500-100	169.9	PLLA2-2000-100	164.8
PLLA1-3500-125	169.9	PLLA2-2000-125	164.8
PLLA1-3500-150	170.0	PLLA2-2000-150	165.2

4.3.3 Crystallinity

The crystallinity changes after annealing are shown in **Figure 4.18**. The crystallinity of both PLLAs increases after annealing at 125°C for 30 minutes, but PLLA1 fibers increased to a greater extent. The highest crystallinity that PLLA2 reached was 50.9% (DSC) and that of PLLA1 56.1% (DSC). The crystallinity of PLLA2 tends to level off (or very slightly decrease) for fibers spun at speeds greater than 2000m/min. Due to the higher spinline stress during spinning of PLLA2 than PLLA1 fibers, a lot more stress-induced crystallization took place in PLLA2 fibers, resulting in higher initial crystallization in as-spun PLLA2 fibers and much higher crystallization potential of as-spun PLLA1 fibers during the annealing procedure. As mentioned in a previous section, it was believed that long L lactide sequences are capable of crystallization and the attachment of D lactide units interfere with the growth of L-lactide crystals. As PLLA1 contains 0.8% D- content, which is less than 1.3% in PLLA2, the final crystallinity of PLLA1 after annealing would be expected to be a little higher than that of PLLA2, which was indeed observed.

WAXD patterns also suggest that PLLAs are highly crystalline after annealing, an example is shown in **Figure 4.19**. In the case of annealed samples, we found that the crystallinity calculated from WAXD is actually closer to the DSC value than to the DGC values. This may be because that after annealing, the “cold crystallization” does not exist which eliminated the uncertainty of correcting it as in as-spun fibers.

The influence of annealing temperature on the crystallinity of fibers is shown in **Figure 4.20**. The crystallinity of both PLLAs increased abruptly under annealing temperature higher than 60°C and tends to level off, with PLLA1 at a higher amount

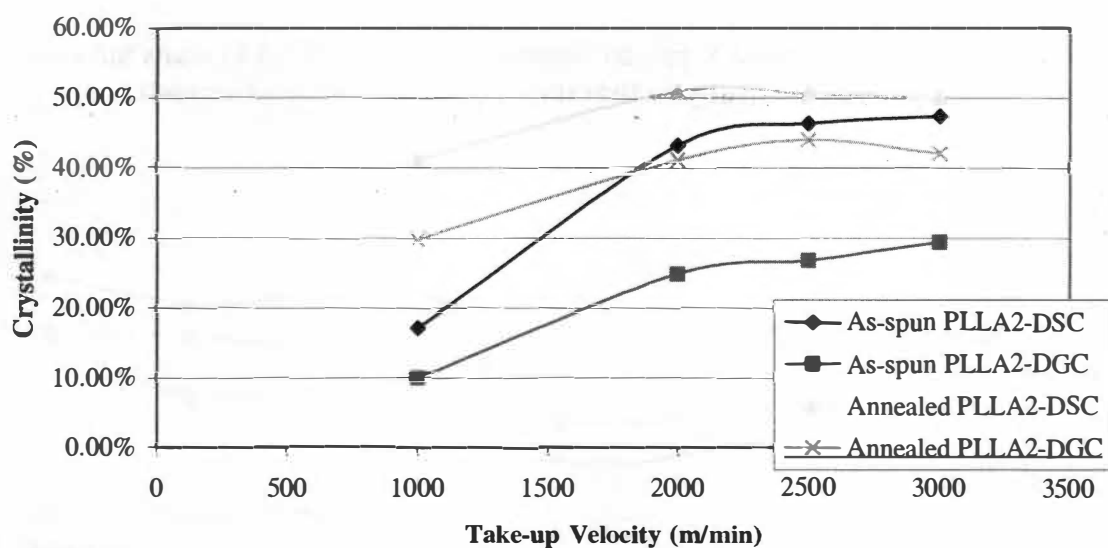
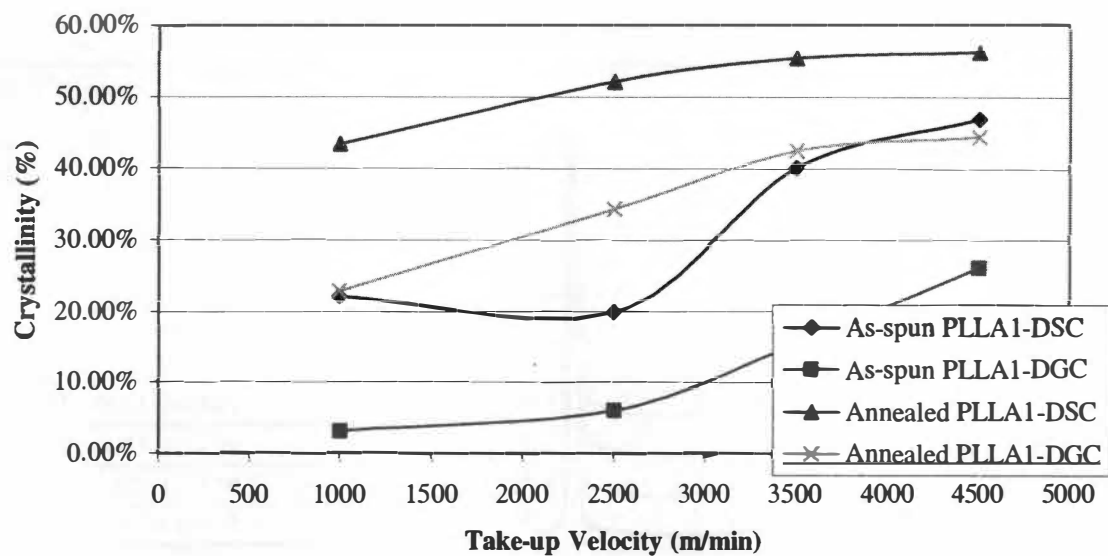


Figure 4.18 Percentage Crystallinity vs. Take-up Velocity of As-spun and Annealed PLLA1 (upper) and PLLA2 (lower). Annealed 30 minutes

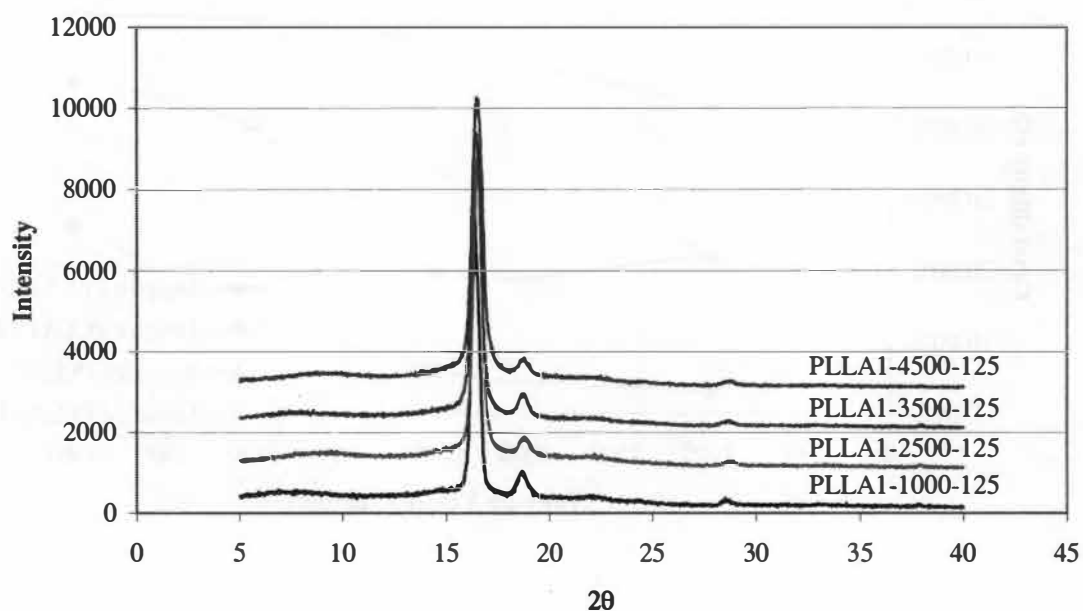


Figure 4.19 Normalized X-ray 2θ Scans of Annealed PLLA1 (scans have been shifted vertically so that they are more readily observed)

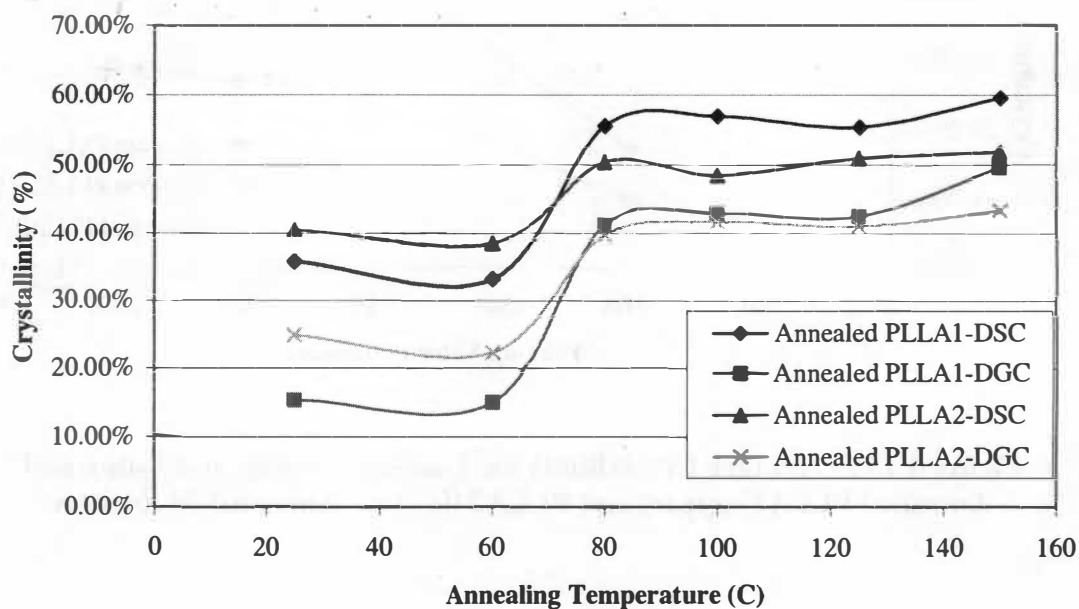


Figure 4.20 Percentage Crystallinity vs. Annealing Temperature of PLLA1-3500 and PLLA2-2000. Annealing time was 30 minutes

4.3.4 Crystalline and Amorphous Orientation Factors

As indicated in Figure 4.21-22, annealing substantially increased the orientation as we compare the results with as-spun fibers. We noticed that crystalline orientation factor increased substantially for those poorly oriented as-spun fibers spun at lower take-up velocities, while improved a fair amount for the as-spun fibers developed quite strong orientation during the processing. The c axis becomes more aligned with the fiber axis and the a and b axes becomes more nearly perpendicular to it. This is the same tendency that was observed for increasing take-up velocity. And it tends to level off at take-up velocities greater than 2500 m/min (PLLA1) and 2000 m/min (PLLA2). $f_{a,z}$, $f_{b,z}$, $f_{c,z}$ reach ~ -0.5 , ~ -0.4 and ~ 0.9 in most cases with PLLA1-4500-125 reaches $f_{a,z} = -0.481$, $f_{b,z} = -0.465$, $f_{c,z} = 0.946$ and PLLA2-2500-125 reaches $f_{a,z} = -0.485$, $f_{b,z} = -0.440$, $f_{c,z} = 0.925$ for the highest value observed.

The effect of increasing annealing temperature is illustrated in Figure 4.23-24. In the case of PLLA1, spun at 3500m/min, $f_{a,z}$ gradually turns to -0.5 , which is perpendicular to the fiber axis. $f_{c,z}$ increased dramatically to ~ 0.9 above annealing temperature 60°C , while $f_{b,z}$ decreased substantially to ~ -0.4 . Further increase in annealing temperature had minor influence on the orientation factors. As for PLLA2, spun at 2000m/min, change of annealing temperature didn't change the orientation distribution appreciably possibly because molecular chains of PLLA2 were mostly oriented during the melt spinning process when take-up velocity was 2000m/min.

Amorphous orientation factor of annealed PLLAs, as shown in Figure 4.25, increased with the take-up velocities and is at a higher level than as-spun PLLAs, while in Figure 4.26, the higher the annealing temperature, the higher the amorphous

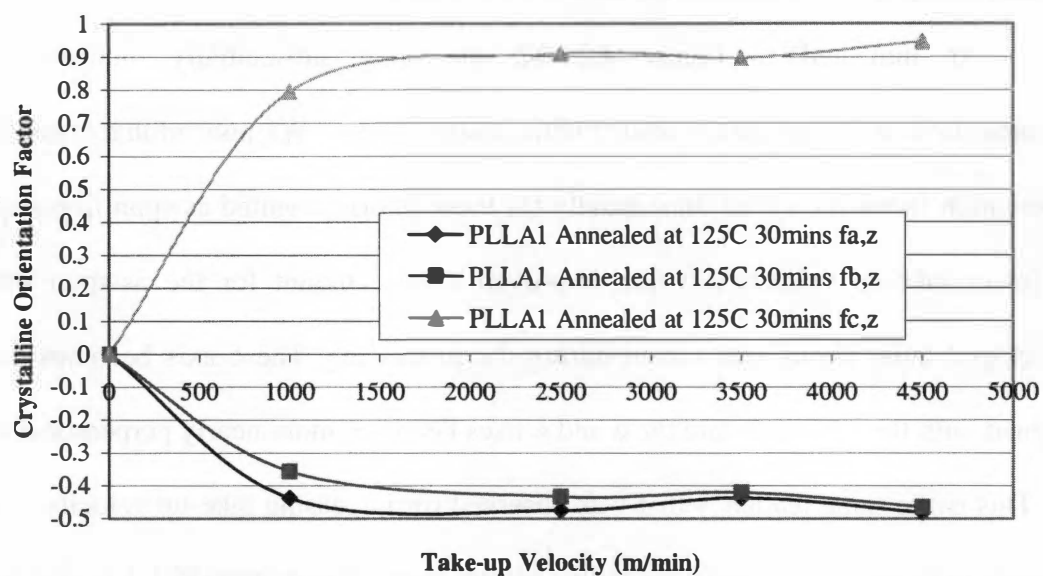


Figure 4.21 Annealed PLLA1 Crystalline Orientation Factor vs. Take-up Velocity

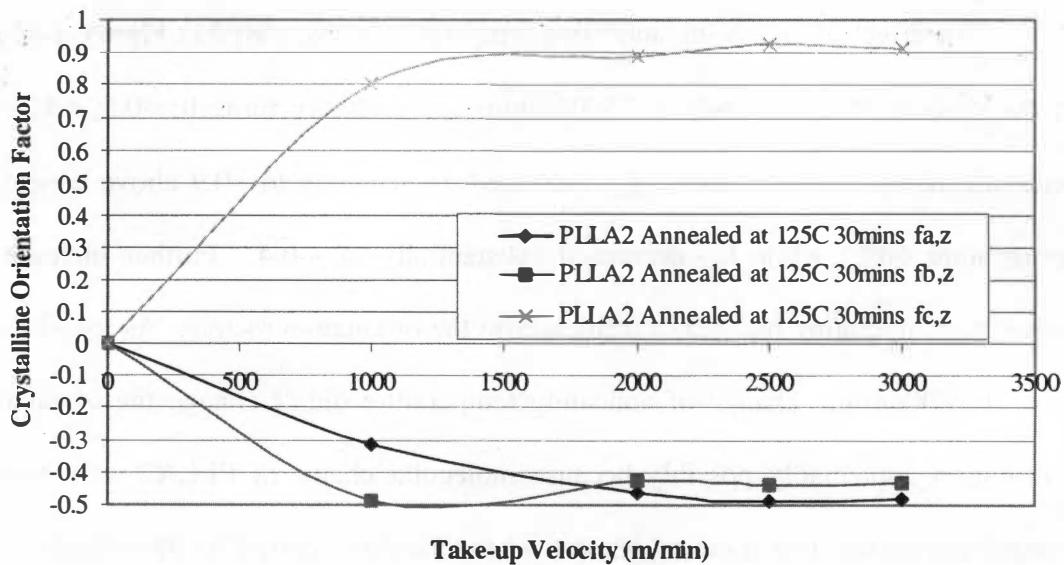


Figure 4.22 Annealed PLLA2 Crystalline Orientation Factor vs. Take-up Velocity

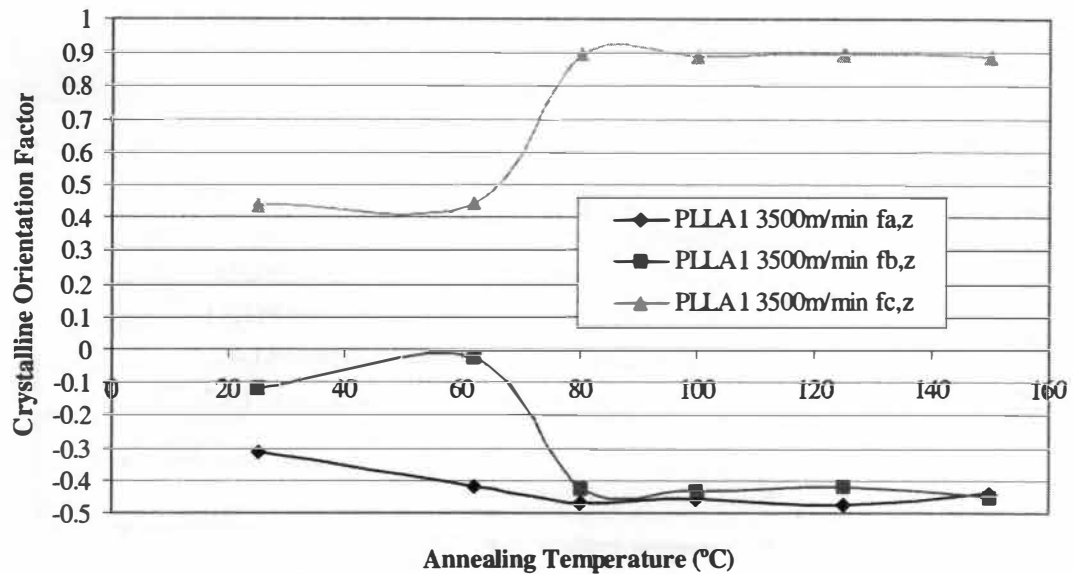


Figure 4.23 PLLA1 Crystalline Orientation Factor vs. Annealing Temperature

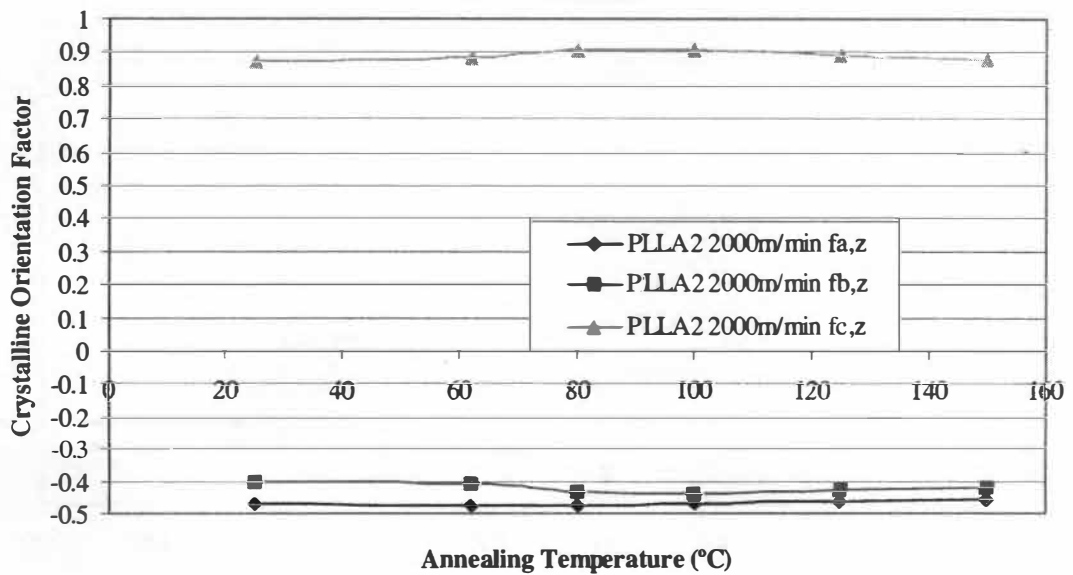


Figure 4.24 PLLA2 Crystalline Orientation Factor vs. Annealing Temperature

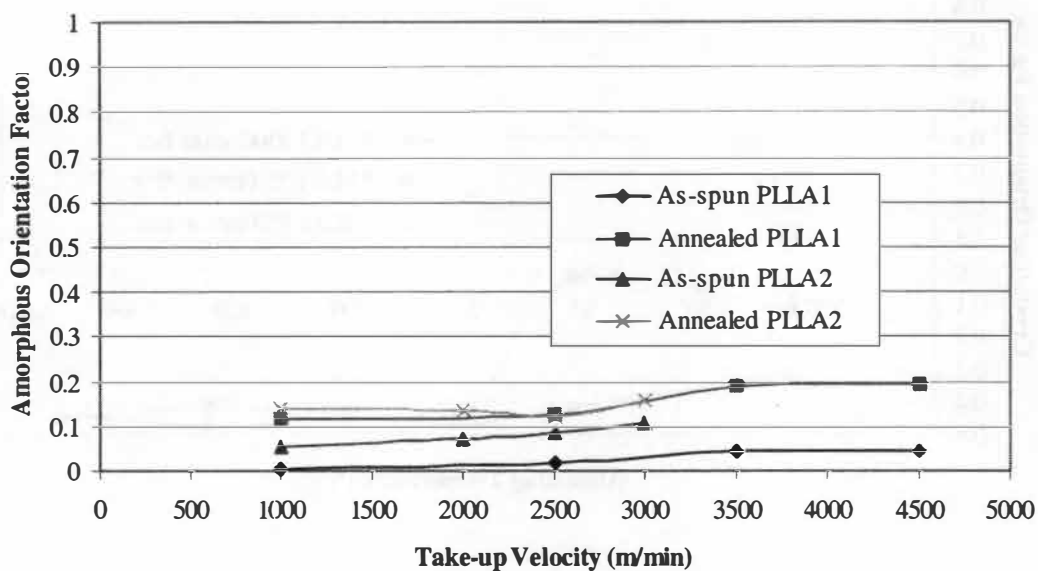


Figure 4.25 Amorphous Orientation Factor vs. Take-up Velocity of As-spun and Annealed PLLAs

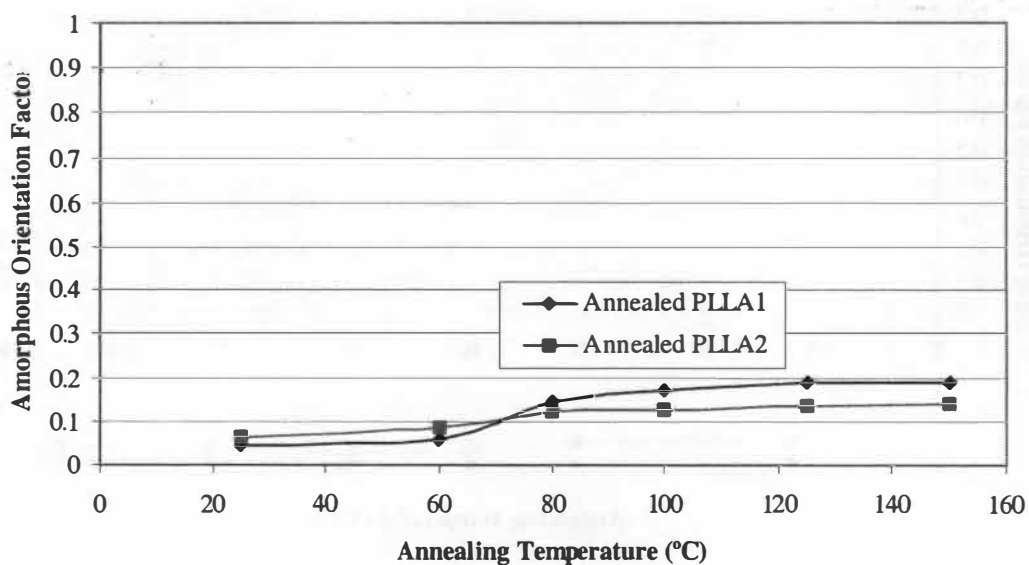


Figure 4.26 Amorphous Orientation Factor vs. Annealing Temperature of As-spun and Annealed PLLAs

orientation. The annealing temperature had larger impact on PLLA1 than PLLA2. The highest f_{am} reached in all cases is close to 0.2. One would expect to observe the decrease of amorphous orientation factor after annealing due to the sharp increase of crystalline orientation factor when more amorphous orientation turned in to crystalline orientation. What we observed is contradictory to this rationale. This may possibly due to the factor that the calculation of f_{am} involved lots of experimental data, thus more sources of error. Being very low in the amorphous orientation, these effects of errors could be enlarged. If reliable intrinsic birefringence of the crystalline and amorphous phase (Δ_c^o and Δ_{am}^o) were available, using $\Delta_T = X_c \Delta_c^o f_c + (1 - X_c) \Delta_{am}^o f_{am}$ and other known experimental values, f_{am} may be determined with less errors.

4.3.5 Optical Birefringence

The effect of annealing on the birefringence of as-spun fibers is shown in **Figure 4.27**. It is obvious that annealing increased substantially the birefringence, thus the overall molecular orientation of both PLLAs. Annealed fibers still carried the same tendency as seen in as-spun fibers, i.e. molecular orientation of PLLA1 increases gradually and that of PLLA2 hit a maximum with increasing take-up velocity.

Further studies on the effect of annealing temperature on the fibers showed that the birefringence remained unchanged at annealing temperature of 60°C, which is mentioned before as the crystallization would not initiate. Major birefringence improvement occurs at annealing temperature 80°C and further increase in annealing temperature increases the birefringence only slightly. (**Figure 4.28**)

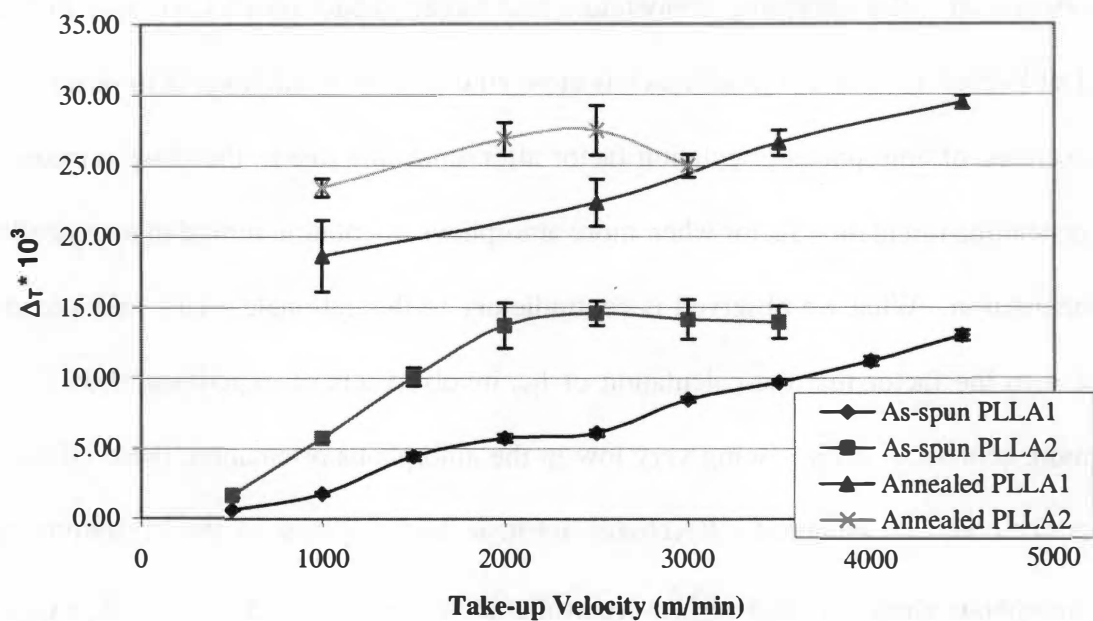


Figure 4.27 Birefringence of As-spun and Annealed PLLAs vs. Take-up Velocity

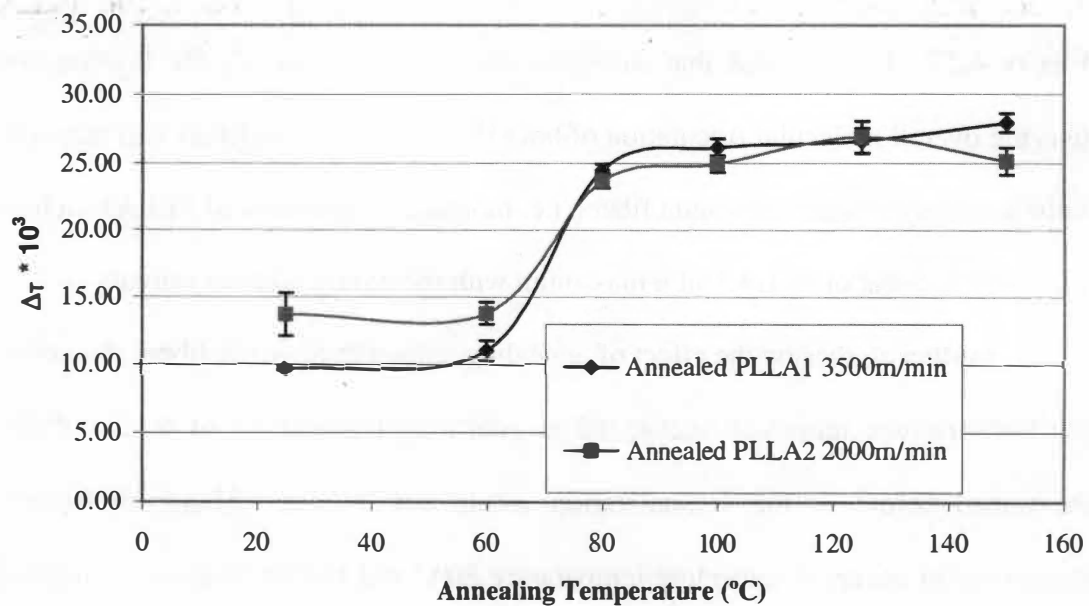


Figure 4.28 Birefringence of Annealed PLLAs vs. Annealing Temperature

4.4 Experimental Measurement of Intrinsic Birefringence

Now that we obtained amorphous orientation factor f_{am} , with the knowledge of other parameters such as f_c , X_c , Δ_T from various experiments, we are able to estimate the intrinsic birefringences Δ_{am}^o and Δ_c^o of PLLA. The appropriate equations are:

$$\Delta_T = X_c \Delta_c^o f_c + (1 - X_c) \Delta_{am}^o f_{am} \quad (4.5)$$

$$\frac{\Delta_T}{X_c f_c} = \Delta_c^o + \frac{(1 - X_c)}{X_c} \frac{f_{am}}{f_c} \Delta_{am}^o \quad (4.6)$$

The plot of $\frac{\Delta_T}{X_c f_c}$ vs. $\frac{(1 - X_c)}{X_c} \frac{f_{am}}{f_c}$ gives Δ_c^o as the intercept and Δ_{am}^o as the slope.

Since the f_c values obtained from some of the (0 0 10) plane showed really broad peaks and the R^2 of the fitting was not as good as others, those samples were excluded from the calculation of the intrinsic birefringence. Those excluded samples include PLLA1-1000, PLLA1-2500, PLLA1-3500, PLLA1-3500-60 and PLLA2-1000. The rest of the data were used in the calculation even though they are processed or treated under different conditions because, in principal, the intrinsic birefringence of a material is a material property, that doesn't change. The experimental data are tabulated in **Table 4.9** and plotted in **Figure 4.29** accordingly. The value of intrinsic birefringences become $\Delta_c^o = 0.040$ and $\Delta_{am}^o = 0.114$.

A preliminary attempt has been made to calculate the intrinsic birefringence from bond polarizabilities, the values are $\Delta_c^o = 0.033$ and $\Delta_{am}^o = 0.420$ using $\rho_a = 1.2503 \text{ g/cm}^3$ and $\rho_c = 1.2762 \text{ g/cm}^3$. We found that the value of intrinsic birefringence of crystalline phase is close in both cases. However, the value of

Table 4.9 Structural and Mechanical Data of PLLAs

Sample ID	C (km/s)	ρ (g/cm ³)	X _c (%)	Δ_T	E $\times 10^{-10}$ (dyne/cm ²)	f _c	f _{am}
PLLA1-4500	2.114	1.2570	26.3%	1.30E-02	5.618	0.877	0.044
PLLA1-1000-125	2.136	1.2561	22.8%	1.86E-02	5.731	0.794	0.118
PLLA1-2500-125	2.337	1.2591	34.4%	2.24E-02	6.875	0.908	0.126
PLLA1-3500-125	2.556	1.2612	42.6%	2.66E-02	8.240	0.897	0.188
PLLA1-4500-125	2.638	1.2617	44.5%	2.94E-02	8.780	0.946	0.191
PLLA1-3500-80	2.468	1.2609	41.4%	2.45E-02	7.680	0.896	0.141
PLLA1-3500-100	2.532	1.2613	43.0%	2.61E-02	8.086	0.888	0.171
PLLA1-3500-150	2.694	1.2630	49.6%	2.79E-02	9.166	0.890	0.189
PLLA2-2000	2.126	1.2566	24.7%	1.37E-02	5.680	0.873	0.073
PLLA2-2500	2.170	1.2572	27.0%	1.46E-02	5.920	0.889	0.082
PLLA2-3000	2.204	1.2578	29.4%	1.41E-02	6.110	0.856	0.094
PLLA2-1000-125	2.268	1.2579	29.8%	2.34E-02	6.468	0.868	0.138
PLLA2-2000-125	2.475	1.2608	41.0%	2.69E-02	7.723	0.928	0.137
PLLA2-2500-125	2.530	1.2616	44.1%	2.75E-02	8.075	0.950	0.121
PLLA2-3000-125	2.532	1.2610	41.8%	2.50E-02	8.084	0.943	0.159
PLLA2-2000-60	2.124	1.2560	22.4%	1.38E-02	5.666	0.922	0.087
PLLA2-2000-80	2.436	1.2605	39.9%	2.37E-02	7.480	0.938	0.120
PLLA2-2000-100	2.478	1.2610	41.8%	2.49E-02	7.743	0.938	0.124
PLLA2-2000-150	2.522	1.2614	43.4%	2.51E-02	8.023	0.920	0.142

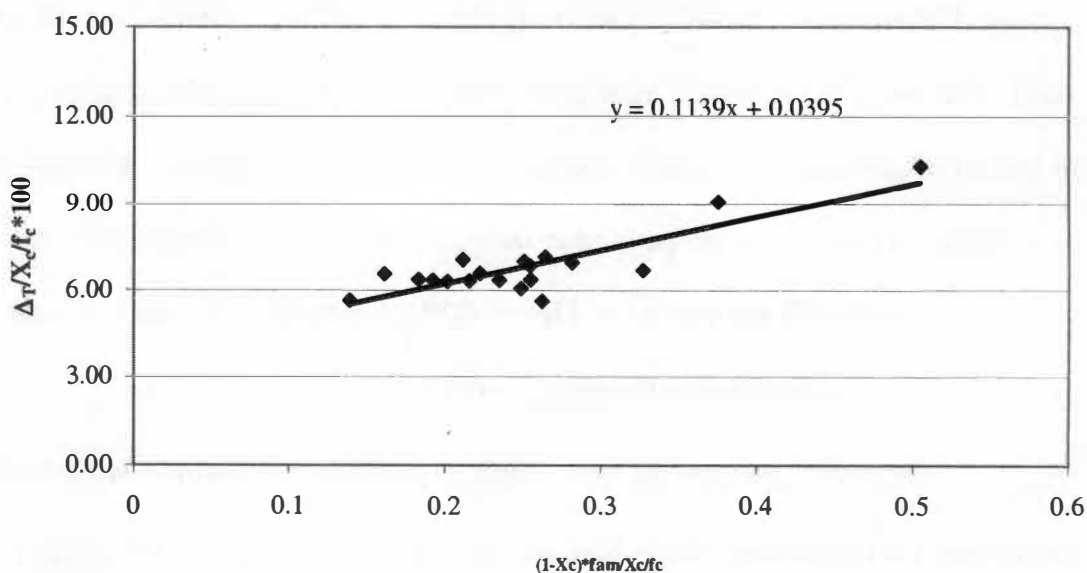


Figure 4.29 Plot from the Experimental Data for Calculation of Intrinsic Birefringence for the Crystalline and Amorphous Phases

intrinsic birefringence of amorphous phase presented large difference.

The reason could be (1) when we calculated the intrinsic birefringence from bond polarizabilities, we assumed that the molecular chains are planar, which simplified the calculation procedure, but may oversimplify the real chiral structure of PLLA; (2) the density of fibers deviates from the real value due to the air trapped between them, which makes the observed value lower. As we observed in unoriented samples, which were fibers with larger diameters that makes measurement of a single filament possible, the highest crystallinity observed was 70.1% (Table 4.7) for fibers annealed at 150°C for 30 minutes, while the highest DGC crystallinity of all oriented PLLA fine fibers, as we recall, was 49.6%; and (3) the equations we used to calculate the amorphous orientation factor from sonic modulus involved bulk compressibility. The bulk compressibility K is related to the bulk modulus B , Young's modulus E , and the Poisson's ratio ν , by the expression:

$$K = \frac{1}{B} = \frac{3(1-2\nu)}{E} \quad (4.7)$$

We assumed $\nu = 0.33$, which is a value similar to many other materials. This lead to a specific case of the above equation:

$$K = \frac{1}{B} = \frac{1}{E} = \frac{1}{\rho C^2} \quad (4.8)$$

While the real value of Poisson's ratio of PLLA remains unknown, such assumption could lead to possible error.

Chapter 5 . SUMMARY AND CONCLUSIONS

The amorphous and crystalline density values are important to the calculation of many quantities in our research. The amorphous density, $\rho_a = 1.2503 \pm 0.002 \text{ g/cm}^3$, of PLA was determined by measuring the density of the fiber spun under gravity only. The crystalline density, $\rho_c = 1.2762 \pm 0.0013 \text{ g/cm}^3$, was calculated from this unit cell dimension containing 20 monomers. This value happens to be about the mean value of all the literature values. The lattice constants were obtained from indexing of a highly oriented PLLA rod sample which leads to the orthorhombic α phase PLLA with $a = 10.57 \pm 0.084 \text{ \AA}$, $b = 6.13 \pm 0.007 \text{ \AA}$ and $c = 28.91 \pm 0.017 \text{ \AA}$.

Two polymers, PLLA1 and PLLA2, of similar molecular weight; slight difference in percentage D content (0.8% vs. 1.3%) were melt spun at high-speeds under different extrusion temperature (223°C vs. 208°C). Then fibers spun at different take-up velocity were subjected to annealing at 125°C for 30 minutes and the effect of different annealing temperatures (60°C, 80°C, 100°C, 125°C and 150°C) were studied on PLLA1-3500 and PLLA2-2000 fibers. The crystallinity and orientation development of as-spun and annealed fibers was then studied by means of differential scanning calorimetry (DSC), density gradient column (DGC), optical birefringence, wide angle x-ray diffraction (WAXD) and sonic modulus.

The higher extrusion temperature of processing PLLA1 than PLLA2 leads to lower spinline stress and stress-induced crystallization due to lower viscosity at the upper part of the spinline. Moreover, higher extrusion temperature results in larger extent of thermal degradation of PLLA1 than PLLA2 and the resulting lower

molecular weight was expected to further lower the spinline stress during preparation of PLLA1 fibers. Even though PLLA1 contains less D-content, which should enhance crystallization rates, this effect was not observed mainly because of the above two stronger effects. Due to the higher stress in the spinline of PLLA2 than PLLA1, the highest spinning speed reached was 3500m/min for PLLA2 and 4500m/min for PLLA1.

Experimental results support the explanations. The DSC thermograph of as-spun fibers showed that stress-induced crystallization occurs at lower take-up velocity in PLLA2 than PLLA1 (2000m/min vs. 4500m/min) by the appearance of bimodal melting peaks, which consists of the melting of smaller crystals formed during stress-induced spinning and larger crystals formed during the heating of the DSC. Percentage crystallinity values from both DSC and DGC methods bear the same tendency: as take-up velocity increases, so does the crystallinity, with DGC values closer to reality for as-spun fibers having low values of crystallinity. This conclusion is based on a comparison of x-ray patterns and x-ray crystallinity measurements with the DSC and DGC measurements.

Crystalline orientation factor reached $f_{c,z} \sim 0.9$, $f_{b,z} \sim -0.4$ and $f_{a,z} \sim -0.5$ of both PLLAs, but PLLA2 developed the high orientation at much earlier stage of spinning due to the higher stress it experienced. Compared with the development of crystalline orientation factor, the amorphous orientation factor developed much more slowly.

Birefringence values increased gradually with take-up velocity in PLLA1 fibers, but reached a maximum in PLLA2 before it slightly decreases. This decrease is believed to result from the radial temperature distribution caused by rapid cooling

during high-speed spinning process. The outer skin of fiber cools faster, leading to higher viscosity on the fiber surface, when combined with the spinning stress, it crystallized first, which allows the inner part of the fiber to relax. Thus, the inner part actually experiences less stress-induced crystallization.

Percentage crystallinity improved after annealing and tends to level off at higher annealing temperature. Crystalline orientation factor substantially improved for fibers spun under lower take-up velocities and slightly improved for those spun under higher take-up velocities. The effect of annealing temperature did not influence the crystalline orientation of PLLA2-2000 due to the saturation of orientation during the spinning, while for PLLA1-3500, it increased substantially when annealed above 60°C and then levels off. Birefringence showed the same tendency. In all cases, PLLA1 exhibited higher final values than PLLA2 as it contains lower D-content. Amorphous orientation factors also increased over as-spun fibers with regard to take-up velocities and annealing temperature, which is not expected. This may be an artifact due to the small value that could be greatly influenced by errors.

DSC, DGC and WAXD were used to calculate the percentage crystallinity of as-spun and annealed PLLAs. Even though the basic trends observed are mostly the same, the absolute values present large discrepancy. DGC values were in better agreement with WAXD patterns and values for as-spun fibers, while in the case of annealed fibers, DSC and WAXD values are close. From such observation, we tend to believe that at low crystallinity level (especially those fibers that shows “cold crystallization” peaks), the DGC values were more realistic than DSC values because fibers crystallize during the heating procedure and its effect is hard to correct. Such

potential problem does not affect as much with regard to annealed samples so that DSC values would be more reliable, while DGC encounters a common problem of trapping air on the fine fibers, which makes accurate measurements difficult. Since the correct separation of amorphous and crystalline phases of x-ray patterns is still unavailable, WAXD crystallinity of PLLAs would serve more as a qualitative than quantitative method.

X-ray pattern analysis of both as-spun and annealed fibers suggest that all of them are α phase PLLA, which is commonly observed in melt spun PLLA fibers.

The intrinsic transverse modulus of the crystalline and amorphous phase used in the calculation of the amorphous orientation factor from sonic modulus measurements was also obtained from a series of unoriented samples of different crystallinity. The values obtained were $E_{t,am}^0 = 2.72 \times 10^{10}$ dyne/cm² and $E_{t,c}^0 = 4.12 \times 10^{10}$ dyne/cm².

Furthermore, the calculation the intrinsic birefringence of crystalline and amorphous phase by both experimental data and bond polarizabilities has been attempted. Δ_c^o value from both methods are in reasonable agreement, but Δ_{am}^o exhibited a large difference. The reason behind the difference is still unclear at present.

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VITA

Xiaoyun Ling was born in Shanghai, China on November 7, 1975. She went to Fudan University in Shanghai, where she received her Bachelor of Science degree in Polymer Materials and Engineering with a minor in Business Administration in July 1998. In the fall of 1999, she enrolled in the program of Polymer Engineering at the University of Tennessee, Knoxville and received her Master degree in August 2003. Her professional affiliations include the Society of Plastics Engineers and American Chemical Society.

Xiaoyun is currently continuing on to pursue her doctorate in Polymer Engineering at the University of Tennessee, Knoxville.