A STUDY OF THE STRUCTURE AND MOLECULAR DYNAMICS OF
ORIENTED, SEMI-CRYSTALLINE POLY(LACTIC ACID)

A Thesis in
Materials Science and Engineering

by
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ABSTRACT
Poly(lactic acid), a semi-crystalline polymer, is used in a wide range of applications because it is biodegradable, biocompatible, versatile, and easy to process. Some of these applications include oriented fibers and films. In this research, poly(lactic acid), [PLA], was uniaxially deformed at 70°C, which is above its glass transition temperature. Samples of different magnitudes of deformation (25%, 70%, and 110%) were selected as oriented samples. For use as controls, amorphous and crystalline unoriented PLA sample were produced under similar temperature and pressure conditions. Differential scanning calorimetry was used to confirm a constant glass transition temperature of 63°C and a constant melting temperature 149°C independent of orientation. Differential scanning calorimetry confirmed that the degree of crystallinity increased with orientation. Wide angle x-ray diffraction demonstrated that the α crystal structure was formed during initial crystallization and amorphous chains orient parallel to the deformation direction and convert to crystalline regions during orientation. Small angle x-ray scattering verified that orientation did not affect the long period spacing. Finally, dielectric relaxation spectroscopy was able to confirm that orientation lead to the formation of additional rigid amorphous regions in between crystalline regions and at the crystalline and amorphous interface. Uniaxial orientation lead to a decrease in dielectric strength and a broader segmental relaxation, but the mean relaxation time and temperature were unaffected.
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Chapter 1: Introduction and Motivation

Poly(lactic acid), PLA, is a thermoplastic, semi-crystalline polymer. Because of its extensive list of favorable properties: easy to process, biocompatible, biodegradable, and easy to modify, PLA is used in applications ranging from textiles and fabrics, to food packaging and bottles, to credit cards and films.1–6 PLA is also of interest in biomedical devices, as well as oriented films and fibers.1–3,5,7 Continuing to add to our basic understanding of its structure-property relationships will facilitate the use of PLA in an even larger product market.

1.1 Synthesis and Stereochemistry of PLA

With the recent push toward environmentally friendly and green materials, one of the most promising features of PLA is that it is produced from a renewable resource. PLA can be synthesized using one of two methods: condensation or ring opening polymerization. The less expensive method is condensation polymerization, but usually this method results in a low molecular weight polymer because of the difficulty in removing residual water and the likelihood of a back-biting reaction. Ring-opening polymerization results in higher molecular weight polymer that is easier to stereochemically control. Prior to polymerization by either condensation or ring-opening reactions, lactic acid is created chemically or naturally through fermentation from starchy products, such as corn. A condensation polymerization reaction is then used to either bulk polymerize PLA or to make a low molecular weight pre-polymer for ring-opening polymerization. In ring-opening polymerization, the pre-polymer is then depolymerized with a catalyst to make cyclic dimeric lactide monomers. After purifying through
distillation, anionic, cationic, or coordination insertion ring-opening polymerization can be conducted to produce high molecular weight (>100,000 g/mol) PLA. A simple schematic of ring opening polymerization is shown in Figure 1.1.

![Diagram of ring-opening polymerization](image)

Figure 1.1: Basic schematic showing the ring-opening polymerization method of producing PLA.

It is the stereochemistry of the lactide that, once polymerized, control the properties of the resulting PLA. Each monomeric unit contains a chiral carbon atom, leading to either left-handed (S) or right-handed (R) stereoisomers. This leads to the possibility of three cyclic dimeric lactides: D-lactide, L-lactide, or meso-lactide. The L-lactide consists of two S-stereoisomers and the D-lactide is made up of two R-stereoisomers. Meso-lactide contains one R- and one S-stereoisomer. Figure 1.2 shows the three cyclic dimeric lactides and their polymerized forms.
The amount of each lactide produced is dependent on the lactic acid feedstock, reaction
temperature, and catalyst used. For example, if produced through fermentation of corn, L-lactide
is preferentially created in a 99.5% to 0.5% L- to D-lactide ratio.\(^4\)

![Figure 1.2: The three cyclic dimer of lactide and their corresponding polymer.\(^8\)](image)

When polymerized, poly(L-lactic acid) and poly(D-lactic acid) are optically active and
both have a glass transition temperature around 55°C and a melting temperature around 175°C.\(^3\)
When D-lactide or meso-lactide is copolymerized with L-lactide, the melting temperature
decreases and has been shown to fall between 145°C-175°C depending on the concentration of
stereoisomer.\(^3,8\) The stereochemistry also has an important effect on the crystallizability and
degree of crystallinity. This has important consequences for the thermal, mechanical, and
degradation properties of PLA, and an important research topic is to understand the relationships
between stereochemistry, crystallinity, and resulting properties. The findings of some of these previous studies are discussed in detail later in this introduction.

1.2 Chain Conformation and Crystal Structure

The crystal structure of poly(L-lactic acid) and poly(D-lactic acid) has been widely investigated using wide angle X-ray and electron diffraction\textsuperscript{9–11} and conformational energy analysis\textsuperscript{12}. The $\alpha$ and $\beta$ crystal forms are the focus of most of the previous studies, but a $\gamma$ form has also been noted to occur during epitaxial crystallization.\textsuperscript{13} The crystallization parameters dictate which crystal structure will form.

The $\alpha$ crystal structure was first described in detail by DeSantis and Kovacs.\textsuperscript{9} This unit cell structure is believed to form at low mechanical drawing temperatures and low draw ratios, as well as during quiescent crystallization above 120°C.\textsuperscript{10} The $\alpha$ crystal structure consists of a pseudo-orthorhombic unit cell containing two chains and with dimensions: $a = 10.7\text{Å}$, $b = 6.45\text{Å}$, and $c = 27.8\text{Å}$. The chains in this structure adopt a 10/3 helical conformation.\textsuperscript{9,14} Hoogsteen et al also proposed a similar $\alpha$ crystal structure with a pseudo-orthorhombic unit with the dimensions: $a=10.6\text{Å}$, $b=6.1\text{Å}$ and $c=28.8\text{Å}$. A modified $\alpha$ ($\alpha'$) crystal structure occurring at crystallization temperatures below 120°C was proposed by Zhang et al.\textsuperscript{11} The $\alpha'$ crystal structure was first investigated to understand the discontinuation of the spherulite growth rate, the formation of significantly smaller spherulites, and the minimum value obtained for the long period and lamellar thickness at a temperature between 100° to 120°C. The $\alpha'$ crystal structure has been called a “disordered” $\alpha$ crystal structure because the $\alpha'$ diffraction results in similar peak locations and magnitude.\textsuperscript{11,15}
The β crystal structure was described by Hoogsteen et al to arise during stretching of the α crystal form at high drawing temperatures and high draw ratios. This structure consists of an orthorhombic unit cell containing six chains with $a = 10.31 \, \text{Å}$, $b = 18.21 \, \text{Å}$, and $c = 9.00 \, \text{Å}$ dimensions and the chains adopt a 3/1 helical conformation.\textsuperscript{10} More recently, Puiggali et al. suggested that the β crystal system is a frustrated crystal structure that forms from three three-fold helices, as seen in Figure 1.3. The helices adopt a trigonal unit cell with parameters $a=b=10.52 \, \text{Å}$ and $c=8.8\, \text{Å}$. This proposed crystal structure takes into account the frustrated random up-down orientation that occurs because of fast quenching.\textsuperscript{12}

Figure 1.3: The frustrated trigonal unit cell proposed by Puiggali et al.\textsuperscript{12}
1.3 Crystallization of PLA

The effect of crystallization temperature and time, degree of supercooling, and chain stereochemistry on the resulting crystallinity and microstructure of PLA has been a highly researched topic and discussed in additional detail throughout the introduction.

Semi-crystalline polymers have three main structural regions: relatively mobile amorphous regions, crystalline regions, and so-called ‘rigid’ amorphous region. The rigid amorphous regions are located in the order to disorder regions at surfaces or regions where the segments are confined between crystalline regions. In most semi-crystalline polymers, the polymer chains fold back and forth on themselves to form ordered lamella. In unoriented, isotropic systems, lamella grows out in all directions from a nucleation point to form a spherulite. A schematic of a spherulite with lamella growing three-dimensionally is shown in Figure 1.4. An inset in the diagram also shows the folded polymer chains which makes up the lamella.

![Schematic of a spherulite](image)

Figure 1.4: Schematic of a spherulite showing lamella-containing fibrils growing out from a nucleation point. The inset give a close up of the folding chain lamella that make up the fibrils.16
In order to characterize the effect of time and temperature on the crystallization kinetics, the spherulite growth can be monitored with polarized optical microscopy. Polarized optical microscopy images of semi-crystalline PLA are shown in Figure 1.5.

Figure 1.5: Polarized optical microscopy images of PLA spherulites crystallized at (A) 125°C, (B) 130°C, (C)135°C, and (D)145°C. [Note: The scale of 100 nm is the same for all four images.]^{17}

The spherulite radius is monitored as a function of time to determine the growth rate. Previous work by Huang, et al., shown in Figure 1.6, explored the spherulite growth rate as a function of temperature for random co-polymer samples of varying meso-lactide content. Table 1.1 is from a paper by Baratian et al. that compared the results from Huang et al. to PLA containing D-lactide units. The values in Table 1.1 can be used as a reference for the Figure 1.6. The
maximum spherulite growth rate occurs at a temperature around 120°C-130°C depending on the co-monomer concentration.\textsuperscript{18,19} An increase in meso-lactide content led to a decrease in the spherulite growth rate, as well as a decrease in the temperature of maximum spherulite growth rate. The sample with the highest meso-lactide content (12%) did not show any change in spherulite growth rate because the R-stereoisomer defects inhibited ability for crystal to form in the PLA.\textsuperscript{19} It is clear from these findings that the R-stereoisomers in the meso-lactide serve as defect structures within the S-lactide PLA. Several previous studies have come to conclusion that the R-stereoisomer defects are rejected from the crystals.\textsuperscript{18–20}

Table 1.1: Indicated the R-isomer content and molecular weight information for the PLLA contain D-lactide and meso-lactide co-monomers.\textsuperscript{18}

<table>
<thead>
<tr>
<th>polymer</th>
<th>(PLLA)</th>
<th>1.5% D-lactide</th>
<th>3% D-lactide</th>
<th>6% D-lactide</th>
<th>3% meso-lactide</th>
<th>6% meso-lactide</th>
<th>12% meso-lactide</th>
</tr>
</thead>
<tbody>
<tr>
<td>nominal comonomer content</td>
<td>% R isomer</td>
<td>$M_n$</td>
<td>$M_w$</td>
<td>no. av S run length</td>
<td>$M_n$</td>
<td>$M_w$</td>
<td></td>
</tr>
<tr>
<td>polymer A</td>
<td>0.4</td>
<td>65 500</td>
<td>127 400</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copolymer E</td>
<td>1.7</td>
<td>72 900</td>
<td>110 800</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copolymer F</td>
<td>3.0</td>
<td>81 900</td>
<td>143 500</td>
<td>67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copolymer G</td>
<td>6.2</td>
<td>75 100</td>
<td>128 500</td>
<td>33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copolymer B</td>
<td>2.1</td>
<td>65 800</td>
<td>122 600</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copolymer C</td>
<td>3.4</td>
<td>63 900</td>
<td>119 100</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copolymer D</td>
<td>6.6</td>
<td>65 500</td>
<td>121 300</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1.6: Plot of the spherulite growth rate as a function of crystallization temperature, where samples have varying meso-lactide co-monomer content. [Co-monomer content is listed in Table 1.1] \(^{19}\)

Other studies have shown that the bulk crystallinity, \(\varphi_c\), is strongly influenced by the crystallization temperature \((T_c)\), the degree of supercooling \((\Delta T = T_m^0 - T_c\), where \(T_m^0\) is the equilibrium melting temperature\), and the stereoisomer content. Increasing the crystallization temperature, generally leads to a higher degree of crystallinity, as shown in Figure 1.7a. At crystallization temperatures above that associated with the maximum spherulite growth rate higher crystalline ordering occurred due to a slower crystal growth rate. The degree of supercooling is sample dependent.\(^{18,19}\) Increasing the co-monomer content lowers the equilibrium melting temperature; therefore, the crystallization temperature must be adjusted to compare the effect of degree of supercooling between samples with different equilibrium melting temperatures. For a particular sample, a decrease in the degree of supercooling, \(\Delta T\), leads to an increase in the bulk crystallinity, as shown in Figure 1.7b. Table 1.1 serves as a reference to
Figures 1.7 (a) and (b) to show important information about the R-isomer content in each sample.

Figure 1.7: The bulk crystallinity of PLA with co-monomer content of D-lactide or meso-lactide is shown as a function of the crystallization temperature (a) and degree of supercooling (b). [The sample properties are described in Table 1.1.]
The size and spacing of the co-monomer defects determines the magnitude of the decrease. Baratian et al. compared the effect of meso-lactide and D-lactide co-monomer defects on the crystallinity and lamellar thickness of PLA. The D-lactide containing PLA contains two R-stereoisomers placed together along the chain, whereas the meso-lactide containing PLA has individual R-stereoisomers randomly placed throughout the chain. If samples containing the same concentration of R-stereoisomers are compared, meso-lactide will result in a lower degree of crystallinity as a result of having shorter chain lengths between defects. If samples containing equal concentrations of co-monomer defects are compared, the PLA containing D-lactide results in a lower degree of crystallinity due to the larger size of the defect present. These trends can be seen in Figure 1.7 (a) and (b).

The long period (L), the average distance between crystal centers, was determined using the relationship \( L = \frac{2\pi}{q_{\text{max}}} \), where \( q_{\text{max}} \) is the first order maximum in the intensity versus q plot. The long period, as investigated with small angle X-ray scattering, increased with increasing the addition of co-monomer defect during isothermal crystallization at a constant temperature since lower degrees of crystallinity would be expected to lead to a larger distance between lamella. Figure 1.8 plots the long period as a function of the degree of supercooling for PLA samples containing D-lactide co-monomer.
Figure 1.8: The long period plotted as a function of the degree of supercooling for samples containing varying amounts of D-lactide. [The sample names correspond to data given in Table 1.1]^{18}

Along with the first order maximum, PLA crystallized at higher temperatures had a second order maximum indicating the presence of relatively well oriented lamellar stacks.^{18} The magnitude of the second order peak decreased for the 3% meso-lactide co-polymer and completely disappeared for the PLA containing 6% meso-lactide co-monomer; therefore, indicating less defined lamellar stacks in PLA containing a higher meso-lactide concentration.^{20}

The lamellar thickness and the interlamellar amorphous material were also estimated from the small angle X-ray results. The correlation function, shown in Equation 1.1, was used to derive the thickness of crystalline lamella, L_c, from the linear crystallinity, x_c, shown in Equation 1.2.
\[ \gamma(r) = \int_0^\infty q^2 I(q) \cos(qr) \, dq \quad (Equation \, 1.1) \]

\[ \frac{B}{L} = x_c (1 - x_c) \quad (Equation \, 1.2) \]

In Equation 1.1, \( r \) is the distance and \( I(q) \) is the intensity for a specific \( q \) value. In Equation 1.2, \( B \) is the value where \( \gamma(r) \) equals zero and \( L \) is the first maximum of \( \gamma(r) \). To differentiate between the thickness of the crystalline lamella and the thickness of the amorphous material between the lamella, \( L_a \), the definition of linear crystallinity and the assumption that the lamella thickness should increase with crystallization temperature were used. The definition of linear crystallinity states that \( x_c \geq \varphi_c \). If \( x_c = \varphi_c \), then amorphous material is present only in between lamella, but if \( x_c > \varphi_c \), then amorphous material is located between the lamella and lamellar stacks.\(^{18-20}\) The thickness of the crystalline lamella, \( L_c \), and the amorphous entanglements, \( L_a \), can be determined from the relationships in Equation 1.3 and Equation 1.4, respectively.

\[ L_c = x_c L \quad (Equation \, 1.3) \]

\[ L_a = (1 - x_c) L \quad (Equation \, 1.4) \]

The crystalline lamellar thickness calculated using the above method was confirmed with tapping mode AFM studies conducted by Kanchanasopa, et al.\(^{21}\)

Application of the definition of linear crystallinity suggests that amorphous material is not only located between lamella, but also between the spherulites and fibrils. Previous
polarized optical microscopy studies determined that even at low crystallinitities, the spherulites in PLA impinge on each other indicating that a substantial amount of amorphous material did not exist between spherulites. Therefore, amorphous segments exist in interfibrillar regions. The fraction of amorphous material located in the interfibrillar regions ($\eta_{if}$) is calculated using Equation 1.5, where $v_s$ is equal to the ratio, $\varphi_c/x_c$.

$$\eta_{if} = \frac{(1 - v_s)}{(1 - \varphi_c)} \quad (Equation \ 1.5)$$

The lamellar thickness continues to increases with crystallization temperature for particular PLA samples containing co-monomer defects. If the crystallization temperature is held constant, the lamellar thickness decreases with an increase in co-monomer content, indicating that the co-monomer defects are rejected from the crystal. Therefore, the addition of co-monomer defects lead to more amorphous material between lamella and lamella stacks.\textsuperscript{18-20}

1.4 Effect of Crystallinity and Stereochemistry on the Dynamics of PLA

The crystallinity and stereochemistry of PLA has an effect on the molecular dynamics of PLA. Several previous studies to understand the molecular dynamics of PLA used common characterization techniques such as, dynamic mechanical analysis and differential scanning calorimetry. A less commonly used but just as informative technique, dielectric relaxation spectroscopy, is also useful to investigate the dynamics of amorphous and semi-crystalline PLA.\textsuperscript{22-26}
The dielectric spectra of amorphous and crystalline PLA show two relaxation processes, local and segmental relaxations. The local, β, relaxation is a broad relaxation that occurs at lower temperatures while the polymer is in its glassy state. This process arises from rotations of the methyl group on the polymer backbone. The segmental, α, relaxation occurs at temperature at or above the glass transition temperature. The dielectric spectrum of amorphous PLA also shows a normal mode relaxation, α_n, that is caused by the net dipole motions along the entire chain. The normal mode relaxation does not occur in crystalline materials because both ends of the amorphous chains are fixed in either loop chains, tie chains, or between crystalline lamella. Figure 1.9 shows the dielectric loss spectra of amorphous and semi-crystalline PLA and labels the local, segmental, and normal mode relaxations for each.

Figure 1.9: Dielectric loss spectra of amorphous PLA (open circles) and semi-crystalline PLA (closed circles).
The focus of previous work has been on the effect of crystallinity on the shape, dielectric strength, and mean relaxation time and temperature of the $\alpha$ relaxation. An extensive study by Kanchanasopa et al. investigated the effect of crystallinity and stereoisomer content on the dynamics of the segmental relaxation.\textsuperscript{23}

For both amorphous and crystalline PLA, the effect of temperature on the segmental relaxation was investigated. The dielectric strength of the segmental relaxation of the amorphous PLA fulfilled the expectations from the Kirkwood-Onsager-Fröhlich equation, which predicts that the dielectric strength will decrease with increasing temperature. On the other hand, the dielectric strength of the segmental process of crystalline PLA increased with temperature. This occurred because of the presence of rigid amorphous segments. The rigid amorphous region, discussed in an earlier section of this introduction, includes segments along the surface of crystals and those trapped between crystallites. These regions lack mobility at temperatures where other amorphous segments have mobility and are able to relax. As temperature increases, the confined amorphous regions become progressively more mobile; therefore the dielectric strength should increase with increasing temperature. At a constant temperature, the dielectric strength of crystalline PLA is lower than amorphous PLA, as expected due to the inhibited mobility in crystalline PLA.\textsuperscript{22,23} This trend can be seen in Figure 1.10, where the dielectric loss is plotted as a function of frequency for a sample of PLA that is being crystallized at 80°C.
Figure 1.10: The dielectric loss as a function of frequency for PLA isothermal crystallized at 80°C over different increments of time (minutes) as indicated in the legend.\textsuperscript{23}

A longer crystallization time leads to a higher degree of crystallinity, which lowers the dielectric strength of the segmental relaxation. As discussed in a previous section, the addition of stereoisomer content leads to a lower crystallinity. Therefore, the dielectric strength increased for samples with increasing R-stereoisomer concentration.\textsuperscript{23}

As shown by previous studies, crystallinity also plays a key role in the shape of the segmental relaxation and mean relaxation time. It was determined that a higher degree of crystallinity lead to a broader relaxation because more crystallinity inhibits the segmental relaxation. Kanchanasopa et al. showed that the difference between the relaxation time of the crystalline sample and amorphous sample decreased with an increase in stereoisomer content.
This trend is shown in Figure 1.11 (a). At a meso-lactide content of 12%, the mean relaxation time of the crystalline and amorphous samples is the same, as shown in Figure 1.11(b).23

Figure 1.11 (a) and (b): The mean relaxation times of (a) polylactide and (b) 12% meso-lactide co-polymer are shown in a semi-logarithmic plot as a function of the inverse temperature.23

1.5 Effects of Orientation on PLA

PLA has the versatility and ease to be processed using several manufacturing techniques, including extrusion and fiber drawing, which results in anisotropic materials. Also, a recent interest in using PLA in uniaxially and biaxially oriented films has sparked an interest in understanding the effects orientation has on the structure, dynamics, and resulting properties of PLA. The superstructure changes in semi-crystalline polymers with orientation are generally well-understood and several previously discussed techniques can be used to understand the effects of orientation on semi-crystalline PLA.
During uniaxial orientation, this superstructure becomes anisotropically altered. The spherulites break up and form smaller crystalline regions and the tie-chains are the first to orient in the direction of stretching. Following the tie chains, the crystalline regions orient themselves so that the lamella growth direction is perpendicular to the stretching direction. Finally, the amorphous regions begin to orient and order. Depending on the degree of deformation, some amorphous segments may order and crystallize.\textsuperscript{27,28} Figure 1.12 shows the breaking up of the lamella into smaller crystalline regions, as well as the extension of tie chains as a semi-crystalline polymer is uniaxially oriented.

![Figure 1.12: Extension of tie-chains and breaking up of spherulites during the orientation of a semi-crystalline polymer.\textsuperscript{29}](image)

Orientation increases the fraction of rigid amorphous segments.\textsuperscript{30,31} As the spherulites break-up, the crystallites become smaller, but the total surface area of crystalline regions increases. The increase in crystallinity from newly oriented and ordered amorphous regions, as
well as the extension of amorphous segments will increase the number of confined segments.\textsuperscript{27,28} Effects of orientation on semi-crystalline polymers has been studied using wide angle and small angle X-ray scattering techniques, while its effect on resulting properties and dynamics has been investigated using differential scanning calorimetry, tensile testing, and dynamic mechanical analysis.\textsuperscript{14,32,33}

Wide angle X-ray diffraction patterns of uniaxially oriented and unoriented PLA are shown in Figure 1.13.

![Figure 1.13: The wide angle X-ray diffraction pattern for oriented (solid red line) and unoriented (dashed blue line) PLA samples that were crystallized at 105°C.\textsuperscript{14}](image)

Comparison of the two wide angle X-ray scattering patterns shows that the unoriented PLA sample is in the $\alpha$ crystal form discussed earlier in the introduction, while the oriented PLA
sample starts to form the “disordered” α crystal form, $\alpha'$. The loss of the smaller peaks and the slight shift of the peaks located at 2θ of 16.7° and 19.1°, which correspond to the (200)/(110) and (203) crystal planes, respectively, indicates formation of the $\alpha'$ crystal structure.\textsuperscript{14,15}

The effect of orientation on the glass transition temperature, melting temperature, and the degree of crystallinity has been investigated using differential scanning calorimetry. As shown in the thermograms shown in Figure 1.14, from a study by Wong et al., the glass transition temperature and melting temperature only increased by a few degrees with an increase in the stretching ratio.\textsuperscript{32} The samples in this study were uniaxially stretched at a temperature of 85°C.

![Figure 1.14: Differential scanning calorimetry thermograms of PLA stretched at 85°C.\textsuperscript{32}](image)
Directly after the glass transition, an exothermic peak arises and increases in magnitude with stretching ratio as a result of the melting of strain-induced crystallization. Lastly, as the sample was stretched to a higher extension ratio, the degree of crystallinity increased.\textsuperscript{32}

1.6 Motivation for this Thesis

Several studies have investigated the effect of crystallization and stereochemistry on properties and dynamics of PLA. Differential scanning calorimetry, wide angle X-ray diffraction, and small angle X-ray scattering have been very helpful in determining the effect of crystallization parameters, stereochemistry, and orientation on semi-crystalline PLA. Dielectric relaxation spectroscopy is a very powerful characterization tool that allows us to gain a greater insight into the relaxation dynamics of amorphous and semi-crystalline PLA, but there are no previous studies investigating the uniaxial orientation of PLA using this method. Dielectric spectroscopy was recently used to investigate the effect of orientation of the molecular dynamics of semi-crystalline poly(vinylidene fluoride) by Linares et al.\textsuperscript{30} The purpose of this study was to investigate the effect of uniaxial orientation of semi-crystalline PLA on the microstructure and molecular dynamics using dielectric relaxation spectroscopy. Semi-crystalline PLA samples were stretched to different magnitudes and characterized using differential scanning calorimetry, wide angle X-ray diffraction, small angle X-ray scattering, and dielectric relaxation spectroscopy.
References


Chapter 2: Experimental Section

Amorphous, non-oriented semi-crystalline, and oriented semi-crystalline samples were formed from PLA. A variety of characterization techniques were used to investigate the changes in structure and molecular dynamics caused by external orientation. Differential scanning calorimetry (DSC) was used to determine the glass transition and melting temperatures, as well as an estimate of the percent crystallinity. Wide angle X-ray diffraction (WAXD) gave some insight into the unoriented and oriented semi-crystalline PLA crystal structure and was used to estimate the degree of crystallinity, while small angle X-ray scattering (SAXS) was used to determine the long period of the materials. Lastly, dielectric relaxation spectroscopy (DRS) was used to characterize the molecular dynamics of each material.

2.1 Sample Preparation

Poly(lactic acid) was obtained in bulk from NatureWorks LLC (via Professor John Dorgan at the Colorado School of Mines). This PLA has been reported to consist of predominately L-lactide, but does contain about 4% R-stereoisomer$^{1,2}$. Three types of samples were prepared for this study: amorphous, unoriented semi-crystalline, and oriented semi-crystalline. Prior to preparing samples, the PLA pellets were melted to form a continuous mass in order to facilitate later processing. The pellets were sandwiched between two metal plates with a sheet of Teflon on each side between the pellets and the metal plates. The Teflon prevented sample contamination and made it easier to remove the polymer after melting. The PLA, Teflon, and metal plates were placed in a preheated Carver hot press at 170°C with no
pressure for 15 minutes. After melting, the melt was removed from the hot press and allowed to cool to room temperature before further processing.

The continuous polymer mass was once again placed between two Teflon sheets and two metal plates and placed back into the Carver hot press at 170°C. The two metal plates, sandwiching the polymer and Teflon, were given 6 minutes to also reach 170°C before pressure was applied to the system. About 1 metric ton of pressure was applied to the sandwiched material for 30 minutes. After 30 minutes under pressure, the melt was removed from the hot press and quenched to room temperature in air to create the amorphous sample. For the unoriented and oriented semi-crystalline PLA samples, the sample was left overnight in the hot press to slowly cool from 170°C to room temperature under pressure allowing for crystallization to occur.

Oriented samples were created by uniaxially stretching the semi-crystalline sample in a Model 5866 Instron using a 1 kN load cell and a stretching rate of 1 millimeter per minute. Prior to stretching, the material was cut into dog bone tensile test sample using an ASTM D638 Type III die. A diagram of the dog bone sample die is shown in Figure 2.1 and the corresponding dimensions are shown in Table 2.1.
Figure 2.1: ASTM D638 Type III dog bone tensile test sample diagram (corresponding dimensions are shown in Table 2.1)\(^3\).

Table 2.1: Dimension of ASTM D638 Type III dog bone tensile test sample (corresponding diagram in Figure 2.1)\(^3\).

<table>
<thead>
<tr>
<th>Dimension (in millimeters)</th>
<th>Tolerances (in millimeters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Narrow Section Width (W)</td>
<td>19</td>
</tr>
<tr>
<td>Narrow Section Length (L)</td>
<td>57</td>
</tr>
<tr>
<td>Overall Width (WO)</td>
<td>29</td>
</tr>
<tr>
<td>Overall Length (LO)</td>
<td>246</td>
</tr>
<tr>
<td>Gage Length (G)</td>
<td>50</td>
</tr>
<tr>
<td>Grip Distance (D)</td>
<td>115</td>
</tr>
<tr>
<td>Fillet Radius (R)</td>
<td>76</td>
</tr>
</tbody>
</table>
Also prior to deformation, lines were drawn on the dog bone samples at 10 millimeter increments to determine the percent extension of specific sections of the sample after stretching, as shown in Figure 2.2. Stresses within the sample were concentrated in the necking region, the region in which plastic deformation occurred, and was the focus in selecting oriented samples for this study. A photograph of a uniaxially deformed PLA sample is shown in Figure 2.2.

![Necking Region](image)

Figure 2.2: Uniaxially deformed PLA dog bone sample showing the necking region (in box).

Early in this investigation, it was determined that PLA was too brittle to be deformed significantly at room temperature. To encourage flow and plastic deformation, the stretching
was performed above the PLA glass transition temperature. A furnace attachment to the Instron was used to deform the PLA at 70°C. In order to maintain consistency among all samples, a heat treatment was created for the furnace and stretching. After insertion of the dog bone in the Instron clamps and furnace, the system was heated up from room temperature to 70°C over a 15 minute time period and then allowed to equilibrate at 70°C for an additional 15 minutes prior to starting the stretching. The sample was deformed to 100% extension, where it was held until the system cooled down to room temperature. The stress-strain curve for this sample is shown in Figure 2.3.

![Stress-strain curve of the 100% extended sample.](image)

Figure 2.3: Stress-strain curve of the 100% extended sample.
In order to quickly cool the system, the heater was turned off and the furnace door was opened immediately after 100% elongation had been reached. The sample was held at 100% extension for 30 minutes to ensure no major recovery occurred. Measurements of each section, which were initially 10 millimeters, were taken to calculate the percent elongation in the individual sections of the sample. Three sections were then selected as the oriented semi-crystalline PLA samples: 25%, 70%, and 110% extension.

To maintain consistency, the same heat treatment in the Instron furnace used on the oriented semi-crystalline samples was performed on the unoriented semi-crystalline samples. Results from differential scanning calorimetry, wide angle X-ray diffraction, and small angle X-ray scattering experiments demonstrated that the heat treatment had little effect on the unoriented semi-crystalline sample’s crystalline structure. The heat treated unoriented semi-crystalline sample is used through-out the discussion of the results along with the amorphous and oriented semi-crystalline samples.

2.2 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a Seiko DSC220CU with a liquid nitrogen gas cooling system. The DSC was calibrated using both an indium and tin standard. Each sample was sealed in a standard aluminum lid and pan. All sample masses were between 5.4 and 6.7 mg. Each sample underwent the same temperature scan cycle per measurement. Because PLA is glassy at room temperature, the measurement was started at 25°C. The temperature was increased at a rate of 10°C per minute to an upper limit of 250°C.
The glass transition temperature, melting temperature, and enthalpy of fusion were determined from this first heat.

### 2.3 Wide Angle X-ray Diffraction

Wide angle X-ray diffraction (WAXD) was performed on a Rigaku DMAX Rapid Micro-Diffraction System in the Materials Characterization Lab at Pennsylvania State University. A Cu Kα (λ=1.541 Å) point focus radiation source with a 0.8 mm pinhole collimator was used along with a curved image plate detector to obtain the diffraction patterns. Prior to experiments, the X-ray source was conditioned to a voltage of 50 kV and a current of 40 mA. In order to maintain consistency, a constant exposure time of 30 minutes for each sample was used.

### 2.4 Small Angle X-Ray Scattering

Small angle X-ray scattering (SAXS) was performed using a Rigaku Molecular Metrology small angle X-ray instrument with a q range of 0.008 to 0.15 Å⁻¹ in the Materials Characterization Lab at Pennsylvania State University. This SAXS uses a copper Kα radiation source with a wavelength (λ) of 1.5418 Å and a collimated beam diameter of about 0.8 millimeters. The small angle chamber was 1.5 meters away from the two dimensional detector. Prior to measurements, the X-ray source was conditioned to a voltage of 45 KV and a current of 0.67 mA. A silver behenate standard was used for calibration of q, where q is defined by Equation 2.1.
2.5 Dielectric Relaxation Spectroscopy

Dielectric relaxation spectroscopy (DRS) samples were placed between two brass electrodes, with the top and bottom electrode having a diameter of 10 mm and 25 mm, respectively. The dielectric permittivity was measured using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. Isothermal frequency sweeps between 10 MHz and 0.01 Hz were performed for a temperature range of -130°C to 160°C at 5°C increments. The measurements started at low temperature (-130°C) and completed at 160°C in order to preserve the thermal history of the sample.
References


Chapter 3: Results and Discussion

3.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is able to provide an important analysis of the effect of uniaxial deformation on the thermal characteristics of semi-crystalline PLA. Even with a limited amount of sample, two measurements were performed for each sample. The reported glass transition temperatures ($T_g$), melting temperatures ($T_m$), and degrees of crystallinity are the average of the two measurements.

For comparison with the results of other characterization techniques, all thermal information was obtained from an initial heat scan, shown in Figure 3.1 for the amorphous, unoriented, 25% extended, 70% extended, 110% extended samples.
Figure 3.1: DSC thermograms of the various PLA samples vertically shifted for comparison.

The transitions in Figure 3.1 can be directly compared because all samples were approximately the same weight. For each sample, there are two main features on this plot: the glass transition temperature and the melting temperature.

In all glass forming materials, a change in the heat capacity accompanies the glass transition temperature ($T_g$) and $T_g$ is conventionally defined as the midpoint of the change. The glass transition region in PLA samples exhibits a heat capacity change and a superimposed endothermic response associated with the non-equilibrium nature of the glassy polymer.\footnote{1} The peak is more dramatic for the amorphous PLA because there was more free volume as compared
to the unoriented and oriented semi-crystalline PLA for the chains to relax and less crystal
hindrances to prevent it from physically aging to a more stable state.²

The glass transition temperature (T_g) is unaffected by the addition of crystallinity and
orientation. The T_g values, shown in Table 3.1, are all within the typical uncertainty of ±3°C
confirming that there is no change in T_g with the addition of crystallinity or orientation. Uniaxial
defor...mation also led to an additional peak shown as a small endothermic peak after the glass
transition temperature. Others have proposed that this represents the melting of strain induced
crystals formed during deformation at an annealing temperature above the glass transition
temperature.³ This assignment is in keeping with the increase in the peak magnitude with
increasing deformation.

Table 3.1: Summary of the glass transition temperature, melting temperature, and enthalpy of
fusion determined by the DSC measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass Transition Temperature, T_g (°C)</th>
<th>Melting Temperature, T_m (°C)</th>
<th>Enthalpy of Fusion, H_f (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>59</td>
<td>148</td>
<td>&gt;1</td>
</tr>
<tr>
<td>Unoriented</td>
<td>60</td>
<td>149</td>
<td>17</td>
</tr>
<tr>
<td>25% Extension</td>
<td>62</td>
<td>149</td>
<td>25</td>
</tr>
<tr>
<td>70% Extension</td>
<td>62</td>
<td>148</td>
<td>30</td>
</tr>
<tr>
<td>110% Extension</td>
<td>62</td>
<td>148</td>
<td>33</td>
</tr>
</tbody>
</table>
The melting exothermal peak in DSC, shown in Figure 3.1, presents the melting temperature, where all crystalline regions have melted, and can also be used to estimate the amount of crystallinity in the sample. The introduction of crystallinity and orientation to these PLA samples did not affect the primary melting temperature of PLA, as shown in Figure 3.1 and Table 3.1. Table 3.1 also displays the heat of fusion for each sample. The heat of fusion determined from differential scanning calorimetry is calculated at the melting temperature; therefore, is known to be an underestimate of the true value due to the pre-melting of smaller crystalline regions. When the measured heat of fusion is compared to that of the heat of fusion of 100% crystalline PLA ($\Delta H_f^\circ$), the percent crystallinity of the sample can be determined.\textsuperscript{4,5}

$$X_c = \frac{\Delta H_f}{\Delta H_f^\circ} \times 100 \quad (\text{Equation 3.1})$$

$\Delta H_f^\circ$ for PLA has been reported to be 100 J/g.\textsuperscript{6} As shown in Table 3.1, the degree of crystallinity increases with orientation.

### 3.2 Wide Angle X-ray Diffraction (WAXD)

Wide angle X-ray diffraction is a powerful technique used to better comprehend the effects of orientation on the crystalline structure of semi-crystalline PLA. As discussed in the introduction, PLA can exhibit several crystal forms, which occur depending on how the system was crystallized. In this investigation, it is believed that one type of crystal is formed when the PLA is crystallized from the melt. Upon deformation above the glass transition temperature at
an annealing temperature, another crystal form develops along with the previously formed crystals. Unfortunately, these two crystals, formed under different conditions, could not be differentiated by the characterization techniques used in this study. WAXD provides some insight into how the amorphous and crystalline regions orient with uniaxial deformation. Lastly, the amount of crystallinity in PLA can be estimated with this technique.

The wide angle X-ray diffraction patterns are shown in Figure 3.2 for the unoriented semi-crystalline PLA and the 25%, 70%, and 110% extended semi-crystalline PLA samples. These diffraction pattern images were rotated in order to vertically orient the stretching direction along with the meridian axis. It is important to note that the diffracted intensity cannot be compared between multiple samples.
Figure 3.2: WAXD diffraction patterns for the semi-crystalline unoriented (a), the 25% extended (b), the 70% extended (c), and the 110% extended (d) samples.

Because the unoriented PLA contains both crystalline and amorphous regions, both crystalline diffraction rings and an amorphous halo can be seen in Figure 3.2(a). When uniaxially deformed, arcing along the equatorial axis occurs. This is a result of the amorphous segments orienting in the direction of uniaxial deformation. In the most deformed sample, 110% extended, shows the arcing in the (200)/(100) crystal system indicating preferential orientation.$^{3,7,8}$
Figure 3.3 displays the intensity of all samples averaged over 180 degrees, avoiding the beam stop. The intensity values are vertically shifted so all four scattering patterns can be readily compared.

![Graph showing WAXD scattering profiles](image-url)

**Figure 3.3**: WAXD scattering profiles of the unoriented, 25% extended, 70% extended, and 110% extended PLA samples.

Because the semi-crystalline unoriented and oriented samples were crystallized from the melt, the α crystal form is expected to form.\(^3\,7\,9\) As shown in Figure 3.3, crystalline peaks are found at 2θ values of 12.5, 14.8, 16.7, 19.1, and 22.4 degrees for the (103), (010), (200) and/or (110), (203), and (015) crystalline planes, respectively. Diffraction of the (200)/(110) and (203) planes
are the most distinct. The scattering patterns in this study are confirmed with expectations for the α crystal structure from the literature.

The crystalline and amorphous contributions to the diffraction patterns can be separated by resolving the crystalline peaks from the rest of the scattering pattern using the amorphous scattering pattern, as shown in Figure 3.4. The scattering pattern from the amorphous sample was shifted to fit under the crystalline peaks and then subtracted, leaving the resolved crystalline peaks.

Figure 3.4: Plot showing the original scattering pattern for the unoriented PLA sample along with the amorphous scattering pattern and the resulting resolved crystalline peaks for the unoriented PLA pattern.
The area of the resolved crystalline peaks ($A_c$) can then be compared to the area of the entire sample’s scattering pattern ($A_t$), as shown in Equation 3.2, to calculate the relative crystallinity in the samples ($X_c$).

$$X_c (\text{in } \%) = \frac{A_c}{A_t} \times 100 \quad (\text{Equation 3.2})$$

The degrees of crystallinity determined in this fashion are shown in Table 3.2, along with those calculated from the DSC measurement. Both measurements clearly show that as the sample becomes more oriented, the degree of crystallinity increases. Because the degree of crystallinity in a sample is temperature dependent, there is a consistent difference between the degree of crystallinity calculated from the DSC measurement at the melting temperature and the WAXD measurement at room temperature.\textsuperscript{4,5} The degree of crystallinity measured from DSC was consistently lower than that calculated from the WAXD measurements because the heat of fusion used to calculate the degree of crystallinity is determined at the melting temperature. At this temperature, the strain-induced crystallization that was formed during annealing and deformation, as well as some smaller crystalline regions had relaxed prior to the melting temperature.
Table 3.2: Degrees of crystallinity as determined from WAXD and DSC measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>X_c (from WAXD)</th>
<th>X_c (from DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unoriented</td>
<td>29 %</td>
<td>17 %</td>
</tr>
<tr>
<td>25% Extended</td>
<td>30 %</td>
<td>25 %</td>
</tr>
<tr>
<td>70% Extended</td>
<td>44 %</td>
<td>30 %</td>
</tr>
<tr>
<td>110% Extended</td>
<td>42 %</td>
<td>33 %</td>
</tr>
</tbody>
</table>

As discussed in the introduction, when a semi-crystalline polymer is oriented, the spherulites break up and lamellar reorganization occurs; therefore, reducing the crystallite size. The Scherrer equation, shown in Equation 3.3, represents the inverse relationship between the scattering profile peak breadth and the crystallite size (D), the latter being the perpendicular distance through the set of crystallographic planes in question. A broader crystalline peak indicates a decrease in crystallite size.

\[
D = \frac{K\lambda}{B\cos(\theta)}
\]

(Equation 3.3)

In this equation, B is the peak breadth as determined from the full width at half maximum (FWHM) of each crystalline reflections, K is the Scherrer Constant (which is taken to be 1), \( \lambda \) is the wavelength, and \( \theta \) is the Bragg angle.\textsuperscript{10,11} The crystallite size for each sample is shown below in Table 3.3.
Table 3.3: The crystallite size (Å) as calculated from the Scherrer Equation for each sample and each crystalline peak.

<table>
<thead>
<tr>
<th></th>
<th>(103)</th>
<th>(101)</th>
<th>(200)/(110)</th>
<th>(203)</th>
<th>(105)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unoriented</td>
<td>888.2</td>
<td>178.1</td>
<td>157.7</td>
<td>125.4</td>
<td>83.8</td>
</tr>
<tr>
<td>25% Extended</td>
<td>888.2</td>
<td>114.6</td>
<td>134.9</td>
<td>113.2</td>
<td>85.6</td>
</tr>
<tr>
<td>70% Extended</td>
<td>888.2</td>
<td>105.9</td>
<td>122.6</td>
<td>99.1</td>
<td>79.4</td>
</tr>
<tr>
<td>110% Extended</td>
<td>888.2</td>
<td>104.8</td>
<td>115.9</td>
<td>89.9</td>
<td>73.6</td>
</tr>
</tbody>
</table>

Even though the crystalline regions are decreasing in size, the DSC measurements and WAXD calculations indicate an increase in the crystallinity with deformation indicating that amorphous chains are orienting and converting to the crystalline state with uniaxial deformation. The intensity was azimuthally integrated at a 2θ value of 18°, which is between crystalline peaks, and plotted as a function of the azimuthal angle, Φ to create three-dimensional radial plots of the amorphous halo. These plots are shown in Figure 3.5. It is important to note that the stretching direction for all samples is at a Φ value of 135°. Also, the beam stop is located at a Φ value of 80°. As the PLA becomes more oriented, arcing occurs along the axis perpendicular to the stretching direction. Therefore, indicating ordering and orientation of the amorphous regions within the PLA.
Figure 3.5: Radial plots with intensity around the Φ direction at a 2θ value of 18° for the amorphous (a), unoriented (b), 25% extended (c), 70% extended (d), and 110% extended (e) PLA along with an intensity color scale bar. [Note: Stretching Direction is at Φ = 135°]
3.3 Small Angle X-ray Scattering (SAXS)

Small angle X-ray scattering (SAXS) was performed to estimate the long spacing of unoriented and oriented semi-crystalline PLA. The two dimensional scattering patterns for the unoriented, 25% extended, and 110% extended PLA samples are presented in Figure 3.6.

![2D scattering patterns for unoriented and oriented PLA samples](image)

Figure 3.6: The 2D scattering patterns for the unoriented (a) and 110% (b) oriented PLA samples.

The bright red region in the center of the scattering pattern above arises from the spillover of the incident radiation from the beam stop. An isotropic ring is observed at higher q values indicative of randomly oriented crystalline lamella within the sample. As expected, the isotropic ring disappears with orientation. With orientation in horizontal direction, the 2D scatting pattern shows anisotropic lobes in the meridian axis. This indicates orientation of crystalline lamellae or lamellar fragments perpendicular to the deformation direction. Although the original purpose of
the SAXS experiments on the oriented samples was to determine lamellar orientation as a function of deformation, the long spacing of the oriented samples could not be clearly distinguishable from the high intensity near the beam stop.

Even though the extent of the lamellar organization could not be determined from the two-dimensional scattering profiles, experimental data was azimuthally averaged and Lorentz-corrected, as shown in Figure 3.7.

![Figure 3.7: Azimuthally averaged and Lorentz-corrected SAXS data as a function of q for the unoriented and 25%, 70%, and 110% extended PLA samples.](image)

The long period ($L$) can be calculated from the maximum ($q_{\text{max}}$) of each set of data using Equation 3.4. The long period is the average distance between the crystalline centers in a sample.
\[ L = \frac{2\pi}{q_{\text{max}}} \quad (Equation \ 3.4) \]

As seen in Figure 3.7, the mean lamellar long periods are all about 18.9 nanometers and independent of orientation. This value agrees with previous values reported in the literature.\(^{12}\)

### 3.4 Dielectric Relaxation Spectroscopy (DRS)

Dielectric relaxation spectroscopy is a valuable characterization technique for gaining an understanding of the molecular dynamics of materials. As is the case with several semi-crystalline polymers, PLA has two observable relaxations: segmental and local glassy state relaxation. The segmental (\(\alpha\)) relaxation occurs at temperatures at or above the glass transition temperature. On the other hand, the local (\(\beta\)) relaxation occurs at lower temperatures and represents the localized motions of side groups or of the main chain depending on the polymer. The segmental relaxation refers to the relaxation of the polymer chain with length scales in the 1 to 10 nanometer range, whereas the local relaxation has a shorter length scale, typically on length than 1 nanometer. In PLA, the local relaxation peak is the result of the side methyl group rotating perpendicular to the backbone.\(^6,^{13,14}\) PLA is also one of a few polymers that have dipole motions both parallel and perpendicular to the backbone chain, but the normal mode was not observed in the present study.\(^{13}\) Figure 3.8 shows these two relaxations in a three-dimensional plot of the dielectric loss as a function of frequency and temperature for the unoriented PLA sample.
Figure 3.8: Dielectric loss as a function of frequency and temperature for the unoriented PLA sample.

The sharp increase in dielectric loss at high temperatures and low frequencies is the result of ionic conduction of impurities in the PLA and possibly electrode polarization. Both the unoriented and oriented semi-crystalline PLA samples exhibited a segmental and local relaxation.

As described in detail in the introduction, the Havriliak-Negami equation, shown in Equation 3.5, is a commonly used fitting function to quantitatively describe the dielectric strength ($\Delta\epsilon$), relaxation time ($\tau_{\text{max}}$), and shape (a and b) of both the segmental and local relaxations. In order to accurately fit the dielectric relaxation data, a conduction term was
add to the equation to take into account and remove the ionic conduction contribution caused by impurities.\textsuperscript{15}

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega) = \varepsilon_\infty - \frac{i\sigma_R}{(\varepsilon_0\omega)^s} + \frac{\Delta\varepsilon}{\Delta(1+(i\omega\tau_{\text{max}})^{a}b)} \quad (\text{Equation 3.5})
\]

\[
\Delta\varepsilon = \varepsilon_{\text{relaxed}} - \varepsilon_{\text{unrelaxed}} \quad (\text{Equation 3.6})
\]

The dielectric strength, $\Delta\varepsilon$, shown in Equation 3.5, is defined in Equation 3.6. The relaxed dielectric constant refers to the limiting value at low frequencies. The unrelaxed dielectric value is the limiting dielectric constant at high frequencies. Also in Equation 3.5, $\tau_{\text{max}}$ is the mean relaxation time, $\omega$ is the angular frequency ($\omega=2\pi f$), and $a$ and $b$ describe the broadness of the relaxation and the symmetry of the relaxation peak, respectively. The symmetry shape parameter, $b$, can range from a value of 0 to 1, with a value of 1 indicating a symmetric relaxation peak. Crystalline polymers have been shown to previously display a symmetric segmental relaxation peak.\textsuperscript{17} Therefore, the segmental relaxation of unoriented and oriented PLA was analyzed using a peak symmetry parameter value of 1.\textsuperscript{6,15} Amorphous polymers have asymmetric segmental relaxations. When allowed to freely fit, the symmetry shape parameter, $b$, of the amorphous PLA sample was consistently around 0.5 for all temperatures.\textsuperscript{6} Therefore, the amorphous polymer was analyzed using a constant symmetry parameter value of 0.5. Fixing the symmetry shape parameter improves the fitting. The peak breadth shape parameter, $a$, takes on a value between 0 and 1, with 0 being a more broad relaxation and 1 being a very narrow relaxation.\textsuperscript{15}
The local relaxations of semi-crystalline polymers are often broad and overlap the segmental relaxation.\textsuperscript{17,18} This effect is shown in an isochronal plot of 110% extended PLA in Figure 3.9. The local relaxation overlap is minimal, but still needs to be taken into consideration with fitting the segmental relaxation.

Figure 3.9: Isochronal plot of the 110% extended PLA sample showing the overlap of the local and segmental relaxation.

In order to account for the tail of the local relaxation overlapping with the segmental relaxation, the Havriliak-Negami equation was modified using a method described by Coburn and Boyd.\textsuperscript{17} In this method, the local relaxation is fit using Equation 3.6 and the resulting dielectric strength and broadness shape parameter (a) are plotted as a function of temperature and the relaxation time was semi-logarithmically plotted as a function of inverse temperature. Theses plots were
then fit with linear equations and values for each parameter were extrapolated to temperatures in the segmental relaxation temperature range. These extrapolated values were considered the local relaxation contribution to the segmental relaxation and an extra term was added to the Havriliak-Negami equation.\textsuperscript{17,18} Equation 3.7 shows the modified Havriliak-Negami fitting function used to fit the segmental relaxation for each PLA sample.

\[
\varepsilon^*(\omega) = \varepsilon_\infty - \frac{i\sigma_R}{(\varepsilon_0 \omega)^s} + \left\{ \frac{\Delta \varepsilon_\alpha}{\left[ 1 + (i\omega \tau_{max\alpha})^{a_\alpha} \right]^{b}} + \frac{\Delta \varepsilon_\beta}{\left[ 1 + (i\omega \tau_{max\beta})^{a_\beta} \right]^{b}} \right\} (Equation 3.7)
\]

The shape parameters, the mean relaxation time, and the dielectric strength were determined for the segmental relaxation for each PLA sample. Unlike the local relaxation, the segmental relaxation was affected by the addition of crystallinity and orientation into the sample. The results for both the local and segmental relaxation are discussed in the following sections.

3.4.1 The Local Relaxation

As previously mentioned, the local relaxation remained unaltered by the addition of crystallinity or orientation. Figure 3.10 displays the local relaxation of the amorphous, unoriented, 25% extended, 110% extended samples with a plot of the dielectric loss as a function of frequency at 80°C.
Figure 3.10: Isothermal plot of the local relaxation of amorphous, unoriented, and oriented PLA samples at 80°C.

Using the Havriliak-Negami equation, shown in Equation 3.5, the peak breath shape parameter, mean relaxation time, and dielectric strength confirm that crystallinity and orientation does not affect the PLA local motions. Figure 3.11 and Figure 3.12 show the broadening shape parameter and dielectric strength, respectively, as a function of temperature for the local relaxation. Figure 3.13 is a semi-logarithmical plot of the mean relaxation time as a function of inverse temperature.
Figure 3.11: The broadness shape parameter, a, as a function of temperature for the local relaxation.
Figure 3.12: Dielectric strength as a function of temperature for the local relaxation for the amorphous, unoriented, and oriented PLA samples.
The average relaxation time ($\tau_{\text{max}}$) plotted as a function of the inverse temperature follows an Arrhenius form.\textsuperscript{19} When fitted with the Arrhenius equation in Equation 3.8, the activation energy ($E_a$) of the local relaxation can be determined.

$$\tau = \tau_0 e^{\frac{E_a}{RT}} \quad (Equation \ 3.8)$$

The activation energy for all samples was about 10.7 kcal/mol, which compares well with other values reported for PLA.\textsuperscript{6,13}
3.4.2 The Segmental Relaxation

Unlike the local relaxation, the segmental relaxation is effected by crystallinity and orientation. As discussed in the introduction, when a semi-crystalline polymer is drawn, lamellar reorganization occurs and the spherulites are generally believed to break up into smaller crystallites and orient. The amorphous regions begin to order and orient parallel to the stretching direction. Also, tie chains become stretched and elongated. The increase in crystallite surface area and extension of tie chains lead to more confined amorphous regions with inhibited mobility. The increased crystallinity and the addition of confined amorphous regions affect the dynamics of the segmental relaxations by broadening the relaxation and lowering the dielectric strength. Both results can be seen in the isothermal plot in Figure 3.14. The relaxation time of the remaining mobile segments remains unchanged with increasing crystallinity and orientation.
Equation 3.7 was used to calculate the peak breadth shape parameter, mean relaxation time, and dielectric strength.

As shown in Figure 3.14, as expected, the unoriented and oriented crystalline PLA samples have a broader segmental relaxation than the amorphous PLA. Figure 3.15 plots the peak breadth shape parameter as a function of temperature.
Shown in Figure 3.15, the breadth of the relaxation peak is controlled by the addition of crystallinity to the PLA. The additional crystallinity hinders the mobility of the amorphous segments; therefore, creating a broader relaxation. Samples with any crystallinity have breadth parameters that are consistently lower than the breadth parameter of the amorphous sample. A similar result was found by Coburn and Boyd in their study of amorphous and semi-crystalline poly(ethylene terephalate). The addition of orientation leads to a slight decrease in the breadth parameter indicating a broader relaxation for PLA with a higher degree of orientation.
Even though the segmental relaxation is significantly broader, the mean relaxation time and temperature remains unchanged between the amorphous, unoriented semi-crystalline, and oriented semi-crystalline PLA. This is shown in an isochronal plot in Figure 3.16 and in the semi-logarithmic plot of the mean relaxation time as a function of inverse temperature in Figure 3.17.

![Isochronal plot of the amorphous, unoriented, and oriented PLA at 11952 Hz.](image)

Figure 3.16: Isochronal plot of the amorphous, unoriented, and oriented PLA at 11952 Hz.
Figure 3.17: The average relaxation time as a function of the inverse temperature for the segmental relaxation.

Along with indicating a constant mean relaxation time between samples, the semi-logarithmic plot in Figure 3.17 does follow the Vogel-Fulcher-Tammann (VFT) form. Normally, this data would be fit to the VFT equation and the fragility of the polymer could then be determined.\textsuperscript{19} Unfortunately, there were an insufficient number of data points in the segmental relaxation range to reliably fit the VFT equation.

The dielectric strength of the segmental relaxation is shown in Figure 3.18 as a function of temperature.
Figure 3.18: Dielectric strength as a function of temperature for the α relaxation.

As crystallinity and orientation is added to the polymer system, the dielectric strength decreases. The dielectric strength of the unoriented, semi-crystalline PLA decreased by one-third of the strength values of the amorphous polymer. The dielectric strength of the oriented samples decreased by an additional one-third; therefore, decreasing by two-thirds of the amorphous sample’s dielectric strength. The extent of orientation does not have an effect on the resulting dielectric strength.

Because the magnitude of orientation did not affect the dielectric strength, it was concluded that the segmental motion of the polymer system was being constrained in rigid amorphous regions. The rigid amorphous region refers to amorphous segments that are
constrained by the presence of crystalline regions, with correspondingly slowed dynamics. Even though rigid amorphous regions are amorphous, they have restricted mobility until the surrounding crystals are able to relax. The dielectric strength values for both the unoriented and the oriented systems can be compared to that of the amorphous sample to estimate the mobile amorphous fraction, as shown in Equation 3.9. The mobile amorphous fraction is not significantly constrained and is able to relax at the alpha transition temperature.

\[ X_{MAP} = \frac{\Delta \varepsilon_{sample,T}}{\Delta \varepsilon_{amorphous,T}} \quad (Equation \ 3.9) \]

Ideally, if no rigid amorphous phase existed, then the crystalline fraction and the mobile amorphous fraction would make up 100% of the sample. The calculated mobile amorphous fraction is plotted against the crystalline portion in Figure 3.19.
Figure 3.19: The mobile amorphous fraction is plotted against the crystalline fraction proving the existence of a rigid amorphous phase.

Ideally, the fraction of crystalline regions and mobile amorphous regions should equal 1 if those were the only two components present. A linear slope of -1 is not present; therefore, confirming the existence of a third component, the rigid amorphous regions. Similarly, a rigid amorphous region has been determined and discussed in several other studies. ⁶,¹⁴,²⁰,²¹
References


Chapter 4: Conclusion and Future Work

Being environmentally friendly, biodegradable, biocompatible, and easy and versatile to process has made PLA a polymer of interest in a wide range of applications. Some of these applications include medical scaffolds and drug delivery devices, food packaging, and oriented films and fibers.\textsuperscript{1–7} The latter has become a widespread research focus in order to gain an understanding of oriented PLA to better control the degradation rate of PLA, as well as, for use of PLA in barrier applications. Several studies have been performed to investigate the effect of uniaxial and biaxial deformation on the structure and properties of semi-crystalline PLA.\textsuperscript{8–12} Until now, no previous study has used dielectric relaxation spectroscopy to characterize the effects of orientation on the crystalline, mobile amorphous, and rigid amorphous regions, as well as the molecular dynamics of PLA. The current research used dielectric relaxation spectroscopy along with differential scanning calorimetry, wide angle X-ray diffraction, and small angle X-ray scattering to investigate the effects of uniaxial orientation on the structure and dynamics of semi-crystalline PLA.

Oriented samples were prepared by uniaxially stretching PLA and selecting three samples with different degrees of extension. The oriented samples were compared to two control samples: unoriented semi-crystalline PLA and amorphous PLA. DSC was used to determine the glass transition and melting temperature, and to estimate the bulk degree of crystallinity for each sample. The findings demonstrated that orientation did not affect the glass transition or melting temperature. The bulk crystallinity was shown to increase with uniaxial deformation.

WAXD gave insight into how uniaxial deformation affected the crystal structure of PLA and crystalline and amorphous orientation, while SAXS was used to determine long period for unoriented and oriented crystalline PLA. The two-dimensional wide angle X-ray diffraction
patterns indicated that deformation led to amorphous segmental organization in the stretching direction. Additional arcing in the most oriented sample indicated orienting of the crystalline regions. WAXD scattering profiles were also used to estimate the degree of crystallinity and it was demonstrated that the crystallinity increased with orientation. The degree of crystallinity determined from WAXD and DSC displayed the same trend. The degree of crystallinity was consistently higher when determined from WAXD because that value is determined at ambient temperature, as opposed to being determined at the melting temperature where some crystallinity may have already relaxed. Using the Scherrer equation and the FWHM of the crystalline peaks in the WAXD scattering pattern, the crystallite size was found to decrease with increasing deformation. Lastly, SAXS showed that the long spacing of semi-crystalline PLA was unaffected by orientation.

Dielectric relaxation spectroscopy is a useful technique to characterize the molecular dynamics of polymers, yet had never been used in previous literature to study oriented, semi-crystalline PLA. The Havriliak-Negami equation\textsuperscript{13} was modified using the Boyd and Coburn method\textsuperscript{14} and used to fit the segmental and local relaxation of the DRS results of each sample and determine the dielectric strength, mean relaxation time, and the breadth of the relaxation. The results of this study showed that the addition of crystallinity and orientation did not affect the local relaxation; while on the other hand, they did influence the segmental relaxation. The breadth of the segmental relaxation was affected by crystallinity, but not orientation. All crystalline samples had breadth shape parameters that were consistently lower than the amorphous sample indicating that the crystalline regions inhibit the segmental relaxation motion of PLA. Orientation leads to lamellar reorganization and break up of spherulites, which leads to continual broadening of the relaxation with orientation. Finally, the dielectric strength
decreased with the addition of crystallinity and was even lower for the oriented samples. The dielectric strength remained unchanged between samples with differing degrees of orientation.

The oriented PLA samples in this study were derived from a tensile testing dog bone sample that was stretched to a total of 100% extension. The breadth of the relaxation, the mean relaxation time, and the dielectric strength were significantly affected with increasing crystallinity. Orientation continued to inhibit segmental relaxation, as shown in the peak breadth and dielectric strength results for sample with difference magnitudes of orientation. In the future, similar measurements on samples taken from a tensile test dog bone stretched to other total degrees of deformation would extend these results. Also this study would provide insight into the degree to which orientation affects the properties of semi-crystalline PLA. Another interesting study would be to investigate the effect of strain rate on the structure and molecular dynamics through DRS measurements. This would give insight into how the method of orientation would affect the resulting properties of PLA. Lastly, because this study only investigated the effects from uniaxial orientation, the next step naturally would be to investigate the effect of biaxial orientation on the structure and molecular dynamics of PLA.
References


