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Monitoring the molecular weight of poly(lactic acid) during fiber spinning and coloration

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MONITORING THE MOLECULAR WEIGHT OF POLY(LACTIC ACID) DURING
FIBER SPINNING AND COLORATION

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ABSTRACT

One fiber that is being researched as a possible alternative to the petroleum based polyester fibers currently being used is polylactic acid (PLA). Being aware of the low heat resistance and degradation of PLA during processing is a concern for practical production and the performance of the polymer.

Disperse dyed PLA film and solution dyed PLA film, along with un-dyed film and the original PLA pellets have been investigated to determine molecular weight. Infrared analysis has been conducted to examine the compounds found in the PLA samples at different steps in the polymer processing. Un-dyed PLA samples have been subjected to different heat treatments to observe the changes associated with temperature exposure. PLA has also been analyzed after dyeing to view the effects of the coloration method to the PLA structure.

CHAPTER 1 INTRODUCTION

1.1   Research Objectives

The recent increase in petroleum prices and the uncertainty of future supplies has caused many people to be concerned about reducing the dependency of petroleum. More and more consumers are resisting the wide consumption of petroleum based products and seeking alternatives that are more environmentally friendly.

One fiber that is made from petroleum and accounts for 40% of textile fiber use is polyester. The consumption of polyester fibers is second only to cotton (Blackburn, et al. 2006). The production and disposal of polyester fibers has negative impacts on the environment. The reduction of petroleum used in the production of man-made fibers can benefit the environment. By using resources that are renewable and sustainable to produce polyesters, the negative impact on the environment can be reduced.

One fiber that is being researched as a possible alternative to the petroleum based polyester fibers is polylactic acid (PLA). PLA is made from lactic acid, HOOC-CH(CH$_3$)-OH) that is obtained by fermentation of glucose. Glucose is at its turn a product of starch fermentation. The starch is derived from plants such as corn. Polymers produced from PLA can be used to make a wide range of products, e.g., plastic bottles, packaging, apparel, non-wovens, household fabrics, fiberfill and many others.

One of the main advantages of PLA is that it is an alternative to petroleum-based synthetic polymers, such polyesters for textile industry. PLA production uses 30 to 50 percent less fossil fuel than does the production of conventional petroleum based polyesters, such as poly(ethylene terephthalate) (PET) (Verespej, 2000). During the fiber spinning process, there is almost no waste due to almost all wastes being recycled (Perepelkin, 2002).

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Another advantage that PLA has over petroleum-based polyesters is that it biodegrades into nontoxic biomasses. Biobased polymers such as PLA are capable of biodegrading to carbon dioxide and water. Thus the products will totally biodegrade back to these atmospheric components in 20-30 months in soil and in 30-40 days in standard compost (Perepelkin, 2002).

The biodegradability of PLA makes it a good choice to replace single use plastic packaging which is commonly made from PET. PLA packaging can be sent to an industrial compost facility along with food and plant waste. By using PLA to replace disposable plastic containers, the amount of petroleum based plastics in the landfills can be reduced.

In 2002 a joint venture, Nature Works, between Dow and Cargill, developed a lower cost production process of PLA. Using the starch from wheat and corn, these simple sugars are converted to lactic acid using anaerobic bacteria. The lactic acid is converted to the lactide monomer and then ring-opening polymerization produces PLA. (Evans, 2010)

The Federal Trade Commission has designated PLA as a new generic fiber category. To achieve this classification, PLA had to show radically different properties and chemical composition from other fibers (Federal Trade Commission, 2002). This classification will allow other companies to create sustainable textiles from this product.

PLA can perform equally to comparable petroleum-based products in many respects. Moisture regain, wicking and self-extinguishing characteristics of PLA fibers are superior to that of PET, the most commonly used polyester fiber (Gupta & Kumar, 2007). The inherent benefits of PLA fiber that are used for apparel are increased breathability, water vapor absorbency, thermal insulation and overall comfort (Walzer, E. 2001). When blended with cotton or wool, the garments are more comfortable and have a silky feel. PLA also shows self-extinguishing

properties that are desirable (Gupta & Kumar, 2007). PLA lends itself to the sportwear and active garments market due to the higher moisture regain in comparison to PET.

One of the disadvantages of PLA is the low heat resistance. The blending of PLA with other plant based materials, or blending with polypropylene produces a product with greater heat resistance than a pure PLA product (Evans, 2010). Being aware of the heat resistance and degradation of PLA during processing is a concern for practical production and the performance of the polymer.

For PLA fibers to be seen as a suitable replacement for polyester there needs to be successful coloration methods that are practical for production. Because PLA is a hydrophobic fiber, disperse dyes that have a high affinity for other hydrophobic fibers such as PET are expected to have affinity for PLA. An important point to remember, however, is that PET is commonly dyed at 130°C, which is above the melting point of PLA. PLA fibers are generally dyed at 110°C and for shorter periods of time than PET fibers. Excessive heat or extended dyeing time will cause fiber degradation and loss of tensile strength, molecular weight and elongation at break (Choi and Seo, 2006).

Due to the fiber degradation that has been observed, alternative methods to the disperse dying of PLA fibers should be investigated. One possible method is solution dying during the melt spinning of the fibers. The process of melt spinning PLA fibers does not require the use of solvents, produces a more even fiber, and can be accomplished at higher production speeds (Solarski, et al. 2005).

The hypothesis is that there will be increased degradation of the PLA polymer during the disperse dyeing process in comparison to the solution dyed PLA. This will be observed by comparing the variations of the molecular weight of PLA during various heating times and

temperatures, and during the disperse dying and solution dying processes. The variations in molecular weight will be determined by monitoring the glass transition temperature (T_g), activation energy, decomposition temperature, and molecular size ratio.

1.2   Definitions

Table 1-1 Definitions

| Poly(lactic acid) (PLA) |

Lactide   Polylactide

a manufactured fiber in which the fiber-forming substance is composed of at least 85% by weight of lactic acid ester units derived from naturally occurring starches |
|---|---|
| Poly(ethylene terephthalate) (PET) | a manufactured fiber in which the fiber-forming substance is a long chain synthetic polymer composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalate units. |
| Solution dying | pigments or dyes are added to the polymer melt or spinning solution prior to extrusion. |
| Disperse dying | slightly water-soluble dyes are applied from fine aqueous suspensions; widely used for man-made fibers. |
| Melt spinning | the process of melting the polymer and extruding into air, other gas, or into a liquid, where it is cooled and solidified. |
| Polymer | a long chain of repeating monomers. |
| Melting Point (T_m) | the temperature at which the substance changes from a solid to a liquid. |
| Glass Transition Temperature (T_g) | above this temperature, polymers are brittle like glass and below this temperature polymers are either fluid or rubbery depending on the structure. |
| Viscosity | the resistance to flow at the molecular level |
| Differential Scanning Calorimetry (DSC) | the application of heat and the measurement of heat flow during transitions, calculates T_m and T_g. |
| Thermogravimetry Analysis (TGA) | the application of heat and measurement of weight loss due to decomposition. Calculates decomposition temperature and rate of decomposition |
| Modulated Thermogravimetry | a TGA method in which the results are obtained by application of a waving temperature signal |

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Analysis (MTGA)	
Rheology	the science of flow (from Greek rheo = flow)
Size Exclusion Chromatography (SEC)	also known as gel permeation chromatography (GPC), process of when material in solvent is pumped through a porous column and detectors. Larger molecules elute faster while the small molecules are retained in the column due to interactions with the porous column. Ratios of various molecular size are obtained
Fourier Transform Infrared Spectroscopy (FTIR)	a spectroscopic method in the infrared region of light in which the results are analyzed using a Fourier transform of data
Wide Angle X-Ray diffraction (WAXRD)	analysis of materials using the scattering of reflected X-rays under an angle higher than 2°
Activation Energy	The least amount of energy required for a reaction to take place.

CHAPTER 2 LITERATURE REVIEW

2.1 Synthesis of Poly(Lactic Acid)

PLA is most frequently synthesized from the cyclic lactide using ring-opening

polymerization technique. The catalyst that is most widely used is tin(II) bis-2-ethylhexanoic

acid. This is due mainly to its FDA approval and the ability to produce high-molecular weight

polymers with low racemization (Garlotta, 2001).

2.2 PLA Isomers

There are two optically active isomers of the monomer, HOOC-CH*(CH$_3$)-OH, D and

L forms, present as such in PLA. The ratios of each can be controlled during synthesis of the

polymer. PLA with more than 15% D-lactic acid isomer does not crystallize (Ghosh and

Vasanthan, 2006). Lactic acid can be chemically synthesizes or produced by fermentation. The

chemically derived lactic acid produces a 50/50 mixture of the two isomers, D and L. Fermented

lactic acid is composed of 99.5% L and 0.5% D isomers. Polymers with higher D-isomer levels

have more amorphous regions. PLA produced with a blend of D an L isomers has a higher

melting point than PLA produced from D or L alone. A very small concentration of the D-

isomer is needed to aid in production processing (Blackburn et. al, 2006).

2.2.1 Effect of Isomer Levels on Dyeing Conditions

In a study conducted by Blackburn et. al., the dyeability of commercial PLA fabrics of

two different levels of D-isomer levels were examined. It was found that fabrics with higher d-

isomer concentrations have a lower melting temperature. This can influence the temperature at

which the fabrics can be safely dyed. Fabrics with a higher level of D-isomers have a higher rate

of dye exhaustion. This is because dyes only diffuse into the amorphous regions of the fiber.

This is expected, as the fiber with higher d-isomers content have lower crystallinity and more

amorphous regions. Fibers with higher d-isomer content also have higher color strength when compared to the fibers with low d-isomer content (Blackburn et. al, 2006).

There is little difference in the washfastness and staining on adjacent polyester between fibers with high and low d-isomer concentrations (Blackburn et. Al, 2006).

2.3 Spinning Conditions

There are many different methods to produce PLA fibers, each with different equipment used and different outcomes. Solution spinning of PLA uses solvents such as chloroform and toluene and has slow production speed.

2.3.1 Melt Spinning

Melt spinning of PLA fibers does not require the use of solvents and a more even fiber is produced and at higher production speeds. In this method of spinning, PLA is melt-extruded through a die and is collected on a winder at speeds up to 5000m/min. Spin drawing is another method that does not require the use of solvents. The PLA is melt-extruded through a die and then the filaments are drawn between two hot rollers and collected on a winder (Solarski et. al, 2005).

2.3.2 Dry-Jet-Wet Spinning

Degradation of fibers during spinning is a concern for many of the methods. Severe degradation is due to the heat exerted on the polymer during many of the spinning methods. A way to control the degradation and maintain fiber strength was studied by Gupta et al. In this study, the PLA fibers were formed by a dry-jet-wet spinning process. In this method, the PLA was dried at 110°C for 24h and then dissolved in chloroform and extruded through a 0.5mm spinneret. The fibers coagulated in a methanol bath and collected on take-up rollers at a speed of 10m/min at a temperature of 90°C and heat set at 120°C. This method of spinning showed less

fiber degradation than melt spinning (Gupta et. al, 2006).

It has been shown that tensile strength and other mechanical properties of PLA fibers are dependent on draw ratio and drawing temperature during melt spinning. The solvent composition and molecular weight of PLA are also important to these properties during solution spinning. Fibers spun from highly volatile solvents have higher tensile strength and a faster degradation rate (Gupta et. Al, 2006).

The take-up speed of the rollers the fiber is collected on, drawing ratio and temperature, and the heat-setting temperature can influence the physical structure of the PLA fibers. The crystallinity of the fibers was observed to increase as the take-up speed increased. A maximum crystallinity of 28% was achieved at a take-up speed of 12m/min. Also, as take-up speed increased, the maximum draw ratio decrease. This may be because as the take-up speed increases, the wet stretch increases and improves the molecular chain orientation of the fibers (Gupta et. al, 2006).

2.4 Coloration

For PLA fibers to be seen as a replacement for polyester, it needs to have successful coloration methods that are practical. Since PLA is a hydrophobic fiber, disperse dyes that have a high affinity for other hydrophobic fibers such as PET are expected to have affinity for PLA. An important point to remember is that PET is commonly dyed at 130°C, which is above the melting point of PLA. PLA is generally dyed at 110°C and for shorter lengths of time. Excessive heat or extending the dyeing time will cause degradation and loss of tensile strength, molecular weight and elongation at break (Choi and Seo, 2006). It is because of the this loss of tensile strength that is it important to have a de method that will provide "right first time" dyeing and reduce the need for additional processing and dyeing.

The PH of the dye bath has impact on the strength and degradation of the PLA fiber. A pH of 5-6 has the least amount of effect on the reduction of the elongation at break of PLA fibers. Increased alkalinity has a greater reduction of fiber strength than increased acidity. Controlling the dye bath PH closely can have impact on color consistency also. Higher pH dye baths have better dye uptake, yet the fiber has a reduction in strength (Yang and Huda, 2003).

It has been found that PLA has poorer wash and crock fastness than PET with the same dyes and concentrations. For most dyes, wash fastness is 0.5-1.0 class lower rating for PLA than for PET on the AATCC standard grayscale rating system. In this study there was no significant difference between the photostability for six of the eight dyes examined (Choi and Seo, 2006). The crockfastness rating of PLA is 0.5-1.0 class lower than PET for five of the ten dyes studied when using the AATCC standard grayscale rating system (Yang and Huda, 2003).
In a study conducted by Choi and Seo, the dyeability of PLA is investigated using various commercial disperse dyes. Two fabrics of 100% PLA and 100% PET were dyed with 20 different disperse dyes at the appropriate dyeing temperature and length of time for each fabric. Dye exhaustion yields, wash and light fastness, and colormetric measurements were taken. A wide range of exhaustion rates on the PLA fabrics were found. A quarter of the dyes had exhaustion of less than 30% and just under half exhausted at 70% or higher (Choi and Seo, 2006).

Of the 20 dyes tested, the eight that exhausted well (over 70%) on PLA were applied to PET with an adjusted application level so that a similar depth of shade would be obtained. It was found that most of the dyes on PLA where lighter and brighter than the dyeing on PET. Because of a lower refraction index for PLA, less light is reflected back and shades will appear deeper than on PET. Except for one blue dye, yellow and blue dyes were greener on PLA than

on PET, and orange and red dyes were yellower (Choi and Seo, 2006).

The exhaustion rates were also examined for these eight dyes. When the dyeing rates were examined at different points of the process it was found that there was almost no dye uptake below 80°C for both fibers. There was a sharp increase in dye absorption around 90-100°C for PLA and around 110-120°C for PET. This is consistent with the higher glass transition temperature of PET (Choi and Seo, 2006).

In general, PLA has a lower dye affinity than PET to disperse dyes. In a study by Yang and Huda, only two out of ten dyes reviewed had exhaustion levels above 80% on PLA, while all ten dyes had exhaustion levels above 90% on PET. Although PLA has a lower dye uptake in comparison to PET, the depth of shade of the same dye is similar due to the lower reflectance and reflectivity of PLA.

CHAPTER 3 METHODS

3.1 Introduction

Excessive heat or extending the dyeing time will cause degradation and loss of tensile strength, molecular weight and elongation at break (Choi and Seo, 2006). Besides external fiber structural damage, the molecular chains that compose the fiber are damaged and this causes the loss of molecular weight (M_w).

During disperse dying, PLA fibers are exposed to moisture and heat that cause damage to the molecular chain, hence causing a loss of M_w. An alternative to disperse dying is solution dying. During solution dying, the fibers are not exposed to additional heat and moisture during the dying process. Disperse dyed PLA film and solution dyed PLA film, along with un-dyed film and the original PLA pellets have been investigated to determine M_w.

IR Analysis has been conducted to examine the compounds found in the PLA sample during different points in the processing. Un-dyed PLA samples have been exposed to different heat ranges to observe the changes associated with temperature exposure. PLA has also been analyzed after dyeing to view the effects of applying dye compound to the PLA structure.

3.2 Materials

There have been 13 variations of PLA analyzed in this study:

(1) PLA-A pellets

(2)- (3) PLA pellets obtained from chemical supply company

(4) PLA pellets after DSC

(5) PLA powder

(6) PLA and tributyl citrate (TBC) mixture

(7) PLA and propyl galate (PG) mixture

(8) Un-dyed PLA film-A

(9) Un-dyed PLA film-B

(10) Atlantic Chemical Corporation Scarlet BA Disperse Dye, batch #30799

(11) Solution dyed PLA film

(12) Disperse dyed PLA film

(13) PLA pellets heated in oven

(14) Lactide

3.2.1 PLA Pellets

PLA-A pellets have been obtained from an unknown industrial source.

3.2.2 PLA Pellets from Chemical Supply Company

Two types of PLA pellets have been purchased from a chemical supply company:

(1) PLA-F: poly(L-lactide) viscosity 0.90-1.20

(2) PLA-G: poly(DL-lactide) viscosity 0.55-0.75

3.2.3 PLA Pellets after DSC

PLA-A pellets have been be heated at a rate of 10° C/min from 40^oC to 200^oC in air. Sample size is less than 10 mg. DSC was conducted using the TA Instruments Modulate DSC 2920. Pellets were retained for use in GPC analysis.

3.2.4 PLA powder precipitated from chloroform solution

10g of PLA-A pellets were added to 400 ml of chloroform ($CHCl_3$). The solution was stirred with a stir bar and stir plate for 24 hours. 2 L of methanol (CH_3OH) was slowly added to solution. The solution was filtered though filter paper and the PLA powder was collected.

3.2.5 PLA and tributyl citrate (TBC) mixture

PLA, TBC and chloroform were combined in a Burrel wrist action shaker. The solution then was placed in a shallow container and the chloroform was allowed to evaporate. This created a 99.37% PLA mixture.

3.2.6 PLA and Propyl Galate (PG) Mixture

PLA, PG (a thermal stabilizer), and chloroform were combined in a Burrel wrist action shaker. The solution then was placed in a shallow container and the chloroform was allowed to evaporate. This created a 98.91% PLA mixture.

3.2.7 Un-dyed Film

A PLA film was created by dissolving PLA-A pellets in chloroform and placed in a Burrel wrist action shaker. The solution was then placed in a shallow Teflon dish and the chloroform was allowed to evaporate to create a film (PLA film-A). A second PLA solution was created using the same method and placed in a shallow glass dish and the chloroform was allowed to evaporate to create a film (PLA film-B).

3.2.8 Disperse Dyed Film

PLA film was dispersed dyed using the Atlantic Chemical Corporation Scarlet BA Disperse Dye, batch #30799. The film was dyed with a liquor to goods ratio of 10:1. It was heated at $110\,^{o}C$. for 30 minutes. The film was then rinsed with $65\pm5\,^{o}C$ for 30 minutes. The disperse dyed PLA film was then allowed to air dry.

3.2.9 Solution Dyed Film

0.1165g of PLA-A pellets were combined with 0.0015g of Atlantic Chemical Corporation Scarlet BA Disperse Dye, batch #30799 in chloroform. The solution was placed in a Burrel wrist action shaker. The solution was then placed in a shallow glass dish and the chloroform was allowed to evaporate to create a film.

3.2.10 PLA Pellets Heated in Oven

PLA-A pellets heated in glass vial at $175\pm 5\,^{o/}$C.

3.2.11 Lactide

Lactide was obtained from the Aldrich Chemical Supply company.

3.3 Methods of Analysis

3.3.1 Thermogravimetric Analysis (TGA)

In the present study the samples (10-20mg) were heated at a rate of 5°C/min to 600°C in air.

TGA investigations were conducted using the TA Instruments Hi-Resolution TGA-2950.

3.3.2 Modulated Thermogravimetry Analysis (MTGA)

The MTGA analysis is similar to TGA. The following MTGA program has been used operating

a TA Instruments Hi-Resolution TGA-2950 thermobalance:

1. High Resolution Sensitivity 1

2. Modulate +/-5ºC every 200 sec

3. Select gas (Air or N2)

4. Ramp 2.00ºC/min Res 4 to 600ºC

3.3.3 Differential Scanning Calorimetry (DSC).

The PLA film sample for DSC investigations was heated at a rate of 10° C/min to 200°C

and then held at a constant 200°C for 2 minutes. Sample size was 0.0064g and analysis was

performed in air.

The PLA film-A sample was obtained after the heating and FTIR analysis. The sample

was heated at a rate of 10° C/min to 200°C and then held at a constant 200°C for 2 minutes.

Sample size was 0.0201g and analysis was performed in air.

The PLA film-B sample was obtained after the heating and FTIR analysis. The sample was heated at a rate of 10° C/min to 200^oC and then held at a constant 200^oC for 2 minutes. Sample size was 0.000392g and analysis was performed in air.

The solution dyed film sample was heated at a rate of 10° C/min to 200^oC and then held at a constant 200^oC for 2 minutes. Sample size was 0.0064g and analysis was performed in air.

The PLA and TBC mixture sample was heated at a rate of 10° C/min to 200^oC and then held at a constant 200^oC for 2 minutes. Sample size was 0.0189g and analysis was performed in air.

The PLA and PG mixture sample was heated at a rate of 2° C/min to 200^oC and then held at a constant 200^oC for 2 minutes. Sample size was 0.0313g and analysis was performed in air.

DSC was conducted using the TA Instruments Modulate DSC 2920.

3.3.4 Dynamic Shear Rheology (DSR)

In Figure 3.2 are presented two of the most utilized rheological geometries for analysis of polymer solutions and composites.
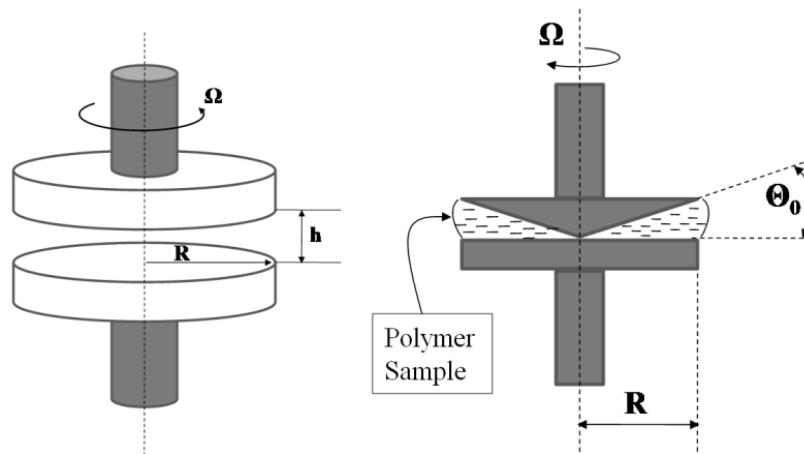

Figure 3.1 Schematic representation of the parallel-disk (left) and cone-and-plate (right) geometries. The parameters are: h is the distance between the plates, Ω is the constant angular velocity of the plate or cone in rotation, θ is the angular displacement, R is the radius of the plate and/or cone

Since the viscosity of molten polymers is rather high, the cone-and-plate geometry was preferred in the present investigations. The PLA-A sample was melted at 180ºC for 30 minutes and analyzed using a TA 1000 Rheometer (Thermal Analysis Instruments, USA). Figure 3-1 represents the set up of the Rheometer during this analysis. The angular displacement was 2 degree and the plate diameter was 4 cm.

3.3.5 Size Exclusion Chromatography (SEC)

The general scheme for a SEC experiment is presented in Figure 3.2. Because the separation is based on the exclusion of molecular species of the polymer according to their macromolecular size while permeating the gel with which the SEC columns are filled, the technique is usually called Gel Permeation Chromatography (GPC).In the present work, the PLA-A, PLA-F, PLA-G, and PLA powder samples were dissolved in chloroform ($CHCl_3$) to make a 0.25% solution. Three Phenogel 300 x 7.8 mm columns (Phenomenex, Torrance, CA), connected in series as follows, i.e., (1) 5µ, 500Å (1K-15K); (2) 5µ, 10-4Å (5K- 500K); 10µ, MXM (100-10,000K), as well as with a guard column (5 µ, 50x7.8mm), were used for separation. The GPC instrumentation consisted of an Agilent 1100 pump (Agilent Technologies, Palo Alto, CA), and an Agilent 1100 auto-sampler. Three detectors connected in series were used for detection: A Wyatt Heleos Multi Angle Light Scattering (MALS) detector equipped with a QUELS (DLS) detector (Wyatt Technology Corp., Santa Barbara, CA), a Wyatt ViscoStar viscosity detector, and a Wyatt rEX Differential Refractive Index detector. All separations were done using an injection volume of 100µL. Chloroform (1mL/minute) was used as the solvent. Data acquisition and the molar masses (Mw), sizes (radius of gyration (Rg) and hydrodynamic radius (Rh), and intrinsic viscosity calculations were performed using the Astra V software (Wyatt). The MW for

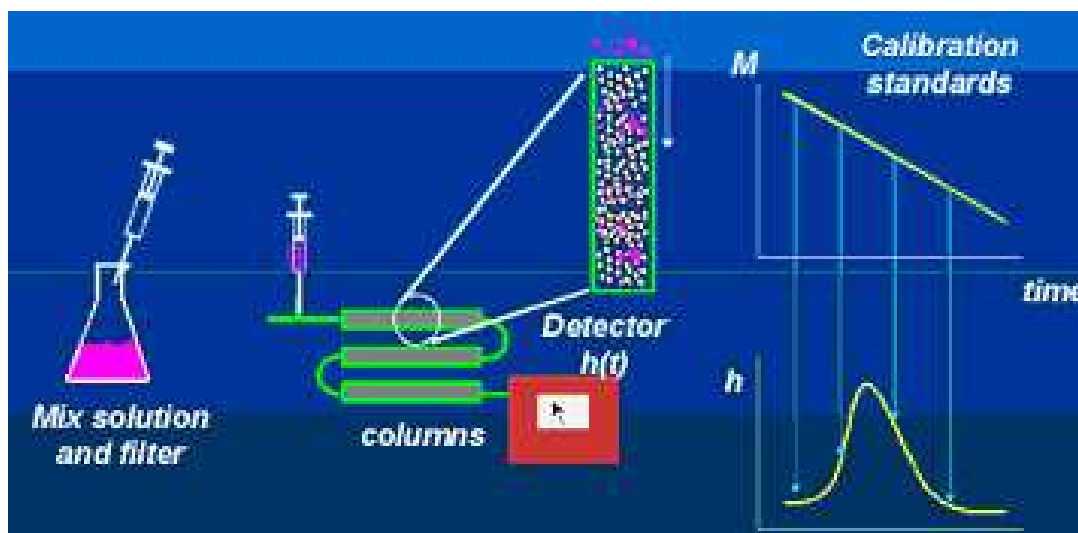PLA samples was determined using the dn/dc value of 0.0237 ml/g reported earlier (Malmgren et al., 2006)

Figure 3-2 General Scheme for a SEC Experiment

3.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

A *Fourier Transform Infrared (FTIR)* spectrometer uses the technique of Michelson interferometry. A beam of radiation from the source, S, is focused on a beam splitter constructed such that half the beam is reflected to a fixed mirror. The other half of the beam is transmitted to a moving mirror which reflects the beam back to the beam splitter from where it travels, recombined with the original half beam, to the detector, D. The recombined beam passes through the sample before hitting the detector. The sample absorbs all the different wavelengths characteristic of its spectrum, and this subtracts specific wavelengths from the interferogram. The detector now reports variation in energy versus time for all wavelengths simultaneously. Energy versus time is an odd way to record a spectrum. Because *time* and *frequency* are reciprocals, a mathematical Fourier transform function allows the conversion of an intensity-vs.-time spectrum into an intensity-vs.-frequency spectrum. The IR intensity variation with optical

path difference (interferogram) is the Fourier transform of the (broadband) incident radiation. A laser beam is superimposed to provide a reference for the instrument operation. The IR absorption spectrum can be obtained by measuring an interferogram with and without a sample in the beam and transforming the interferograms into spectra.

Most spectra using electromagnetic radiation are presented with wavelength as the X-axis. Originally, IR spectra were presented in units of micrometers. However, a linear axis in micrometers compresses the region of the spectrum (10-15 μm) that usually has the largest number of peaks. Therefore, a different measure, the wave number (ν), was derived as follows: ν (cm^{-1}) = 10,000/λ (μm). On the wave number scale (4000-400 cm^{-1}) the vibration of carbon dioxide, O=C=O, mentioned before is seen as a band at 2400 cm^{-1}. The C-H from C single bonds appears at around 2800-3000 cm^{-1} and the carbonyl C=O double bonds, of particular interest for the analysis of polyesters, such as PLA, appear in the region of 1650-1800 cm^{-1}, with specific bands for esters at1740-1750 cm^{-1}.Samples can be analyzed as very thin PLA films or as pellets made from PLA powder and potassium bromide (KBr), a compound transparent in the IR region of interest.

In the present investigations PLA film-A was combined with potassium bromide (KBR) to create a 2% PLA mixture. The mixture was place in a shaker to blend. Mixture was then placed in a die and pressed to create a transparent sample. FTIR analysis of transmittance and absorbance was performed using 100 scans and a resolution of 2 on a ThermoNicolet 300 Fourier Transform Infrared spectrophotometer.

PLA film-B was combined with KBR to create a 2% PLA mixture. The mixture was place in a shaker to blend. Mixture was then placed in a die and pressed to create a transparent

sample. FTIR analysis of transmittance and absorbance was performed using 100 scans and a resolution of 2 on a spectrophotometer.

Both un-dyed film samples were then placed in an oven heated at 117 $\pm$5 ºC for 2 hours and then allowed to cool. FTIR analysis of transmittance and absorbance was completed on both samples using 100 scans and a resolution of 2 on a spectrophotometer.

The disperse dyed PLA film was combined with KBR to create a 2% PLA mixture. The mixture was placed in a shaker to blend. Mixture was then placed in a die and pressed to create a transparent sample. FTIR analysis of transmittance and absorbance was performed using 100 scans and a resolution of 2 on a spectrophotometer.

Both un-dyed film samples were then place in an oven heated at 165 $\pm$5 ºC for 30 minutes and then allowed to cool. FTIR analysis of transmittance and absorbance was completed on both samples using 100 scans and a resolution of 2 on a spectrophotometer.

3.3.7 Wide Angle X-Ray diffraction (WAXRD)

The PLA powder was examined using the back packing method. The X-ray diffraction measurements were made using a Siemens-Bruker D5000 X-ray diffractometer with a Cu K_{α} radiation of 1.54 Å. Diffraction patterns were collected from $2\theta = 2$ to 35° with steps of 0.02^{o} and a scan time of 2s per step.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 WAXRD of PLA Powder

X-ray diffraction is a powerful non-destructive technique capable of providing information on the averaged volume characteristics of a crystalline sample. It is used predominantly in crystallography and it involves projecting an X-ray beam against a crystalline structure and analyzing the pattern produced by the diffraction of rays through the closely spaced grate of atoms. The diffractometer consists of three basic elements, an X-ray tube, a sample holder, and an X-ray detector. The X-radiation is produced in the X-ray tube through the emission of electrons from a tungsten cathode. Following emission, electrons are accelerated in vacuum and forced to collide with the metal anode, also called target. The detector records and processes this X-ray signal and converts the signal to a count rate which is afterwards output to a computer monitor. One type of resultant X-radiation is known as the "white or continuous radiation", and is characterized by a broad, continuous spectrum of wavelengths. On the other hand, the "characteristic radiation" is a set of X-rays described by very sharp peaks of discrete wavelengths that are characteristic to the analyzed crystal.

Because X-rays belong to the electromagnetic spectrum, they exhibit the characteristics of both waves and particles. This means that when X-ray beam strikes an atom the beam's energy will be partly diffracted and partly adsorbed. Although the X-rays were discovered in 1895 by the German physicist W. Roentgen, it was the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg, in 1913, who explained why the X-ray beams were reflected at angles of certain degrees of incidence by the faces of the crystals, when irradiated. The explanation provided by the two Bragg physicists resulted in a law, widely accepted today as

the Bragg's law of diffraction, which states that when the X-rays strike an atom they force the electronic cloud to travel and re-radiate waves with essentially the same frequency. The equation describing Bragg's law is $n\lambda = 2d\ sin\theta$, where λ is the wavelength of the incident X-ray beam, θ is the angle of incidence, n represents an integer, and d is the distance between atomic layers in the analyzed crystal. When several waves superimpose as a result of diffraction, a new wave is created, which depends on the frequency, amplitude and relative phase of the initial waves. The interference of waves can be constructive, when the two rays are in phase, or destructive when the two waves are out of phase.
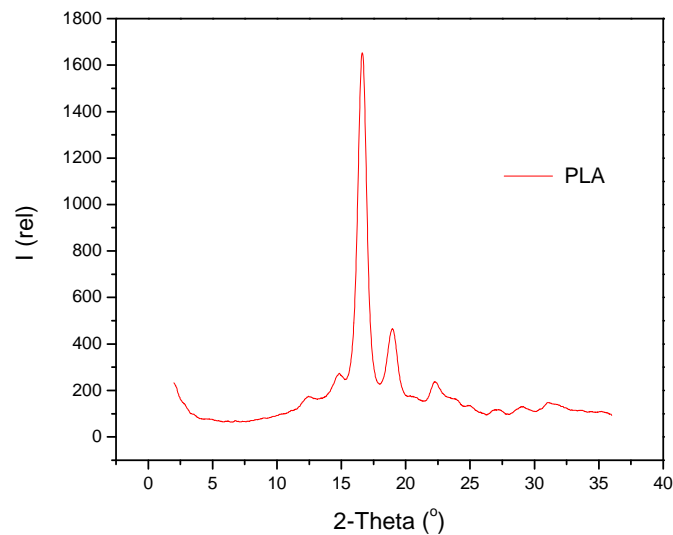

Figure 4-1 Wide Angle X-Ray Diffraction of PLA Powder

The main 2-Theta peak at approximately 17^0 (Figure 4-2) matches the main peak of other X-ray diffraction patterns of published PLA samples. Smaller peaks are seen at approximately 15°, 19°, and 22° also match that of published WAXRD results (Figure 4-2). This is indicative of the crystallinity of the PLA material used in this study matching that of other PLA samples used in research and testing.
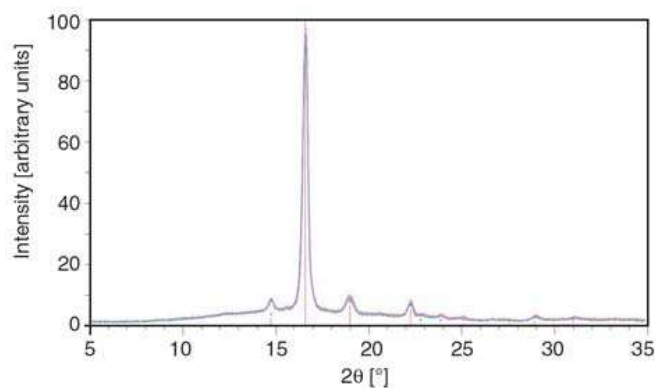
Figure 4-2 WAXRD of PLA annealed at 120C for 10-60 Minutes (Tabi et. al, 2010)

4.2 MTGA of PLA

Thermogravimetry (TGA or TG) is an experimental procedure in which changes in weight of a specimen are recorded as the specimen is heated either in air, or in a controlled atmosphere such as nitrogen, under a rigorously controlled temperature program. In short, a sample of the material of interest is placed into an aluminum, platinum or alumina basket that is supported on, or suspended from an analytical balance located outside of a furnace chamber. Prior to the measurement the balance is tarred, and the sample basket is heated according to the predetermined thermal cycle. When the sample undergoes thermal degradation, volatile components are lost during the TGA experiment and the mass loss can be observed and recorded. Additionally, materials can lose weight from a simple physical process such as drying. The balance sends the weight signal to the computer for storage, along with the sample temperature and the elapsed time. The TGA curve plots the TGA signal, converted to percent weight change on the Y-axis against the reference material temperature on the X-axis.

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The weight loss process emerges as a step in the TGA curve. Although most of the sample's mass is lost around one specific temperature the shape of the curve appears sigmoid, because some reactions start before and/or end after the main reaction temperature. Additionally, because a reaction in the solid state is relatively slow compared to gas or solution reactions, a thermogravimetric trace of such a transformation may be seen to occupy a wide span of temperature. Although other factors may be involved in some cases, the rate of reaction is often controlled by the rate of heat transfer to or from the reaction interface. Since the reaction evolves in time and the temperature always increases with respect to time, graphical representations show the reaction covering a spread of temperature. Because of this spread of reaction over time a careful definition of decomposition temperature must be formulated before comparing results. An alternate and very useful way to represent thermogravimetric results is to plot the temperature-derivative curve of the original data as a function of temperature (time-derivative curves are also possible). The resultant derivative thermogravimetry (DTGA) plot provides critical information about overlapping reactions or about slow reactions concurrent with fast reactions that may take place during the heating cycle. Typical TG experiments are performed raising the temperature at a constant rate. Such experiments are known as non-isothermal or scanning.

The modulated MTGA technique, which was developed by TA Instruments (MTGA^{TM}), superimposes a sinusoidal temperature modulation on the traditional underlying heating profile. This sinusoidal temperature program produces a change in the rate of weight loss. The use of discrete Fourier transformation allows kinetic parameters (activation energy, Ea) to be calculated on a continuous basis.
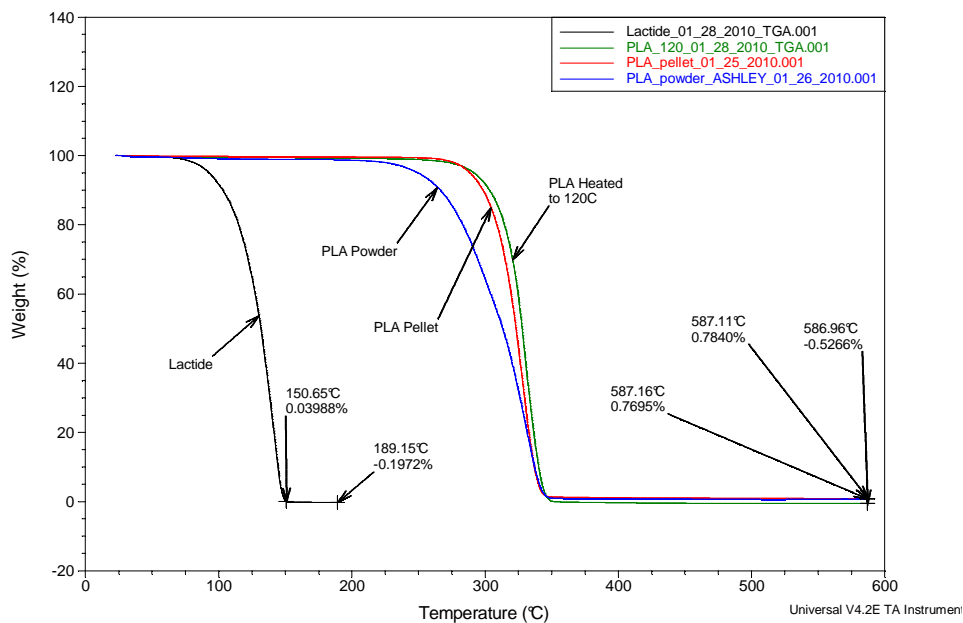
4.2.1 MTGA of PLA in Various Forms

Figure 4-3 Thermal degradation of Lactide and PLA Samples: Weight Loss

The lactide decomposed at a much lower temperature right after melting (92°C) when the

cycle breaks leading to two volatile monomer unit fragments. This shows that the lactide

structure is less stable when exposed to heat than that of the PLA structure.

Table 4-1 MTGA parameters of PLA

Sample	Setting Temp ($^{\circ}$C)	Ea (KJ/mol)	Temp at Max Dec Rate ($^{\circ}$C)	Weight at Max Dec Rate (%)	Dec Rate (%/$^{\circ}$C)	Dec Rate (%/min)
Lactide	117	84	141	22.39	3.24	5.55
PLA Pellet	307	145	328	36.18	3.13	5.06
PLA Powder	288	140	331	21.70	1.87	3.32
PLA heated to 120°C	314	153	330	42.18	3.54	5.43

The PLA backbone breaks also after melting (170°C) in smaller and smaller fragments which became volatile after 200 - 250°C, depending on the polymer aggregation (powder or pellet). The order of thermal stability follows the magnitude of the surface area of samples, i.e., the higher the surface, the lower the thermal stability. The surface area is increased in powder form and decreased in the bulk sample obtained by melting of pellets (Figure 4-3 and Table 4-1).
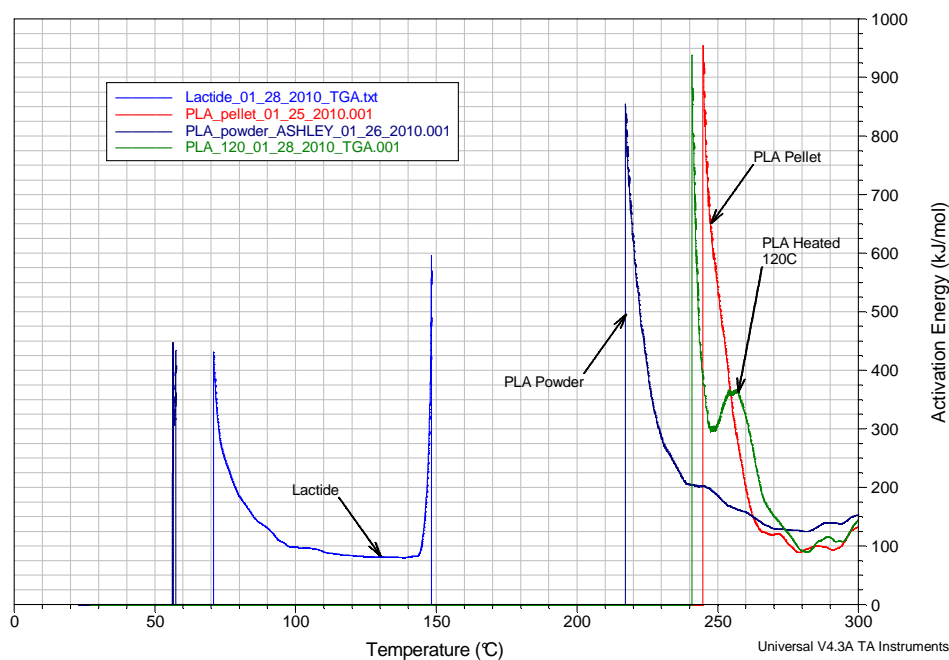

Figure 4-4 Thermal Degradation of Lactide and PLA Samples: Activation Energy

The setting temperature for thermal decomposition and the activation energy (Ea) are much lower for the cyclic lactide (two monomer tensioned ring) as compared to that of multiple PLA monomer unit species. For the high molecular weight polymer, they are again dependent on the aggregation state, both being lower for the PLA powder sample. While the temperature at which the polymers decomposed with the higher rate are similar, the weight loss of the powder sample at this temperature was higher (-79.30%) than that of the pellet or of the PLA heated samples (-63.92% and -57.82%, respectively) and consequently the decomposition rate diminished accordingly (Table 4-1). The PLA sample that was evaluated after heating to 120°C

has a higher Ea at 153KJ/mol and a higher setting temperature at 314°C. The rate of

decomposition though is at a faster rate than the other forms of PLA. This means that the fiber

that is processed from the heated PLA sample would begin decomposing at a higher temperature,

but once it begins decomposition, it will decompose at a faster rate.

The activation energy needed for the lactide is considerably lower than the other PLA

samples. This is due to the more volatile nature of the molecular structure present (Figure 4-4).

Decomposition begins at an earlier temperature and requires lower activation energy (Ea) to

begin the decomposition.

4.2.2 MTGA of PLA Films

Table 4-2 MTGA parameters of PLA Films

Sample	Setting Temp (^{o}C)	Ea (KJ/mol)	Temp at Max Dec Rate (^{o}C)	Weight at Max Dec Rate (%)	Dec Rate (%/^{o}C)	Dec Rate (%/min)
PLA Pellet	307	145	328	36.18	3.13	5.06
Un-dyed Film	307	133	330	31.51		4.55
Solution Dyed Film			322	31.99	2.03	
Disperse Dyed Film	311	149	329	35.27	3.35	5.20

The un-dyed and solution dyed film samples have weight loss beginning around 60°C due

to excess chloroform still retained in the sample from the creation of the film. The boiling point

of chloroform is 61.2^{o}C. Once the chloroform is removed from the samples, the weight loss

levels off until it reaches 200°C. The chloroform has already been removed from the disperse

dyed film during the heat applied during the dyeing processing. The disperse dyed film retains

thermal stability similar to that of the original PLA pellets. (Figure 4-5 and Table 4-2)   The

decomposition rate 3.35%/^{o}C of disperse dyed film is higher than that of the solution dyed film rate of 2.03%/^{o}C, which indicates that the solution dyed film has a more stable structure and is less susceptible to decomposition during heat processing.

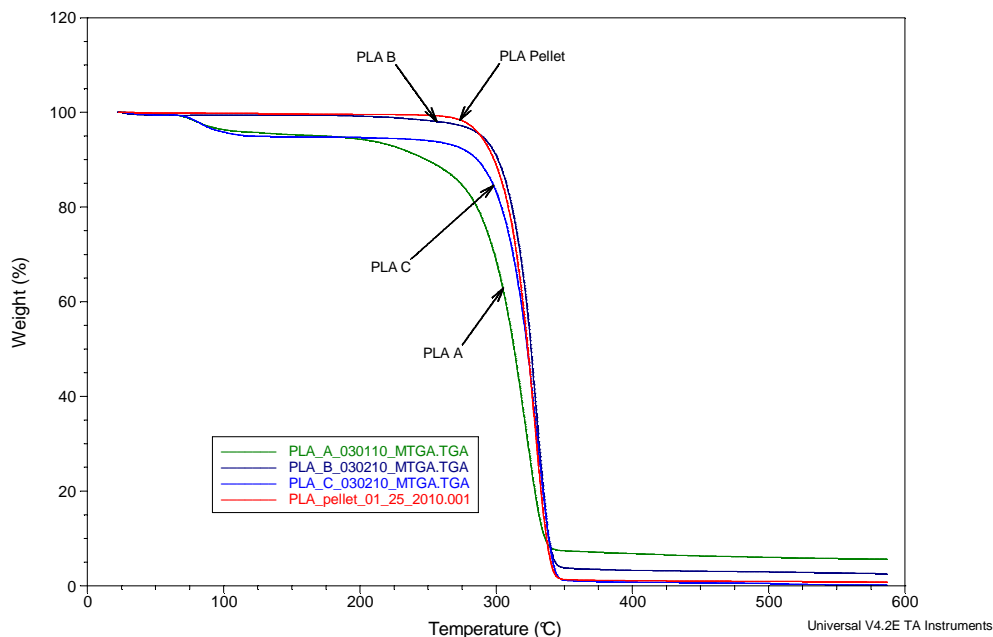Figure 4-5 Comparisons of PLA Films: Weight Loss

4.3 DSC of PLA

Differential Scanning Calorimetry (DSC) is one of the most extensively utilized thermal analysis techniques, in which the difference in the amount of heat needed to elevate the temperature of a sample and reference are measured as a function of temperature. Duplicate matching sensors are employed for measuring the thermal changes of the sample and a reference, with the sample and reference being maintained at nearly the same temperature throughout the entire experiment. The important characteristic of this technique is highlighted by the word "differential" as the concept behind each measurement is to obtain information on the thermal changes in the sample by heating or cooling it next to the inert reference. Due to this differential attribute the resultant signal corresponds exclusively to the thermal variation to be studied, as any potentially unwanted

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thermal effects impact both sensors in the same way. The sample and reference pans are enclosed in the DSC cell, which incorporates also the temperature sensors and the heating devices. A computer is employed to control the parameters of the system, capture the data and analyze it. A very important thermal characteristic of polymers is the melting temperature, Tm. The Tm of a polymer is the temperature at which the macromolecular chains forming the crystalline domains lose their periodicity and order. The size of crystallites, as well as the presence or absence of defects in the crystallite, influences considerably the range of temperatures that typically accompany the melting of a polymer. This range of temperatures is a useful indication on the sample crystallinity. In theory, polymers that are 100% crystalline should show only a Tm transition, while polymers that are 100% amorphous should exhibit only a glass transition Tg transition. In reality, however, 100% crystalline polymers are never possible due to crystallization defects and varying sizes of the crystallites. As a result of such defects, polymers are most of the times semi crystalline and contain crystalline and amorphous domains, thus exhibiting both Tm and Tg. PLA is a semi crystalline polymer. Around Tm the segmental motion of chains is elevated and does not permit the formation of stable nuclei. However, if the temperature is decreased below Tm the translational, rotational, and vibrational energies and the diffusion rate of the polymeric chains decrease, allowing for the formation of crystallization nuclei. The temperature of crystallization is also commonly referred to as freezing temperature T_f. Since crystallization is a complex development that involves formation of crystallites and the expansion of crystalline areas, the freezing temperature is also an interval of temperatures, much like Tm. A very common way to determine the relative crystallinity of polymers is to perform DSC measurements. The enthalpy variation ΔH resulted from the DSC measurements is directly proportional to the amount of crystalline polymer in the sample. When various samples are

considered the ΔH values are typically used to compare their crystallinity with respect to each

other. For comparison purposes, the lowest point in the DSC dip is generally regarded as the *Tm*

of the sample.

Finally, another important thermal characteristic of polymers is the decomposition temperature,

T_d. Thermal decomposition of a chemical, also known as thermolysis, is an endothermic process

in which the chemical is divided into at least two other new chemicals upon heating. Polymers

will typically break up into more than just two chemicals because the macromolecular chains are

long and they can be fragmented at any segmental bond in the chain. This is the case of PLA

which is thermally unstable and decomposes in monomer units which immediately form the

lactide, viz., the more stable six-member ring dimer. For this reason, while small molecules have

a rather well defined T_d, in the case of polymers T_d is in fact a broad range of temperatures. For

practical purposes, the Td of a polymer is generally obtained through thermogravimetric (TGA)

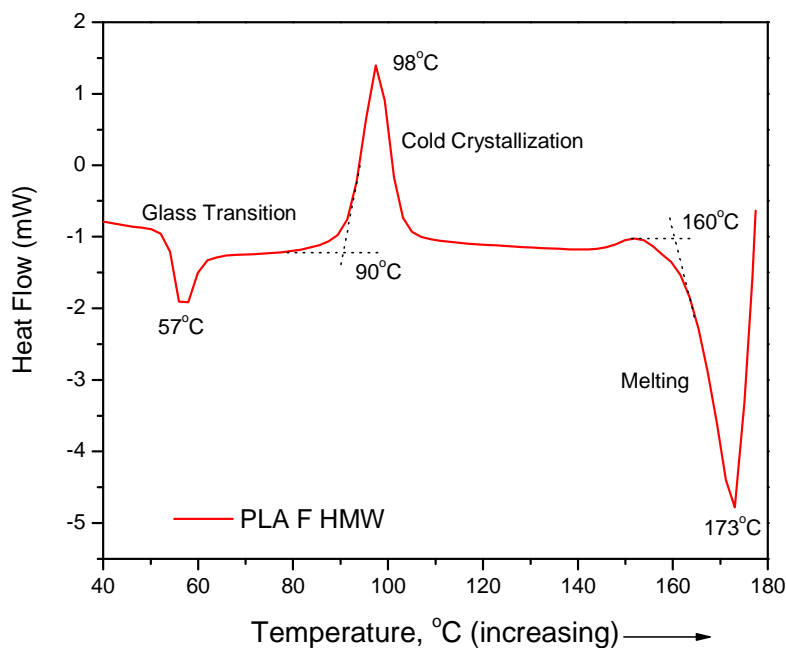measurements, like the one presented in this chapter.

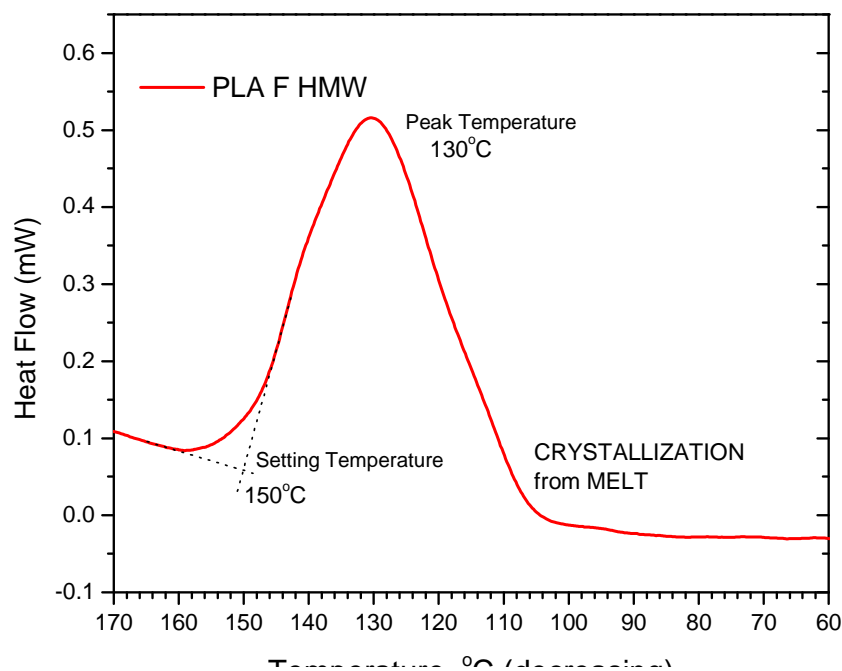Figure 4-6 Melting of PLA with a rate of 20°C/min

Figure 4-7 Crystallization of PLA from the melt with a cooling rate of 1°C/min

The sample was amorphous and crystallized during heating, and cold crystallization occurred above the glass transition of 57°C (Figure 4-6). Higher heating rates precluded crystallization and the polymer crystallized only after being heated above the glass transition temperature, $T_g = 57°C$ (Figure 4-6). Slow cooling rates (1°C/min) allowed crystallization from melt (Figure 4-7). Crystallization peaked at 130°C for the PLA sample that had previously been melted.

4.3.2 DSC of PLA at Various Heating Rates

The thermal characterizations of PLA pellets were observed using DSC under a series of heating rates. Multiple heating rates were used in order to mimic the time of extrusion from melting of polymer to fiber spinning. During the faster heating rates, the two peaks are present in one larger peak. At the heating rate of 5°C per minute, the two peaks become visible. During

the slower heating rates, the two peaks are clearly separated (Figure 4-5). The cause of the two peaks may be two different types of crystals present in the PLA, or that a second form was produced during the heating.
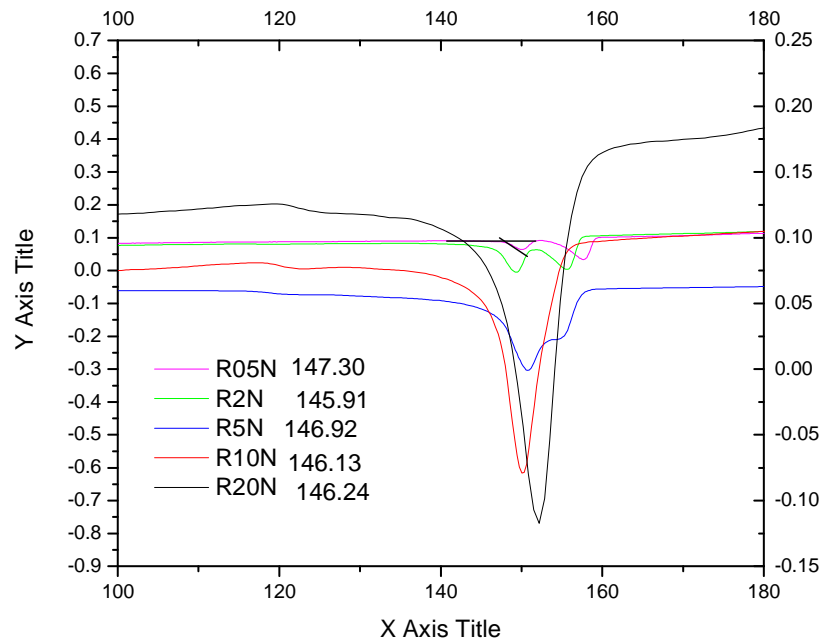

Figure 4-8 PLA DSC heated at rate of 0.5°C/min to 20°C/min

The initial melting temperature for the PLA samples was found to be between 145.91 and 147.30°C and dependent on the rate of heating. During the first heating of PLA, at a heating rate of 20°C per minute, the glass transition is much easier to observe, while the two peaks for melting are combined (Figure 4-8). The combining of the two peaks in the faster heating rates causes the peak to shift to be present at a higher temperature in comparison to the slower heating rates.

4.3.3 DSC of PLA Powder

The PLA powder has a lower glass transition of $57.34^{o}C$ than the original PLA pellet which has a glass transition of $64^{o}C$. The PLA powder has a melting point of $129.7^{o}C$ and the PLA pellets

have a higher melting point of 147.18^{o}C. (Figure 4-9) This indicates that the PLA pellets have

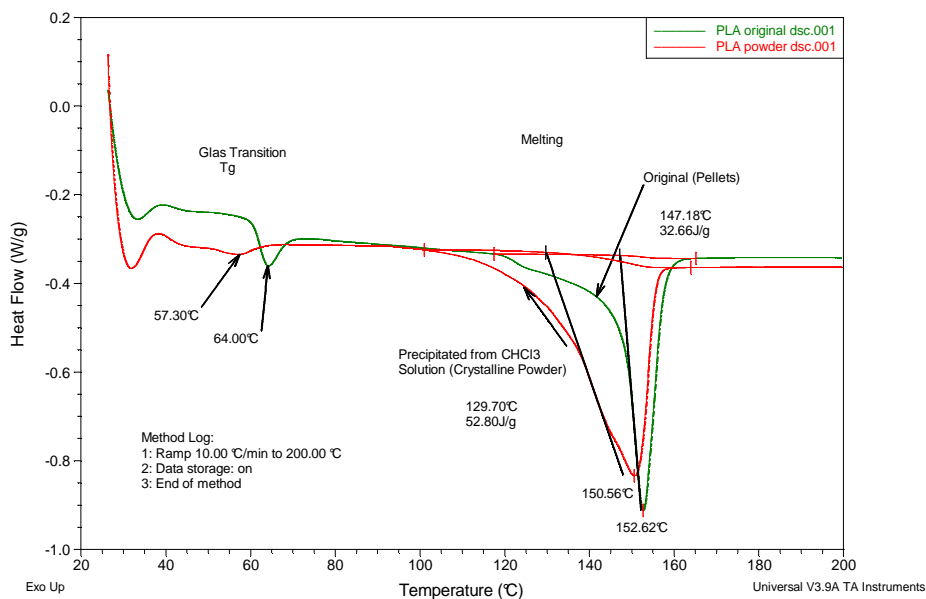better thermal stability than PLA in the powder form

Figure 4-9 PLA and PLA powder comparison

4.3.4 DSC of PLA Films

Disperse dyed PLA has a lower melting point (123.96^{o}C) than the PLA powder and the original
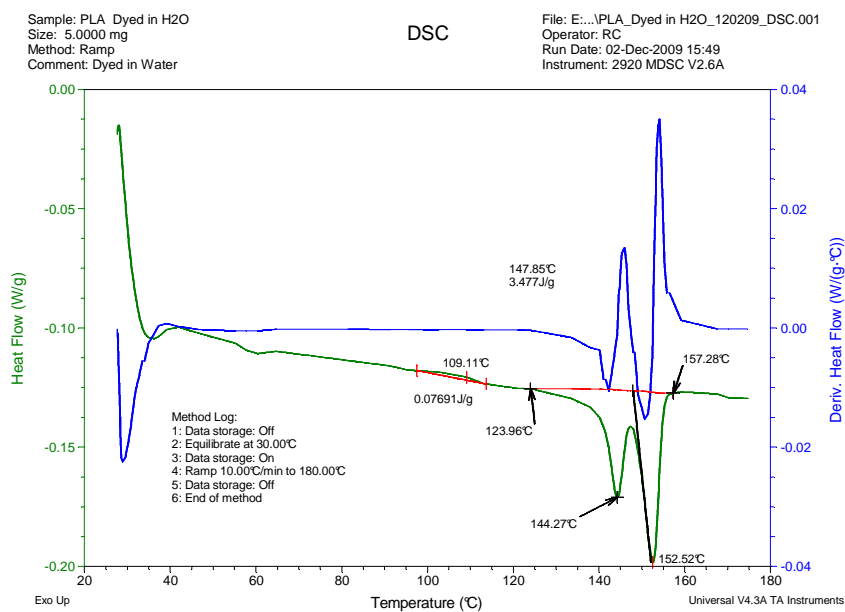

Figure 4-10 Disperse Dyed PLA

PLA pellets (129.70 and 147.18$^\text{o}$C respectively). This reduction of the melting point indicates a loss of thermal stability during the disperse dying process (Figure 4-10).
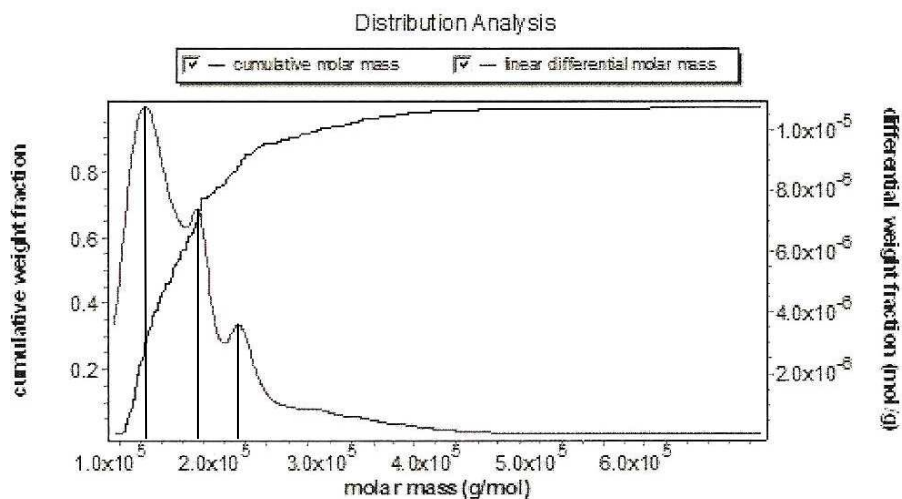
4.4 SEC of PLA

Size-exclusion chromatography (SEC), also called gel-filtration or gel-permeation chromatography (GPC), uses porous particles to separate molecules of different sizes. It is generally used to separate and to determine molecular weights (M_n and M_w) and molecular weight distributions or polydispersity, PD ($PD = M_w/M_n$) of polymers. A mechanical pump provides an eluting solvent from reservoir to push the injected sample along in columns (Figure 3.1). The individual molecules wander around, and sometimes enter the pores of the column packing material (a gel). The columns are designed so that the larger molecules do not fit into many of the pores (they are excluded), so they run through the column quickly. On the other hand, the smaller molecules in the sample can fit into most of the pores, getting occasionally stuck there, and so diffuse along more slowly. Molecules that are smaller than the pore size can enter the particles and therefore have a longer path and longer transit time than larger molecules that cannot enter the particles.

This setup leads to the counter-intuitive result that the biggest molecules come out first, and the smallest ones last. SEC essentially sorts the molecules based on their average size in solution ("hydrodynamic volume"). Molecules of size larger than the pore size cannot enter the pores and elute together as the first peak in the chromatogram (Figure 3.1). This condition is called total exclusion. Molecules that can enter the pores will have an average residence time in the particles that depends on the molecules size and shape. Different molecules therefore have different total transit times through the column. This portion of a chromatogram is called the selective permeation region. Molecules that are smaller than the pore size can enter all pores, and have the

longest residence time on the column and elute together as the last peak in the chromatogram. This last peak in the chromatogram determines the total permeation limit.

PELLETS
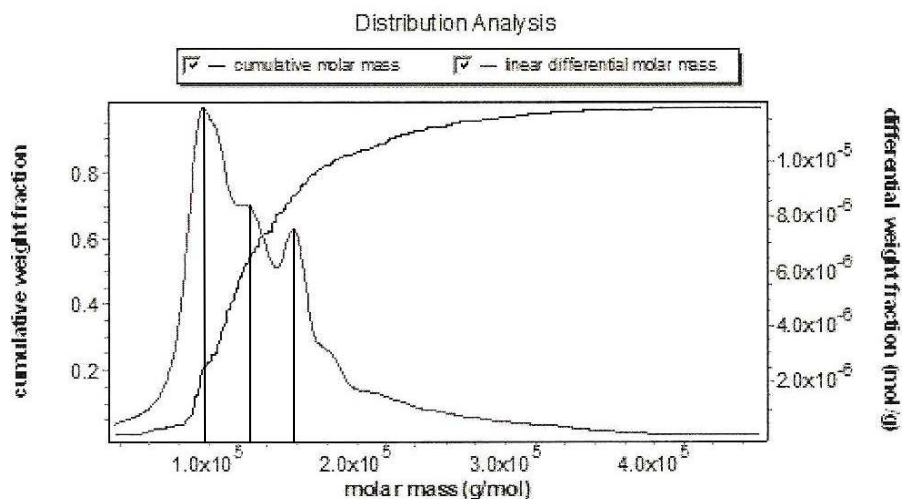
AFTER DSC

Figure 4-11 SEC of PLA before and after DSC heating

As pointed out in the experimental section (Chapter 3), a SEC (GPC) analysis for determination of molecular mass of polymers started with the preparation of a dilute polymer solution (e.g., 0.25%) and filtration of the solution. The solution was then injected into the column at the time

zero (t = 0) min and some characteristics of the elute from the columns, such as absorption of UV light or the refractive index, were compared in the detector to that of the pure solvent. The peak height (h) was related to the polymer sample concentration of molecular species of mass M_n as determined using the dn/dc value of 0.0237 ml/g. The molecular weight determined during the SEC analysis for PLA pellets was 153KD (Negulescu et al.,2008). The molecular weight determined during the SEC analysis for PLA pellets after DSC heating is was 124KD (Figure 4-11). This shows that there was degradation of the molecular structure during the heating of the PLA pellets.   The three peaks visible in the each of the two represent concentrations of different size molecules. In the distribution analysis of the PLA after DSC heating, it can be seen that the peaks have shifted to have concentrations of molecules of smaller sizes.

4.5 FTIR of PLA

4.5.1 FTIR of PLA Film after Heating

Fourier Transform Infrared spectroscopy (FT-IR) analysis provides information about the types of functional groups present in an organic molecule by measuring the characteristic frequencies associated with bond stretching and bending vibration. A stretching vibration (symmetric or asymmetric) is the movement along the bond axis while bending consists of a change in the bond angle between bonds such as twisting, rocking, scissoring, and torsional vibrations. Usually, symmetric stretching vibrations occur at lower frequencies than asymmetric stretching vibrations while the stretching vibrations arise at higher frequencies than bending vibrations. A necessary condition for IR absorption is that a rhythmical change in the dipole moment of the molecule must take place during vibration. Thus, the alternating electric field generated by vibration couples the molecule vibration with the oscillating electric field of the incoming electromagnetic radiation. The above mentioned vibrations are called fundamental absorptions and they develop from excitation from ground state to the lowest-energy excited state.

The vibrational frequencies are affected by the mass of the vibrating atoms and by the strength of the bonds. Bonds between atoms of lighter mass vibrate at higher frequencies than bonds between heavier atoms. Stronger bonds, which correspond to large force constants, vibrate at higher frequencies than weaker bonds.

For this research, C-O bonds were monitored C-O-C(O) (ester bonding) during the thermal treatment of PLA samples.
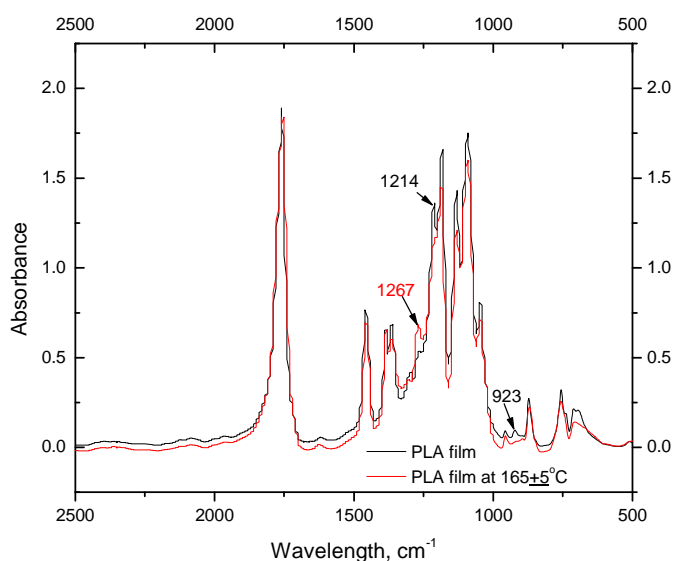

Figure 4-12 FTIR Absorbance of PLA Film Before and After Heating

The appearance of the peak at 1214cm^{-1} indicates C-O-C bonds and the peak at 923cm^{-1} indicates C-H bonds in the PLA film. Some of these bonds disappear after the film sample was heated. The appearance of the peak at 1267cm^{-1} after the sample was heated at 165 ± 5°C indicates the development of C-O molecular bonds.
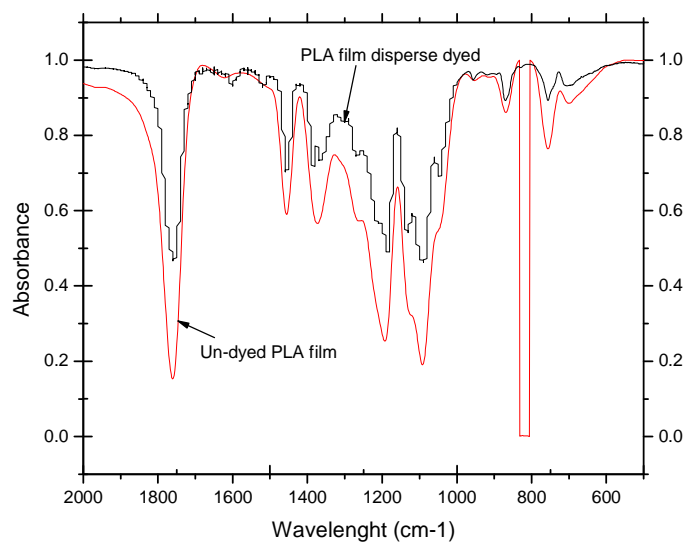
Figure 4-13 FTIR comparison of Disperse Dyed Film and Un-dyed Film

This means there was a change in the structure of the sample during exposure to heat (Figure 4-12). The C-O-C bonds were broken to create more C-O bonds. This indicates that the structure of the polymer is decomposing with exposure to heat.

4.5.2 FTIR of PLA Films

The unseen development or loss of peaks in Figure 4-14 indicates that the structure was not altered during the exposure to the dye compound at 110°C (Figure 4-13).
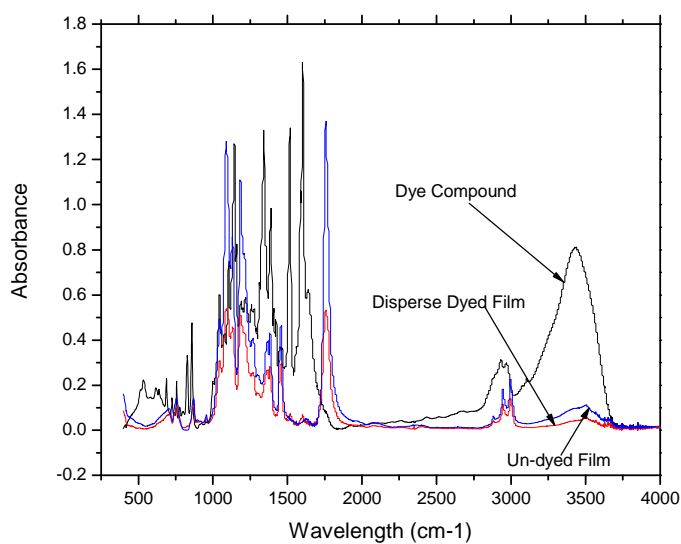

Figure 4-14 Disperse Dyed film and Un-dyed film

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The large dip seen at just under 800cm^{-1} is noise in the data and should be disregarded. The large peak in the dye compound sample in the 3100-3750 range indicates the presence of aromatic rings, which is a characteristic of disperse dyes. In the disperse dyed film sample, there is an increase in the peak in the 3100-3750 range compared to the un-dyed sample. This is expected with the addition of disperse dyes being present in the dyed sample (Figure 4-14).

4.5.3 FTIR of Lactide

The disappearance of a peak at 1250cm^{-1} in the lactide sample indicates that there were no additional structures found in the PLA film sample that were not present in the original lactide that PLA derived from (Figure 4-15).
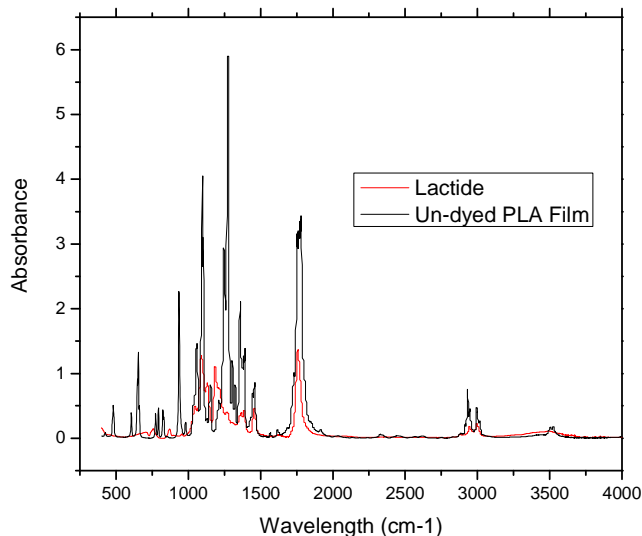

Figure 4-15 Lactide and Un-dyed PLA Film FTIR

4.6 Rheology of PLA

In Figure 3.2 are presented two of the most utilized rheological geometries for analysis of polymer solutions and composites. Both geometries are used for analysis of small quantities of material. While the parallel-disks geometry is usually preferred for the systems of higher

viscosities, the cone-and-plate geometry is typically utilized for systems of moderate viscosities, and involves a smaller gap between the upper and lower tools. The main advantage of the cone-and-plate over the parallel-disks is that the former device eliminates the problem with the radial dependence of the shear rate and shear strain, providing a homogeneous flow of the material independent of the position between the upper and lower tools. For systems of even smaller viscosities (e.g. water) couette geometry is typically utilized for rheological analysis, where the liquid is placed in a barrel-like bottom tool in which a tubular upper tool spins around a centered axis.

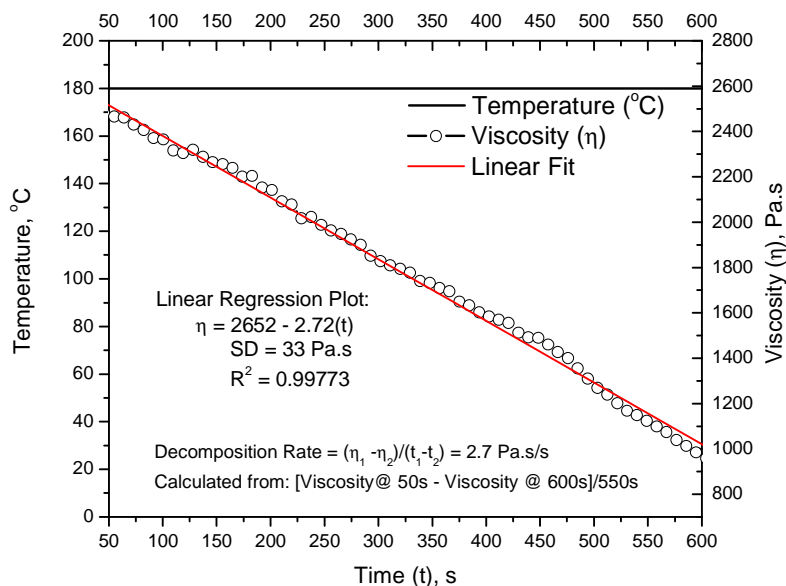Figure 4-16 Rheology of PLA at 180°C: Isothermal degradation indicated by viscosity decrease

The straight line regression of the decomposition of the PLA under application of heat indicates that the polymer begins to have decomposition as soon as the heat and pressure are applied. (Figure 4-16) The lack of a downward curve of the line shows that there was no resistance to the pressures applied to the PLA.

CHAPTER 5 CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

5.1 Conclusions

The novelty of conducting SEC analysis of dyed PLA films has given insight to the molecular decomposition of PLA during the dyeing process. With the loss of molecular weight during heating of the PLA pellets and film, as indicated by the SEC data, it has become apparent that the heat used during disperse dyeing is the reason for the increase degradation the polymer during processing. By employing a dying method, such as solution dyeing, that uses less exposure to heat there was a resulting reduction in the loss of molecular weight during the dying.

As shown by the MTGA analysis, the loss of weight around 60 C was the result of removing the remaining chloroform that was present in the un-dyed film and solution dyed samples. The resulting total weight loss was a combination of the removal of excess chloroform in the sample combined with the weight loss during the sample degradation. It is important to recognize this and examine the weight loss only after 200 C. When reviewing the weight loss of both dyed film samples after 200$^{\text{o}}$C, the disperse dyed film has an increased decomposition rate in comparison to the solution dyed film.

During the examination of the MTGA results, it was discovered that the surface area of the PLA sample also played a role in the degradation of the polymer. The inverse relationship of surface area to thermal stability is important to be taken into account during processing. The use of a PLA source with a lower surface area will allow for dyeing with a lower loss of degradation and loss of molecular weight.

By correlating the DSC results with that of MTGA, the increased loss of molecular mass is observed to be increasing as the PLA sample is exposed to increased heat. The PLA film sample that was solution dyed was exposed to the least amount of heat since the dye was

absorbed by the polymer during the creation of the film. The film that was dispersed dyed was subjected to heat during the dyeing process which then showed increased degradation.

In conclusion of these results, the hypothesis that there will be increased degradation of the PLA polymer during the disperse dyeing process in comparison to solution dyed PLA has been supported by this study. The reduced molecular mass along with the increased decomposition rate of disperse dyed PLA film results in increased degradation.

5.2 Further Research Suggestions

The DSC analysis has shown that multiple melting transitions can occur with the PLA pellets depending on the heating rate used. The results from DSC indicates multiple crystal structures forming during heating, before the last melting peak temperature. A correlation of DSC results along with X-ray mapping of diffraction data of PLA samples annealed at increasing temperatures preceding the melting domain will allow the determination of the most thermally stable crystalline form of PLA. A SEC analysis of annealed samples will indicate if thermal degradation occurred also during the heating.

Continued research using other means of investigation could also be considered. The use of SEC on the dyed film samples would confirm the changes in molecular weight that were assumed during this research. The use of this technique will support the acceptance of the results of molecular degradation caused by the application of heat during dying and fiber spinning of PLA.

The effect of the molecular weight lost during dyeing on the mechanical properties of PLA fibers is another area of study to be considered. Tensile strength and fiber durability will have an impact on fiber end use and could be another reason to prefer solution dyeing over disperse dyeing. The final fiber properties of dyed PLA will have a direct impact on the

appropriate end use of the fiber and resulting yarns and materials. Colorfastness comparisons between solution dyed and disperse dyed PLA fibers will be an area that will need to be researched to provide clear insight into the benefits between the two dyeing methods.

The solution dyeing of a fiber presents implications for production that make it undesirable for some product types. The color lead times are longer and the color minimums are higher for solution dyed fibers since the color is added during the fiber spinning stage of production. This type of dyeing is considered less versatile since the color cannot be changed after the fiber is extruded. The business and logistic implications of using solution dyeing for a replacement of disperse dyeing will need to be evaluated to decide if solution dyeing will be a beneficial endeavor to enter into.

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