2014

The Crystallization Kinetics of Polylactic Acid (Pla) Processed Through Solid-State/Melt Extrusion

Brian Bernard Lynch
Bucknell University, bbl007@bucknell.edu

Recommended Citation

Lynch, Brian Bernard, "The Crystallization Kinetics of Polylactic Acid (Pla) Processed Through Solid-State/Melt Extrusion" (2014). *Honors Theses*. 245.
https://digitalcommons.bucknell.edu/honors_theses/245

The Crystallization Kinetics of Polylactic Acid (PLA) Processed Through Solid-State/Melt Extrusion

by

Brian B. Lynch

A Thesis Submitted to the Honors Council

For Honors in Chemical Engineering

May 8, 2014

Approved by:

K. Wakabayashi

Advisor: Dr. Katsuyuki Wakabayashi

Department Chairperson: Dr. Jeffrey Csernica

Acknowledgements

I would first like to thank Professor Wakabayashi for everything that he has done throughout this past year. He has been an invaluable resource for any and all questions that I have had during this research study and someone that I truly respect for his knowledge and passion for research. His guidance has allowed me to acquire the vast amount of information to complete this thesis and his constant scrutiny has helped me to become the writer that I am today. Without him, this thesis would lack much of the technical content and would certainly not be as well written as it is.

Additionally, I would also like to thank the members of my research group: Andrew Fox, David Frey, Evan Miu, and Ethan Blumer. Their support and suggestions on many results throughout the year allowed me to explore ideas and seek answers to questions that I had not thought of on my own. In the beginning of the year, I especially appreciated the knowledge and training that David gave me to help me get acclimated to the lab and the various testing procedures.

This project would also not have been successful without the help of Diane Hall. Diane was the “go-to” person during this thesis whenever an instrument was malfunctioning. Her ability to troubleshoot many instruments was invaluable at many points during this project.

Most importantly, I would like to thank my family and friends for all of the support that they have given me throughout this year and the last four years. At so many points in time, they have eased the stress and frustrations that have come with school and

research. I truly appreciate all of the encouragement that I have gotten, especially during tough times. I especially want to thank my parents, who have always been my biggest supporters. They have never been more than a phone call away and at so many times, have provided me with the motivation I need.

Table of Contents

List of Tables

List of Figures

Abstract

Polylactic acid (PLA) is a bio-derived, biodegradable polymer with a number of similar mechanical properties to commodity plastics like polyethylene (PE) and polyethylene terephthalate (PETE). There has recently been a great interest in using PLA to replace these typical petroleum-derived polymers because of the developing trend to use more sustainable materials and technologies. However, PLA's inherent slow crystallization behavior is not compatible with prototypical polymer processing techniques such as molding and extrusion, and in turn inhibits its widespread use in industrial applications.

In order to make PLA into a commercially-viable material, there is a need to process the material in such a way that its tendency to form crystals is enhanced. The industry standard for producing PLA products is via twin screw extrusion (TSE), where polymer pellets are fed into a heated extruder, mixed at a temperature above its melting temperature, and molded into a desired shape. A relatively novel processing technique called solid-state shear pulverization (SSSP) processes the polymer in the solid state so that nucleation sites can develop and fast crystallization can occur. SSSP has also been found to enhance the mechanical properties of a material, but its powder output form is undesirable in industry. A new process called solid-state/melt extrusion (SSME), developed at Bucknell University, combines the TSE and SSSP processes in one instrument. This technique has proven to produce moldable polymer products with increased mechanical strength.

This thesis first investigated the effects of the TSE, SSSP, and SSME polymer processing techniques on PLA. The study seeks to determine the process that yields products with the most enhanced thermal and mechanical properties. For characterization, percent crystallinity, crystallization half time, storage modulus, softening temperature, degradation temperature and molecular weight were analyzed for all samples. Through these characterization techniques, it was observed that SSME-processed PLA had enhanced properties relative to TSE- and SSSP-processed PLA.

Because of the previous findings, an optimization study for SSME-processed PLA was conducted where throughput and screw design were varied. The optimization study determined PLA processed with a low flow rate and a moderate screw design in an SSME process produced a polymer product with the largest increase in thermal properties and a high retention of polymer structure relative to TSE-, SSSP-, and all other SSME-processed PLA. It was concluded that the SSSP part of processing scissions polymer chains, creating defects within the material, while the TSE part of processing allows these defects to be mixed thoroughly throughout the sample. The study showed that a proper SSME setup allows for both the increase in nucleation sites within the polymer and sufficient mixing, which in turn leads to the development of a large amount of crystals in a short period of time.

1. Introduction

The introduction of polymers into mainstream culture came in the 1940’s as discoveries in polymerization chemistry coincided with the increasing demand for a light material that could be used to package goods [Society of Plastic Engineers at Texas A&M University, 2013; American Chemical Council, 2014]. This new class of materials replaced metals and ceramics in many applications as polymers were less expensive to process and had more desirable properties for consumers. Throughout the last 75 years, the everyday uses of polymers have expanded from the original nylon polymer to other commodity polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). In 2009, the United States produced 31.1 million tons of plastic products [United States Environmental Protection Agency, 2013]. However, these polymers are often criticized as they are derived from petroleum, and therefore not considered environmentally-friendly nor sustainable [Haas, T., et al. 2009; Mooney, B. P., 2009].

In 1988, the Society of the Plastics Industry (SPI) introduced the Resin Identification Code (RIC) in response to plastic manufacturer’s demands to help preserve natural resources. Table 1, developed by the SPI, shows the 6 types of commonly used polymers as well as a category that includes the remaining polymers that can be recycled [Society of the Plastic Industry, 2013; American Chemical Council, 2014]. These efforts have led to an increase in the rate of recycling in the United States from 8 to 32% over the last 25 years [Zero Waste, 2014]. However, despite these efforts, it was estimated that in 2008, over 80% of post-consumer plastics still went to landfills [History of Plastic, 2013]. Though the amount of recycling has increased over time, it is still not as sustainable as many environmentally-conscious citizens desire.

Table 1: The RIC for each type of polymer that can be recycled [Society of the Plastic Industry, 2013]

Resin Identification Number	Resin	Resin Identification Code –Option A
1	Poly(ethylene terephthalate)	1 PETE
2	High density polyethylene	2 HDPE
3	Poly(vinyl chloride)	3 V
4	Low density polyethylene	4 LDPE
5	Polypropylene	5 PP
6	Polystyrene	6 PS
7	Other resins	7 OTHER

From an industrial standpoint, petroleum-derived polymers are becoming more and more expensive due to the increase in petroleum prices. Between 2000 and 2010, the price of PP increased about from approximately $0.40/lb to $1.00/lb [The Hedging Corner, 2011]. As a result, a need exists for an alternative polymeric material in the commodity plastics market.

For these reasons, significant research efforts have been targeted towards sustainable polymers, which include bio-based, bio-derived, naturally-occurring, and biodegradable polymers [Van de Velde, K. & Kiekens, P., 2002]. One of the most promising bio-derived and biodegradable polymers is polylactic acid (PLA) [Madhavan Nampoothiri, K., et al., 2010; Drumright, R. E., et al., 2000; Mooney, B. P., 2009; Averous, L., 2008]. PLA has emerged as an alternative polymer to PE and PS as it has been found to have similar characteristics. The physical properties of neat PLA can be manipulated, both intrinsically by controlling the level of polymer crystallites (semicrystalline format) and extrinsically by adding plasticizers (amorphous format) [Pillin, I., et al., 2006; Labrecque, L. V., et al., 1997; Baiardo, M., et al., 2003; Jacobsen, S. & Fritz, H, 1999]. PLA is commercially supplied by a variety of companies around the world, and can be processed by many techniques such as blow and injection molding [Bergeret, A., 2011].

However, one of the main hurdles for the widespread use of PLA is the large amount of time and energy needed to process the material into an application-friendly, semicrystalline form, preventing the mass-manufacturing of PLA-based products. When PLA is processed through conventional melt-processes like injection molding, polymer crystals do not form at a sufficiently high rate to complete processing in a time similar to that of petroleum-based polymers [Vadori, R., et al., 2013]. The low level of crystallinity that occurs leads to a low quality and inconsistent polymer product.

In this honors thesis, the processing of PLA will be investigated by comparing the current industrial processing technique of twin-screw extrusion (TSE) to two novel, innovative processing techniques of solid-state shear pulverization (SSSP) and solid-state/melt extrusion (SSME). The mechanical and thermal properties, as well as the structure, of the resulting PLA will be analyzed and compared between each respective processing technique. An optimum processing method will be one that would yield products with similar or enhanced properties relative to the current standards but with faster processing time. Once the processing technique with the greatest set of properties has been determined, that process will be optimized in terms of flow rate and screw design to find the processing conditions at which PLA is most effectively processed.

The balance of this thesis begins in Chapter 2 with a literature review of the PLA material and relevant processing techniques involved. Chapter 3 introduces the methods by which PLA was processed and the techniques by which the extruded samples were analyzed. Results of an initial survey study of the three different processing methods (TSE, SSSP, and SSME) are shown in Chapter 4 and an optimization study will be discussed in Chapter 5. The final chapter will summarize the key findings from this Honor’s thesis work and provide recommendations for future research directions in this field.

2. Background

2.1 Polylactic Acid

Polylactic acid (PLA) was discovered in 1932 by DuPont as a chemical used for drug delivery and has since expanded its use to be one of the most popular biodegradable polymers used in the manufacturing of everyday plastic products [Auras, R.A., et al., 2011]. In 2012, PLA accounted for 41% of the 269,000 metric tons of worldwide biodegradable polymers. A projected increase in total demand for biodegradable polymers to 525,000 metric tons by 2017 [Plastemart, 2013] is due in part to the environmental concerns of petroleum-based polymers and to the increased price of these polymers because of rising oil prices. PLA is not affected by the price of oil as PLA is a bio-derived and biodegradable polymer. In the future, as the cost of processing decreases, the use of PLA will likely supersede the use of petroleum-based polymers. Currently, PLA is used in many applications including packaging, electronics, and agriculture [Avérous, L., 2008; Drumright, R. E., et al., 2000; Garlotta, D., 2001; Plastemart, 2013].

PLA is a polyester, a molecule whose repeat molecule contains a ester and methyl group, as seen in Figure 1. The methyl groups attached to the structure can vary in orientation (chirality) depending on the method of synthesis and processing. PLA is derived from lactic acid, which can be produced from chemical synthesis, starting with cellulose, or more commonly, from the fermentation of the carbohydrate lactate, glucose, or sucrose to produce 100% L-lactic acid or via hydrolysis of lactonitrile to produce a racemic mixture L-lactic acid and D-lactic acid [Lim, L. T., et al., 2008; Garlotta, 2002; Averous, L., 2008].

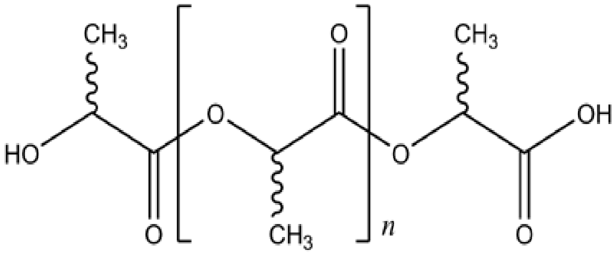

Figure 1: Chemical structure of PLA

Because of cost, the route most typically used is the fermentation of carbohydrates, which are usually extracted from corn [Xiao, L., et al., 2012]. The first step in the synthesis of lactic acid is the hydrolysis of the carbohydrate. Hydrolysis creates a dextrose product, which can be fermented to produce lactic acid [Garlotta, 2002; Averous, L., 2008; Lim, L. T., et al., 2008]. PLA can then be synthesized via direct condensation polymerization or azeotropic dehydration condensation depending on the chirality of the original monomer molecule, as seen in Figure 2 [Avérous, L., & Pollet, E., 2012]. The polymer is then molded into small pellets and sold to manufacturers.

Depending on the method by which PLA is synthesized, the degree of chain-length can vary greatly within the polymer leading to varying properties [Averous, L., 2008; Avérous, L., & Pollet, E., 2012]. If produced with the azeotropic dehydration method, PLA chain lengths are generally longer than when produced via the direct condensation polymerization method [Avérous, L., & Pollet, E., 2012]. PLA's crystalline state can vary from completely amorphous (non-crystalline) to up to 40% crystalline; many physical properties of the polymer depend on the amount of crystallinity that has occurred within the polymer. In most PLA polymers, the glass-transition temperature (T_g) ranges between 50°C-80°C, while the melting temperature (T_m) is between 130°C-180°C [Averous, L., 2008]. PLA is non-flammable, UV resistant, chemically resistant, and insoluble in most solvents [Farrington, D. W., et al., 2005; Lunt, J., & Shafer, A. L., 2000].

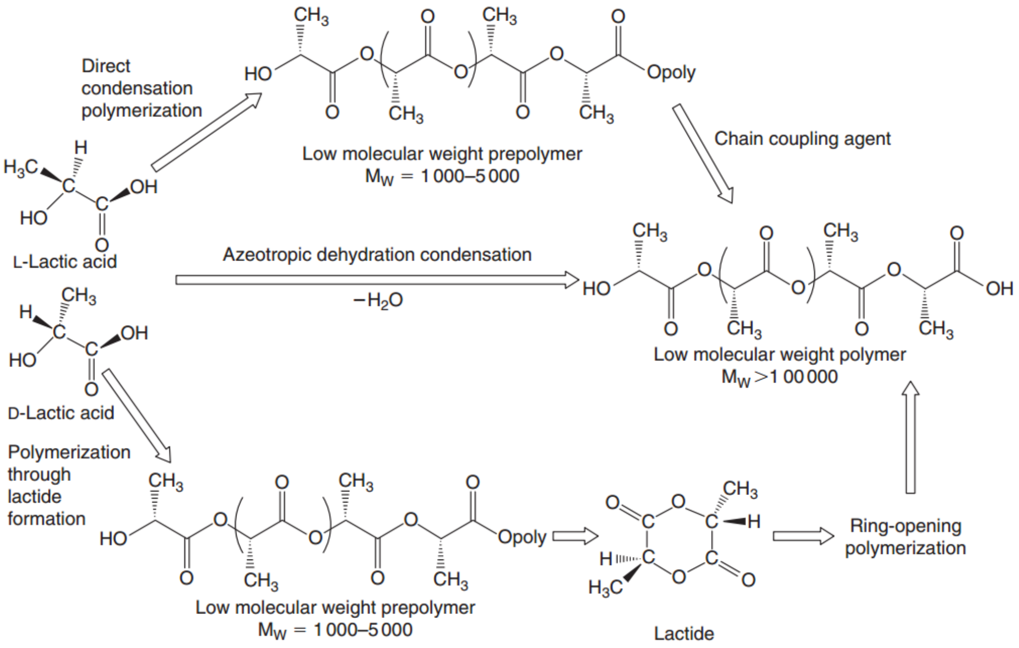

Figure 2: The synthesis steps of PLA from lactic acid [Avérous, L., & Pollet, E., 2012]

PLA, as currently produced, does not necessarily achieve all of the desired technical properties. It has a low thermal stability, low toughness, poor moisture barrier properties due to the glassy state and low crystallinity at ambient temperatures [Brunner,

P. J., 2013]. Improvements in these physical properties can be realized if the PLA is prepared with a higher amount of crystals. However, the kinetic and transport nature of PLA makes it a very slow crystallizing material [Brunner, P. J., 2013]. PLA's slow crystallizing nature restricts fast and/or mass production of products using this material.

Many have attempted to overcome long processing times and low crystallization temperatures of PLA by various methods, the most popular being the addition of nucleating agents [Lunt, J., 1998; Brunner, P. J., 2013; Day, M., et al., 2006]. The addition of nucleating agents decreases the surface free energy barrier towards nucleation, which allows for crystallization at higher temperatures [Liao, R., et al., 2007]. Additives such as carbon nanotubes, talc and microcrystalline cellulose have been successfully used as nucleating agents and have proven to show an increase in crystallization rates [Liao, R., et al., 2007; Xiao, L., et al., 2012]. However, the technique can be costly, and is not considered to be environmentally friendly, causing many in industry to be hesitant about implementing it on a large scale. Therefore, there is a need to develop an environmentally-benign technique that can enhance the crystallization kinetics of PLA.

2.2 Extrusion Processing

Extrusion is a common industrial processing method to mold a polymer from its original, pellet form into the desired product [Plastics Technology, 2005; Polymer Processing, 2001]. This technique is also desired in many polymer blend and composite applications as it allows dispersion and mixing to occur within the polymer matrix [Villmow, T., et al., 2008; Jonoobi, M., et al., 2010; Wang, Y., et al., 2004]. Typically, the polymer pellets are automatically fed into the extruder at a constant rate by an external volumetric feeder. The material enters the extruder at a hopper upstream, and undergoes phase change and mechanical kneading and mixing as the rotating screws push it downstream. The output of an extruder is usually molten strands that are subsequently cooled, though it is possible to extrude a product directly into a desired shape using a mold. Current industrial methods use twin screw extrusion (TSE), but other more advanced methods of solid-state shear pulverization (SSSP) and solid-state melt extrusion (SSME) are being considered as alternative ways to process polymers [Brunner, P. J., et al., 2012; Brunner, P. J., 2013; Fielding, A. S., 2009].

Twin screw extrusion (TSE) is considered to be the most common polymer processing technique in industry [Plastics Technology, 2005; Rauwendaal, C., 2014]. This continuous process allows polymer pellets to enter a feeder, which then feeds the polymer through heated zones with rotating screws, as seen in Figure 3.

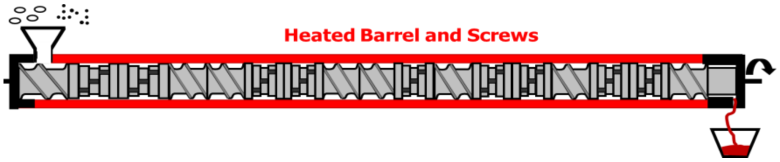

Figure 3: Diagram depicting TSE processing

TSE is an easily-scaled process that can produce polymer strand products at high production rates [Kalyon, D. M., et al., 2013; Daurio, D., et al., 2011]. However, when processing complex polymer systems such as immiscible blends [Lebovitz, A. H., et al., 2002] and composites [Treece, M. A., et al., 2007], or even neat polymers with unpredictable behaviors such as PLA, TSE is not an effective method because of insufficiently rigorous mixing in the molten state. Resulting products often contain non-homogeneous morphology and behave in an inconsistent fashion. In addition, the high-temperature nature of TSE can thermally degrade the materials being processed, especially temperature and moisture sensitive polymers like PLA.

Because of the ineffectiveness of TSE to process certain polymers and composite materials, a new production technique was developed at Northwestern University in the 1980's, termed solid-state shear pulverization (SSSP). This method can use the same extruder as TSE, but instead of melting the polymer, SSSP cools the polymer with an ethylene glycol-water cooler throughout all zones, as shown in Figure 4. SSSP applies large amounts of shear force to the polymer in the solid state by rotating the screws at a high speed. The product is a powder that can exhibit large amounts of homogeneous mixing in polymer blends and composite systems and consistent morphology.

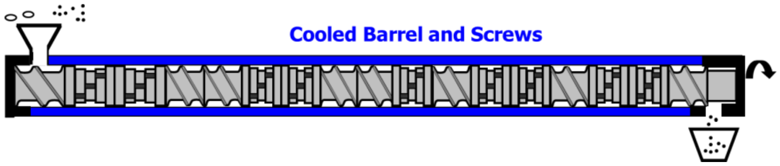

Figure 4: Diagram depicting SSSP processing

In a specific scenario involving PLA, SSSP has been used to show increases in the crystallinity of the polymer [Brunner, P. J., 2013]. SSSP was found to induce crystallinity within PLA by creating an increased amount of nucleation sites because of the many defects created by the harsh processing of the SSSP technique. However, there are also two main disadvantages to using SSSP to process a material. Because shearing and compressive forces in the solid state create a large amount of friction, heat needs to be removed constantly by the chilling fluid. As a result of this limiting factor, SSSP processing is confined to low production rates. The second disadvantage is that the final product is a powder, which is undesirable in industry because of challenges in handling as well as health and environmental hazards.

A new processing method was developed several years ago at Bucknell University to overcome the shortcomings of SSSP processing. Solid-state/melt extrusion (SSME) combines SSSP and TSE in one instrument, essentially combining the advantages and removing the constraints of the two previously-discussed processes. The first portion of the instrument cools the polymer and applies similar processing steps as SSSP to create nucleation sites within the polymer, while the second portion heats the polymer to give the easily-handled, molten stands/pelletized product as seen in Figure 5.

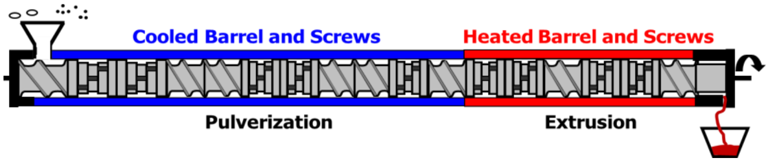

Figure 5: Diagram depicting SSME processing

SSME can be conducted at high production rates, relative to SSSP processing, and can provide a high level of dispersion for nanocomposite materials [Whittington, A. M., et al., 2013]. Based on these composite results, SSME is expected to be effective in creating nucleation sites for neat materials akin to the success in SSSP [Brunner, P. J., 2013].

3. Materials and Methods

3.1 Materials

The material used throughout all trials is PLA 2002D, supplied by NatureWorks LLC in the form of approximately 5-mm-diameter pellets, as seen in Figure 6.

Figure 6: Sample of PLA pellets

NatureWorks 2002D is a commercial-grade thermoplastic resin designed for extrusion/thermoforming applications. This high molecular weight polymer has a number-average molecular weight (M_n) of 110,000 g/mol and a weight-average molecular weight (M_w) of 194,000 g/mol, as determined by gel permeation chromatography (GPC) in our laboratory. According to NatureWorks specifications, this type of PLA is rated to have a specific gravity of 1.24, a melting temperature of 210°C, tensile strength of 53 MPa and yield strength of 60 MPa [NatureWorks, 2005].

NatureWorks 2002D PLA is a commercially well-known biodegradable polymer derived from corn [NatureWorks, 2005]. The starch within corn is hydrolyzed to form dextrose, which is fermented to produce a lactic acid product [Inskeep, G. C., et al., 1952].

The lactic acid is then polymerized and shaped into small pellets, which are sold for various purposes. Because the 2002D grade is specifically formulated for extrusion and molding, it is relatively stable in the molten state.

Post-consumer PLA can either be recycled or undergo a 2-step environmentally-friendly degradation process. Studies have shown that the degradation of PLA spans a 60 day period when the material is subject to an ambient compost environment with a moisture content of 52.4% [Iovino, R., et al., 2008]. First, the polymer undergoes chain scission due to moisture and heat in the atmosphere [NatureWorks 2005]. The long PLA polymer chain breaks down into smaller chains so that microorganisms can recognize and metabolize the PLA. Microorganisms have the ability, on their own, to produce lactic acid via fermentation. When degraded PLA is exposed to a microorganism, the microorganisms are able to quickly digest the polymer [Salminen, S., et al., 2004]. The resulting products from the metabolism of PLA are carbon dioxide, water, and humus, a soil nutrient. These components are released into the ground and atmosphere.

3.2 Processing Methods

In this study, PLA was processed through three different methods: twin screw extrusion (TSE), solid-state shear pulverization (SSSP), and solid-state/melt extrusion (SSME). Each method uses the same extruder: the KrausMaffei Berstorff ZE-25A UTX, as seen in Figure 7; however, in each process, the temperatures along the length of the extruder and the screw designs are modified to give the desired product.

Figure 7: KrausMaffei Berstoff ZE-25A UTX Extruder

The extruder has 2 co-rotating, intermeshing screws that can rotate at a speed of up to 600 rpm. The screws have a nominal length, L, of 850 mm and a diameter, D, of 25 mm, giving an L/D ratio of 34. Each screw can be customized with elements that convey or provide shear forces to the polymer, based on the processing mode and the level of compressive and shear forces to be applied. There are 3 different conveying elements that allow the polymer to flow along the length of the screw, as seen in Figure 8.

Figure 8: a. Short conveying element **b.** Medium conveying element
c. Long conveying element

There are also kneading elements, as shown in Figure 9, that provide shear and compression to the polymer in the cold processes (SSSP and the cold part of SSME) and mixing in hot processes (TSE and the hot part of SSME). Each element is available in two different lengths, which is chosen based on the extent of pulverization/mixing and the time desired for that specific function. Each of the three different screw elements shown in Figure 9 provides a different amount of shear forces to the polymer. Reverse kneading elements are considered to be the harshest screw elements, followed by neutral and forward. The reverse element severely pulverizes or mixes the polymer, restricting the polymer's flow along the length of the screw. Neutral and forward kneading elements impart the same pulverizing or mixing action, but in a less severe manner.

Figure 9: Long kneading elements **a.** Forward **b.** Neutral **c.** Reverse

A screw is assembled by combining various screw elements based on the desired level of shear or mixing. Surrounding the screws are 5 temperature-controlled zones seen in Figure 10. Zones 2-6 have the ability to be individually cooled or heated depending on the desired process. The heating is supplied via an electric cartridge heater and the cooling via a recirculating coolant. The following sections describe each processing method and how the method differs from the others.

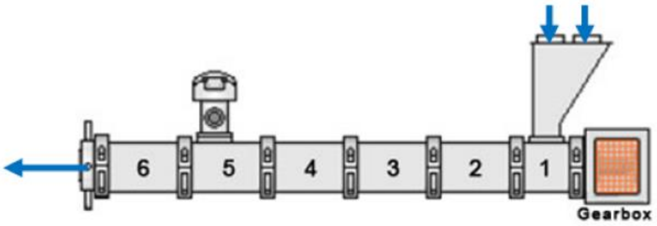

Figure 10: Diagram of KrausMaffei Berstorff ZE-25A UTX extruder showing Zones 2-6 can be temperature-controlled

3.2.1 Twin Screw Extrusion (TSE)

TSE uses six heated extruder barrel zones to melt and transport the polymer. The goal of TSE is to mix a polymer while it is in the molten state within the extruder, and pressurize the molten polymer out a narrow die to shape the polymer, usually into strands. Each zone is set at a specified temperature above the polymer’s melting temperature via a computer interface, which controls an electric heater.

3.2.2 Solid-State Shear Pulverization (SSSP)

SSSP uses the same extruder as TSE; however, all zones within the SSSP are cooled with an external, continuously recirculating chilling fluid. The external chiller employed is from Budzar Industries Model BWA-10AC. In this processing technique, the chiller cools the zones to 11°F, allowing for the polymer to stay in the solid state as it gets pulverized within the instrument. The final output of any SSSP process is a fine powder or flake. Because of the need for the chilling fluid to continuously remove heat generated by the pulverizing friction in all five zones, SSSP is a more energy-intensive process than both TSE and SSME.

3.2.3 Solid-State/Melt Extrusion (SSME)

SSME is a process by which the extruder is modified to combine SSSP and TSE into one process. For SSME processing, Zones 2 and 3 in Figure 10 follow the SSSP processing technique of cooling the polymer, while Zones 5 and 6 heat the polymer to model the TSE processing technique. Zone 4 is moderately heated to make the transition from a chilled state to a molten polymer. The final product is an extruded polymer strand that can be easily shaped into products. As with TSE, the heated zones are heated with an electric heater, while similar to SSSP, the cooled zones are cooled with a recirculating chiller at 11°F. Within the instrumentation lengths of 34 L/D units, the SSSP region has an L/D ratio of 22 and the TSE region has an L/D ratio of 12.

3.3 Characterization Methods

When processing was completed, each sample was prepared into appropriate size and shape specimens and was subjected to many types of characterization by different instruments. These instruments allowed for the determination of thermal and mechanical properties, as well as structural information of each sample.

3.3.1 Sample Pressing

Samples produced from TSE and SSME were in polymer strand form, while samples received from SSSP were provided in powder form. Samples from all forms of processing needed to be molded into a consistent shape so that they could be easily handled and cut into various shapes for various tests. A Carver Laboratory Press was used to heat PLA samples to 200°C and subsequently press the PLA at 200°C into a uniformly flat sheet of 0.5 mm in thickness.

The sheets were pressed by loading the polymer strand or powder onto a non-adhesive Mylar sheet. A brass mold edge, i.e. spacer, was then placed on the Mylar sheet to outline the polymer. Another Mylar sheet covered the polymer and an aluminum plate was placed on either end of the Mylar sheets. The aluminum plates were then placed within the pre-heated press, as seen in Figure 11. Pressure was applied once the press and the aluminum plates had equilibrated to the set temperature of 200°C.

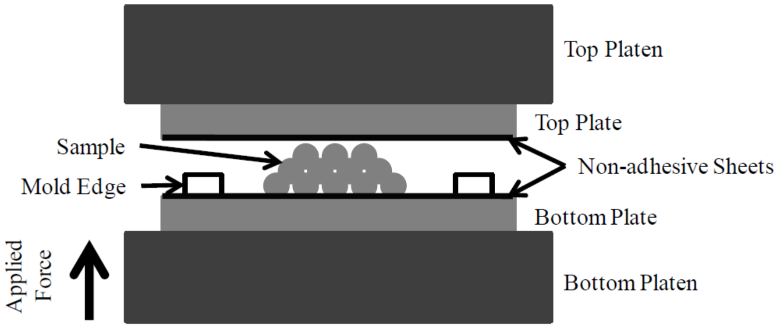

Figure 11: Schematic of sheet pressing procedure

Pressure of 10,000 psig was applied and maintained for 2 minutes after which the aluminum plates were left to cool between 2 refractory bricks, as seen in Figure 12, for 30 minutes.

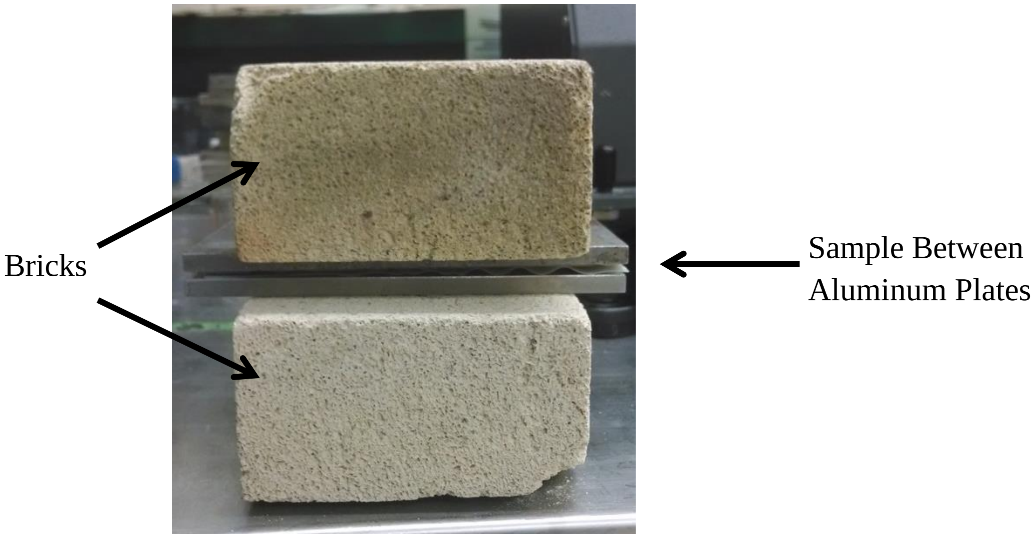

Figure 12: PLA sample cooling between two bricks

It was found that the bricks effectively and consistently dissipated the heat from the aluminum plates as the polymer cooled between them. After 30 minutes, the polymer sheet was removed from the Mylar sheets and placed in an air-tight plastic bag for storage. The polymer was then set aside for at least 24 hours before samples were cut from the sheet. Preliminary tests conducted before the study indicated that initial crystallization occurs within 24 hours of the sample being pressed. After this time period, the polymer assumes a stable structure and can be assumed to be uniform throughout the sample.

3.3.2 Differential Scanning Calorimetry

The thermal properties of each sample were measured and analyzed using differential scanning calorimetry (DSC). DSC measures the heat required to reach the thermal transition points of glass transition temperature, melting, and crystallization. For this study, crystallization was of greatest importance in characterizing the material.

To conduct this test, a sample of 5-10 mg in size was placed in an aluminum hermetic pan. The pan was covered by its accompanying lid and crimped shut. The reference pan contained no materials and was just a crimped lid and pan.

The sample and reference pans were placed on the specimen stage of the TA Instruments Q1000 DSC, as shown in Figure 13.

Figure 13: Clamped hermetic pans within the DSC. Pan R5 is a reference pan and all others contain samples to be tested.

The DSC was then programmed to complete an isothermal or non-isothermal run where the DSC arm loaded each sample into the control furnace where testing took place. Isothermal runs were set at 105°C, PLA’s crystallization temperature, to analyze the development of crystals over a two hour period. Non-isothermal runs were completed by heating the sample at a rate of 5°C/minute from -40°C to 200°C. These runs were completed so that crystallization trends could be compared to trends of mechanical stiffness that were seen in DMA data. When comparing the plots, one can often correlate increases and decreases in stiffness to increases and decreases, respectively, in crystallinity.

All data collected were plotted and analyzed by TA Universal Analysis software. Data were also exported to Microsoft Excel if further analysis was necessary. When analyzing non-isothermal data, heat flows were plotted against a range of temperature during which crystallization occurred, while isothermal data were analyzed by plotting the heat flow over the isothermal holding time. The integral of the heat flow curve over the crystallization range in both plots provided the enthalpy of crystallization. The data were then normalized by taking the ratio the enthalpy of crystallization found to the enthalpy of crystallization of a theoretically 100% crystalline sample, which corresponds to percent crystallinity. For isothermal samples, the crystallization half time was found by plotting the percent crystallinity over the time of crystallization. The crystallization half time was considered the point at which the sample had crystallized to half of its total crystallinity.

3.3.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is an instrument used to measure the modulus of a material at varying temperatures. The instrument applies a sinusoidal strain to a rectangular sample and measures the resulting stress associated with each temperature. The built-in software of the DMA instantaneously determines two types of moduli: the storage modulus (E') and the loss modulus (E''). The storage modulus measures the stored energy or the elastic stiffness of the polymer in the elastic region, while the loss modulus measures the viscous response of the polymer. The loss response is associated with the damping of the polymer and its ability to dissipate energy. When added in Equation 1, these give the complex elastic modulus (E*) of the polymer.

$$E^* = E' + iE'' \qquad (1)$$

Because the focus of this study was to apply results to a solid PLA sample, the loss modulus was not considered in analysis.

A TA Instruments RSA3 was used with a strain frequency of 6.283 rad/s and strain rate of 0.03% to complete a dynamic mechanical strain test, where the resulting stress to PLA was measured while heating the sample from room temperature to 160°C at a rate of 5°C/min. Each sample tested was cut from a pressed sheet into a rectangular strip with dimensions of approximately 40 mm x 5 mm x 0.5 mm. The strip was clamped to either side of film fixture, as shown in Figure 14. The instrument then applied an oscillatory strain as the temperature increased to 160°C. Calculations of the storage and loss moduli were taken and plotted on TA Orchestrator software. The data was then exported to Microsoft Excel for analysis.

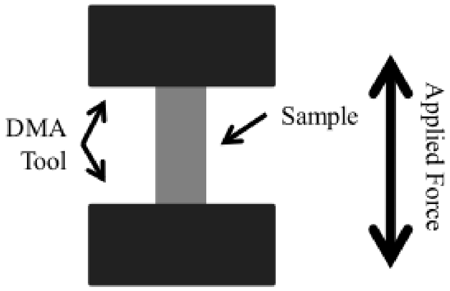

Figure 14: Diagram of DMA testing apparatus showing the direction of tension on a sample

3.3.4 Thermogravimetric Analysis

Thermal degradation behavior of a polymer can characterized using thermogravimetric analysis (TGA). TGA heats a material to a high temperature at a specified rate and measures the residual mass of the material as a function of both time and temperature.

TGA was completed using a TA Instruments SDT-Q600, as seen in Figure 15. The instrument uses two cantilever balances in a nitrogen environment furnace. To conduct the test, an empty alumina ceramic pan was placed on one of the cantilever balances a second alumina pan was filled with 10-20 mg of the sample was placed on the other cantilever balance. The furnace was heated from 30-600°C at 10°C/min. The degree of degradation over the course of times and temperatures was found using the TA Universal Analysis software that accompanied the instrument. The characteristic quantity measured was the heat degradation temperature at a 5% mass loss. Therefore, the data analysis software identified the temperature at which 95% of the total mass still remained.

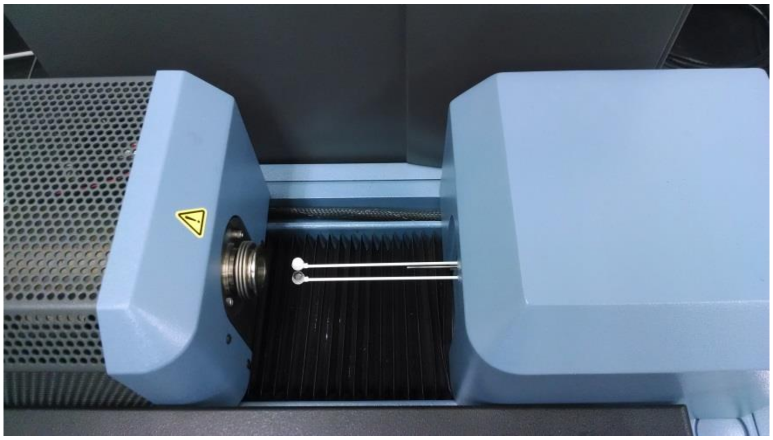

Figure 15: Opened TGA showing the balance and alumina pan

3.3.5 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a size exclusion-based chromatography that can measure the number average (M_n) and weight average (M_w) molecular weight. Molecules with lower molecular weights exit the column later than those with larger molecular weights. The molecular weight was measured to show the degree of degradation that had occurred within the polymer.

An Agilent Technologies 1200 Infinite Series GPC was used for this analysis, using tetrahydrofuran (THF) as the solvent. Before analyzing any sample, a molecular weight calibration was made with polystyrene (PS) standards. PLA samples were dissolved in THF at 30°C and mixed on mixer setting 2 on a VWR VMS-C7 stir plate for 24-48 hours. 300µL of the dissolved PLA was injected into the GPC. The column ran on a 25 minute program with normal elution times between 11-15 minutes. A typical elution time plot can be seen in Figure 16.

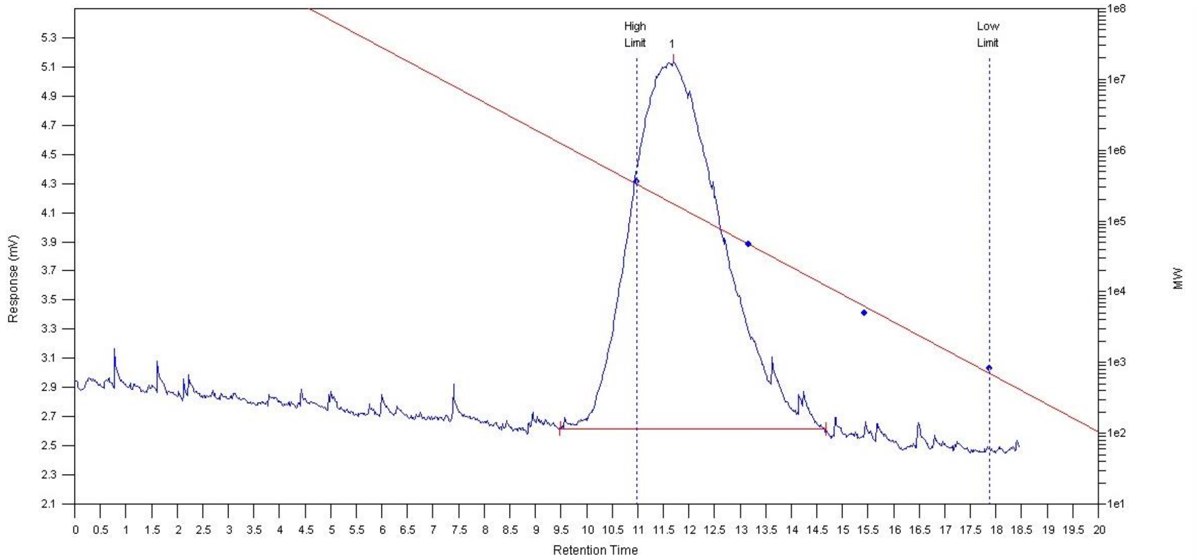

Figure 16: Sample GPC plot of response as a function of retention time

The retention times of each sample were compared to the polystyrene (PS) standard using GPC analysis software supplied by Agilent Technologies. Based on the known molecular weights of the standard, the software computed the number-average and weight-average molecular weight of each sample.

3.3.6 Tensile Testing

All ambient mechanical properties were determined using a tensile tester. A tensile test applies an increasing tensile strain to a sample so that the sample’s stress strain curve can be derived. From the stress-strain curve, yield strength, breaking strain, and the Young’s modulus of each sample can be determined. These parameters give insight into the mechanical robustness of the material. The yield strength is the maximum stress exerted in the elastic region, the breaking strain is the maximum strain a material can tolerate before fracture, and the Young’s modulus is the slope of the stress-strain curve in the elastic region, and is a measure of the stiffness of the material.

For this study, a Tinius Olsen H5K-S tensile tester was used to complete this study. Preliminary tests indicated that PLA in the form of a dogbone would crack upon tightening within the grips, so a rectangular shape was used for this instrument. Tensile testing was completed using samples measured to be approximately 40 mm x 4 mm x 0.5 mm. Both sides of the sample were pulled by a soft grip (Tinius Olsen HT50) as shown in Figure 17. All recorded samples were those with a clean break near the center of the sample.

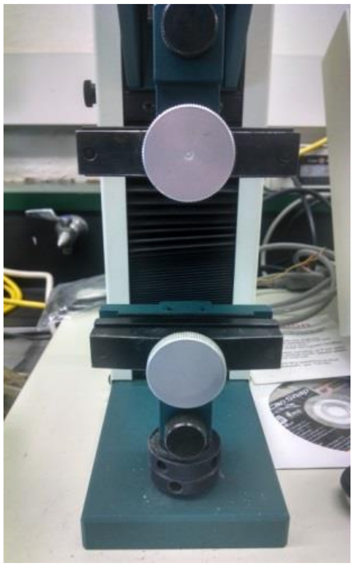

Figure 17: Tensile tester with soft grip attachment

The tensile tester was programmed to pull each strip at a rate of 1 mm/min as this was found to be standard among PLA tensile tests [Jonoobi, M., et al., 2010; Ochi, S., 2007; Suryanegara, L., et al., 2009]. Samples were pulled until the strip broke cleanly between the two grips. Once data had been gathered, the data were analyzed with an in-house MATLAB® interface.

4. Survey of Processing Methods for PLA

4.1 Introduction

Previous studies have shown how PLA processed via SSSP and TSE can affect the properties of PLA in different ways [Fielding, A. S., 2009]. TSE has been shown to increase thermal properties such as percent crystallinity and crystallization half time of PLA, while SSSP has been shown to increase mechanical properties such as yield strength and Young's modulus of PLA. We believe that both processing methods can be combined in SSME to create a product with enhanced thermal and mechanical properties. The initial study, presented in this chapter, compares and contrasts samples processed through the three processing techniques (TSE, SSSP, and SSME) to determine if PLA processed via SSME does, in fact, have the a combination of the superior thermal properties seen in TSE and the superior mechanical properties seen in SSSP.

4.2 Processing Parameters

The control sample for this study was unprocessed, as-received NatureWorks 2002D PLA while 3 other samples were NatureWorks 2002D PLA processed by each of the three processing methods. Processing conditions for each processed sample are listed in Table 2. The three runs were designed such that the processing parameters remain relatively similar in terms of initial pellet condition, screw design and throughput.

Table 2: Processing conditions used for each sample of PLA

Sample	**Dried or As Received**	**Screw Design**	**Screw Number**	**Throughput (g/hr)**
SSME	As Received	Moderate	SSME004	250
TSE	As Received	Standard	EX001	300
SSSP	As Received	Moderate	SS042 M	200
Unprocessed	As Received	N/A	N/A	N/A

The goal of this comparison was to identify the processing method with both desirable mechanical and thermal properties. The samples were tested through various analyses to show which method of processing allowed for the greatest extent of crystallization in the shortest period of time, while also maintaining comparable mechanical properties to the control, neat unprocessed samples of PLA.

Within the extruder, there are 5 different zones in which the temperature can be controlled, as discussed in Chapter 3. Each zone temperature can be specified based on the desired process. For TSE processes, all 5 zones were heated to over the polymer's melting temperature, while in SSSP processes, the barrels were cooled as much as possible to keep the polymer below its melting temperature and cause the polymer to be pulverized in the solid state. Table 3 lists the temperatures at which the extruder zones were set. The chilled zones for any trial included a cooling component, where zones were set to 0°F. The actual temperature was achieved by a using a chiller to recirculate a coolant at 11°F.

Table 3 shows that in experimentation, SSME does indeed combine the two processes of TSE and SSSP by using the set point of 0°F from SSSP for Zones 2 and 3 and the set point of 390°F from TSE for the Zones 5 and 6.

Table 3: Temperatures of each zone within the extruder

	Temperatures (°F)				
Sample	**Zone 6**	**Zone 5**	**Zone 4**	**Zone 3**	**Zone 2**
SSME	390	380	70	0	0
TSE	390	390	380	370	360
SSSP	0	0	0	0	0

Processing screws within the extruder were also carefully constructed so that relatively consistent conditions could be used for all extrusion processes. Table 4 shows the number of conveying and kneading elements, as discussed in Chapter 3, used in the screw design of each process. The TSE process used an industry-standard extrusion screw design, while the screw design for SSSP and SSME screw designs were considered to be of moderate harshness for their respective processing technique. The TSE screw design had 23 conveying elements, and 10 kneading element, while the SSSP screw design had 28 conveying elements and 9 kneading elements. The screw design chosen for SSME combines parts of the TSE and SSSP screw design to create a moderate screw design with 27 conveying elements and 7 kneading elements.

Table 4: Screw element components contained on the screw used for each processing method

Sample	**Conveying Elements**	**Forward Kneading Elements**	**Neutral Kneading Elements**	**Reverse Kneading Elements**
SSME	27	6	1	0
TSE	23	5	3	2
SSSP	28	7	2	0

4.3 Thermal Properties

Detailed thermal analysis was conducted using differential scanning calorimetry (DSC), to evaluate the rate and level of crystallization of each sample. Preliminary tests determined that 105°C was a suitable temperature at which crystal growth occurred over a measureable time period. Therefore, this temperature was selected as the isothermal crystallization temperature.

In each run, the heat flow to the melted polymer at 105°C was measured over the specified time of 120 minutes and plotted. This plot reflected a change in the phase of the polymer, which is the development of PLA crystals. The crystallization curve was integrated to calculate the enthalpy of crystallization. The enthalpy of crystallization was divided by the enthalpy of a theoretically 100% crystalline PLA sample (93 J/g) [Lim, L. T., et al., 2008; Avérous, L., 2008] to find the percent crystallinity. Calculated values of the percent crystallinity calculated can be seen in Figure 18.

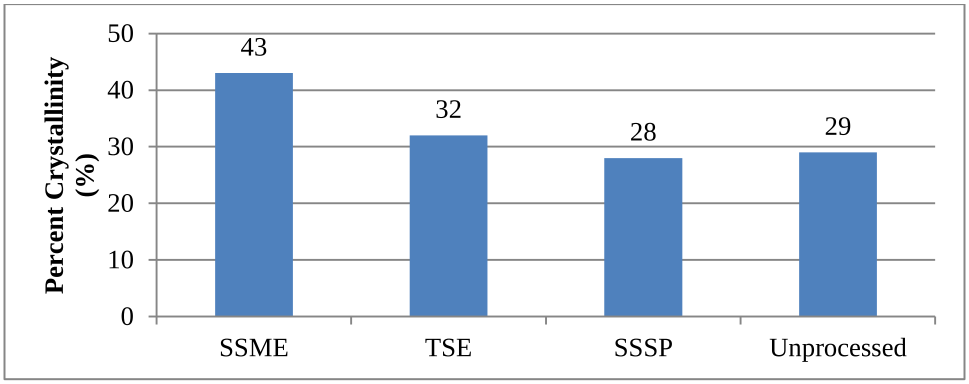

Figure 18: Percent crystallinity for each processing method

SSME-processed PLA has the highest extent of crystallization (percent crystallinity) at 43%, compared to TSE- and SSSP-processed PLA that had 32% and 28% crystallinity, respectively. TSE-processed PLA has a slightly higher degree of crystallization relative to the unprocessed sample, while SSSP-processing shows a slightly lesser degree of crystallization relative to the unprocessed sample. In TSE processing, the creation of crystals is possible because of the large amount of mixing that is facilitated in the heated state. Because of the mixing, nucleation sites are created and polymer crystals form. It is hypothesized that the lower degree of crystallinity in the SSSP sample results from the intense pulverization that occurs in the process. SSSP processes can impart significant mechanical energy to the polymer, potentially destroying some of the intramolecular bonds and reducing the length of polymer chains. As a result, a development of an organized lattice structure from these irregular lengths chains can be more difficult.

However, the increased crystallinity within the SSME sample indicates that the SSSP portion of processing allows for a larger number of defects or more chains available to participate in crystallization, while the TSE portion of SSME mixes the polymer chains so that they are evenly distributed throughout the material. The screws within the extruder are able to facilitate both mechanisms as they co-rotate to process the polymer. SSME processing allows for the optimum amount of both mixing and pulverization to create a sample with a large amount of crystal sites.

The crystallization half time ($t_{1/2}$) for each sample was also calculated using heat flow data from the isothermal crystallization. The crystallization half time was calculated as the time necessary for each sample to crystallize half way to full crystallization. Calculations were completed by graphing the relative amount of crystallization over the time of crystallization as seen in Figure 19. The crystallization half time was determined to be the time at which relative crystallization reached 0.5.

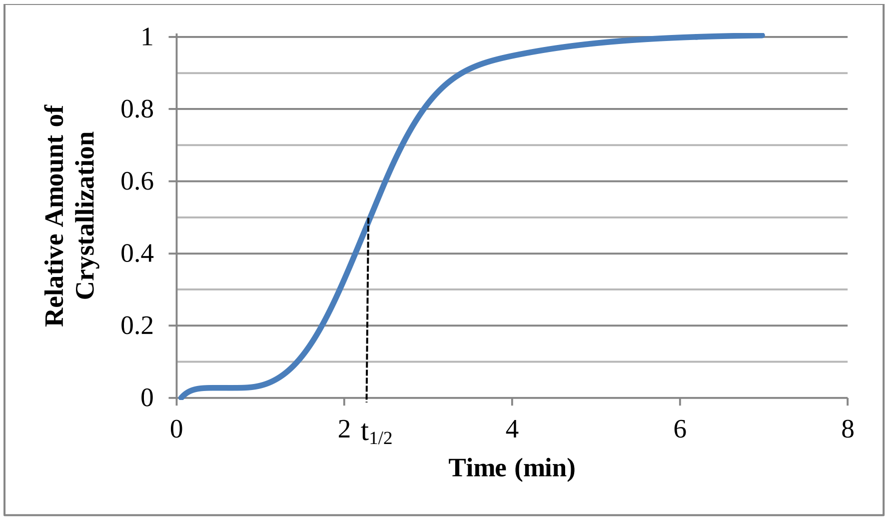

Figure 19: Example crystallization curve showing crystallization half time ($t_{1/2}$)

Table 5 shows the difference in $t_{1/2}$ between SSME, SSSP, and TSE. First, it is noted the rate of crystallization for any processed sample is significantly higher than that of the unprocessed sample. In TSE, this effect is a result of the mixing that occurs within the sample that allows for an even distribution of molecules, while in SSSP and SSME, cold pulverization allows for nucleation sites to form. The SSME-processed sample has the lowest $t_{1/2}$ as the SSSP portion of processing allows for the creation of nucleation sites, which are distributed throughout the polymer in the TSE section of the process. SSSP has the largest $t_{1/2}$ among processed samples. This result could be attributed to insufficient mixing after pulverization of the polymer had completed. In this study, the $t_{1/2}$ of the TSE-processed sample was between that of SSME and SSSP, showing that the melt mixing that occurs impacts the crystallization half time more than the degree of chain scission caused by pulverization does.

Table 5: Crystallization half time for processed and unprocessed samples

Sample	Crystallization Half Time (min)
SSME	2.3
TSE	6.9
SSSP	11.1
Unprocessed	62.4

The large differences in the crystallization behavior between each method are significant, and speak to the advantage of using SSME when faster and higher degrees of crystallization are desired. It is surprising that SSSP-processed PLA showed a smaller degree of crystallinity relative to an unprocessed sample and required the most amount of time to crystallize among the processed samples. Earlier studies at Northwestern University indicated a crystallization half time of approximately 4 minutes for SSSP-processed PLA samples when subject to a specific energy of 8 kJ/g [Brunner, P.J., 2013]. However, many processing parameters between both studies were different so a comparison of nominal times cannot be made.

Non-isothermal DSC analysis was also used to investigate how polymer crystals had developed during sheet pressing. Each sample taken from a pressed sheet was heated from -40°C to 200°C at a rate of 5°C/min and heat flow values were plotted as displayed in Figure 20.

Figure 20 shows that the SSME-processed PLA sample had a higher temperature at which the crystals within the sample melted relative to TSE- and SSSP-processed sample, indicating that the crystallites that formed within the polymer were larger and thus able to withstand higher temperatures before the crystals melted. Since polymer crystallites often contribute to a polymer's stiffness, this result implies that the stiffness of PLA can be maintained for a larger range of temperature when processed via SSME, compared to TSE and SSSP.

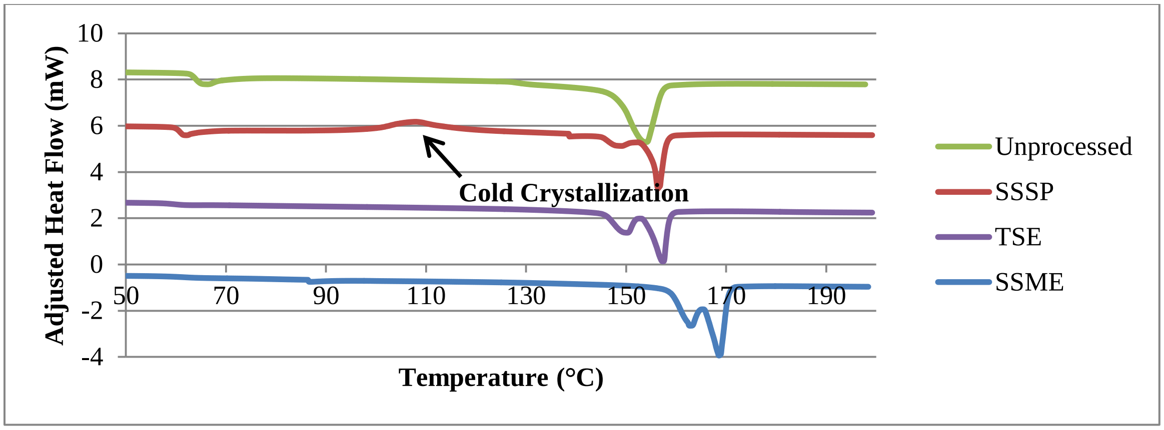

Figure 20: Non-isothermal DSC thermogram for each sample at a heating rate of 5°C/min. The curves were shifted in 3 mW increments for clarity

One can also observe a small increase in heat flow for the SSSP-processed material at approximately 110°C. The increase at this temperature shows that PLA maintains a constant degree of crystallinity from ambient temperatures to this point, but then increases in crystallinity at moderate temperatures before decreasing once again as the crystallites melt. This trend is characteristic of cold crystallization, in which a sample does not completely crystallize during the cooling that occurs after sheet pressing. The sample, at room temperature, cannot form the crystallites. When the polymer is heated to a moderate temperature, crystals form. This increase in crystallinity is expected to lead to an increase in stiffness for at the specific temperature.

4.4 Thermomechanical Properties

Dynamic mechanical analysis (DMA) was completed to quantify the changes in stiffness that were implied in DSC data. As with DSC, the samples analyzed were taken from a pressed sheet. The stiffness was quantified by the storage modulus of each sample (E'), as seen in Figure 21, over a range of temperatures from 25°C to 160°C.

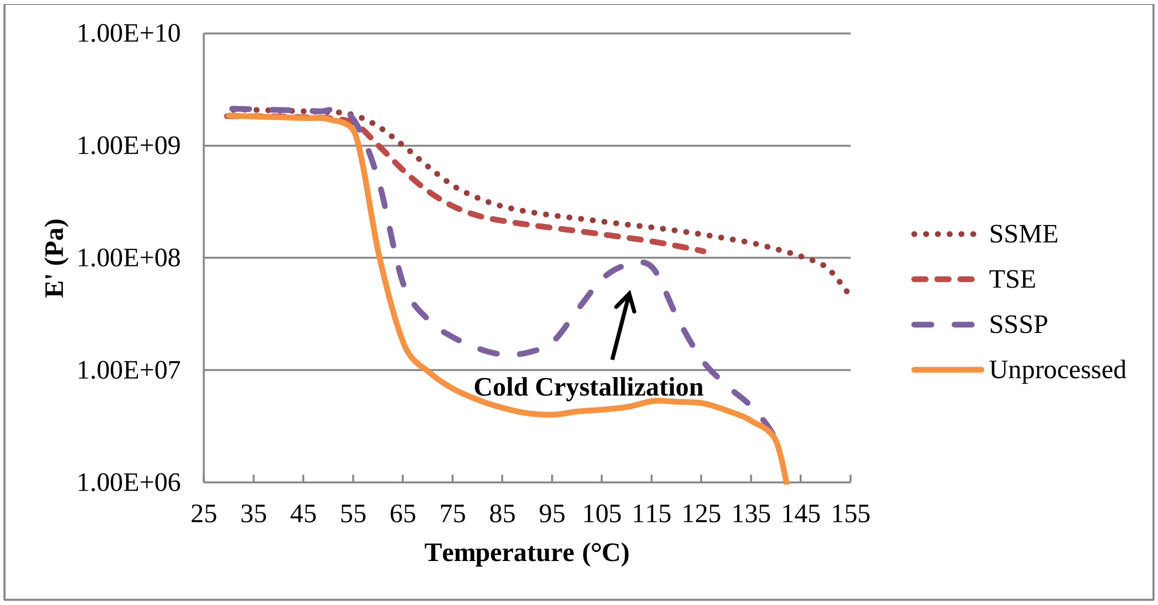

Figure 21: Storage modulus for each processed an unprocessed sample from 30°C to 155°C

Each sample shown in Figure 21 decreases in stiffness at approximately 60°C as this is the glass transition temperature of PLA. Further decreases in stiffness can be seen at approximately 135°C as this is PLA's melting temperature [Lim, L.T., et al., 2008]. Processing through any type of extrusion is shown to increase the stiffness of PLA as a result of an increasing number of crystallites within the sample. The crystallites increase the rigidity of the polymer and allow it to be stiffer across all temperatures.

Though the storage modulus for the SSME-processed PLA resembles the shape of TSE-processed PLA, it is clear from Figure 21 that the magnitude of the storage modulus across all temperatures is less for the TSE-processed sample than the SSME-processed sample. The TSE-processed sample also melted after 125°C, while the SSME-processed PLA sample was able to maintain a storage modulus about 10^8 Pa until 145°C. Compared to the unprocessed sample, both the TSE-processed and SSME-processed PLA sample resemble a similar shape, but the storage modulus for the unprocessed sample is lower at all times because of the lack of crystals.

The magnitude of the storage modulus of each process sample was then compared to one another at various temperatures, as shown in Figure 22. Figure 22 suggests that while all PLA samples have similar stiffnesses at ambient temperatures, only the SSME-processed PLA sample retains most of its stiffness as the temperature increases. PLA processed via SSSP loses stiffness very quickly with only minimal temperature increase past the glass transition temperature. The PLA sample processed via TSE maintains a high value of stiffness similar to SSME, but loses all stiffness after melting at 125°C. The sample processed via SSME holds its stiffness for the longest period of time and maintains a higher stiffness than samples processed via TSE and SSSP throughout a wider range of temperatures. This is consistent with DSC data discussed above. DSC data showed a decrease in crystallinity for both TSE and SSSP-processed samples before that of SSME-processed samples. Figure 22 shows that decrease in crystallinity results in a decrease in stiffness at those temperatures.

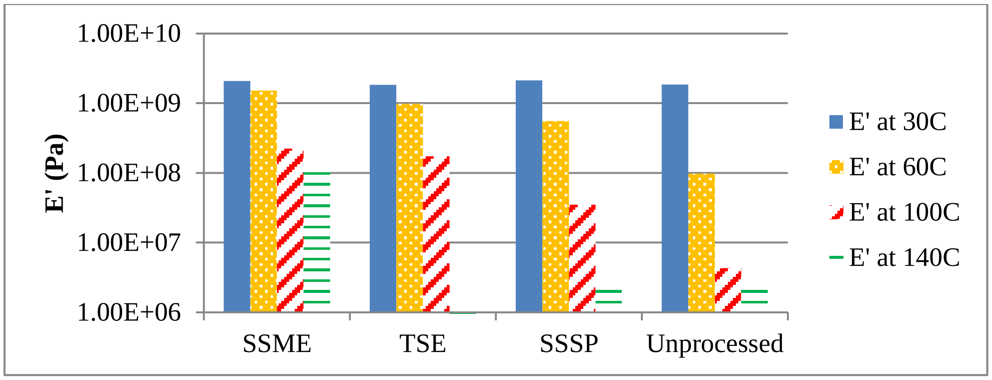

Figure 22: Storage moduli of PLA processed samples at 30°C, 60°C, 100°C, and 140°C

Additionally, it is noted that the stiffnesses at specified temperatures in Figure 22 of the processed samples are all higher than that of an unprocessed sample. The unprocessed sample has a stiffness at 60°C and 100°C that is approximately one order of magnitude less than that of the SSSP-processed PLA, the polymer with the lowest stiffness at these temperatures. Thus, it can be concluded that processing PLA through any of these methods, followed by melting the polymer into a pressed sheet allows PLA to gain an increase in stiffness relative to an unprocessed sample of PLA that is just melted.

DMA data also provided important implications about the heat stability within the material by showing the temperature at which the polymer decreased in stiffness significantly. The softening temperature of the PLA was defined in this study as the temperature at which the polymer decreased in stiffness by at least three orders of magnitude from the original stiffness. Figure 23 displays that the softening temperature of the SSME sample is significantly higher than all other types of processing. The increased amount of crystals within the PLA sample adds to the strength of the material and creates a sample that is much more resistant to higher temperatures.

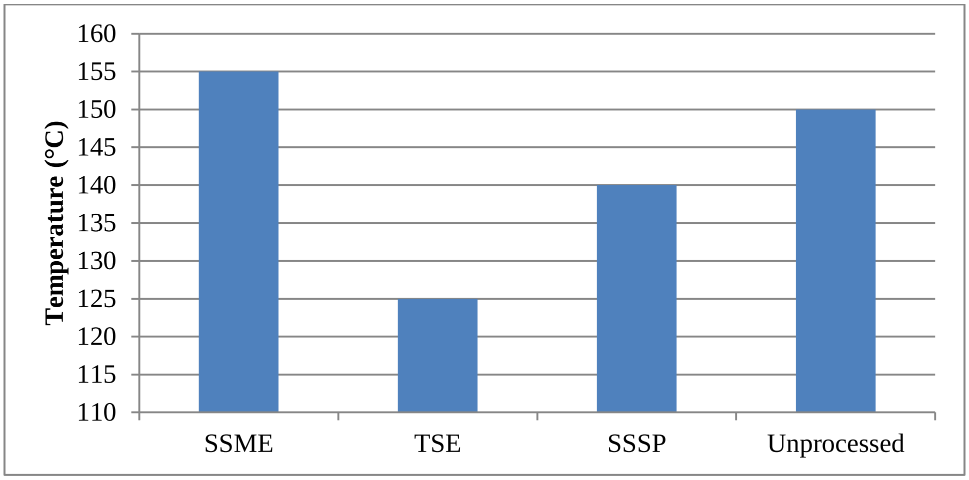

Figure 23: Softening temperature of each processing method

4.5 Thermal Degradability

The next step after comparing each PLA sample's thermal stability and softening temperature was to evaluate each sample's thermal degradation characteristics. A higher degradation temperature indicates a polymer's increased thermal stability, which is often associated with a higher average polymer chain length [Qu, X., et al., 2000]. This concept thus relates to the decomposition of the polymer, by way of chain scission that occurs when the polymer is processed through one of the three processes.

In this analysis, the temperature at which a 5% loss in mass was seen for each polymer was found and compared to other samples in Figure 24. Based on these temperatures, one can infer the relative degree of chain scission and thus degradation that occurred in the polymer through each processing method.

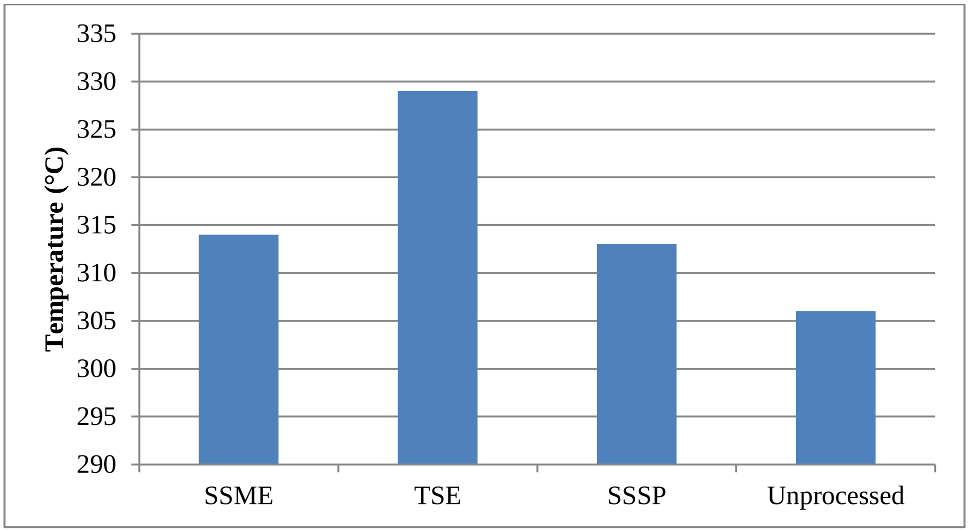

Figure 24: Degradation temperature for each processing technique at a 5% loss

One can observe that all processed sample have a higher degradation temperature than an unprocessed sample, indicating that processing in any of these three methods has an increasing effect on the sample's resistance against degradation. PLA processed through TSE has the highest degradation temperature followed by SSME, and SSSP. This indicates that TSE processing allows PLA to resist chemical degradation more so than SSME and SSSP processes. Though this seems to contradict molecular weight and softening temperature data, one explanation for these results could be related to crystal size. Crystal size was not measured by any method in this study, but an explanation for the results could be that crystals within a TSE-processed sample are larger and thus have a greater resistance to melting under high temperatures. However, further testing needs to be performed to confirm this explanation. When analyzing the other processed samples, one can see that the degree to which SSME allows for thermal degradation of PLA is slightly more than that of SSSP. Through TGA data, it is inferred that the cold pulverization portion of extrusion has the greatest effect on the thermal degradation of PLA. The degradation temperature for SSSP is lower than for TSE, and as expected, SSME is between TSE and SSSP. This shows that the cold pulverization decreases PLA's ability to resist chemical degradation more so than melt mixing. It is therefore implied that cold pulverization causes a higher degree of chain scission within the polymer than melt mixing.

4.6 Molecular Structure

While TGA results suggest relative degrees of chain scission, gel permeation chromatography was chosen as the method to analyze the polymer's true molecular structure. GPC is a size exclusion method of chromatography that can show a polymer's number average molecular weight (M_n) and weight average molecular weight (M_w). Differences in molecular weights can show the varying degrees of chain scission that occurs within a polymer. From these data, implications can be made about the relative harshness of a process by identifying which process breaks the largest amount of bonds and thus, causes the largest amount of degradation. This method of analysis allows one to measure the average chain length of a given polymer in a direct manner. Results for each type of processing method can be seen in Figure 25.

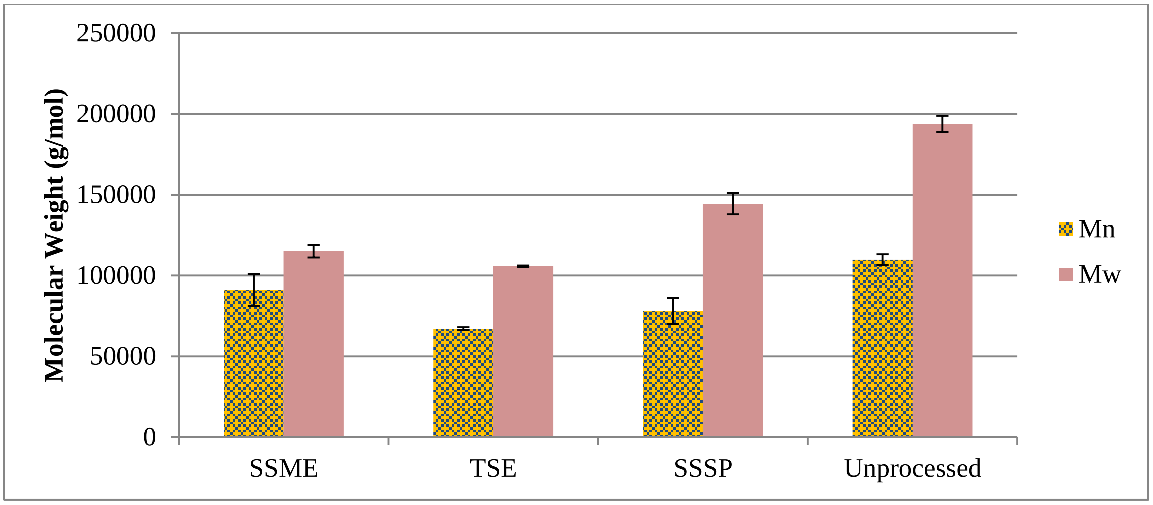

Figure 25: M_n and M_w for each processing technique. All error bars represent 1 standard deviation between the two reported trials

All processed samples have much lower M_n and M_w values than the unprocessed sample as a result of chain scission during processing. The chain degradation in terms of the reduction in M_n is greatest when processing with TSE, followed by SSSP and SSME. M_w data shows a similar trend except that the SSME-processed sample has a higher degree of degradation than SSSP-processed sample. Overall, however, the difference in molecular weights is small and among processed PLA and thus the degree of degradation can be considered minimal when comparing the across processed samples. In this study, the greatest degree of chain degradation occurred in TSE processing. The polymer's M_w

decreased from 194,000 g/mol to 144,000 g/mol and M_n from 110,000 g/mol to 67,000 g/mol.

The data for unprocessed samples are relatively consistent with literature data as most sources report an M_n for NatureWorks PLA at approximately 110,000 and an M_w at approximately 200,000 g/mol [Gámez-Pérez, J., et al., 2011; Mallet, B., et al., 2013; Pantani, R., & Sorrentino, A., 2013]. The SSSP-processed PLA M_n and M_w data, however, are approximately 30% higher than those found at Northwestern [Brunner, P. J., 2013]. This could, again, be due to the harshness of the SSSP process.

4.7 Ambient Mechanical Properties

Mechanical testing at room temperature was completed via a uniaxial tensile testing. Tensile testing results in a stress-strain curve, from which one can calculate the yield strength, breaking strain, and Young's modulus. These three quantities correspond to a polymer's strength, ductility, and stiffness, respectively. All data shown is an average of 5 specimens taken from identical samples.

Figure 26 shows the yield strength of all methods of processing. The average yield strength of all processed PLA is very similar. Samples processed via SSSP have a slightly higher average yield strength than those processed via SSME and TSE, but when considering the error bars representing one standard deviation of each sample, all samples produced relatively the same yield strength as one another.

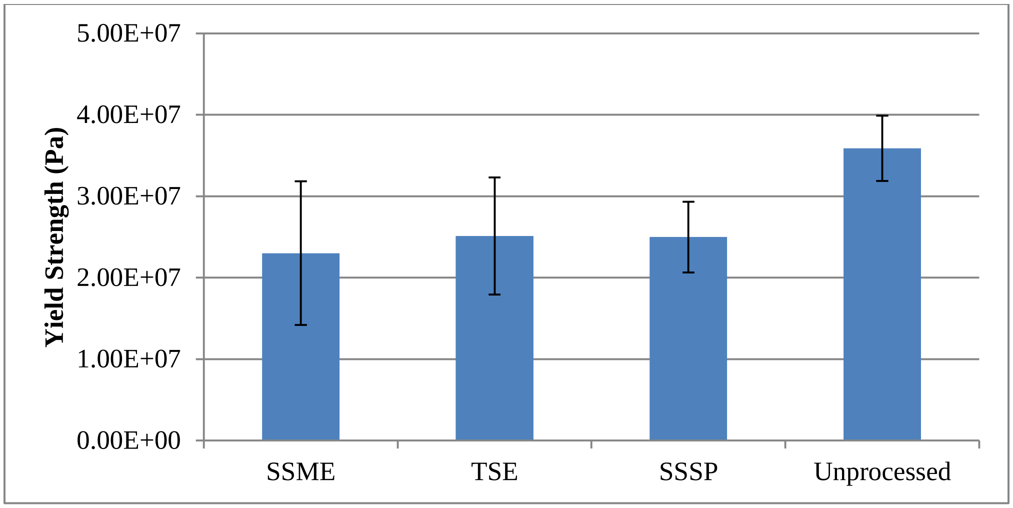

Figure 26: Average yield strength of each processing method. The error bars correspond to one standard deviation in our measurement

Figure 27 shows the average breaking strain of PLA processed through each processing method. As with yield strength, the averages for each method are very similar to one another. Samples processed through TSE have a slightly higher average breaking strain than those processed through SSME and SSSP. The averages, however, for all samples are not significantly different from one another. PLA processed via SSSP has the highest average breaking strain, but that is only approximately 6%. On the contrary, the unprocessed samples have a breaking strain of 12%. These data show how brittle PLA is and how much more brittle it becomes as it is processed. These data can be explained using theory about the degree of processing. When a polymer is subject to a large amount of chain scission, some molecules may get degraded to such an extent that they behave more like short chain molecules (oligomers) rather than polymers. Oligomers, generally, have more brittle properties than polymers and break with much less strain applied to the material. Therefore, the PLA samples could have been processed in such a way that the intensity of the processing lead to a mechanical behavior similar to that of a PLA oligomer. The oligomers would have a much lower breaking strain, like the processed samples seen in Figure 27 where all processed samples have a breaking strain that is, on average approximately half of the unprocessed sample.

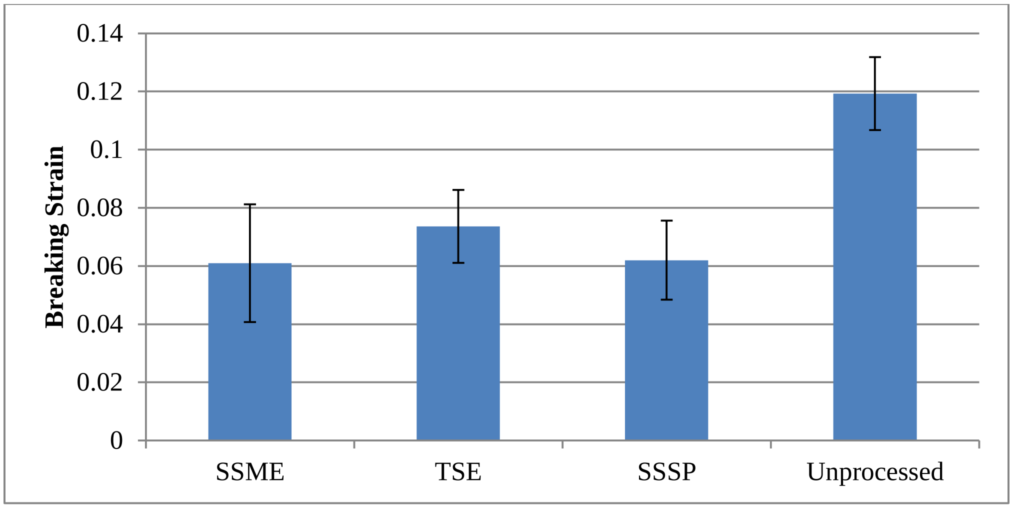

Figure 27: Average breaking strain of PLA processed through each method. The error bars correspond to one standard deviation in our measurement

The average Young's modulus of PLA processed through each processing method is shown in Figure 28. The Young's modulus was also not statistically different from one another across processing methods. SSME is reported to have the highest average Young's modulus of 5.26 x 10^8 Pa, while TSE has the lowest average Young's modulus among processed samples of 5.23 x 10^8 Pa.

This data can be compared to the storage modulus or stiffness data found at 30°C in DMA testing. The data suggests that there is approximately a factor of 2 difference between the two sets of data as the DMA data suggests that the stiffness of PLA at 30°C is approximately 1.00 x 10^9 Pa, while tensile testing suggests that the stiffness is approximately 0.5 x 10^9 Pa. Tensile test data does however agree that the differences in yield strength among processing methods is relatively small when looking at the stiffness of the polymer.

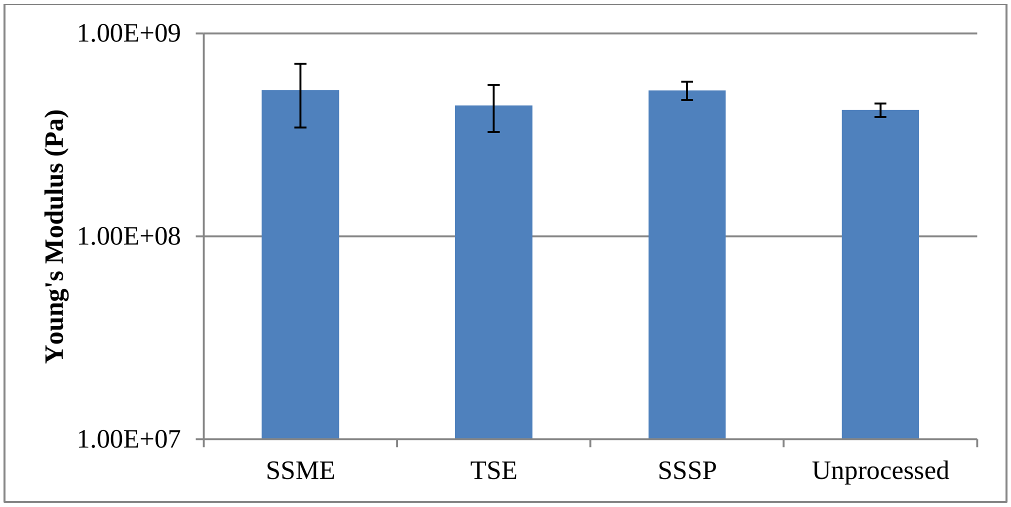

Figure 28: Average Young's modulus of PLA processed through each method. The error bars correspond to one standard deviation in our measurement

Overall, the mechanical properties of yield strength, breaking strain, and Young's modulus provide little information about the superiority of one processing method over any other. All processed samples recorded results that were not statistically different from one another when accounting for one standard deviation of error.

The data also can be compared to the mechanical properties of samples of PLA processed via SSSP and TSE at Northwestern University. Mechanical studies on SSSP-processed PLA show the yield strength to be 6.12 x 10^7 Pa, the breaking strain to be 0.08, and the Young's modulus to be 2.7 x 10^9 Pa. The data collected in this study's mechanical tests seem to be much lower than that of the Northwestern University data in all categories. Similarly, other studies also suggest the yield strength of unprocessed PLA to be approximately 60.0 x 10^6 Pa and the Young's modulus to be approximately 2.5 x 10^9 Pa [Jonoobi, M., et al., 2010; Oksman, K., et al., 2003; Yang, S. L., et al., 2008].

When analyzing mechanical properties, it can be seen that across all three parameters, the processing methods produced relatively similar results and thus, little information can be gained about the superiority of one processing method over another. One reason for the small deviation between samples could be the shape of the polymer tested. From pressed sheets, each sample was cut into a rectangle instead of a dogbone shape. The reason for this change was because of the brittleness of PLA. In initial studies, it was found that when the tensile tester was used to test samples in the ASTM D1708 dogbone shape, the PLA would crack before a test could be completed. However, here it is hypothesized that this rectangular shape does not produce data that is representative of the true mechanical properties of the material. In future studies, a different ASTM standard shape may be considered to verify the results presented above.

4.8 Summary

From all tests completed, the SSME-processed PLA displays much more favorable qualities in terms of the percent crystallinity and the rate at which the polymer crystallizes. It is clear that PLA processed via SSSP and TSE has some desirable properties in regard to mechanical and molecular properties, but fails to surpass SSME processed samples in thermal properties. Even though SSME-processed PLA sample did not always have the greatest degradation and mechanical properties, the results in a given test of an SSME sample were relatively close to the highest performing in the group of samples analyzed.

The results conclude that when processing PLA, SSME is a very viable method if thermal properties are of importance. In the following chapter, the optimization of the SSME process is considered to examine if PLA processed with different SSME conditions results in products with different properties. The optimization chapter will consider variations in screw design and throughput to examine their effect on the thermal and mechanical properties of PLA.

5. Optimization of SSME Processing Parameters

5.1 Introduction

The previous chapter identified SSME as the processing technique with the greatest potential to minimize the time needed to process PLA and maximize the degree to which PLA could crystallize. In this chapter, SSME-processed PLA under different processing conditions will be analyzed to determine which parameters have the most impact in maximizing the thermal and mechanical properties of PLA.

The parametric study employed the same extruder and the same thermal and mechanical property testing and structural characterization techniques as in the previous chapter. Tensile testing was not part of the testing procedures in this study because the previous study found that the rectangular sample shape did not accurately portray the true mechanical properties of the samples. The KrausMaffei Berstoff ZE-25A UTX Extruder was manipulated in two different ways: screw design and flow rate into 9 configurations using 3 different screw designs and 3 different flow rates. The screw designs were selected based on the SSME screw design in the last chapter. One screw was designed to be harsher and one was designed to be milder than the original moderate screw design. The harsher screw design is designated with SMHS, the original (moderate) with SMMD, and the mild with SMML. Table 6 lists each of the three screw designs and their components. Essentially, the screw harshness is a factor of the ratio of conveying to kneading elements with a higher ratio implying less processing and thus a milder screw.

The harsh screw has 9 kneading elements in contrast to the very mild screw, which has only 4 kneading elements.

Table 6: Screw design elements contained within the screws used for optimization trials

Sample Category	**Conveying Elements**	**Forward Kneading Elements**	**Neutral Kneading Elements**	**Reverse Kneading Elements**
SMML	30	4	0	0
SMMD	27	6	1	0
SMHS	24	7	2	0

The flow rate to the extruder, referred to as the throughput of the material, was also varied between slow, medium and fast feed rates. 250 g/hr was used in Chapter 4 as the standard flow rate. Because of the limiting specifications on the feeder, it is difficult to feed pellets at a rate slower than 250 g/hr. As a result, medium and fast flow rates of approximately 500 and 750 g/hr, respectively, were chosen for each screw design. Table 7 lists the processing conditions for each trial.

Table 7: Processing conditions for all samples used in the optimization study

Sample	**Processing Method**	**Dried or As Received**	**Screw Design**	**Screw Number**	**Throughput (g/hr)**
SMML1	SSME	As Received	Mild	SSME007	250
SMML2	SSME	As Received	Mild	SSME007	500
SMML3	SSME	As Received	Mild	SSME007	750
SMMD1	SSME	As Received	Moderate	SSME005	250
SMMD2	SSME	As Received	Moderate	SSME005	500
SMMD3	SSME	As Received	Moderate	SSME005	750
SMHS1	SSME	As Received	Harsh	SSME004	300
SMHS2	SSME	As Received	Harsh	SSME004	500
SMHS3	SSME	As Received	Harsh	SSME004	600

All other parameters such as screw speed and the temperatures of the heated zones were maintained at the values used for the SSME sample presented in Chapter 4 and are listed in Table 8.

Table 8: Parameters used for SSME processing in optimization study

		Temperatures (°F)				
Sample	**Screw Speed (rpm)**	**Zone 6**	**Zone 5**	**Zone 4**	**Zone 3**	**Zone 2**
SSME	200	390	380	70	0	0

5.2 Thermal Properties

Each processed sample was pressed into a 0.5 mm sheet and analyzed for its thermal properties. Isothermal crystallization was completed for all samples at the temperature of 105°C. Figure 29 displays the percent crystallinity of each trial.

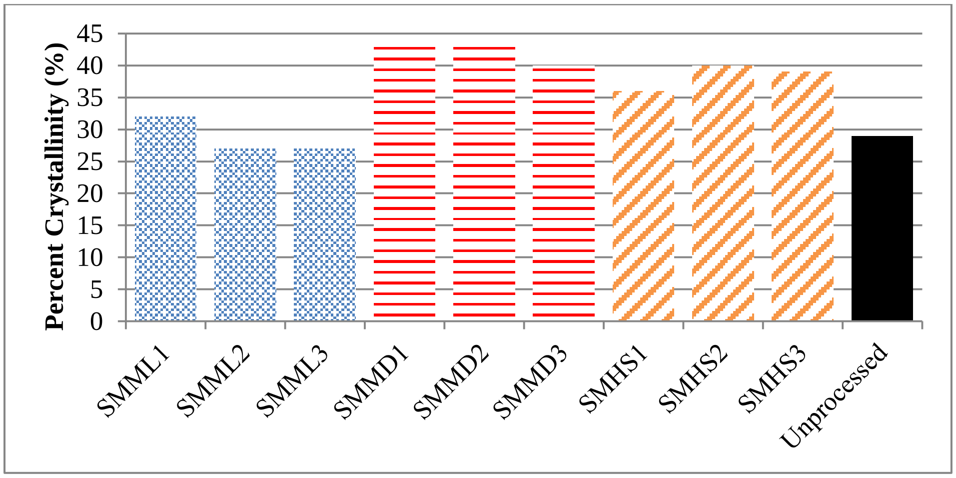

Figure 29: Percent crystallinity for all 9 SSME-processed PLA samples, measured via isothermal crystallization at 105°C

The samples processed with the moderate screw design have the highest degree of crystallinity, followed by those processed with the harsh screw design. Figure 29 shows that the samples processed with the mild screw design have similar levels of crystallinity as the unprocessed sample. From these data, it is surmised that the mild screw design did not process the polymer with sufficient shear and compressive forces to induce an increased crystallization activities in the polymer. However, when PLA is processed using a moderate screw design, the degree of crystallinity greatly increases as this allows for a larger degree of chain scission in the SSSP portion of the extruder. Figure 29 also suggests that screw design is a more important parameter than flow rate. Within each screw design, there is little variation of the percent crystallinity, but when compared with other screw designs, there is a clear difference in crystallinity.

The SMMD1 and SMMD2 sample achieved the highest percent crystallinity of 43 and 44%, respectively. A reason for this could be that the low and medium rate and moderate screw design are optimum for producing crystals within PLA. The moderate screw design allows for pulverization to occur such that an optimum amount of chain scission happens. Within the polymer, some degree of chain scission allows more polymer chains to participate in crystallization. The pulverization in SMMD1 and SMMD2 is not so harsh that the polymer chains are scissioned to a degree where they are unable to crystallize because of their small size but not so mild that an insufficient amount of nucleation sites are created. The moderate flow rate allows for an optimum amount of polymer within the extruder at any given point in time so that effective pulverization can occur. The data show that among screw designs, the moderate screw design produces the highest percent crystallinity and among flow rates, the samples with a medium flow rate tended to have the highest percent crystallinity. The SMMD screw design has fewer kneading elements within the chilled region than the SMHS screw design and therefore pulverizes the polymer to a lesser extent. The mild flow rate allows for a large amount of PLA to melt in the heated zones, but not so much that the melting of the polymer within the zones becomes ineffective to create crystallites. Combined, these two parameters allowed PLA to crystallize to the largest extent within the extruder.

Additionally, from the isothermal crystallization data, the crystallization half times are displayed in Table 9. These data agree with the percent crystallinity data above in that PLA processed with the SMML screw resemble an unprocessed sample more than an SSME-processed PLA sample with an SMMD or SMHS screw design.

Table 9: Summary of crystallization half times for SSME-processed samples

Sample Number	**Crystallization Half Time (min)**
SMML1	13.9
SMML2	14.3
SMML3	13.6
SMMD1	2.3
SMMD2	2.8
SMMD3	3.3
SMHS1	2.2
SMHS2	2.8
SMHS3	3.0
Unprocessed	62.4

Crystallization half times are relatively similar for PLA processed with a moderate and harsh screw design across all three flow rates. The time necessary to crystallize with a mild screw is approximately 5 times that of a moderate or harsh screw. However, compared to an unprocessed sample, the time necessary to crystallize is significantly less, suggesting that some structural change has taken place in the SMML samples, but larger structural changes have occurred in the SMMD and SMHS samples. The SMMD and SMHS samples are shown to have very small crystallization half times as a result of the increased pulverization. The increased pulverization allowed for creation of more nucleation sites within the polymer. A higher number of nucleation sites decreased the overall time necessary for the polymer to crystallize. Between samples produced with these two screws, there is little difference in the crystallization characteristics. These data could suggest that the moderate screw design is an optimum screw design for creating crystals, and when the harshness of the screw is increased, there is little effect on the amount of crystals or the time needed for the sample to crystallize. Thus, these characteristics of the sample start to decrease at this point, but only slightly because both screw designs provide a level of processing that allows the maximum amount of nucleation sites to be created within a polymer sample.

In addition to isothermal DSC, non-isothermal DSC was employed to depict the trends of crystallization when heating pressed PLA from 30°C to 200°C at a rate of 5°C/min. These data were compiled to gain insight into the molecular behavior of the polymer when heated at this rate in the DMA tests. Figure 30 displays all non-isothermal heat flow curves as a function of temperature.

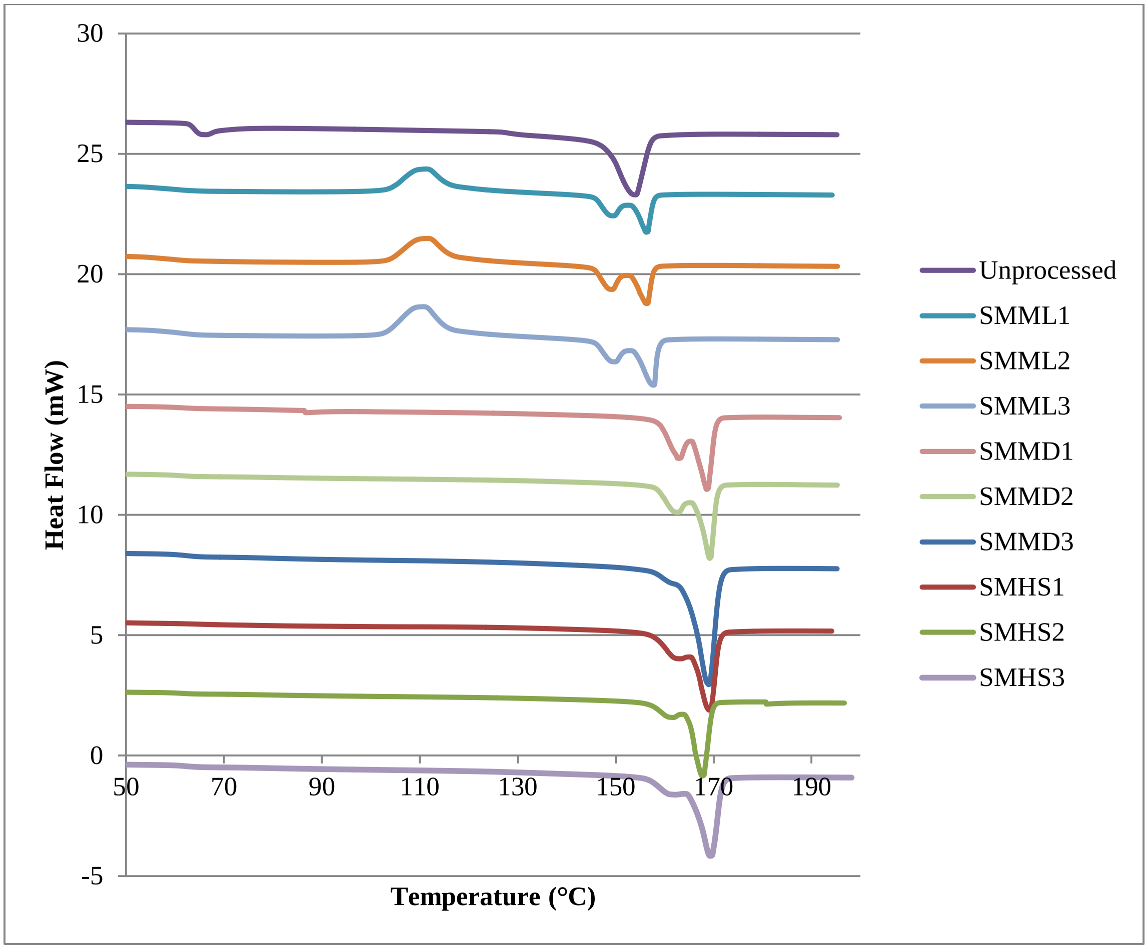

Figure 30: Heat flow for all SSME-processed PLA samples. All trials were shifted in 3 mW increments for clarity

Figure 30 shows that all samples were consistent in shape within a specific screw design. The mild screw design produced a moment of cold crystallization around 110°C that resembles that of SSSP-processed PLA, discussed in the previous chapter. The slight increase in crystallization at that point suggests an increase in the stiffness of the polymer at that temperature. Figure 30 also shows a shift in the melting point of the polymer samples as the processing method increases in harshness. All samples extruded with the mild screw exhibited this characteristic and a melting point that was much less than that of the moderate or harsh screw designs. This shows that harsher processing allows for greater chain scission so that more sites can participate in crystallization.

5.3 Thermomechanical Properties

DMA was used to examine the stiffness of the polymer as the polymer was subjected to a 5°C/min ramp heating over the temperature range of 30°C to 160°C. The stiffness of the polymer was measured with storage modulus (E'), as done in the previous chapter. Figure 31 shows that samples SMML1, SMML2, and SMML3 all started to increase in stiffness at approximately 105°C—the cold crystallization temperature, as expected, and then decreased in stiffness as the crystals melted from the pressed sheet. Though greater in magnitude at the cold crystallization curve, the SMML storage modulus values at temperatures other than the cold crystallization temperature range are similar to the unprocessed sample. Thus, the mild processing can be concluded to have little overall effect on the polymer except for the range of temperature between its cold-crystallization and melting temperatures. The mild screw design allowed the polymer to be pulverized to a lesser extent so that a relatively smaller percentage of the polymer was scissioned. This led to the creation of fewer defect sites relative to the SMMD and SMHS samples, which acted as nucleation sites only at the cold crystallization temperature. Therefore, the storage modulus at the cold crystallization temperature is observed to have increased with mild processing relative to an unprocessed sample.

However, all other storage moduli are similar in magnitude to those of the unprocessed sample at all other temperatures.

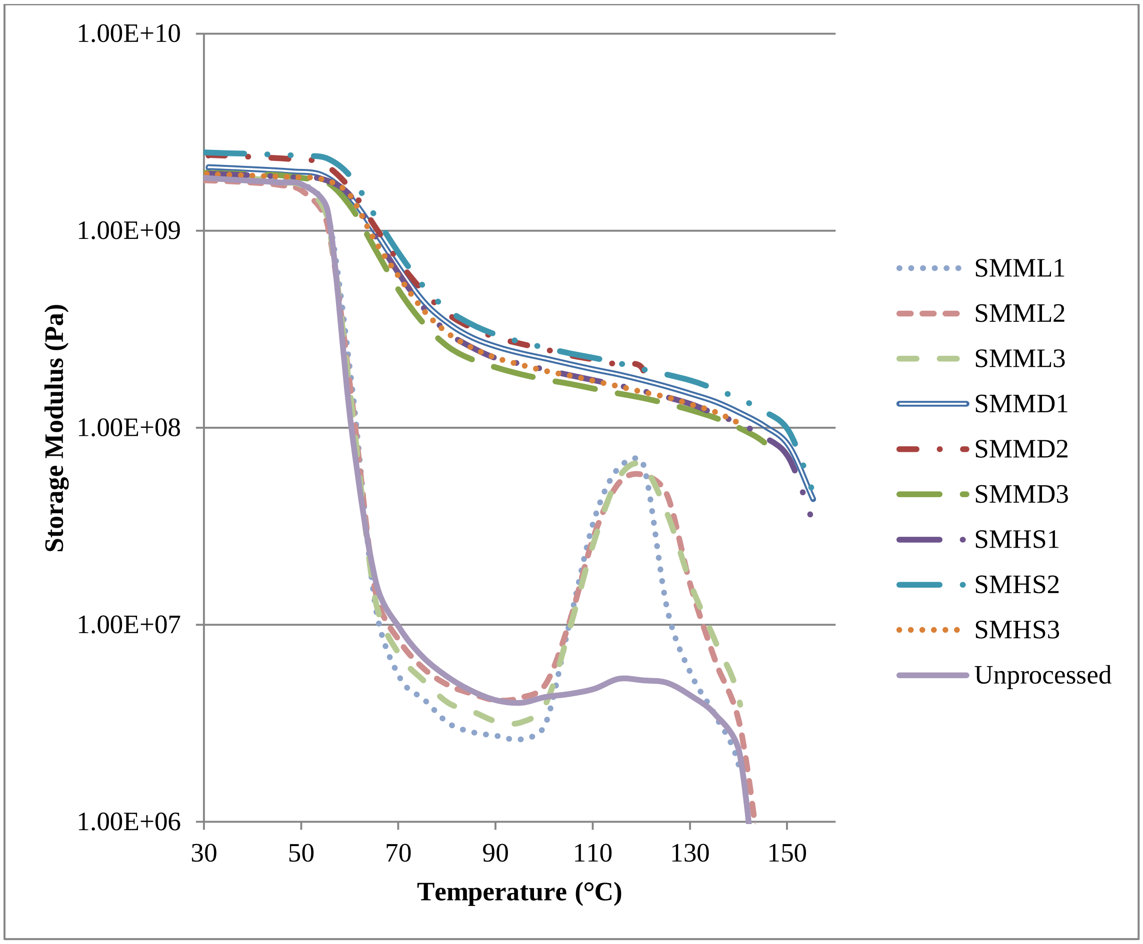

Figure 31: Storage modulus of SSME-processed PLA between 30-160°C

Trends in the samples processed with a moderate and harsh screw design showed very similar shape and magnitude. Samples SMMD1-3 and SMHS1-3 all have a very high stiffness for the majority of the heating process. The stiffness of each sample decreases approximately one order of magnitude at PLA's glass transition temperature

(~60°C) and then loses further stiffness at PLA's crystallization temperature (~140°C). Within these samples, there is very little difference in the magnitude between screw designs and polymer flow rates. This trend agrees with DSC data in that the samples processed with moderate and harsh screw designs have very similar thermal properties. The similarities in crystallinity across a wide range of temperatures translate to similarities in the stiffness of the polymer over the same range of temperatures.

Further differences in the stiffness profile for each polymer is the softening temperature, or the temperature at which the polymer experiences a decrease in stiffness that is greater than or equal to 3 orders of magnitude. The softening temperature for each SSME-processed sample can be seen in Figure 32.

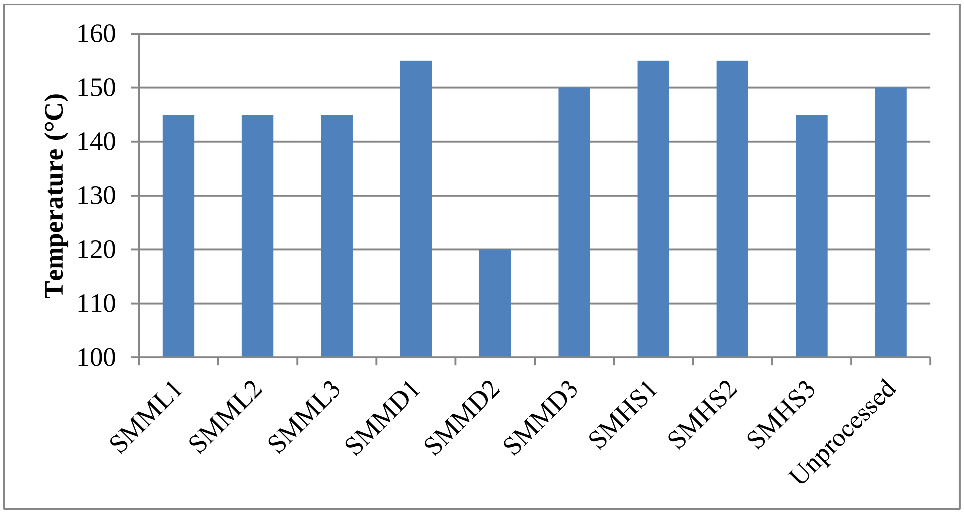

Figure 32: Softening temperature of SSME-processed PLA

This softening temperature for each sample is within 10°C of one another except for sample SMMD2. The SMMD2 sample is shown to have a relatively lower softening temperature. Though all other DSC data and DMA trends indicate SMMD2 to be similar to other SMMD trials, the softening temperature reveals an apparent weakness in the material. All SMML samples have the same softening temperature of 145°C, while the SMMD and SMHS sample seem to decline in softening temperature as the flow rate increases. This indicates that the heat stability of PLA decreases slightly with increasing flow rates. This phenomenon could be explained by the decrease in the total crystallinity as the flow rate of the polymer increases. At a lower flow rate, the polymer is able to melt and mix the material completely, but at higher flow rates, both the melting and the mixing are insufficient and cause a decrease in total crystallinity. Because there are less crystalline structures, the polymer does not retain its rigidity as the temperature increases to larger values.

5.4 Thermal Degradability

The thermal degradation of the polymer was measured by TGA, identifying the degradation temperature at a 5% mass loss. Samples were inserted into the TGA and heated from 30°C to 600°C at a rate of 10°C/min. The degradation temperatures in Figure 33 indicate a decrease in degradation as the flow rate and the harshness of processing increase.

Low thermal degradation temperatures, such as those seen in all SMHS samples, indicate the relative degree of harsh processing that occurred. Harsher processing leads to a larger number of chain scissions and therefore, a larger reduction in molecular weight. This reduction in molecular weight causes the polymer to vaporize at a lower temperature and thus, have a lower degradation temperature.

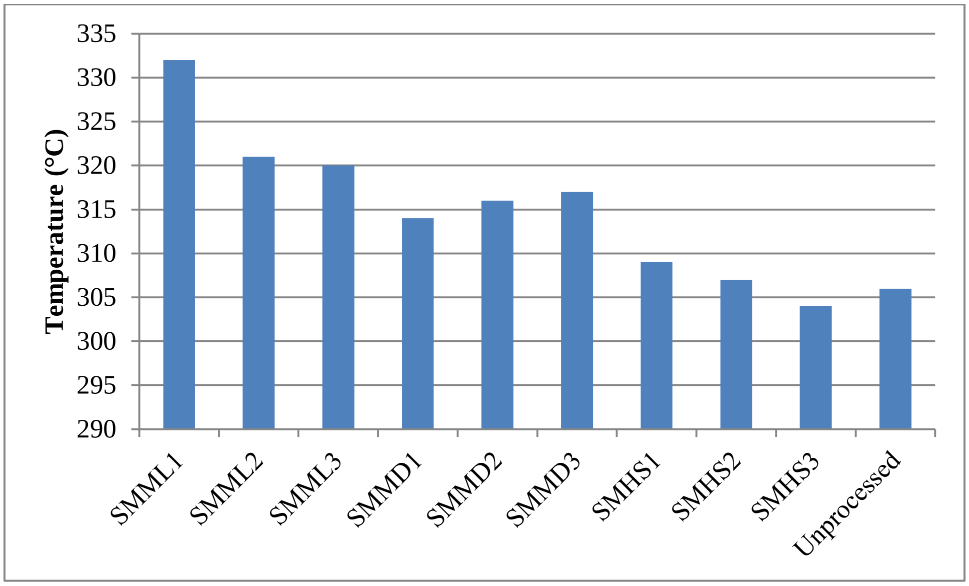

Figure 33: Degradation temperature for each SSME-processed sample, defined as the temperature at a 5% mass loss

SMMD trials show the opposite trend in terms of flow rate, but the magnitude of difference between samples is considerably less than those of the very mild and harsh screw design-processed samples, since the degradation temperature of SMMD1-3 are all within 5°C of one another, showing relatively constant values across the screw design. In the extruder, this indicates that as the pulverization of samples increases in harshness, the amount of chain scissions also increases. Even though the increased chain scission could cause an increase in the amount of crystallites formed, the small polymer chains evaporate at a lower temperature than the longer polymer chains produced by less harsh screw designs.

5.5 Molecular Structure

To confirm hypothesis about chain scission and the physical degradation of the polymer chains, all samples processed by SSME were tested in GPC runs for their number average (M_n) and weight average (M_w) molecular weight, as seen in Figure 34. These data show the degradation at a molecular level, as a lower molecular weight indicates a larger amount of chain scission and thus degradation.

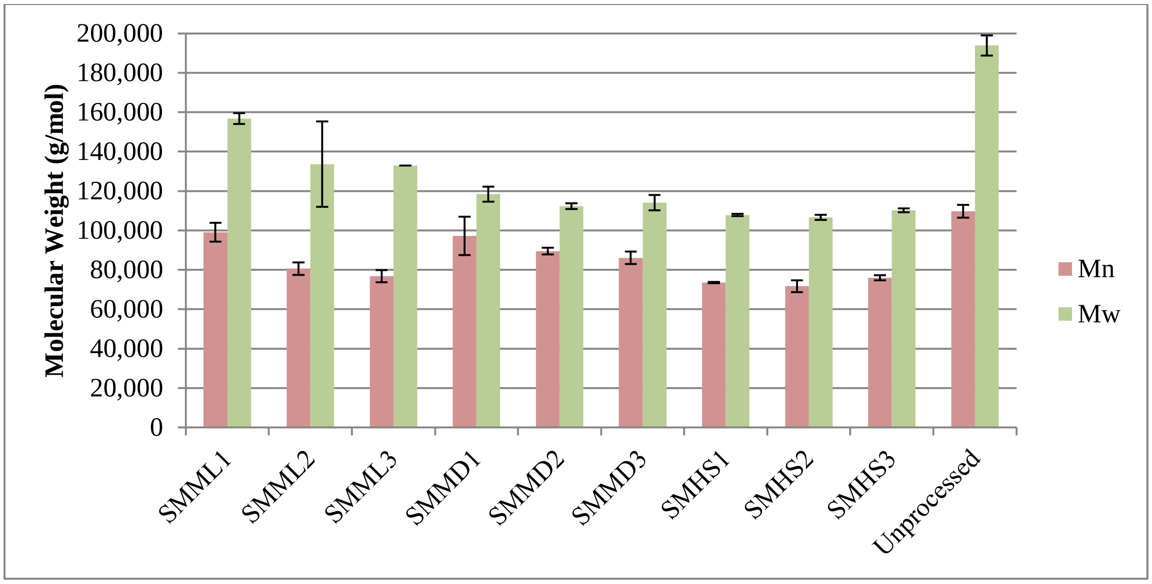

Figure 34: M_n and M_w for all SSME-processed PLA samples. All error bars represent one standard deviation between the two reported trials

Figure 34 displays a decreasing trend in M_n and M_w as the flow rate and harshness of the processing method increase. SMML samples have a larger molecular weight than SMHS samples and within all screw designs, samples processed with increased flow rates have decreased molecular weights. Figure 34 shows that the number average molecular weight is very similar in magnitude in SMML samples as in SMMD samples. There is very little difference when comparing these two sets of data and one can surmise that there was a very similar amount of chain scission that occurred within the polymer. Samples produced with these screw designs may not be distinguishable in a number average molecular weight sense. However, the weight average molecular weight decreases rather consistently as flow rate and screw harshness increase and clearly shows the difference in the degree of chain scission that occurs during processing. Samples processed with a harsh screw design are shown to have a lower M_w.

From the weight and number average molecular weights, the polydispersity index (PDI) was calculated using equation 2:

$$PDI = \frac{M_w}{M_n} \qquad (2)$$

The PDI for a given polymer examines the variation in chain length among the sample. Table 10 shows the PDI for each sample in this study. The PDI with a specific screw design is relatively constant, but between screw designs, there is some variance with the SMML screw designs having the highest PDI followed by the SMHS and SMMD screw designs. The low PDI in the SMMD samples exemplifies ideal pulverization in this study. The moderate screw design chosen gave the polymer sufficient time to pulverize the polymer chains uniformly, causing a relatively narrow distribution of molecular weight. The SMML and SMHS samples have relatively higher PDIs, which can be attributed to a screw design that did not allow for sufficient, uniform pulverization.

Table 10: Polydispersity Index for SSME-processed PLA samples

Sample Number	Polydispersity Index
SMML1	1.58
SMML2	1.66
SMML3	1.73
SMMD1	1.22
SMMD2	1.26
SMMD3	1.33
SMHS1	1.47
SMHS2	1.49
SMHS3	1.45
Unprocessed	1.77

The SMML screw design is considered to be not harsh enough, while the SMHS screw design is considered to be too harsh for PLA. The increased harshness caused an increase in chain scission to a large fraction of the polymer, but much of the polymer remained unchanged.

5.6 Summary

It can be concluded that PLA samples processed via SSME have higher thermal and molecular degradation properties when a moderate screw design is used. A moderate screw design allowed the pulverization within the extruder to induce defects with the polymer, causing large amounts of nucleation sites and therefore, high amounts of crystallinity. Mild screw designs were shown to process the polymer in such a way that less defects were formed so additional nucleation sites contributed to a decreased amount of time necessary to crystallize. PLA processed with a harsh screw design showed an increase in crystallinity, but not to the extent of the moderate screw design. The harsh screw caused an increased amount of chain scission, which allowed for a decreased amount of time to crystallize for the sample to crystallize, but the increased degradation to the polymer caused these values to be less than that of the moderate screw design.

The optimum sample in this study was found to be the SSME sample processed with a low flow rate and a moderate screw design-SMMD1. This sample was found to crystallize in shortest amounts of time (2.2 minutes) and with one of the highest amounts of crystallinity (43%). This degree of crystallinity is relatively high among maximum amounts of crystallinity in many studies [Day, M., et al., 2006; Guinault, A., et al., 2010; Mallet, B., et al., 2013]. In addition, this sample had the highest softening temperature and the largest number and weight average molecular weight among samples processed with a mild or harsh screw design. This indicates that among those samples, SMMD1 had a sufficient level of defects in the polymer chains.

6. Conclusions and Recommendations

PLA is a bio-derived and biodegradable material with similar properties to petroleum-derived polymers such as PE and PETE. The recent rise in the price of petroleum and the heightened environmental awareness by the general public have led to a desire for many manufacturers to consider utilizing PLA for polymer products. Current industrial processing practices use melt-based techniques, which for PLA is neither time- nor cost-efficient. The goal of this thesis was to find a method by which PLA could be processed to produce a high percent crystallinity in a short amount of time without negatively impacting its properties.

In the initial study of the effects of three processing methods (TSE, SSSP, and SSME) upon PLA's structure and properties, SSME was identified as the processing method with the largest increase in desired thermal properties. PLA samples processed with SSME formed 30% more crystals in one-third of the amount of time relative to TSE, while also having comparable or enhanced mechanical properties. The increased crystallinity within the sample is attributed to the large amounts of defects formed within the polymer during SSSP processing that allow for nucleation sites to be created. The nucleation sites are then distributed throughout the sample in the TSE portion of processing.

The second study attempted to optimize the SSME process by varying two fundamental process parameters: throughput and screw design. This study showed that SSME processing with a moderate screw design and low throughput produced a sample that had the largest amount of crystallites within the shortest period of time and had one of the largest resistances to thermal degradation. These properties are a result of the ideal pulverization and mixing that occurred with the moderate screw design. The mild and harsh screw design created a sample that had either insufficient pulverization, which resulted in too few defects, or excessive pulverization, which strained the polymer to the point where chain lengths were not large enough to form crystallites. The low flow rate allowed for a small amount of polymer to be contained within the extruder so that uniform, effective processing could occur.

Though the sample with a moderate screw design and low throughput had the shortest crystallization time and the highest degree of crystallinity, the rate at which the PLA was processed (250 g/hr) was lower than that of a typical laboratory-scale extruder. Therefore, further optimization studies need to be conducted where other variable such as screw speed and the number of heated zones are varied. The goal is to achieve a polymer with similar thermal and mechanical properties at a higher throughput.

In the future, a better understanding of the properties of PLA should also be investigated through additional characterization techniques. The crystallization behavior of PLA could be observed with polarized optical microscopy, and the morphology of the polymer with a melt-flow index test. Since tensile testing was not completed with a method that produced results consistent with that in the literature, proper tensile tests should be completed to determine the true effect that processing has on a polymer’s mechanical properties.

Overall, this study showed that PLA processed via SSME had an increased amount of crystallinity in a decreased amount of time. As PLA continues to be part of today’s environmentally conscious society, some of the inherent challenges associated with the crystallization behavior and less-than-desirable properties of the material can be overcome by the SSME technique.

7. References

American Chemical Council. (2014). *History of Polymers & Plastics for Teachers*. Retrieved from http://plastics.americanchemistry.com/Education-Resources/Hands-on-Plastics/Introduction-to-Plastics-Science-Teaching-Resources/History-of-Polymers-Plastics-for-Teachers.html

Auras, R. A., Lim, L. T., Selke, S. E., & Tsuji, H. (Eds.). (2011). *Poly (Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications* (Vol. 10). John Wiley & Sons.

Avérous, L. (2008). Polylactic Acid: Synthesis, Properties and Applications. In Belgacem, M.N., Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*, 433-450. Oxford, Great Britain: Elsevier.

Avérous, L., & Pollet, E. (2012). *Green Nano-Biocomposites* (pp. 1-11). Springer London.

Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K., & Wintermantel, E. (2003). Thermal and Mechanical Properties of Plasticized Poly (L-Lactic Acid). *Journal of Applied Polymer Science, 90*(7), 1731-1738.

Bergeret, A. (2011). Environmental-Friendly Biodegradable Polymers and Composites. InTech.

Brunner, P. J. (2013). *Overcoming Sustainability and Energy Challenges in Polymer Science via Solid-State Shear Pulverization* (Doctoral dissertation, Northwestern University).

Brunner, P. J., Clark, J. T., Torkelson, J. M., & Wakabayashi, K. (2012). Processing-Structure-Property Relationships in Solid-State Shear Pulverization: Parametric Study of Specific Energy. *Polymer Engineering & Science*, *52*(7), 1555-1564.

Daurio, D., Medina, C., Saw, R., Nagapudi, K., & Alvarez-Núñez, F. (2011). Application of Twin Screw Extrusion in the Manufacture of Cocrystals, Part I: Four Case Studies. *Pharmaceutics*, *3*(3), 582-600.

Day, M., Nawaby, A. V., & Liao, X. (2006). A DSC Study of the Crystallization Behaviour of Polylactic Acid and Its Nanocomposites. *Journal of Thermal Analysis and Calorimetry*, *86*(3), 623-629.

Drumright, R. E., Gruber, P. R., & Henton, D. E. (2000). Polylactic Acid Technology. *Advanced Materials*, *12*(23), 1841-1846.

Farrington, D. W., Lunt, J., Davies, S., & Blackburn, R. S. (2005). Poly (Lactic Acid) Fibers. *Biodegradable and Sustainable Fibres*, 191.

Fielding, A. S. (2009). Characterization of Biodegradable Polymer Nanocomposites Fabricated via Solid-State Processing. Masters Thesis, Bucknell University

Gámez-Pérez, J., Velazquez-Infante, J. C., Franco-Urquiza, E., Carrasco, F., Santana, O. O., & Maspoch, M. L. (2011). Fracture Behavior of Quenched Poly (Lactic Acid). *Express Polymer Letters*, *5*(1).

Garlotta, D. (2001). A Literature Review of Poly (Lactic Acid). *Journal of Polymers and the Environment*, *9*(2), 63-84.

Guinault, A., Sollogoub, C., Domenek, S., Grandmontagne, A., & Ducruet, V. (2010). Influence of Crystallinity on Gas Barrier and Mechanical Properties of PLA Food Packaging Films. *International Journal of Material Forming*, *3*(1), 603-606.

Haas, T., Kircher, M., Kohler, T., & Wich, G. (2009). Basics of PLA. *Bioplastics Magazine* Jan. 2009, (4), 38-40.

The Hedging Corner. (2011). *Resin Prices: A New Paradigm*. Retrieved from http://hedgingcorner.wordpress.com/2011/09/27/resins-prices-a-new-paradigm/.

History of Plastic. (2013). *History of Plastic Recycling*. Retrieved from http://www.historyofplastic.com/plastic-history/history-of-plastic-recycling/.

Inskeep, G. C., Taylor, G. G., & Breitzke, W. C. (1952). Lactic Acid from Corn Sugar. *Industrial & Engineering Chemistry*, *44*(9), 1955-1966.

Iovino, R., Zullo, R., Rao, M. A., Cassar, L., & Gianfreda, L. (2008). Biodegradation of Poly (Lactic Acid)/Starch/Coir Biocomposites under Controlled Composting Conditions. *Polymer Degradation and Stability*, *93*(1), 147-157.

Jacobsen, S., & Fritz, H. G. (1999). Plasticizing Polylactide—The Effect of Different Plasticizers on the Mechanical Properties. *Polymer Engineering & Science*, *39*(7), 1303-1310.

Jonoobi, M., Harun, J., Mathew, A. P., & Oksman, K. (2010). Mechanical Properties of Cellulose Nanofiber (CNF) Reinforced Polylactic Acid (PLA) Prepared by Twin Screw Extrusion. *Composites Science and Technology*, *70*(12), 1742-1747.

Kalyon, D. M., Yu, X., Wang, H., Valdevit, A., & Ritter, A. (2013). Twin Screw Extrusion Based Technologies Offer Novelty, Versatility, Reproducibility and

Industrial Scalability for Fabrication of Tissue Engineering Scaffolds. *Journal of Tissue Science Engineering, 4*, e126.

Labrecque, L. V., Kumar, R. A., Dave, V., Gross, R. A., & McCarthy, S. P. (1997). Citrate Esters as Plasticizers for Poly (Lactic Acid). *Journal of Applied Polymer Science*, *66*(8), 1507-1513.

Liao, R., Yang, B., Yu, W., & Zhou, C. (2007). Isothermal Cold Crystallization Kinetics of Polylactide/Nucleating Agents. *Journal of Applied Polymer Science, 104*(1), 310-317.

Lebovitz, A. H., Khait, K., & Torkelson, J. M. (2002). Stabilization of Dispersed Phase to Static Coarsening: Polymer Blend Compatibilization via Solid-State Shear Pulverization. *Macromolecules*, *35*(23), 8672-8675.

Lim, L. T., Auras, R., & Rubino, M. (2008). Processing Technologies for Poly (Lactic Acid). *Progress in Polymer Science*, *33*(8), 820-852.

Lunt, J. (1998). Large-scale production, properties and commercial applications of polylactic acid polymers. *Polymer degradation and stability*, *59*(1), 145-152.

Lunt, J., & Shafer, A. L. (2000). Polylactic Acid Polymers from Com. Applications in the Textiles Industry. *Journal of Industrial Textiles, 29*(3), 191-205.

Madhavan Nampoothiri, K., Nair, N. R., & John, R. P. (2010). An Overview of the Recent Developments in Polylactide (PLA) Research. *Bioresource Technology, 101*(22), 8493-8501.

Mallet, B., Lamnawar, K., & Maazouz, A. (2013). Improvement of Blown Film Extrusion of Poly (Lactic Acid): Structure–Processing–Properties Relationships. *Polymer Engineering & Science, 54*(4), 840-857.

Mooney, B. P. (2009). The Second Green Revolution? Production of Plant-Based Biodegradable Plastics. *Biochemical Journal, 418*, 219-232.

NatureWorks®, (2005). *NatureWorks® PLA Polymer 2002D.* Retrieved from http://www.historyofplastic.com/plastic-history/history-of-plastic-recycling/.

Ochi, S. (2008). Mechanical Properties of Kenaf Fibers and Kenaf/PLA Composites. *Mechanics of Materials*, *40*(4), 446-452.

Oksman, K., Skrifvars, M., & Selin, J. F. (2003). Natural Fibres as Reinforcement in Polylactic Acid (PLA) Composites. *Composites Science and Technology*, *63*(9), 1317-1324.

Pantani, R., & Sorrentino, A. (2013). Influence of Crystallinity on the Biodegradation Rate of Injection-Moulded Poly (Lactic Acid) Samples in Controlled Composting Conditions. *Polymer Degradation and Stability*, *98*(5), 1089-1096.

Pillin, I., Montrelay, N., & Grohens, Y. (2006). Thermo-Mechanical Characterization of Plasticized PLA: Is the Miscibility the Only Significant Factor? *Polymer*, *47*(13), 4676-4682.

Plastemart. (2013). *Biodegradable Plastics Demand to Grow 15% Annually to 2015.* Retrieved from http://www.plastemart.com/Plastic-Technical-Article.asp?LiteratureID=1958&Paper=biodegradable-plastics-demand-to-grow-15-percent-annually-to-2015.

Plastics Technology. (2005). *No. 5-Twin-Screw Extrusion*. Retrieved from http://www.ptonline.com/articles/no-5---twin-screw-extrusion.

Polymer Processing. (2011). *Twin Screw Extrustion*. Retrieved from http://www.polymerprocessing.com/operations/tscrew/index.html.

Qu, X., Wirsen, A., & Albertsson, A. C. (2000). Effect of Lactic/Glycolic Acid Side Chains on the Thermal Degradation Kinetics of Chitosan Derivatives. *Polymer*, *41*(13), 4841-4847.

Rauwendaal, C. (2014). Polymer Extrusion. Germany: Carl Hanser Verlag GmbH & Company KG.

Salminen, S., Von Wright, A., & Ouwehand, A. (2004). *Lactic Acid Bacteria: Microbiology and Functional Aspects*, *33*(2), 191-197.

Society of Plastic Engineers at Texas A&M University. (2013). *Brief History of Polymers*. Retrieved from http://plastics.tamu.edu/content/11-brief-history-polymers.

Society of the Plastic Industry. (2013). *Recycling*. Retrieved from http://www.plasticsindustry.org/AboutPlastics/content.cfm?ItemNumber=1271&navItemNumber=1125.

Suryanegara, L., Nakagaito, A. N., & Yano, H. (2009). The Effect of Crystallization of PLA on the Thermal and Mechanical Properties of Microfibrillated Cellulose-Reinforced PLA Composites. *Composites Science and Technology*, *69*(7), 1187-1192.

Treece, M. A., Zhang, W., Moffitt, R. D., & Oberhauser, J. P. (2007). Twin-Screw Extrusion of Polypropylene-Clay Nanocomposites: Influence of Masterbatch

Processing, Screw Rotation Mode, and Sequence. *Polymer Engineering & Science*, *47*(6), 898-911.

United States Environmental Protection Agency. (2013). *Plastics*. Retrieved from http://www.epa.gov/osw/conserve/materials/plastics.htm.

Vadori, R., Mohanty, A. K., & Misra, M. (2013). The Effect of Mold Temperature on the Performance of Injection Molded Poly (Lactic Acid)-Based Bioplastic. *Macromolecular Materials and Engineering*, *298*(9), 981-990.

Van de Velde, K., & Kiekens, P. (2002). Biopolymers: Overview of Several Properties and Consequences on Their Applications. *Polymer Testing*, *21*(4), 433-442.

Villmow, T., Pötschke, P., Pegel, S., Häussler, L., & Kretzschmar, B. (2008). Influence of Twin-Screw Extrusion Conditions on the Dispersion of Multi-Walled Carbon Nanotubes in a Poly (Lactic Acid) Matrix. *Polymer*, *49*(16), 3500-3509.

Wang, Y., Chen, F. B., & Wu, K. C. (2004). Twin-Screw Extrusion Compounding of Polypropylene/Organoclay Nanocomposites Modified by Maleated Polypropylenes. *Journal of Applied Polymer Science*, *93*(1), 100-112.

Whittington, A. M., Brouse, S. M., Malusis, M. A., & Wakabayashi, K. (2013). Efficient Fabrication of Polymer Nanocomposites with Effective Exfoliation and Dispersion by Solid-State/Melt Extrusion. *Advances in Polymer Technology*, *32*(1).

Xiao, L., Wang, B., Yang, G., & Gauthier, M. (2012). Poly (Lactic Acid)-Based Biomaterials: Synthesis, Modification and Applications. *Biomedical Science, Engineering and Technology: InTech*, 247-282.

Yang, S. L., Wu, Z. H., Yang, W., & Yang, M. B. (2008). Thermal and Mechanical Properties of Chemical Crosslinked Polylactide (PLA). *Polymer Testing*, *27*(8), 957-963.

Zero Waste. (2014). *Waste & Recycling: Data, Maps, & Graphs*. Retrieved from http://www.zerowasteamerica.org/statistics.htm.