

**DESIGN OF BIOBASED AND BIODEGRADABLE – COMPOSTABLE
ENGINEERED PLASTICS BASED ON POLY(LACTIDE)**

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ABSTRACT

DESIGN OF BIOBASED AND BIODEGRADABLE – COMPOSTABLE ENGINEERED PLASTICS BASED ON POLY(LACTIDE)

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Poly(lactide) (PLA) is a biobased and biodegradable – compostable plastic that is derived from renewable resources such as corn and sugar cane. It possesses excellent strength and stiffness properties and is recognized as safe for biomedical and food packaging applications. Commercially, it costs ~\$1/lb and is now competitive with petroleum based polymers that have dominated the industry for decades. However, the material has some inherently weak properties that prevent it from certain applications – most notably, its rheological properties, brittleness, and poor high temperature performance. Cost effective modifications of the polymer to enhance these deficiencies could allow for increased applications and further its commercial growth. Multiple synthetic strategies have been developed to address PLA's performance property deficiencies.

PLA typically exhibits poor melt strength and does not have the ability to strain harden, partially a result of its highly linear nature. Strain hardening and high melt strength are crucial elements of a material when producing blown films, a large untapped market for PLA. By increasing molecular weight and introducing long-chain branching into the material, these properties can be improved. Epoxy-functionalized PLA (EF-PLA) was synthesized by reacting PLA with a multifunctional epoxy polymer (MEP) using reactive extrusion processing (REX). These modified PLA polymers can function as a rheology modifier for PLA and a compatibilizer

for blends with other biopolyesters. The modified PLA showed an increased melt strength and exhibited significant strain hardening, thus making it more suited for blown film applications. Blown films comprised of PLA and poly(butylene adipate-co-terephthalate) (PBAT) were produced using EF-PLA as a reactive modifier for rheological enhancement and compatibilization. This resulted in films with better processability (as seen by increased bubble stability) and improved mechanical properties, compared to a common rheology modifier used in industry. These modifiers have been successfully scaled up to a 400 kg/hr process and are currently used to make high quality biodegradable blown films for multiple commercial applications.

PLA is an extremely brittle material, typically experiencing only 3-4% elongation prior to fracture. This hinders some of its applications and therefore toughening is needed for future commercial growth. Two different methods of modifying PLA with polysiloxanes are studied and discussed. Polysiloxanes serve as a highly attractive material for toughening PLA due to their inherent properties. Because of the longer bond and higher bond angle of the -Si-O-Si- (siloxane) backbone compared to a carbon based backbone, there is a reduced energy barrier for rotation leading to substantial flexibility. Polysiloxanes also possess good thermal and oxidative stability, biocompatibility, and very low surface tension values, all which could benefit PLA greatly.

Lastly, most injection molded PLA products lose their rigidity above T_g ($\sim 55^\circ\text{C}$) due to a rubbery amorphous phase and low crystallinity. This prevents products like PLA cutlery from being used effectively at elevated temperatures, like those of hot foods. The high temperature mechanical properties of injection molded PLA are enhanced using a combination of nucleating agents and processing improvements to impart high levels of crystallinity, resulting in a substantial increase in the mechanical performance at these temperatures.

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Chapter 1 – Introduction to Bioplastics and Poly(lactide)

1.1 Plastics Industry and Environmental Impact

Plastics have become an essential aspect to our modern lifestyle and have greatly improved our daily lives. They are used everywhere from “lightweighting” cars to medical applications such as artificial prosthetics, and especially in packaging food (~20% of plastic production). With the world’s population continuing to grow and increased applications for plastics, the world wide plastic production is ever increasing. The global yearly production has increased from 1.7 million tons in 1950, to 99 million tons in 1989, and with over 300 million tons today.¹ Plastics are now an integral part of the modern world, and have many benefits over more traditional materials such as wood, metal, and ceramics.

However, with the global increase in plastics, we are beginning to run into many environmental challenges. The overwhelming majority of plastics today are synthetically derived from petroleum sources. Typically, these hydrocarbon based polymers are inherently bioresistant and therefore cannot take part in nature’s carbon cycle. The disposal of these materials is becoming a major issue. As an example, it is estimated that the common poly(ethylene terephthalate) (PET) water/soda bottle will take around 450 years to decompose naturally.² With the rate at which bottles are produced, this is obviously not sustainable. While PET recycling is an efficient method of reusing the plastic, in the United States only 9% of plastics are recycled. And based off of the U.S. plastics production in 2014, this equates to 32 million tons being discarded into landfills.³ This “Landfill Crisis” is posing a major detriment to our climate in the form of ground water and greenhouse gas pollutions. The methane produced from anaerobic

degradation in landfills account for 18% of the global methane emissions and methane is 25 times more harmful to the atmosphere than carbon dioxide as a greenhouse gas.⁴

Plastic disposal on land is not the only environmental issue we are currently experiencing. The effect on the marine environment is lately of increasing concern, as it is a detriment to oceans, wildlife, and potentially humans. This plastic debris can be eaten by animals such as fish, turtles, and birds and is quickly becoming a significant cause of their deaths. And due to circular ocean currents, or gyres, we are beginning to observe large collections of floating plastic particles in all major oceans. The “Pacific Trash Vortex” is the largest of these collections and is estimated to be the size of Texas.⁵ Plastics in the ocean also behave as a “chemical sponge” which can concentrate the ocean’s pollutants to these plastic pieces, and be harmful to wildlife if ingested. It is estimated that between 4.8 and 12.7 million tons of plastic waste enter the oceans yearly, and that number is still growing.⁶

The average person living in North America or Western Europe uses 100 kilograms of plastic each year.³ The majority of this plastic is in the form of packaging products, which are materials that are designed for one time use and then immediate disposal. This packaging accounts for 62.2% of the plastic waste that is thrown into landfills. Due to this growing plastic consumption and our inability to efficiently recycle that which we use, plastics with different end of life options are becoming increasingly desirable.

1.2 Biobased and Biodegradable/Compostable Materials

These growing environmental concerns are the driving force for the growth of biobased and biodegradable/compostable plastics in the plastic industry. Biobased polymers, or those manufactured from biomass feedstocks, offer interesting material value propositions. Plastics

produced from these renewable carbon sources result in a more sustainable carbon cycle, thus yielding essentially a zero material carbon footprint. Their reliance on agricultural biomass can also be beneficial to the agricultural industry. There are some naturally occurring biobased polymers such as starch and cellulose that have already found industrial applications, while other biobased polymers, such as poly(lactide) (PLA), are synthesized from biomass feedstocks. In this case, lactic acid is fermented from starch and is used as the building blocks to produce PLA. Recently, there has been increasing interest in producing traditional petroleum based plastics from bio-resources. For example, in Coca-Cola's "Plant Bottle", they have synthesized one of the reactants, ethylene glycol, from biomass sources. This makes the resultant PET bottle ~30% biobased.

Biodegradable/compostable polymers are ideal materials to battle the landfill and ocean plastics crises. Biodegradability is an end of life option for these polymers in which microorganisms such as bacteria fully decompose the polymer through enzymatic action in a timely, safe, and efficacious manner.⁷ While many biobased polymers are biodegradable, this is not always the case. A biobased poly(ethylene) (PE) is produced by the Brazilian petrochemical company Braskem, and is derived from biobased ethanol. However, PE is a polyolefin which are very chemically resistant, and is therefore not biodegradable. In contrast, poly(butylene adipate-co-terephthalate) (PBAT), known more commonly by the trade name EcoFlex, is a petroleum based aliphatic/aromatic polyester that is fully biodegradable.

These biobased and biodegradable plastics are becoming more common on a commercial scale, but are struggling to find way into the existing plastics industry. As stated earlier, plastic packaging accounts for ~40% of the plastic industry and over 60% of the plastic waste found in landfills. These single use packaging materials are the ideal application for biobased and

biodegradable/compostable polymers. A switch to these more environmentally responsible products could have a large beneficial impact on our current environmental issues. However, material performance and/or cost barriers must first be overcome prior to them being commonplace.

1.3 Poly(lactide)

Poly(lactide) (PLA) is a biobased and compostable aliphatic polyester resin derived from biobased feedstocks such as corn. PLA polymers are strong, stiff, and brittle plastics that possess mechanical and visual properties (such as clarity) that very closely resemble the petrochemical polystyrene (PS). Through the fermentation of corn starch, lactic acid is obtained which can be used to create lactide, its cyclic dimer. Ring-opening polymerization can then be used to efficiently produce a controlled high molecular weight polymer.⁸ Currently NatureWorks, LLC is producing PLA at a rate of almost 300 million pounds (140 thousand tons) per year in Blair, Nebraska. Thanks to the increasingly large production of PLA polymers, the costs of the material continues to decrease. PLA is currently being sold for ~\$1/lb, which is similar to the petrochemical based plastics that it is competing with.

While PLA is most commonly produced from corn feedstocks, it is also currently being produced from sugar cane. In October of 2014, the U.S. Department of Energy announced a grant of up to \$2.5 million to NatureWorks to support their aim of converting biomethane to lactic acid via a fermentation process for PLA production.⁹ Methane is 25 times more harmful than carbon dioxide as a greenhouse gas, and sequestering this would transform a harmful greenhouse gas to a useful material. If this succeeds, this would result in feedstock diversification and lower PLA

production costs by greatly simplifying the number of steps for lactic acid production. This could be revolutionary in the PLA field, driving increased growth.

Lactide has two stereocenters, resulting in four possible stereometric conformations – SS, RR, SR, and RS. However, RS and SR are in effect the same, as they are achiral superimposable images of each other. Therefore lactide has only three *unique* isomers: (SS) L-lactide, (RR) D-lactide, and (SR/RS) meso-lactide which are shown in **Figure 1.1**.

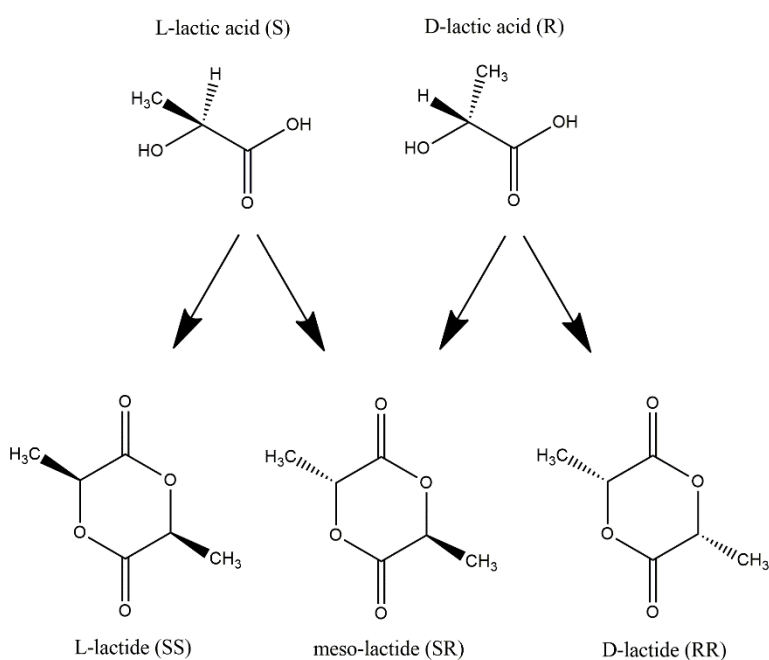


Figure 1.1: Stereoisomers of lactic acid and lactide.

PLA polymers can then be made from any combination of these monomeric units, most commonly as random copolymers. The resultant polymers are largely affected by the isomers they contain, allowing PLA to range from semi-crystalline to amorphous. PLA produced from pure L-lactide possesses a high level of crystallinity (~65%), melting temperature ($T_m = \sim 187^\circ\text{C}$), and faster crystallization rate in comparison to typical PLA polymers. A molecular simulation of

P(L)LA can be seen in **Figure 1.2(a)**.¹⁰ This polymer exhibits a very linear and ordered structure which is the reason for the good crystallization properties. As D- and meso-lactide content is introduced they form kinks in the otherwise very regular P(L)LA molecular architecture. This change decreases both the rate and extent of crystallization achievable, to the point where the PLA becomes strictly amorphous (>13% meso-lactide content). Figure 1.2(b) shows a molecular simulation of a PLA polymer that contain 7.5% meso-lactide with the remainder L-lactide. This structural change has a large effect on the thermal properties of the PLA polymers.

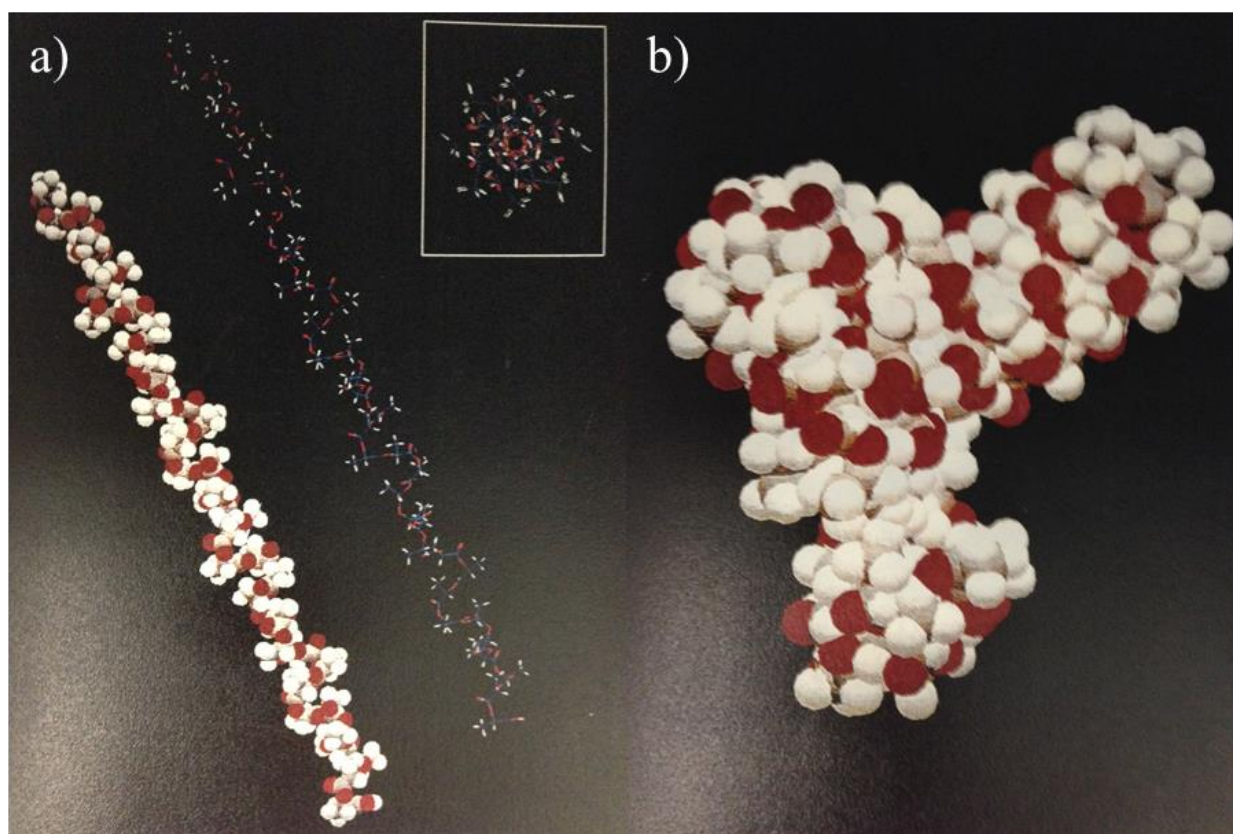


Figure 1.2: 3-D molecular simulations of a) P(L)LA and b) P(L - 7.5 wt% meso)LA.

Initially, lactic acid is polymerized to form PLA oligomers which are depolymerized to produce lactide. By assuming the ratio of L-lactic acid to D-lactic acid before oligomerization is

the same after depolymerization, we can theoretically predict the percentages of L-, D-, and meso-lactide formed based on the initial lactic acid concentrations.

$$w_{L-Lactide} = l_L^2; \quad w_{D-Lactide} = l_D^2; \quad w_{meso-Lactide} = 2l_L l_D, \text{ **Equation 1.1**}$$

where l_L and l_D are percentages of L-lactic acid and D-lactic acid in the oligomerization reaction, respectively. As an example, a lactide production reaction starting with 95% L-lactic acid and 5% D-lactic acid should result in lactide consisting of 90.25% L-, 0.25% D-, and 9.5% meso-lactide. From this it can be seen that the production of meso-lactide is much greater than D-lactide, therefore the meso-lactide content in the PLA polymers is the primary determiner of their thermal properties.

Another interesting effect of the isomeric makeup can be seen in the equimolar stereocomplex of P(L)LA and P(D)LA. The resultant material exhibits a significantly higher melting temperature ($\sim 230^\circ\text{C}$) than either of the homopolymers, due to the ordered structure it creates.¹¹

While PLA possesses high strength, stiffness, optical clarity, and is recognized as safe for food contact and biomedical applications, its brittleness and certain other properties are limiting its commercial growth. Currently in the market, PLA is being used in niche applications such as single-use disposable products like plastic cutlery and clamshell food packaging. These low performance, one-time use food applications are ideal for neat PLA. However, efficient low cost modifications of PLA could potentially open up an entirely new market for the material. As mentioned earlier, for the commercial growth of bioplastics both the material's performance and cost must be similar to the current petroleum based plastics that dominate the market. PLA is

already cost competitive, but improvement of its properties in a few areas could lead to increased use.

Since the cost of PLA needs to remain low, the modification must be done in a scalable and efficient manner. Reactive Extrusion (REX) is the ideal processing method for such modifications because it is a cost-effective continuous process in which an extruder is used as the reactor vessel. Low cost modifications of PLA result in cost-competitiveness of these new engineered plastics and increase its commercial viability. Extruders are capable of resolving heat and mass transfer problems that have been an issue in batch processing as viscosity increases due to polymerization.¹² The large surface area within an extruder barrel creates thin surface layers which enhance the degree of mixing and minimize temperature gradients. These characteristics allow for the reaction times in REX to be much faster than those of a traditional batch reaction, making high throughput possible. REX has proven to be an effective method in various chemical reactions, including polymerization, grafting, branching, and functionalization of polymers.

In the past couple years PLA has started to garner more commercial interest as we learn ways of modifying the material. For example, in November of 2010, Stonyfield Farms announced their switch to using PLA for all of their yogurt multi-packs.¹³ Stonyfield Farm is the world's largest organic yogurt producer, including brands such as Oikos. The company produces approximately 200 million multi-pack yogurt cups a year, and all of these are now made with PLA, replacing the previous material, high impact polystyrene (HIPS). The switch resulted in 48% less greenhouse gas emissions from the plastic production. Also because of the increased strength of PLA, they were able to use 30 mil rollstock of PLA compared to the 35 mil HIPS rollstock. This resulted in a light weighting of the product, and therefore the switch did not cause any price increase. Stonyfield's president and CEO said of the material switch, "It's a win-win-win. It's

price neutral, a big win on carbon, and a much stronger package.” Not only is there interest in PLA for its biobased and biodegradable nature, but its material properties are an improvement over petroleum based plastics in certain applications as well.

1.4 Dissertation Objective

The objective of this work was to efficiently improve selected properties of PLA through cost-effective modification processes. The goal was to create improved engineered PLA materials for potential commercial application. As of writing this thesis, one of the discussed projects (Chapters 2&3) has been scaled up to a commercial level. An estimated 20 million of these PLA based bags were sold to Levi’s in 2015 for shipping their clothing around the world.

The major inherently weak properties holding back PLA are i) weak melt strength and poor rheological properties (Chapters 2-4), ii) brittleness/low toughness (Chapters 4-6), and iii) poor high temperature mechanical properties (Chapter 7). These will be discussed throughout the 6 remaining chapters that make up this thesis.

Chapter 2 discusses the synthesis of an Epoxy Functionalized – Poly(lactide) (EF-PLA) reactive modifiers for rheological modification to aid in blown film processing. Efficient film blowing requires a polymer with strong enough melt strength so that it does not tear when undergoing the biaxial stretching involved. Because of this neat PLA cannot be efficiently blown into films, or only low blow up ratios are achievable. Commercially scalable modifications involving the creation of ultra-high molecular weight branched polymer structures with epoxy functionality are discussed for use as a rheological modifier for PLA and other polyesters in blown film applications.

Chapter 3 discusses the application of the EF-PLA reactive modifiers as a rheological modifier and compatibilizer in blown films comprising of PLA and PBAT. The properties of these enhanced biodegradable/compostable packaging films are compared to physical blends as well as films created with a common industrial rheological modifier used in the PLA blown film industry. Mechanical properties and morphology of these films are discussed to explain the results.

In Chapter 4, poly(siloxanes) containing multiple epoxy groups (EPS) are synthesized for use as a reactive modifier to enhance rheological properties and toughness of PLA. The concept of this project was to produce a reactive modifier similar to that in EF-PLA but comprised of a flexible siloxane backbone to impart both a rheological and toughening benefit. The molecular weight and epoxy functionality of these polymers are controllable, making them capable of a wide range of properties. A model compound study was used to look at the EPS reactivity with the carboxylic acid and hydroxyl functional groups of a polyester (like PLA), and the effect of a catalyst.

Chapter 5 discusses a very different technique at toughening PLA through the use of the flexible siloxanes. Vinyltrimethoxysilane (VTMOS) is grafted onto the backbone of PLA through REX processing in the presence of a silanol-terminated PDMS (OH-PDMS). Processing modifications from a previous study resulted in significant improvement in the grafting efficiency of VTMOS onto PLA. After processing, the modified thermoplastic PLA is capable of undergoing a moisture cured siloxane crosslinking reaction in which the methoxy groups of VTMOS condense with OH-PDMS and each other to create a siloxane crosslinked PLA. Tensile and impact properties are measured to determine the toughening effect, and morphology is investigated.

Chapter 6 deals with toughening PLA using aminopropyl-poly(dimethylsiloxane) (NH-PDMS) to synthesize PLA block copolymers via REX. The PLA is processed in the extruder with

a typical polymerization catalyst, however since PLA polymerization is an equilibrium reaction the polymer gets broken down through chain scission. The newly created carboxyl groups of these shorter PLA chains react with the amine functionality of the NH-PDMS, forming block copolymers while building the molecular weight back up. Processing effects are studied looking at molecular weight and NH-PDMS reactivity to determine the most efficient process. The mechanical properties of these copolymers are analyzed and their potential use as an impact modifiers in virgin PLA is explored.

In Chapter 7, a combination of nucleating agents and processing improvements are used to enhance the high temperature properties of PLA. Most PLA polymers, because of meso-lactide in the polymer, are not capable of a high enough level of crystallinity to achieve good mechanical properties at temperatures greater than their glass transition temperature ($T_g \sim 60^\circ\text{C}$). Therefore, a combination of nucleating agents were blended into PLA resulting in a synergistic nucleating effect greatly increasing both the crystallinity and the crystallization rate. To streamline the injection molding processing of the resultant parts, in mold annealing was used to impart crystallinity into the samples. The Heat Deflection Temperature (HDT) was determined to quantify the effect on the high temperature resistance of the injection molded products.

Chapter 2 – Epoxy Functionalized Poly(lactide) Reactive Modifier for Blown Film Applications

2.1 Introduction

PLA is an excellent candidate for blown film products like carry-out bags, wrapping films, and waste bags/bin liners. The blown film process requires polymer melts to exhibit a certain level of melt strength as well as nonlinear viscoelastic properties like strain hardening. However, PLA exhibits low melt strength and does not show strain hardening behavior. Long-chain branching or a small fraction of high molecular weight polymer can be introduced to neat PLA to improve these rheological properties.^{14,15} Chain extenders have been widely used to improve the rheological properties of polyesters by reacting with either the carboxylic acid and/or hydroxyl end groups. For example, diisocyanates have proven to be an effective chain extender of PLA and improve its rheological properties.^{16,17} However, the toxicity of isocyanates as well as the high propensity to form gels have limited its application. Epoxy-based chain extenders like the one used in this study, can increase the molecular weight of polyesters and introduce long-chain branching.^{18–24} These chain extenders can be available in both solid and liquid forms allowing for easier processing. They show low toxicity and can be introduced via reactive extrusion. The chemistry involves reaction of the carboxylic acid or the hydroxyl chain ends of PLA with its epoxy groups to form an ether or an ester linkage.^{25–28} Very few studies have focused on the reactivity difference between the hydroxyl and carboxylic acid chain ends. In the need to prevent undesirable crosslinking, previous studies have “avoided” using high concentrations of chain extenders. The epoxy-based chain extender used in this study is a copolymer consisting of styrene, acrylic, and glycidyl methacrylate blocks. There are multiple poly(glycidyl methacrylate) blocks per polymer chain

and these blocks contain primary epoxide rings which make it an excellent modifier for fast processes such as reactive extrusion.

In this study, we exploit the reactivity difference between the carboxylic acid and the hydroxyl end groups of PLA to synthesize Epoxy Functionalized PLA (EF-PLA) molecules through reaction with a multi-functional epoxy polymer (MEP). Model compound studies helped establish the reactivity difference between the end groups, and the process parameters driving the chemistry. A series of EF-PLA compounds containing 1-10% MEP content were prepared with no gel formation. These new epoxy modified PLA polymers function not only as chain extenders but as rheology modifiers and compatibilizers in PLA and other biodegradable polyesters to give resin formulations that have the required melt strength and strain hardening properties to be blown into films and foams. Molecular weight and rheological studies are presented to help understand and establish the improved properties and processability. A statistical simulation was created to model the properties of the EF-PLA materials at various MEP content, to support the results presented.

2.2 Experimental

2.2.1 Materials

PLA 3051D resin pellets with a molecular weight of ~130,000 and 8% meso-lactide content were purchased from NatureWorks, LLC (NE, USA). The MEP (Joncryl 4368F) was purchased from BASF (MI, USA). Reagent grade stearic acid and Poly(ethylene glycol) with a molecular weight of 400 were purchased from Sigma Aldrich (MO, USA).

2.2.2 Compounding

The PLA resin pellets were dried overnight at 70°C prior to compounding. The MEP was powdered using a mortar and pestle to ensure differences in pellet size did not affect distribution. The PLA and MEP (1, 5, and 10 wt%) were fed into a ZSK 30 twin-screw extruder (Werner Pfleiderer, NJ, USA) with an L/D ratio of 30 using two separate gravimetric feeders. All samples were compounded at a throughput of 4.8 kg/hr, cooled in a water bath, and then pelletized. After drying overnight at 70°C, the 5 wt% MEP sample (EF-PLA-5%) was used as a rheology modifier to further compound with neat PLA resin pellets and extruded again to obtain diluted specimens with 0.25, 0.5, and 1 wt% MEP. The temperature profile for all compounding was 140, 165, 170, 175, 175, and 170°C while the screw speed was kept constant at 125 rpm. The screw configuration for all of the compounding processes is shown in Figure 2.1. This configuration includes three major kneading zones, which were included to impart additional mechanical energy into the extrusion system helping the reaction proceed. These zones also increase the distributive mixing and residence time of the extruder, allowing for enhanced reactive blending and additional time for the reaction to occur.

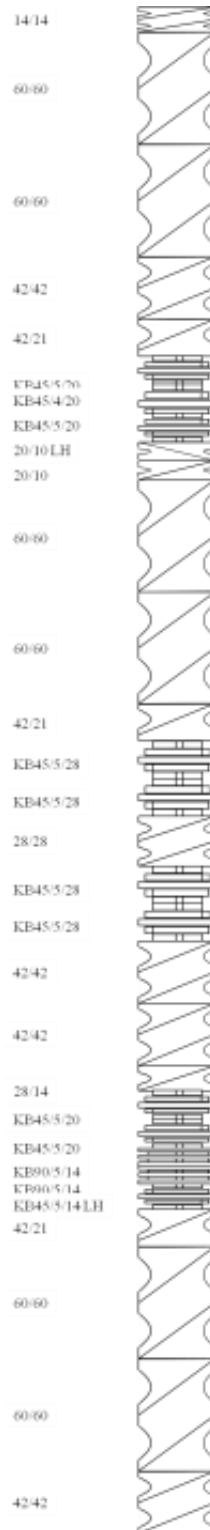


Figure 2.1: A schematic showing the screw configuration used in all compounding.

(Feed at top, die at bottom)

2.2.3 Model Compound Reaction Study

The model compound reaction kinetics were monitored by Differential Scanning Calorimetry (DSC). Stearic acid and PEG were used as the model compounds for this reaction because they contain terminal carboxylic acid and terminal hydroxyl groups, respectively. The model compounds were premixed with powdered MEP at 1:1 weight ratio. Samples (~10 mg) were sealed in a Tzero aluminum pan and heated from room temperature to 220°C at 10°C/min in the furnace of a Q20 Differential Scanning Calorimeter (TA Instruments, DE, USA). The heat flow from the exothermic transition of the epoxy ring opening reaction was recorded.

2.2.4 Characterization of EF-PLA Compounds

Soxhlet extraction was performed for 72 hours using dichloromethane as the solvent. The weight of the dried cellulose thimbles before and after the extraction was recorded for gel content analysis. For each Soxhlet extraction experiment, at least 1 g of the compounded resin was used and each experiment was repeated twice.

The molecular weight characteristics of all the materials and final products were determined by gel permeation chromatography (GPC) (Shimadzu, Japan, RID-10A) using a combination of three columns (Waters Co., Israel). Tetrahydrofuran was the mobile phase at a flow rate of 0.500 mL/min at 40°C. Polystyrene standards were used as a reference for the molecular weight calculations.

Intrinsic viscosity measurements were determined using Ubbelohde viscometers and dilute solutions in tetrahydrofuran. A size 0C Ubbelohde viscometer was carefully cleaned and dried to remove dust and contaminants. Size 0C was chosen since it resulted in an elution time for pure THF of ~185 seconds (ideally the elution time for the pure solvent should be >160 seconds for an

accurate measurement). The viscometers were placed in a 20°C water bath to ensure consistent temperature within the testing environment. Prior to the samples being added to the viscometer they were filtered to avoid any dust or contamination entering the viscometer. The viscometer was then charged and allowed to flow back through the capillary, while carefully measuring the time between the two indicators. This process was completed three times for each solution concentration, and five different concentrations were tested. The reduced and inherent viscosities for each sample were calculated (as shown below) and plotted against concentration to create Huggins and Kraemer Plots.

$$\eta_{red} = \frac{\eta_{sp}}{c}, \quad \text{where } \eta_{sp} = \frac{t - t_0}{t_0}, \text{ Equation 2.1}$$

$$\eta_{inherent} = \frac{\ln(\eta_r)}{c}, \quad \text{where } \eta_r = \frac{t}{t_0}, \text{ Equation 2.2}$$

Where t_0 is the elution time (s) for the pure solvent to flow through the indicator marks on the capillary, t is the elution time (s) for the solutions at varying concentrations, and c is the concentration (g/dL) of these solutions. Extrapolation of the solution concentration to zero results in the inherent and reduced viscosities converging at the intrinsic viscosity (dL/g). This extrapolation to zero is intended to eliminate polymer intermolecular interaction effects.^{29,30}

Complex viscosity was measured by dynamic rotational experiments using an ARES rheometer (TA Instruments, DE, USA) with a parallel-plate geometry and a plate separation of 1.05 mm. A frequency sweep was performed using a frequency range of 1 – 100 rad/s and a strain of 1%. When testing with frequencies lower than 1 rad/s (e.g. 0.1 – 100 rad/s), severe degradation

of PLA was observed due to the long testing time at elevated temperature. Four temperatures (170, 180, 190, and 200°C) were used.

The extensional viscosity was also measured on the ARES rheometer equipped with an EVF fixture at 180°C.³¹ The test specimens were compression molded into dimensions of 18 x 10 x 1 mm prior to testing. Four different Hencky strain rates (0.1, 0.5, 1.0 and 5.0 rad/s) were tested. Equation 2.1 was used to calculate the extensional viscosity of the PLA melt at steady strain rate:

$$\eta_E^+ = \frac{(T)}{2R \dot{\epsilon}_H A_0 \left(\frac{\rho_s}{\rho_m} \right)^{2/3} \exp(-\dot{\epsilon}_H(t))} , \text{Equation 2.3}$$

where η_E^+ is the value of tensile stress growth, $\dot{\epsilon}_H$ is the applied Hencky strain rate, T is the torque, R is the drum radius, A_0 is initial area of the sample measured in the solid state, and t is time in seconds. The density of PLA in the solid state, ρ_s , was assumed to be 1.25 g/cm³, and the density for PLA melt at 180°C, ρ_m , was 1.115 g/cm³.

2.3 Results and Discussion

2.3.1 Model Compound Reaction Study

Previous researchers have discussed the possible reaction between PLA and epoxy-based chain extenders.^{18,20,28} However there is still some uncertainty related to the reactivity of the two major functional groups present in PLA, hydroxyl and carboxyl groups. These previous studies have not created high MEP content samples for fear of crosslinking or gelation. It is well known that PLA has the tendency to hydrolytically degrade through extrusion processes as a result of

back-biting and intermolecular transesterification reactions.¹² To counteract this, triphenylphosphine can be added to suppress/delay these degradation phenomena. However, the slight degradation caused by the extrusion processing is not an issue in this study since the reaction with MEP results in a dramatic increase in molecular weight. A series of experiments was designed with two different model compounds to study the chemistry and the effect of temperature on the reaction between MEP and the functional groups of PLA. Stearic acid and low molecular weight PEG were used as the model compounds to represent the carboxyl and hydroxyl functional groups, respectively. The exothermic signal from the epoxide ring-opening reaction was monitored in the DSC.

In the case of stearic acid, an exothermic signal was observed which indicates that a reaction had occurred between the carboxyl group of PLA and the MEP (**Figure 2.2**). The reaction temperature was between 130 – 200°C with a peak temperature of 168°C. In contrast, no exothermic signal was seen in the spectra of PEG/MEP at these temperatures, indicating that there was no reaction between the hydroxyl functional groups and MEP in the processing temperature range of PLA, typically between T_m and 200°C. The absence of an exothermic signal with the hydroxyl model compound and a signal observed with the carboxyl model compound indicates that MEP only reacts with carboxyl functional groups under the typical processing temperatures seen with PLA. It has been reported that at higher temperatures, around 250°C, the hydroxyl end group of PLA reacts with the epoxide ring. Therefore by staying in the correct processing range, we can ensure no gelation occurs.

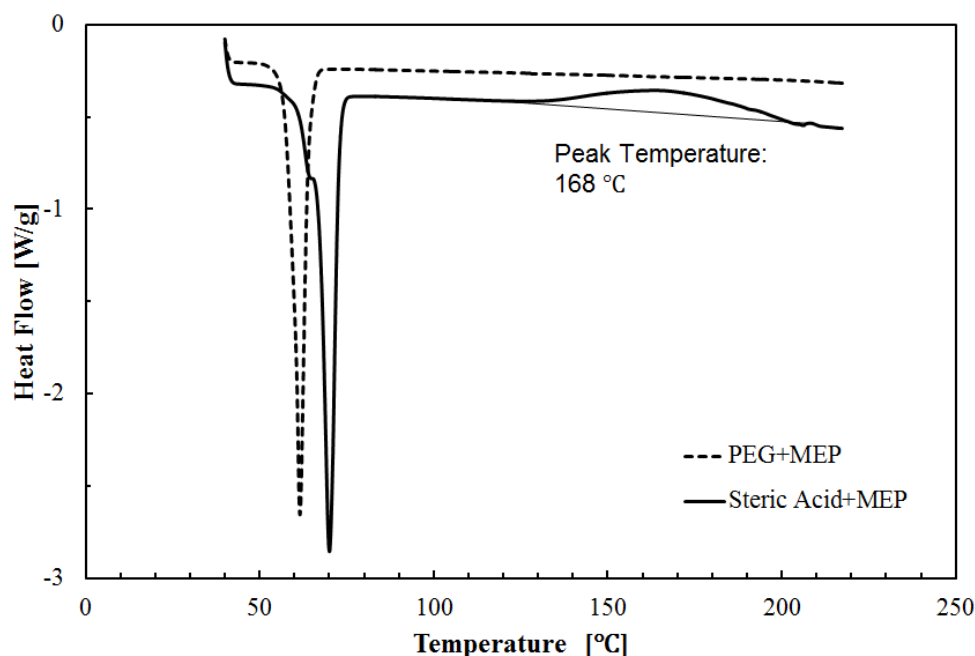


Figure 2.2: DSC of PEG-MEP and stearic acid-MEP mixtures.

The gel formation reported in previous studies is due to improper processing conditions. Either the processing temperature used was too high or the screw configuration resulted in areas of extreme high shear. These high shear zones can result in a dramatic increase in the temperature of the melt locally, which can lead to the formation of gels caused by the hydroxyl group reaction.

2.3.2 Synthesis and Characterization of EF-PLA

The results of the DSC model compound study indicated that only the carboxyl chain end of PLA reacts with the MEP under typical PLA processing conditions. Thus, only branched PLA structures form instead of a crosslinked network (gel), irrespective of the MEP content. Utilizing specific processing conditions, materials can be made without fear of gelation. In order to verify this conclusion, two samples of EF-PLA with high MEP content (EF-PLA-5% and EF-PLA-10%)

were synthesized by REX and subjected to soxhlet extraction to determine if any gel was formed. As expected, no gels were found, indicating no crosslinking during the REX process.

There are multiple epoxy groups present in each MEP, which on average has a molecular weight of 6800 g/mol and an epoxy equivalent weight of 285 g/mol. Reactive compounding with higher molecular weight PLA (~100,000 g/mol) results in more epoxy groups present than the carboxyl groups, even at low total weight percent of MEP. If all PLA chains reacted with epoxy groups during the reactive extrusion of EF-PLA, the resulting material would still be capable of further reaction since it still possesses unreacted epoxies. This potential for further reaction makes the EF-PLA good modifier compounds.

The concentration of MEP in the reaction with PLA to make EF-PLA has a dramatic impact on the structural architecture of the polymers (**Figures 2.3 and 2.4**) as shown through the molecular weight and molecular weight distribution analysis. At lower concentrations of MEP, less than ~5%, there are multiple PLA chains grafting onto one MEP molecule as shown schematically in Figure 2.3. This occurs because at these ratios there are more PLA carboxylic chain ends available for grafting than MEP molecules. Therefore on average, there will be more than one PLA chain reacting with each MEP. This is shown by the observed increase in molecular weight values (M_w and M_n) and the polydispersity index (PDI). Very interestingly, as the concentration of MEP was increased from 5 to 10%, the molecular weight and PDI decreased (**Table 2.1**). This can be explained on the basis that there are more MEP molecules than PLA chains for grafting, and therefore generate the structure in Figure 2.4. In this material, there is one PLA chain per MEP molecule, as opposed to structure in Figure 2.3 with multiple PLA chains per MEP molecule. This suggests that as the MEP concentration in the reaction with PLA is increased,

the structure from Figure 2.4 forms with more unreacted epoxy groups available in the EF-PLA modifier, increasing its overall potential reactivity.

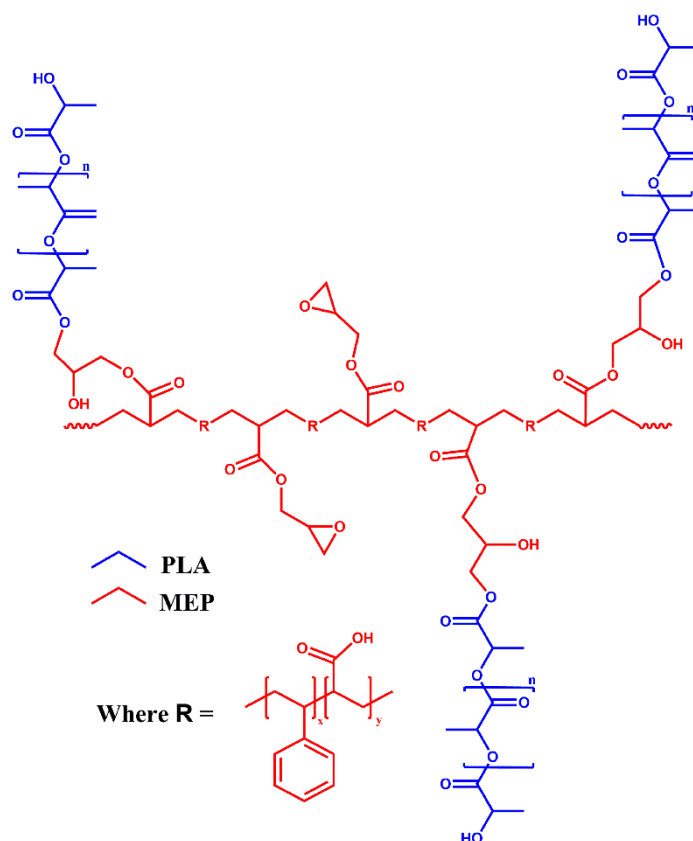


Figure 2.3: Molecular structure of EF-PLA modifiers at low MEP concentrations.

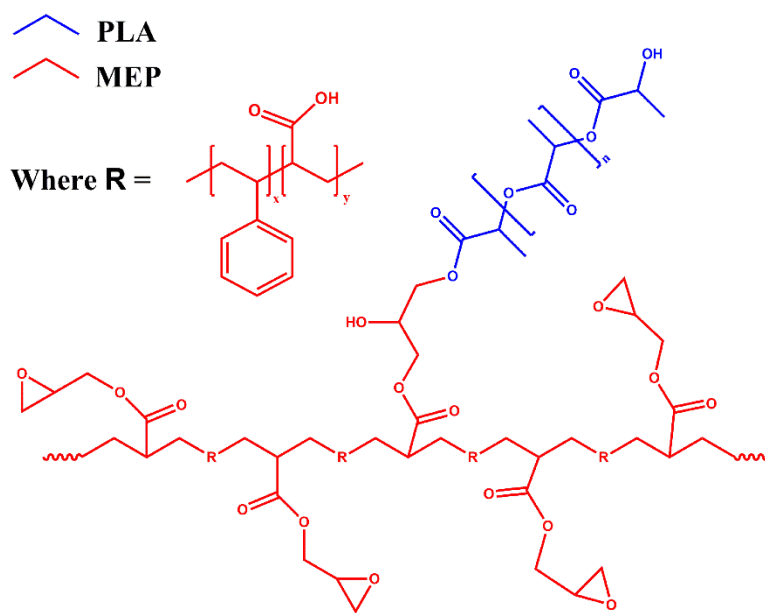


Figure 2.4: Molecular structure of EF-PLA modifiers at high MEP concentrations.

Table 2.1: Effect of MEP content on molecular weight of EF-PLA

MEP [wt. %]	M _w [10 ³]	M _n [10 ³]	PDI
0	139	95	1.46
1.0	248	143	1.73
5.0	327	171	1.91
10.0	211	115	1.83

2.3.3 Synthesis of EF-PLA Modified PLA Resins

The EF-PLA modifier formed by reactive extrusion of 5% MEP in PLA has been reactively blended with neat PLA to obtain resin formulations containing MEP concentrations of 0.25, 0.5 and 1.0 wt%. The molecular weight of these modified PLA formulations increased with increasing MEP content (1.84×10^5 to 3.61×10^5 g/mol). As discussed earlier, the EF-PLA modifier has

additional epoxy groups available for reaction. These react with PLA chains to give branched, high molecular weight products (**Table 2.2**) with suitable rheological properties (discussed in section 2.3.4) for blown film operations.

Table 2.2: Molecular weight characteristics of EF-PLA modified PLA

MEP [wt. %]	M_w [10³]	M_n [10³]	PDI
0.25	184	77	2.39
0.5	250	102	2.45
1.0	361	121	2.98

The value of using EF-PLA as a reactive modifier in neat PLA is clearly observed when comparing samples containing 1 wt% MEP. Higher PDI and molecular weight were observed in the PLA samples modified with EF-PLA to give 1 wt% MEP ($M_w=3.61 \times 10^5$, PDI=2.98) compared with a sample containing 1 wt% MEP obtained by directly blending PLA with 1 wt% MEP ($M_w=2.48 \times 10^5$, PDI=1.73). With the same total amount of MEP in the samples, modification with EF-PLA utilizes the reactive material present in a much more effective way. Rather than just mixing the MEP throughout the neat PLA, making the same a slightly high molecular weight as is seen in the direct blending method, modification with EF-PLA creates a portion of the sample that is highly branching with an ultra-high molecular weight. This is seen by the introduction of a shoulder in the GPC curves.

GPC curves of these samples and the original PLA resin used in this study are shown in **Figure 2.5**. The presence of a high molecular weight shoulder is clearly observed in the samples modified with EF-PLA. This high molecular weight fraction is clearly the result of the epoxy ring-

opening reaction connecting multiple PLA chains to a single MEP. The data further indicates that the amount of the high molecular weight fraction increased as the total concentration of MEP in the sample was increased, at these low concentrations.

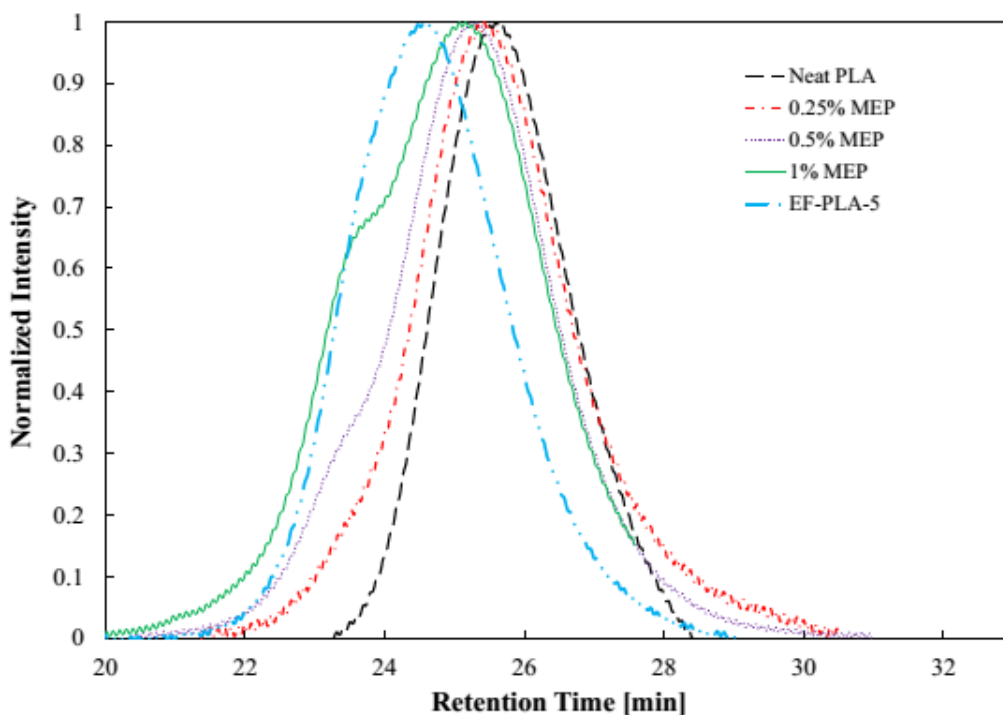


Figure 2.5: GPC traces of neat PLA, PLA modified with EF-PLA-5%, and EF-PLA-5%.

GPC is a technique in which the retention time of a material is a function of its hydrodynamic volume. This hydrodynamic volume is typically related to linear, monodisperse polystyrene polymers of known molecular weights. This calibration data is then used to relate the retention time of a polymer to an experimental molecular weight. However, since GPC is really a measure of hydrodynamic volume rather than molecular weight, densely branched polymers do not necessarily give an accurate result. A densely branched polymer, compared to a linear polymer of similar molecular weight, will have a smaller hydrodynamic volume. Therefore through GPC

analysis, a lower molecular weight would be determined. Because of this, solution viscosity determined with Ubbelohde viscometers was used to determine the intrinsic viscosity ($[\eta]$) of the modified PLA compounds. Intrinsic viscosity is expressed in the units dL/g and essentially represents the volume of a polymer per unit mass. This conceptually simple test is one of the most precise measurements in polymer science and can provide considerable physical insight.

Table 2.3: Intrinsic viscosity data determined by solution viscosity for modified PLA samples

Sample	Intrinsic Viscosity (dL/g)
Neat PLA	1.375
0.25% MEP	1.315
0.5% MEP	1.450
1% MEP	2.209
1% MEP from Single Step	1.507
EF-PLA-5%	1.705

Table 2.3 shows the intrinsic viscosity data for the modified PLA samples as determined through Ubbelohde viscometry. The same trend is seen as that for the molecular weight characteristics. With increasing MEP content up to 1%, an increase in intrinsic viscosity is observed, with EF-PLA-5% being lower than the 1% MEP sample but yet slightly higher than the 0.5% MEP sample. Also the 1% MEP samples modified with EF-PLA and single step blending of MEP show drastically different results that mimic those of the molecular weights. A graphical comparison of M_w and Intrinsic Viscosity showing how the same trend is followed for both measurements is portrayed in Figure 2.6. If the polymers were highly branched resulting in a dense structure, then the Intrinsic Viscosity should follow a different pattern than the M_w . However,

since the same trend is experienced for both measurements this indicates that the long chain branching in the EF-PLA modifier does not result in a densely packed structure. The long linear polymers connected by a single MEP does not yield the densely branched structure typically seen by more traditional short chain branching.

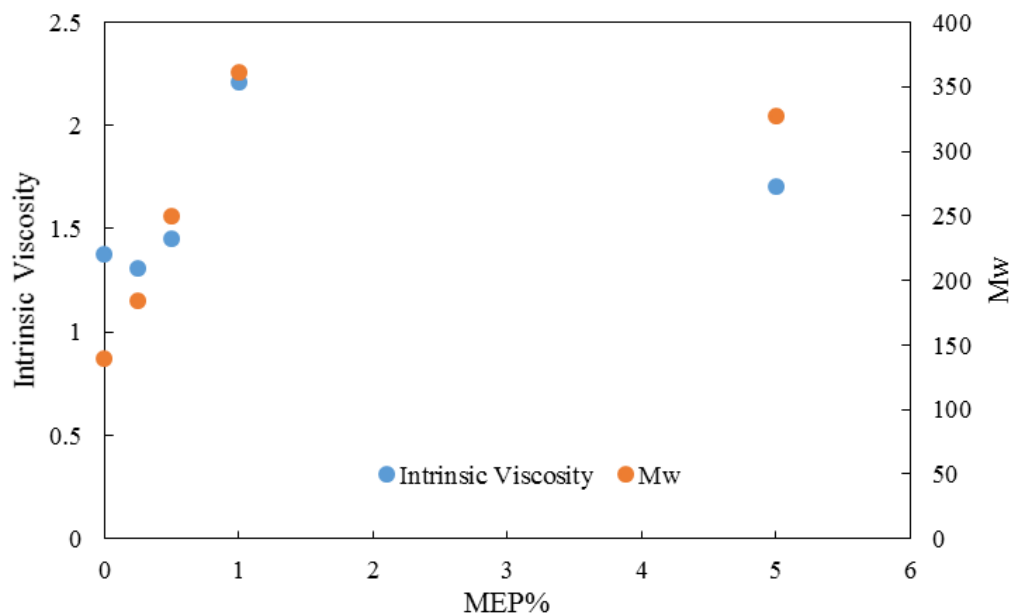


Figure 2.6: Graphical comparison of intrinsic viscosity and weight average molecular weight of EF-PLA modified samples as a function of MEP concentration.

2.3.4 Rheological Properties

At high shear rates the viscosity of a branched polymer system is lower than that of a linear system of the same molecular weight. This is due to the branched polymer's more compact structure, also leading to the branched polymers exhibiting more pseudoplastic behavior.³² At high shear rates the chains disentangle and flow past each other, so the branching doesn't really effect viscosity. As the MEP content in the samples increased, a more significant shear thinning behavior

was observed (**Figure 2.7**) indicating that a branched structure was obtained via reaction with EF-PLA. Long chain branching has a significant effect on the zero shear viscosity (low shear rates in general) because of the increase in relaxation times caused by the branches. Polymer relaxation usually occurs by motion along the backbone, but the branch points hinder this therefore a significant effect on viscosity at low shear rates is observed.³³ There was a dramatic difference in low shear rate viscosity between the 1% MEP samples synthesized through reactive blending with EF-PLA and the sample synthesized by direct blending with 1 wt% MEP. This direct blending method is what has been done in previous studies and what is currently used for industrial processes involving PLA films. The sample modified with EF-PLA showed a complex viscosity ~4 times greater than direct blending with 1 wt% MEP. This is due to the distribution of the MEP in the samples made from the different processing conditions. As mentioned earlier, by modification with EF-PLA, a branched high molecular weight fraction is created in the sample, as opposed to an even distribution in the direct blending which just account for a slight increase in molecular weight evenly. This high molecular weight fraction has a much more substantial effect on the viscosity of the sample, as seen by the large increase in melt strength. Even with higher MEP content, the complex viscosity of the 1% MEP sample obtained through direct blending was lower than that of the sample containing 0.25% MEP prepared through modification with EF-PLA. Again, this shows how the distribution of MEP can show large effect on the properties. This phenomenon can either be used to create better blown films or used to create the similar rheological properties with much less MEP.

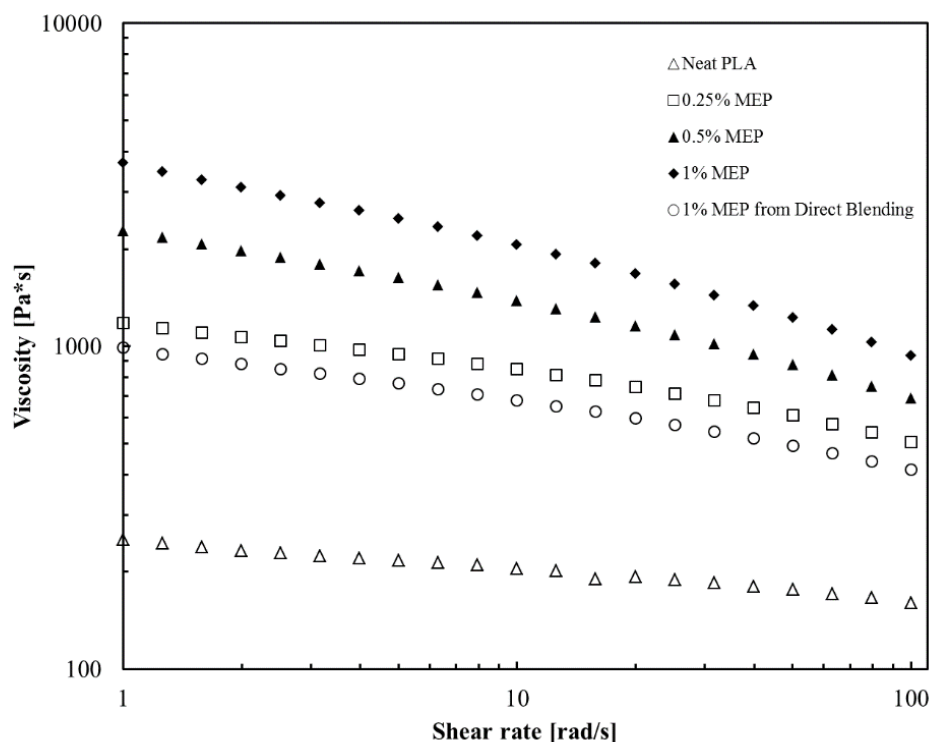


Figure 2.7: Comparison of complex viscosity frequency sweep at 180°C between neat PLA, PLA modified with EF-PLA-5%, and 1% MEP from direct blending.

A complex viscosity-temperature correlation study was conducted to compare the rheological properties of the EF-PLA modified materials. Four temperatures (170, 180, 190, and 200°C) were studied (**Figure 2.8**). A significant viscosity decrease was observed as the temperature was increased for all formulations. However when the temperature was ~180°C, the modified PLA (1% MEP) showed a comparable complex viscosity to LDPE, which could be used as a guide for the viscosity needed for effective film blowing.

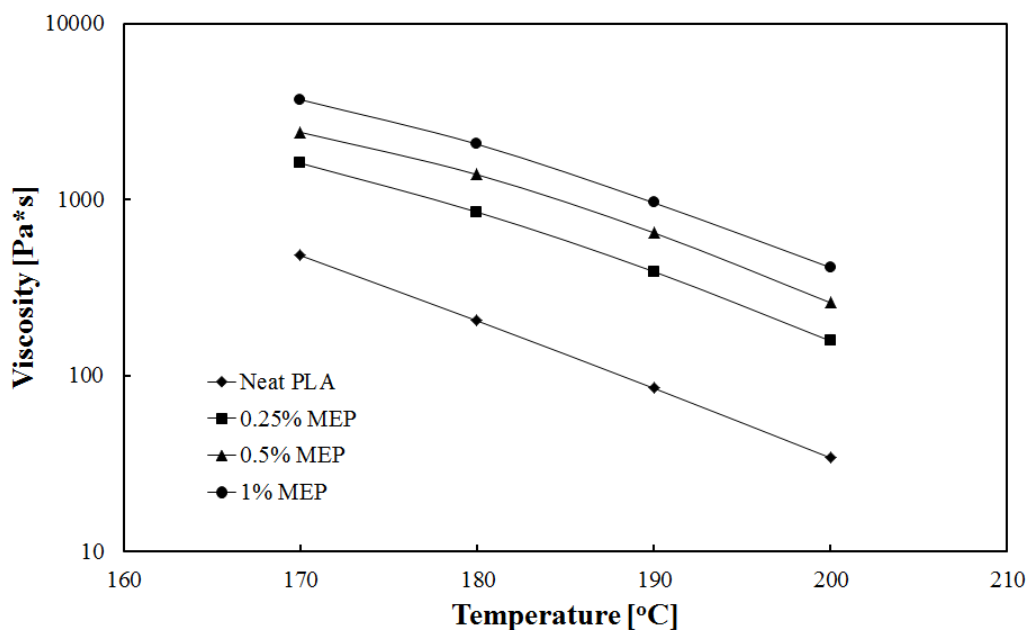


Figure 2.8: Complex viscosity at 10 rad/s at various temperatures for neat PLA, and EF-PLA-5% modified PLA.

Extensional viscosity is an important property for polymer processing, especially for film blowing and foaming operations. The extensional viscosity of a polymer can be increased by increasing the molecular weight as well as the number of entanglements, which can be done through branching. The extensional viscosity of the EF-PLA modified PLA products was tested at 180°C (which is a common PLA processing temperature) at varying strain rates (in rad/s). In **Figure 2.9**, the extensional viscosity of neat PLA was compared to that of the EF-PLA modified PLA products containing 1 wt% MEP. The modified PLA exhibited over 1000 times higher extensional viscosity at the same strain rate compared with neat PLA due to an increase in melt strength and dramatic strain hardening. Also pictured is varying strain rates for the 1% MEP sample through EF-PLA modification. Note that as the strain rate is increased the strain hardening and therefore extensional viscosity increases. It should be noted that increasing the MEP content

resulted in both an increase in extensional viscosity as well as strain hardening (for the low MEP content modified samples), again resulting in rheological properties similar to that of LDPE. Strain hardening is a crucial property in film blowing and foaming operations as it impacts bubble stability and size of the foam cells.

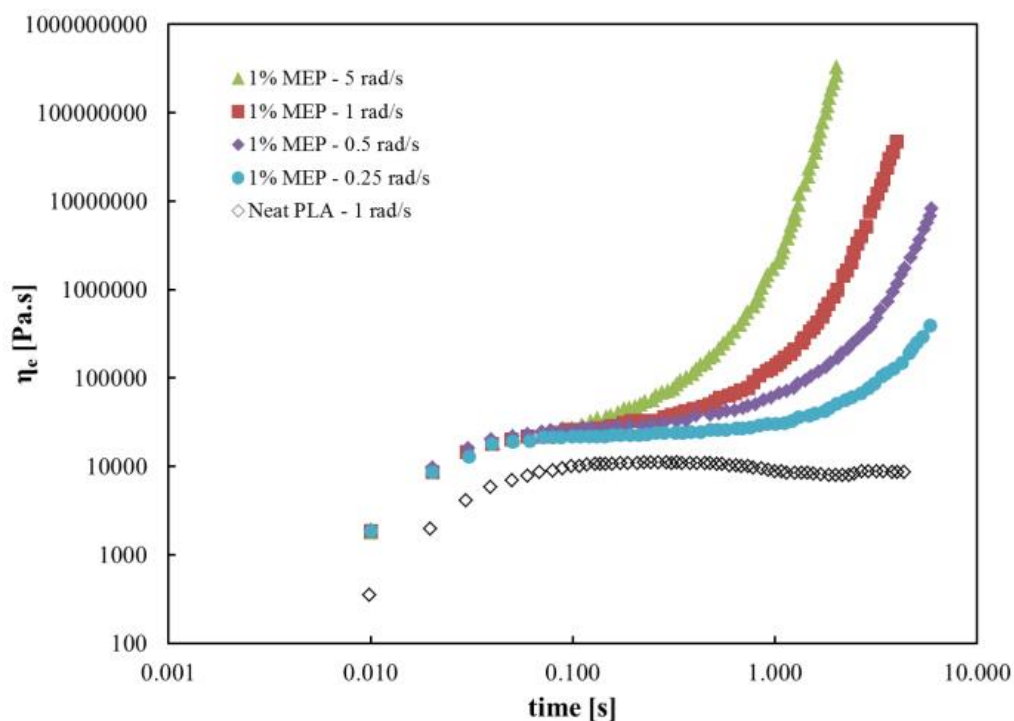


Figure 2.9: Comparison of extensional viscosity at 180°C between neat PLA at 1 rad/s and EF-PLA modified PLA (1% MEP) at varying strain rates.

2.3.5 Statistical Modeling of EF-PLA

The synthesis of EF-PLA and reactive blending with PLA can be statistically modelled to provide more fundamental understanding of the reaction and experimentally observed properties. The model is based on random interaction and reaction of the polymer chains. The molar percentages of the components are calculated using the relative mass percentages of the

components in the reactive blends and the molecular weight data provided by the suppliers. The molecular weight data was experimentally validated using GPC. The molar % is needed to determine how PLA and MEP interact in the synthesis of EF-PLA. At a specific MEP concentration, there exists different extents to which the materials react. For example, 1 PLA chain can be grafted onto an MEP molecule, or 2 PLA chains can attach, and so on. There can also exist free/unreacted PLA and MEP depending on the relative molar ratios used. Each of these combinations of PLA and MEP has a theoretical molecular weight (ex. The molecular weight of 2 PLA chains grafted on 1 MEP molecule = $2 \cdot MW_{\text{PLA}} + MW_{\text{MEP}}$). The probability of each of these species occurring at a specific MEP concentration can be calculated based on the molar % using Standard Probability Theory. This is done much like in the example where there is a bag of red and blue marbles, of the marbles, 60% are red and 40% are blue. The probability that if two marbles are picked from the bag and they are both red, would be $0.60 \cdot 0.60 = 0.36$ or 36%. Thus, probabilities for each of the PLA/MEP species existence can be calculated, and that coupled with their theoretical molecular weights can lead to molecular weight characteristics being calculated. Weight and number average molecular weights can be calculated by determining the theoretical molecular weight and probability of each species existing using the following equations.

$$M_w = \frac{\sum p_i M_i^2}{\sum p_i M_i} , \text{Equation 2.4}$$

$$M_n = \sum p_i M_i , \text{Equation 2.5}$$

where M_i is the theoretical molecular weight of each PLA and MEP combination and p_i is the probability of its occurrence. A factor in the simulation that needed to be experimentally determined was the maximum number of PLA chains that can react with a given MEP, which is equivalent to the maximum number of epoxy groups that can react on a given MEP molecule. If

there were 10 active epoxy groups present on each MEP, then a small percentage of the MEP molecules would contain 10 PLA chains. This would significantly increase the theoretical weight average molecular weight of EF-PLA compared to the assumption that only 5 epoxies are active. **Figure 2.10** shows the simulated weight average molecular weights at varying MEP mass content assuming three different number of maximum epoxy groups per MEP molecule. The experimental weight average molecular weight data obtained for EF-PLA by GPC appears to follow the curve of 5 reactive epoxy groups per MEP in the simulation model. Four and six epoxies were also used to calculate the theoretical molecular weights (not pictured in the figure) however the best fit occurred with five epoxies.

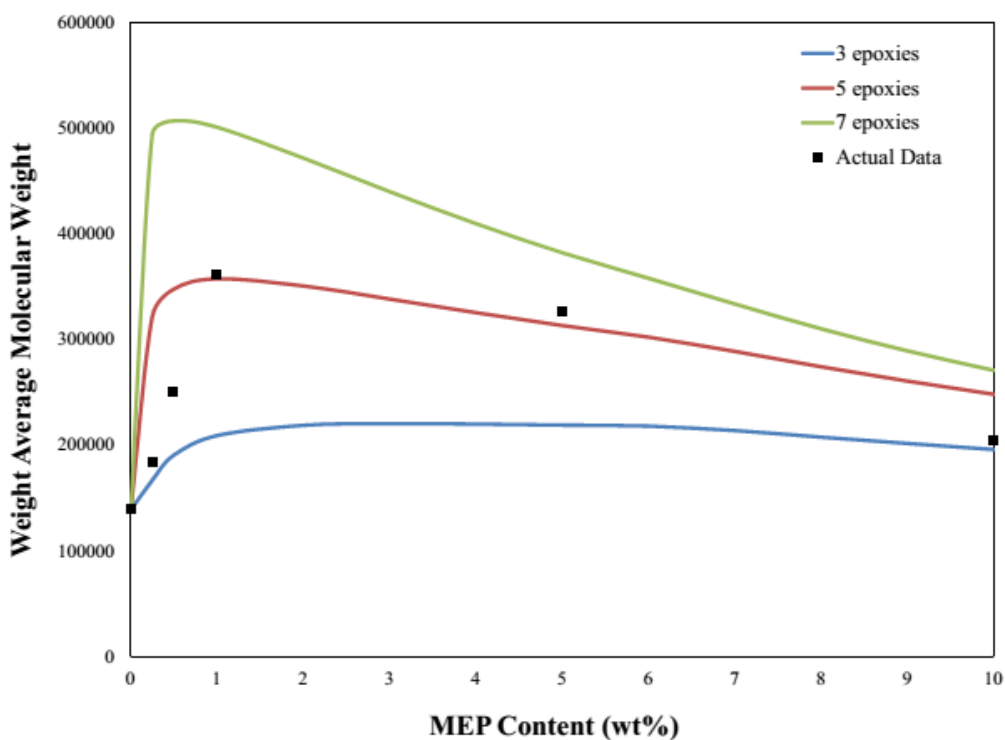


Figure 2.10: Comparison of actual data with simulated weight average molecular weight of PLA compounds modified with EF-PLA assuming different number of epoxy groups per MEP.

The following assumptions were made for the statistical simulation to operate correctly; 1) all epoxy groups have equal probability to react with PLA (Markovian behavior), 2) only the carboxyl groups of PLA react (experimentally validated using model compounds), 3) MEP does not react with MEP, 4) when $[\text{mol\% PLA}] > [\text{mol\% MEP}]$, all MEP reacts (there is no free MEP left in the blend), 5) when $[\text{mol\% PLA}] < [\text{mol\% MEP}]$, all PLA reacts (there is no free PLA left in the blend), and 6) a maximum of 5 epoxy groups per MEP molecule can react (validated experimentally by measuring M_w values using GPC results). This model can be used as a tool to tailor properties of the EF-PLA modifier for specific applications.

As can be seen from Figure 2.10, the simulation shows good fit with the actual data except at the extreme ends, high and low MEP concentrations. This is because the model assumes that at high MEP concentrations there is no free PLA because it has all reacted with epoxy groups (Assumption 5). 100% reaction is difficult to achieve in practice and the experimental data shows that there is free PLA remaining which lowers the molecular weight of the sample. Conversely, the simulation shows more rapid molecular weight increase at very low MEP concentrations compared to the actual data. This is due to Assumption 4 requiring every MEP molecule to react. Assuming 100% reaction shifts the maximum molecular weight to lower MEP concentration than observed experimentally because in practice 100% reaction is not obtained.

The model can also be used to determine the percentage of unreacted epoxy groups remaining on the MEP molecules in the modified compounds and the EF-PLA modifiers as shown in **Figure 2.11**. The model shows good fit between predicted unreacted epoxy content and the experimentally determined epoxy content following ASTM D1652. For example, the simulated epoxide weight percentage of the 5 and 10 wt% MEP EF-PLA compounds had 0.33 and 0.94 wt%

epoxy groups remaining, respectively, while experimental titration data showed epoxy percents of 0.299 and 0.95 wt%.

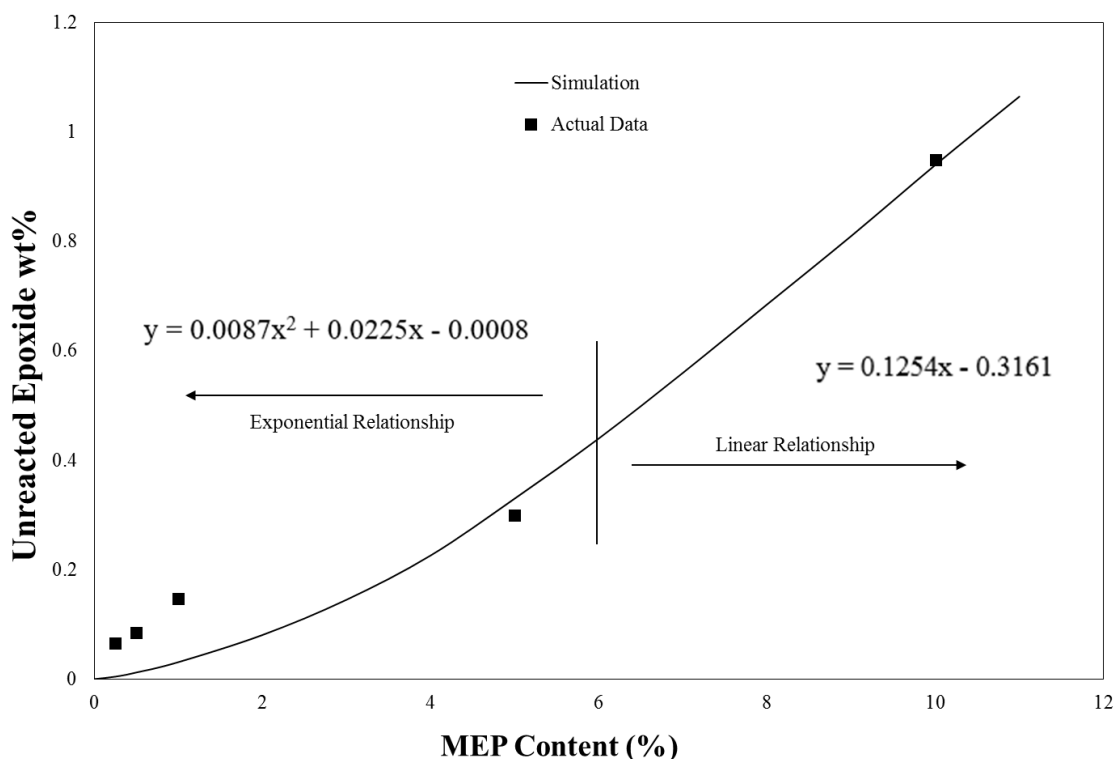


Figure 2.11: Simulated reactive epoxide weight percent compared to experimental data of EF-PLA modified compounds.

The epoxide content calculated by the model follows an exponentially increasing relationship at low MEP concentrations before switching to a linear relationship at ~6.4 wt% MEP. This switch over point is where an equimolar ratio of PLA to MEP is observed. At this specific point, the simulation is assuming that all MEP molecules have one PLA chain attached to them. Any additional increase in MEP content after this point results in fully unreacted MEP molecules in the system, making the relationship linear. At MEP concentrations lower than this equimolar

point the extent of MEP reaction is determined by probability. As more MEP is introduced the average extent of reaction goes down and the reactive epoxide wt% goes up, and this model predicts this as an exponential increase.

EF-PLA molecules containing higher MEP concentrations are capable of more reaction than molecules containing lower concentrations, and could potentially be better used as compatibilizers and precursors for copolymer synthesis. Physically, this is seen as a material that has more unreacted epoxy groups present and is capable of further reaction with the carboxyl groups of PLA or other polymers. Large potential for further reactivity combined with the fact that PLA is covalently bonded to the material makes this high MEP content EF-PLA an excellent compatibilizer, in addition to the processing benefits due to rheological property modifications. The statistical model developed can be used as an excellent guide for tailoring the properties of the EF-PLA compounds for targeting specific applications as the model shows a good fit with respect to both molecular weight and epoxide content.

2.4 Conclusion

The reaction mechanism between MEP and PLA was investigated concluding that under careful processing conditions only the carboxyl end-groups of PLA react with the epoxy groups of MEP. An EF-PLA rheology modifier has been synthesized through reactive extrusion containing a relatively high concentration of MEP (up to 10 wt%) without gel formation. Reactive blending of EF-PLA with neat PLA provided significant rheological property improvements, such as increased viscosity and strain hardening characteristics that are necessary for blown film and foam applications. These improvements cannot be achieved by directly blending the MEP polymer with PLA in a single step blending process. The rheological enhancement is due to the uneven

dispersion of the MEP into PLA forming ultra-high molecular weight species. Direct blending does not result in the formation of these ultra-high molecular weight species do to the even dispersion of MEP. Therefore the EF-PLA modification resulted in a significant improvement in melt strength and strain hardening, making materials better suited for film blowing. A statistical model was developed to simulate the molecular weight effects and unreacted epoxide content of PLA modified with EF-PLA at varying MEP concentrations to serve as a tool to better understand the reaction.

Chapter 3 – Reactive Modification and Compatibilization of Poly(lactide) and Poly(butylene adipate-co-terephthalate) Blends with Epoxy Functionalized-Poly(lactide) for Blown Film Applications

3.1 Introduction

PLA is continuing to find increasing applications including injection molded and thermoformed products, especially packaging, and disposable one time use products like plastic cutlery.^{34,35} PLA exhibits excellent strength properties and is therefore a good candidate for applications like wrapping films, waste bag/bin liners, and carry out bags. However, PLA's weak melt strength due to its highly linear structure hinders its use in blown film applications.³⁶ Polymers that are ideal for film blowing have high melt strength and exhibit nonlinear viscoelastic properties like strain hardening. Another inherent weakness of PLA is its ductility and toughness.³⁷ Typical PLA exhibits ~3% elongation to failure which limits its potential applications unless modified through plasticization or blending with other polymers.

3.1.1 Rheological Enhancement of PLA

The rheological behavior of PLA can be easily enhanced using reactive modifiers, allowing for easier production of blown films. Incorporating long chain branching and a small fraction of high molecular weight polymer can increase the strain hardening and melt strength of PLA, respectively. Chain extension is a common method to boost the rheological properties in polyesters, where the chain extender either reacts with the polymer's carboxyl or hydroxyl groups. Reactive functional groups on these chain extenders can include isocyanate, peroxide, and epoxide groups. Isocyanates undergo the chain extension reaction readily however their toxicity greatly

limits their use, especially in films, where a major application is food packaging.¹⁶ Peroxide chain extenders also have been shown effective at modifying the rheological properties, however their high reactivity causes gels at concentrations as low as 0.7 wt%.³⁸ Multifunctional epoxy polymers (MEP) can function as rheology modifiers through reaction of the carboxyl and/or hydroxyl groups with the epoxy groups of MEP. This increases molecular weight and imparts branching leading to an improvement in properties.^{26,28,39,40} In our previous work, high concentrations of MEP were reacted with PLA to produce Epoxy Functionalized-PLA (EF-PLA) reactive modifiers.⁴¹ Controlling the reaction temperature below 200°C resulted in the epoxy's preferential reaction with the carboxyl group of PLA leading to no gel formation. We observed a significant increase in the molecular weight, melt strength, and strain hardening properties for EF-PLA modified materials, even compared to traditional MEP modified PLA processing. Therefore, modifying PLA with EF-PLA is an extremely effective and efficient method for enhancing the rheological behavior of PLA, making it more suitable for blown film applications.

3.1.2 Compatibilization of PLA/PBAT Blends

Melt blending PLA in an extruder with other flexible polymers is an excellent method to increase the elongation and toughness of the resulting material and is a highly economical and efficient production method. A common polymer combined with PLA in melt blending is Poly(butylene adipate-co-terephthalate) (PBAT). It is also a biodegradable polymer that possesses excellent ductility, around 700%. Blends of these polymers are still biodegradable and can theoretically possess both the strength and ductility of PLA and PBAT, respectively. By incorporating PBAT into PLA, it has been observed that the ductility of the blended product is increased with increasing PBAT concentration.⁴² The addition of PBAT also decreases the rate of

hydrolytic degradation, which is another issue plaguing PLA.⁴³ However PLA and PBAT are immiscible, so the properties of the blends are highly dependent on the morphology.⁴⁴ As the PBAT content in the blend is increased from 20 to 50 wt%, the blend becomes heterogeneous leading to decreased properties.⁴⁵ Therefore, for manufacturing high performance PLA/PBAT blown film materials, a compatibilizer is an essential requirement.

Literature reports the use of MEP for compatibilizing PLA/PBAT blends, resulting in improved mechanical properties.⁴⁶⁻⁴⁸ However, very few papers report the use of these materials for blown film applications.^{38,49} As discussed earlier, EF-PLA is a highly effective rheology modifier of PLA. EF-PLA is a high molecular weight branched PLA polymer, in which its molecular weight and reactive epoxide percentage can be tailored. It can function as an effective compatibilizer in PLA/PBAT blends because the unreacted epoxy groups on the EF-PLA can react with PBAT forming EF-PLA-*g*-PBAT copolymers (**Schematic 3.2**). This copolymer localizes at the interphase and provides for compatibilization resulting in more stable and smaller dispersions of PLA in the PBAT matrix. In turn this results in improved mechanical properties. This makes EF-PLA not only an excellent rheological modifier but also an efficient compatibilizer as well, resulting in a final product that has significantly improved processability (improved melt strength and strain hardening) and performance properties (dart strength).

Based on the discussion above, we report the use of EF-PLA as a rheology modifier and compatibilizer to produce blown films of PLA/PBAT blends with enhanced ease of processing and excellent mechanical properties compared to unmodified control films. Two different EF-PLA modifiers were used containing different MEP concentrations (5% and 10%). Physical characteristics and processing of the films are discussed with emphasis on bubble stability and texture while mechanical properties of the films were determined by tensile and dart impact testing.

Molecular weight and epoxy content characterizations were used as a method of monitoring the reactivity of EF-PLA in the film blends. The morphology of the resulting films was studied and used as a comparative tool for the change in mechanical and physical properties. The EF-PLA modifiers are also compared to a rheological modifier commonly used in the blown film industry, and the previously mentioned characterization techniques are used to describe the mechanical improvements seen with EF-PLA modifiers.

3.2 Experimental

3.2.1 Materials

PLA resin pellets (Ingeo 3052D) were purchased from NatureWorks, LLC (NE, USA) with a weight average molecular weight of ~175,000 and 4% D-lactide (8% meso-lactide) content. The MEP (Joncryl 4368C), PBAT (Ecoflex F Blend C1200), and a PBAT masterbatch containing an erucamide slip agent (Ecoflex Batch SL 1) were obtained from BASF (IL, USA). The PBAT had a weight average molecular weight of ~90,000 and the slip agent masterbatch had a 10% loading of erucamide. The Industrial Modifier, described at the end of the chapter, is CesaExtend (OMAN698493) from Clariant (NC, USA) and possesses a MEP loading in PLA of ~30 wt% (Reactive epoxy content = 4.56 wt%).

3.2.2 Reactive Extrusion of EF-PLA

The PLA resin pellets were dried for a minimum of 6 hours at 60°C in a vacuum oven. PLA and MEP pellets were carefully weighed and physically blended to obtain mixtures containing various percentages of each (5 and 10% MEP in PLA). The physical blend was then fed into a 26 mm diameter LabTech (Thailand) co-rotating, twin screw extruder with an L/D ratio

of 44:1. All samples were compounded at a throughput of ~6 kg/hr, cooled in a water bath, and then pelletized (LZ-120, LabTech, Thailand). The screw speed was held constant at 140 rpm for all compounding, as it was shown to provide the greatest reaction in previous testing where the speed was adjusted. The temperature profile used for all compounding was:

143 – 154 – 171 – 177 – 177 – 177 – 177 – 185 – 185 – 185 – 185°C

The EF-PLA compounds that were created consisted of 5% (EF-PLA-5%) and 10% (EF-PLA-10%) of MEP by weight.

3.2.3 Production of PLA/PBAT Based Films

All resin pellets were dried a minimum of 6 hours at 60°C in a vacuum oven to remove any residual moisture. This is crucial when dealing with PLA because it can hydrolytically degrade through extrusion processes as a result of hydrolysis, back-biting, and intermolecular transesterification reactions, which can result in decreased properties.¹² The various materials were carefully weighed to determine accurate weight percentages, which also included an additional 2% of the slip masterbatch to enhance the ease of handling after production. The films produced had PLA content ranging from 20 – 70% and for each concentration three different films were made; a control sample containing neat PLA and PBAT, and two samples modified with EF-PLA so that the total MEP content in the films was 1%. To get to 1% total MEP in the films, 20% of EF-PLA-5% and 10% of EF-PLA-10% are needed. Therefore all modified films, regardless of PLA or PBAT content, had 1% MEP in the system. Since the reactive content is the same for all films, the differences in the film's properties are due to how the MEP is incorporated with the different

EF-PLA reactive modifiers. The preweighed mixture of pellets was added to the hopper of a LabTech (Thailand) Extrusion Blown Film Line. The single extruder (Type LE20-30/C) had a 20 mm diameter with an L/D ratio of 30:1, and the attached blown film unit (LF250) had a 2 inch die diameter.

The processing parameters of films such as the Blow-up Ratio (BUR) and nip roller speed have a large effect on the resulting properties of the films and therefore all conditions were held constant. BUR is the ratio of the diameter of the blown film bubble to the diameter of the extrusion die. It can be difficult if not impossible to accurately measure the diameter of the inflated bubble, so instead it can be calculated using the width of the bubble after it has been flattened (Layflat Width) through the nip rollers according to the equation below. The Layflat Width is half of the circumference of the bubble, therefore relating the bubble diameter to Layflat Width is done through the factor of $2/\pi = 0.637$.

$$BUR = \frac{0.637 * \text{Layflat Width}}{\text{Die Diameter}}, \text{Equation 3.1}$$

The temperature of the extruder across all heating zones and the die was held at 185°C and maintained at a consistent screw speed of 40 rpm, which resulted in a residence time of ~5 minutes. The nip roller speed was held constant and pulled the film at 5.3 ft/min and the bubble was blown to a consistent layflat width of 7.5 inches. These processing parameters resulted in an average film thickness of ~1 mil (25.4 µm) and a BUR of 2.4.

3.2.4 Mechanical Properties Characterization

3.2.4.1 Tensile Properties

The tensile properties of the films were characterized in both the machine (MD) and transverse (TD) directions following ASTM D882-12: Standard Test Method for Tensile Properties of Thin Plastic Sheeting.⁵⁰ Films were conditioned for at least 24 hours prior to testing in a temperature and humidity controlled environment. The testing specimens were cut from the blown film using a parallel blade sample cutter with a fixed width of 1 inch. Specimens were long enough to ensure that at least 1 inch of additional material was on each side of the gage length, to prevent any slippage. The testing apparatus was an Instron 5544 (MA, USA) testing machine using Bluehill 2 software. The ultimate strength and elongation data were determined with a grip separation rate of 20 in/min (508 mm/min) in accordance with the ASTM for films with elongations at break greater than 100%. For determination of modulus of elasticity, a grip separation rate of 1 in/min (25.4 mm/min) was used. A minimum of 6 specimens were tested for each orientation of the film samples. The properties recorded were max load, max stress and strain, elastic modulus, and thickness.

3.2.4.2 Dart Impact Properties

The impact resistance of the films was determined with testing following ASTM D1709-09: Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method.⁵¹ This test method determines the energy needed to cause a plastic film to fail 50% of the time under specified conditions by a free-falling dart. The energy needed for failure is expressed as a weight (mass) of the dart. Method A was employed for this testing utilizing the standard testing technique, the staircase method.

The blown film samples were cut and separated lengthwise so that only a single layer of film could be tested at a time. Prior to testing, the thicknesses of the films throughout the tested area were measured to ensure consistent film thicknesses. Sections of the films that did not possess uniform and consistent thickness were not subjected to testing.

3.2.5 Gel-Permeation Chromatography

The molecular weights characteristics of all raw and manufactured materials were determined by gel-permeation chromatography (GPC). The intensity was measured by a Refractive Index Detector (RID-10A, Shimadzu, Japan) using a combination of columns (Waters Co., MA, USA). Tetrahydrofuran was used as the mobile phase with a flow rate of 0.500 mL/min at 40°C. Polystyrene standards were used as a reference for molecular weight calculations.

3.2.6 Epoxy Content Titrations

Titration was performed to determine the remaining reactive epoxy groups present in the reactive modifiers and the films. The procedure used is outlined in ASTM D1652-11: Standard Test Method for Epoxy Content of Epoxy Resins.⁵² In this method, the titration is done using a perchloric acid solution in the presence of an excess of tetraethylammonium bromide. The combination of perchloric acid and tetraethylammonium bromide generate hydrogen bromide in situ, which with the quaternary ammonium halide rapidly opens the oxirane ring. The epoxide weight percent, E, is determined by the equation:

$$E = F \times \frac{V}{W_e} , \text{Equation 3.2}$$

where F is the perchloric acid solution reagent factor, determined through standardization with potassium hydrogen phthalate, V is the volume of the perchloric acid solution needed to reach the equivalence point, and W_e is the weight of the sample used in grams.

3.2.7 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was used to determine any differences in thermal properties of the films created. Samples of film (~5 mg) were placed in a Tzero aluminum pan and heated from room temperature to 200°C, then cooled to -50°C, and reheated to 200°C at 10°C/min using a Discovery DSC from TA Instruments (DE, USA).

3.2.8 Scanning Electron Microscopy

The morphologies of the films were studied using a JEOL 6610LV (Japan Electron Optics Laboratories, Japan) Scanning Electron Microscope (SEM). The samples were cut from the films and cryofractured using liquid nitrogen. They were mounted vertically to look at the fractured cross-section followed by coating with approximately 8 nm platinum.

3.3 Results and Discussion

3.3.1 Blown Film Processing and Physical Characteristics

Modification with EF-PLA resulted in different physical characteristics and processability compared to the control films. EF-PLA modified films resulted in improved bubble stability, as observed by less popping and tearing of the bubble. Due to this, it was possible to blow PLA/PBAT films with higher PLA concentrations than the control films. The highest PLA concentration that could be blown for the control films was 40% PLA, whereas with EF-PLA

modification a 70% PLA film was produced. The control films at these high PLA concentrations were not able to achieve the same BUR outlined in the procedure due to overstretching and tearing. The reason the bubble instability occurs for the control samples is because neat PLA possesses very weak melt strength and little to no strain hardening, both of which are critical for film blowing. By incorporating EF-PLA, PLA has higher melt strength and can strain harden which makes the film blowing more effective and efficient. The free epoxy groups on EF-PLA continue to react with neat PLA and PBAT, thereby enhancing its ability to be blown into a film by further increasing melt strength and strain hardening. This allows EF-PLA to not only act as a rheological modifier but as a compatibilizer as well, making more stable films.

The control films were also more difficult to process because they possessed a lot of static charge. Due to the static, once the nip rollers flattened the bubble it became difficult to separate the layers, regardless of how much slip additive was in the film, resulting in a poor quality final product. The EF-PLA modified films did not possess this static charge which resulted in a film with much better slip (i.e. the layers were easier to separate).

There were also physical differences observed between the modified and control films, most notably texture and color. The EF-PLA modified films had a much softer texture, which probably correlates with better slip. This occurs because EF-PLA acts as a compatibilizer for PLA and PBAT resulting in better dispersion. For the lower PLA content samples (20% and 30%), PLA is the dispersed phase and by decreasing the sizes of these dispersed particles it decreases the overall rigidity of the film resulting in a softer feel. The other physical difference between the films was the color, or more correctly, transparency. Both films were white in color but the control samples were translucent while the modified films were more opaque. This is indicative of films

with higher crystallinity and can also be affected by morphological differences, which will be discussed later.

3.3.2 Molecular Weight Characteristics

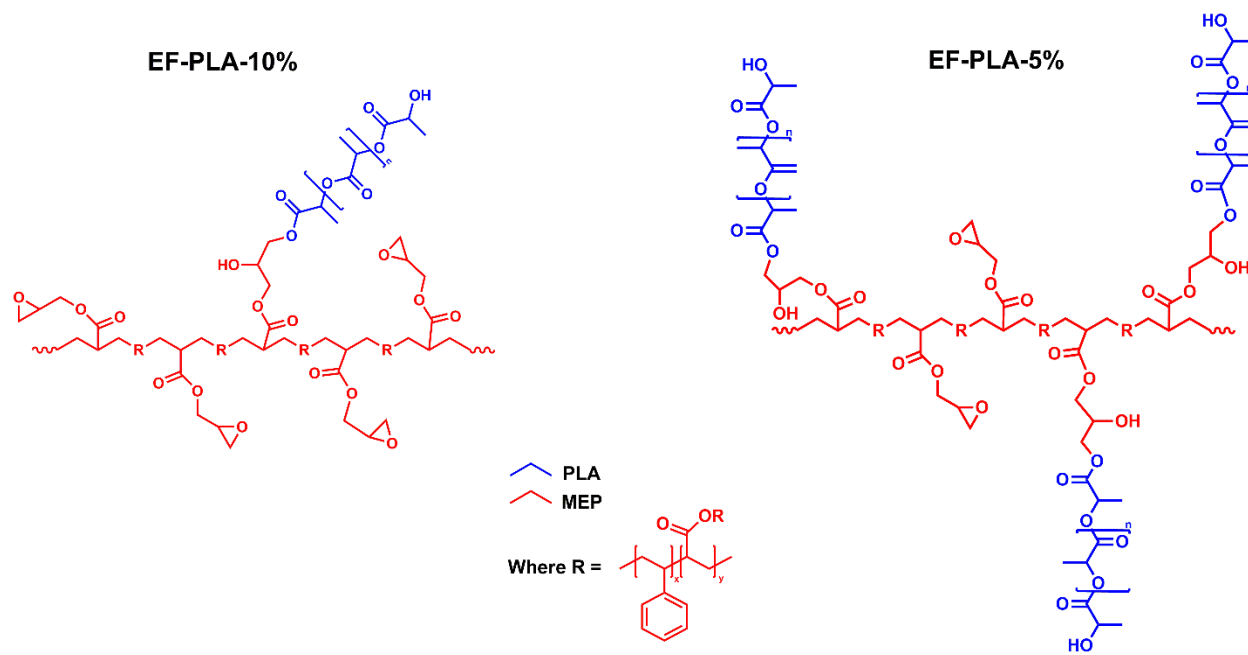
The different EF-PLA reactive modifiers possess different starting characteristics which should have different effects on the resulting molecular weights of the films. The molecular weight characteristics of the films produced should give insight into the property differences from the various reactive modifiers used, as well as the controls. First, we look at the neat resins and the EF-PLA reactive modifier compounds (5% and 10%).

Table 3.1: Molecular weight characteristics of neat resins and reactive modifiers

	M_w [10³]	M_n [10³]	PDI
Neat PLA	175	105	1.67
Neat PBAT	115	55	2.09
EF-PLA-5%	300	170	1.76
EF-PLA-10%	210	120	1.75

Table 3.1 shows that the neat PLA has a higher molecular weight than neat PBAT. So as more PLA is introduced into the films, the molecular weights of the films will increase, even for the controls. EF-PLA-5% is a higher molecular weight modifier than EF-PLA-10%, however it possesses less unreacted epoxy groups which makes EF-PLA-10% the more reactive molecule. In comparing the molecular weights, it is clear that EF-PLA-5% on average has 2-3 PLA chains connected to one MEP molecule.⁴¹ This results in a higher molecular weight, and more branched structure. EF-PLA-10% however shows molecular weight characteristics close to 1 PLA chain

per MEP, yielding a more linear structure with higher reactivity from the additional epoxy groups available (**Schematic 3.1**).



Schematic 3.1: A schematic comparison of the EF-PLA reactive modifiers based on molecular weight characteristics.

Figure 3.1 shows the weight average molecular weights of the films produced. As expected, when the PLA content in the films is increased, the molecular weight increases. In comparing the EF-PLA modifiers, EF-PLA-5% results in films with higher weight average molecular weights (M_w) than seen in modification with EF-PLA-10%. However, there is no significant difference observed in number average molecular weight (M_n) or polydispersity (PDI). This leads to the conclusion that the differences in M_w are due to the creation of ultra-high molecular weight species, which would have a large effect on M_w , but a small effect on M_n . EF-

PLA-5% starts at a higher M_w and further reaction during film blowing results in formation of high molecular weight species resulting in the higher M_w .

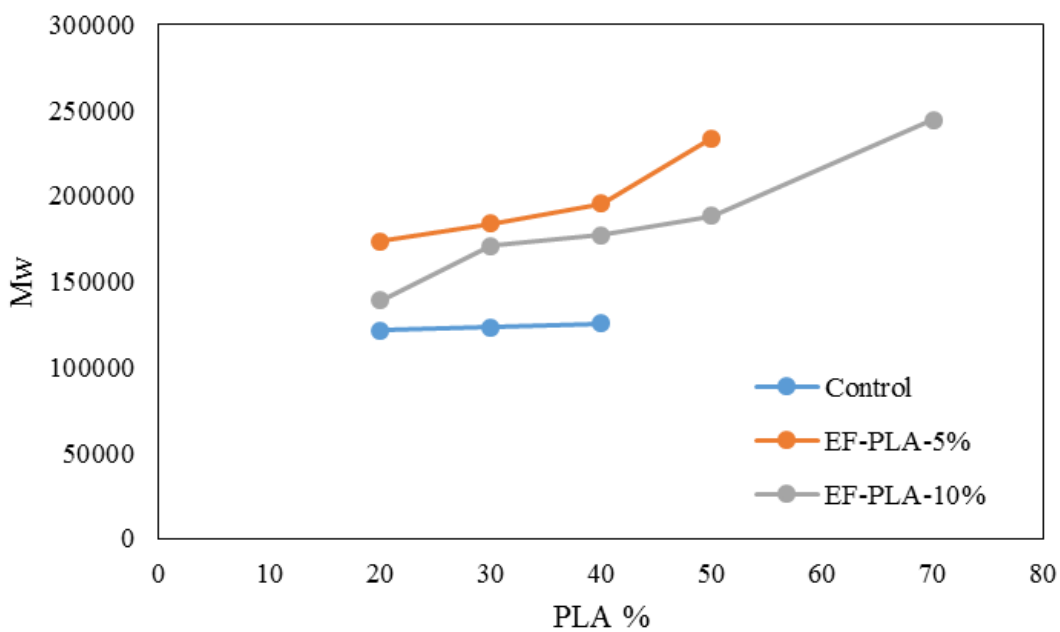
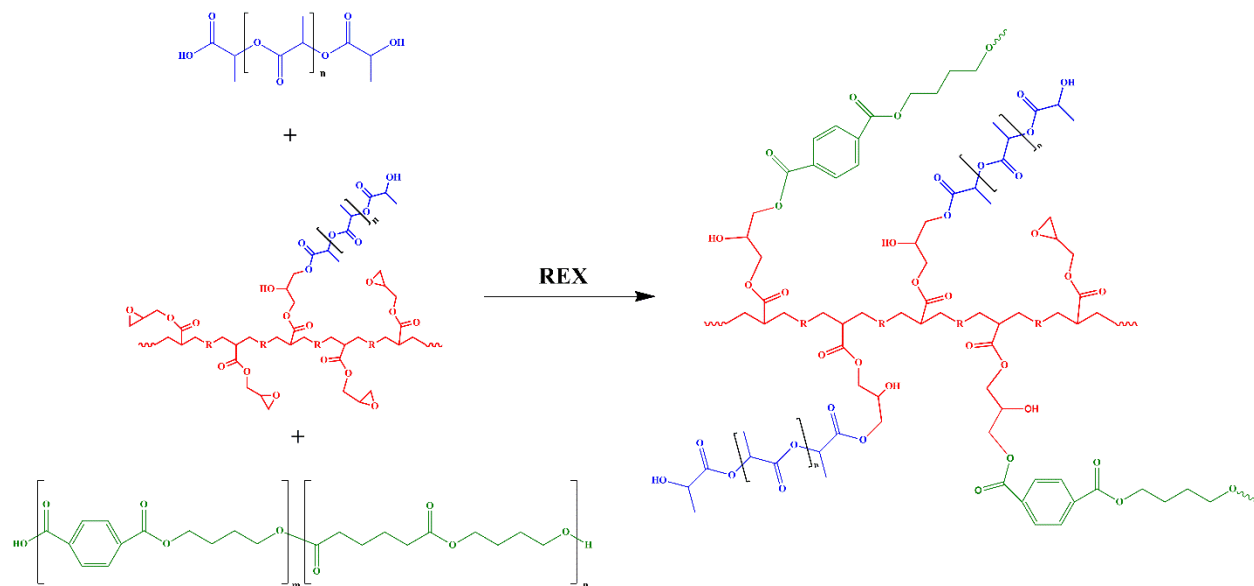


Figure 3.1: Weight average molecular weight as a function of reactive modifier and PLA content.

The reactive epoxy groups on the EF-PLA modifiers are capable of reaction with both neat PLA and PBAT, since they are both polyesters containing carboxylic acid end groups. The resultant chemical species is a branched copolymer of PLA and PBAT, with an MEP center as shown in **Schematic 3.2**. These copolymers are created in situ and aid in compatibilization of the blends by localizing at the interphase between the two phases. This results in better dispersion as well as smaller dispersed particles.



Schematic 3.2: The reaction of neat PLA and PBAT with EF-PLA-10% to yield a high molecular weight, branched copolymer.

3.3.3 Epoxide Content Analysis

The molecular weight and property differences observed in the films made with reactive modifiers containing different epoxide content can be understood by reviewing the epoxide content analysis and molecular structure. EF-PLA-5% is a higher molecular weight, highly branched material with less reactivity (unreacted epoxide content of 0.30 wt%). In comparison, EF-PLA-10% is lower molecular weight, more linear structure and higher reactivity (epoxide content of 0.95 wt%). The total MEP content in all of the films was kept at 1%, but the structure and epoxy content of the modifier used accounts for the property differences.

The reactive epoxide content (weight percent of unreacted epoxide groups in the polymer) is shown in **Table 3.2**. In comparing the EF-PLA modifiers, the data clearly shows that the film samples with the EF-PLA-10% modifier have more residual unreacted epoxy groups than the films

from EF-PLA-5%. EF-PLA-10% with its lower molecular weight and linear structure would be a more effective compatibilizer. EF-PLA-5% with its higher molecular weight and branched structure would be more effective as a rheology modifier.

Table 3.2: Residual epoxide content in the modified films

Film Sample	Epoxide %	% Increase over EF-PLA-5%
<i>20% PLA (EF-PLA-5%)</i>	0.116	-
<i>20% PLA (EF-PLA-10%)</i>	0.121	3.87
<i>30% PLA (EF-PLA-5%)</i>	0.102	-
<i>30% PLA (EF-PLA-10%)</i>	0.111	8.32
<i>40% PLA (EF-PLA-5%)</i>	0.127	-
<i>40% PLA (EF-PLA-10%)</i>	0.137	7.87

3.3.4 Morphological Comparison

The cryofractured surfaces of the films were analyzed using SEM to determine the effect of modification on the resultant morphology and to give explanation for the differences in mechanical properties. Since the TD properties best predict the overall film quality, discussed later, SEM micrographs of the TD cross-sections are shown in **Figure 3.2**. Figure 3.2(a) and 3.2(b) show the 30% PLA films modified with EF-PLA-10% and control, respectively. At this PLA concentration, PBAT is the continuous phase with PLA fibrils dispersed in it. See Figure 3.2(a) and 3.2(b) where the PLA fibrils can be seen dispersed in the dark PBAT matrix. The SEM shows that the interface for the control film, Figure 3.2(b), is sharply defined and separated indicating poor compatibility between the two blend components. The addition of the EF-PLA provides compatibilization of the two phases and one can see better dispersion of the PLA fibrils in the PBAT matrix in Figure 3.2(a). This is observed as a diffused interface in the SEM demonstrating

compatibilization. Increasing the PLA content of the films to 40% results in a change in morphology for the control samples with the white PLA fibrils beginning to connect and forming the continuous phase with PBAT becoming the dispersed phase (Figure 3.2(d)). This morphology change at 40% PLA in PLA/PBAT blends was also noted by Arruda et al.⁴⁹ The EF-PLA-10% modified film seen in Figure 3.2(c) shows smaller and better dispersed fibrils than those in the control film. The interface is diffused showing better compatibilization. The increased compatibility from the EF-PLA results in better and more stable dispersion at this high PLA content. Indeed, the EF-PLA modified films exhibit superior dart properties of these films, discussed next, because of the morphology change to the continuous PLA matrix and incompatibility of the two phases in the control film. Therefore EF-PLA modifiers can be used to create a high PLA content films (40%) with superior mechanical properties compared to control blends.

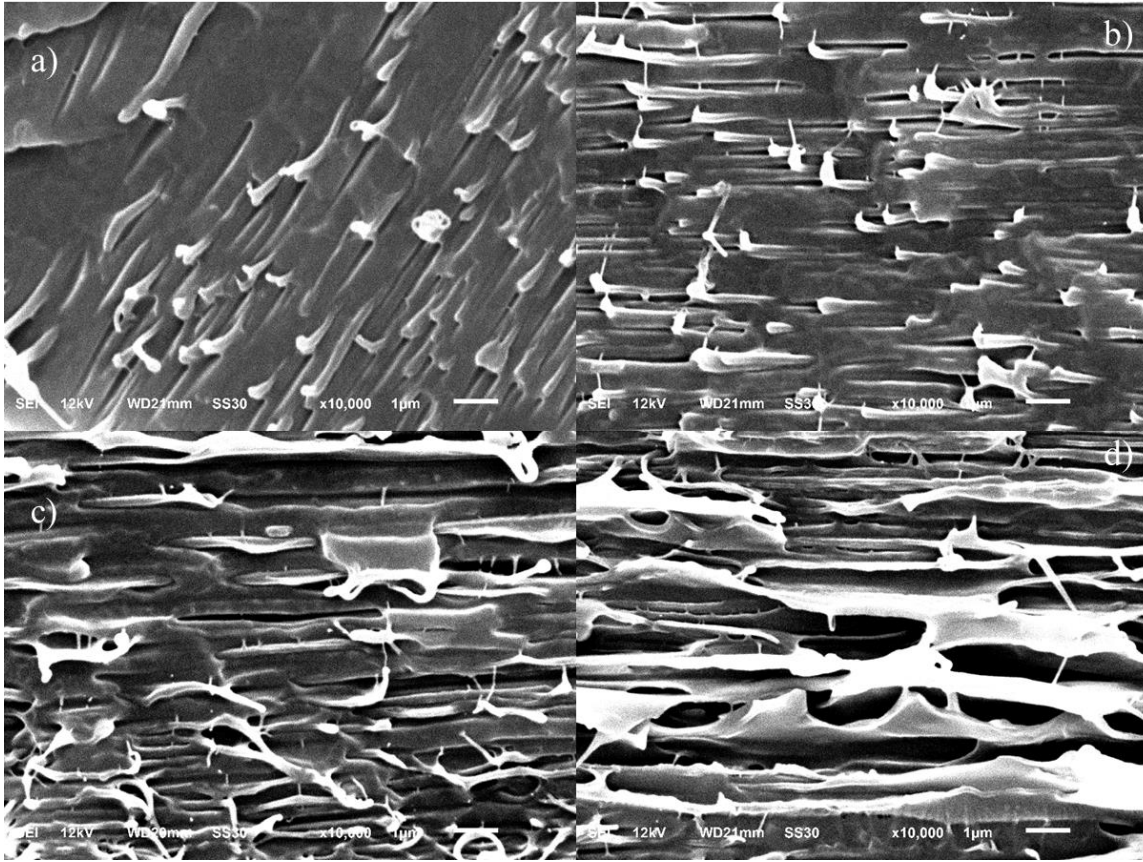


Figure 3.2: SEM micrographs of modified films, a) 30% PLA with EF-PLA-10%, b) 30% PLA control, c) 40% PLA with EF-PLA-10%, and d) 40% PLA control.

3.3.5 Mechanical Properties of Films

3.3.5.1 Dart

The impact resistance of the films were tested through the free-falling dart method in which varying weights are dropped onto the samples in a consistent manner. The results are measured in the weight (in grams) of the dart required for failure 50% of the time. However it is actually a determination of the energy required to puncture the film. Therefore, a higher failure weight results in a more impact/puncture resistant film. This resistance is a combination of the film's strength and ductility in its ability to deform and absorb the energy. Therefore dart testing is a

good measure of the overall performance of a film because it is a dynamic test that is a combination of mechanical properties.

EF-PLA modification resulted in an increase in dart performance. The EF-PLA modified film samples showed failure at much higher weights than the control samples at all PLA concentrations. The EF-PLA enhances the molecular weight and branching of the polymers, which increases the number of chain entanglements. This leads to more strain hardening and therefore an increase in toughness. The EF-PLA modifiers also act as a compatibilizer between PLA and PBAT which can increase miscibility allowing for better dispersion, increasing properties. The films modified with EF-PLA-5% showed a maximum dart weight at 20% PLA content while films with EF-PLA-10% reached a maximum at 30% PLA (**Figure 3.3**). This supports the earlier discussion that the lower molecular weight and linear structure of EF-PLA-10% provides more compatibilization compared to EF-PLA-5% modifiers, resulting in better properties for the high PLA content films. The most significant result is seen in films containing 40% PLA, where the failure weight of the EF-PLA modified films is >4 times that of the control film. At this high PLA content without compatibilization, immiscibility occurs and the two components are phase separated, as previously shown in Figure 3.2.

A significant decrease in the failure weight is seen once the PLA content reaches 50% for the modified films and at 40% for the controls. This sudden drop off in impact resistance can be attributed to the change in morphology of the films. At lower PLA concentrations, PLA is dispersed in the continuous PBAT matrix. The PBAT provides good flexibility to the film while the dispersed PLA imparts strength and stiffness, resulting in a film with high dart properties. The EF-PLA modification provides for better dispersion and a more stabilized morphology resulting in improved properties. As the PLA content is increased, a morphological change occurs resulting

in a continuous PLA phase being formed. Figure 3.2 shows the white PLA fibrils connecting to form a continuous fibrular matrix and phase separation from the dark PBAT matrix. The continuous PLA matrix properties dominate, and its inherent brittleness greatly detracts from the films properties, as seen by the drastic reduction in dart performance. The EF-PLA modifiers hold off this morphology change until higher PLA content allowing for significantly better dart performance than control films at 40% PLA. The EF-PLA modified films show only a 17% decrease in dart properties from the 30% to 40% PLA films. In contrast, the control films with no EF-PLA added, showed a 77% decrease in dart performance.

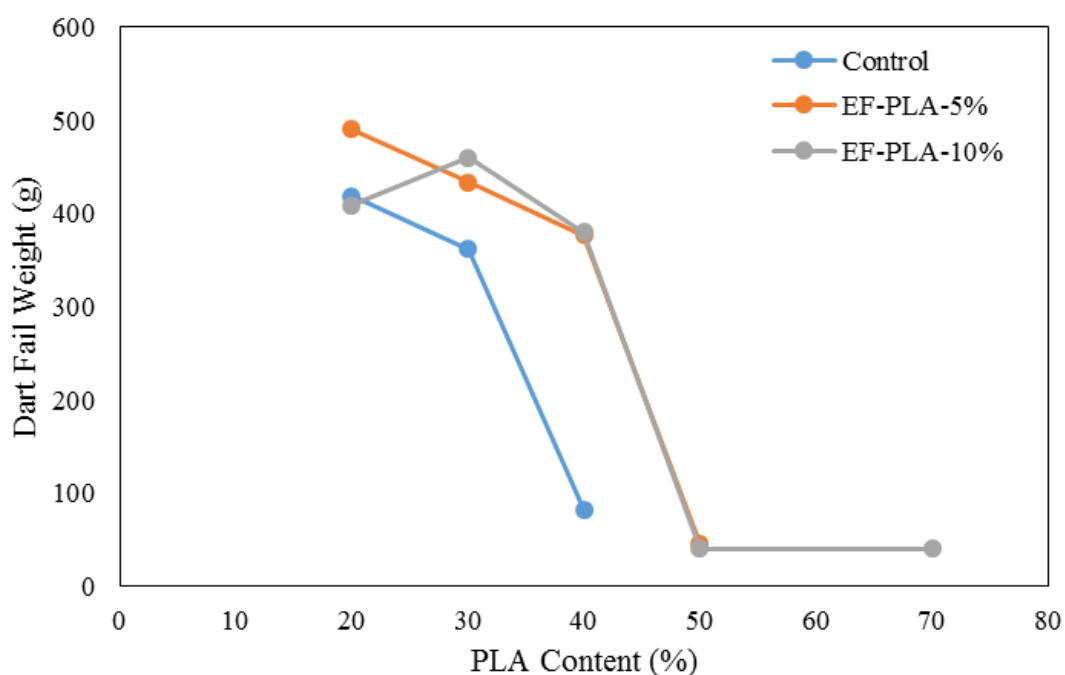


Figure 3.3: Dart impact performance as a function of reactive modifier and PLA content.

3.3.5.2 Tensile

Film blowing involves biaxial stretching of the polymer melt, therefore the resultant films tend to be anisotropic. Because of this, the film samples were tested in both the machine direction (MD) and the transverse direction (TD). The tensile properties of the films for the most part followed the rule of mixtures, where an increase in the PLA content resulted in an increase in modulus and a decrease in ductility (**Figure 3.4**). However, the maximum stress achieved for the films did not occur at the highest PLA content, as would be expected. This maximum typically occurred around 30-40% PLA, most likely due to immiscibility issues. The tensile properties for the EF-PLA-10% films exhibited a slightly different trend than the other films. It is probable that the more unreactive EF-PLA-10% doesn't fully utilize its reactivity until there is 30% PLA, which is why it exhibits different local minima and maxima.

The strength of the films modified with EF-PLA was higher than that of the control films, especially in the MD. The addition of high molecular weight branched polymer chains in the sample increases the number of chain entanglements, which allows the film to withstand a higher stress prior to failure. An interesting result was observed in the fracture strain behavior. The MD fracture strain of the control films was higher than the EF-PLA modified films, while the opposite trend occurred in the TD with the modified films experiencing higher strain.

The most significant result of tensile testing was observed for the TD modulus. At 40% PLA, the TD modulus of the control film showed a dramatic increase. This was the same concentration when the dart performance significantly decreased. The TD modulus appears to show an inverse correlation with the dart performance of the films. This is also seen for the EF-PLA modified films at 50% PLA and higher. The TD moduli of these films increases at a more rapid rate and this is accompanied by the drastic decrease in dart performance. The modulus

significantly increases when the PLA goes from a dispersed phase to a co-continuous phase in the blend. As PLA becomes the matrix it more greatly affects the moduli of the films, and therefore its inherent brittleness decreases the dart properties.

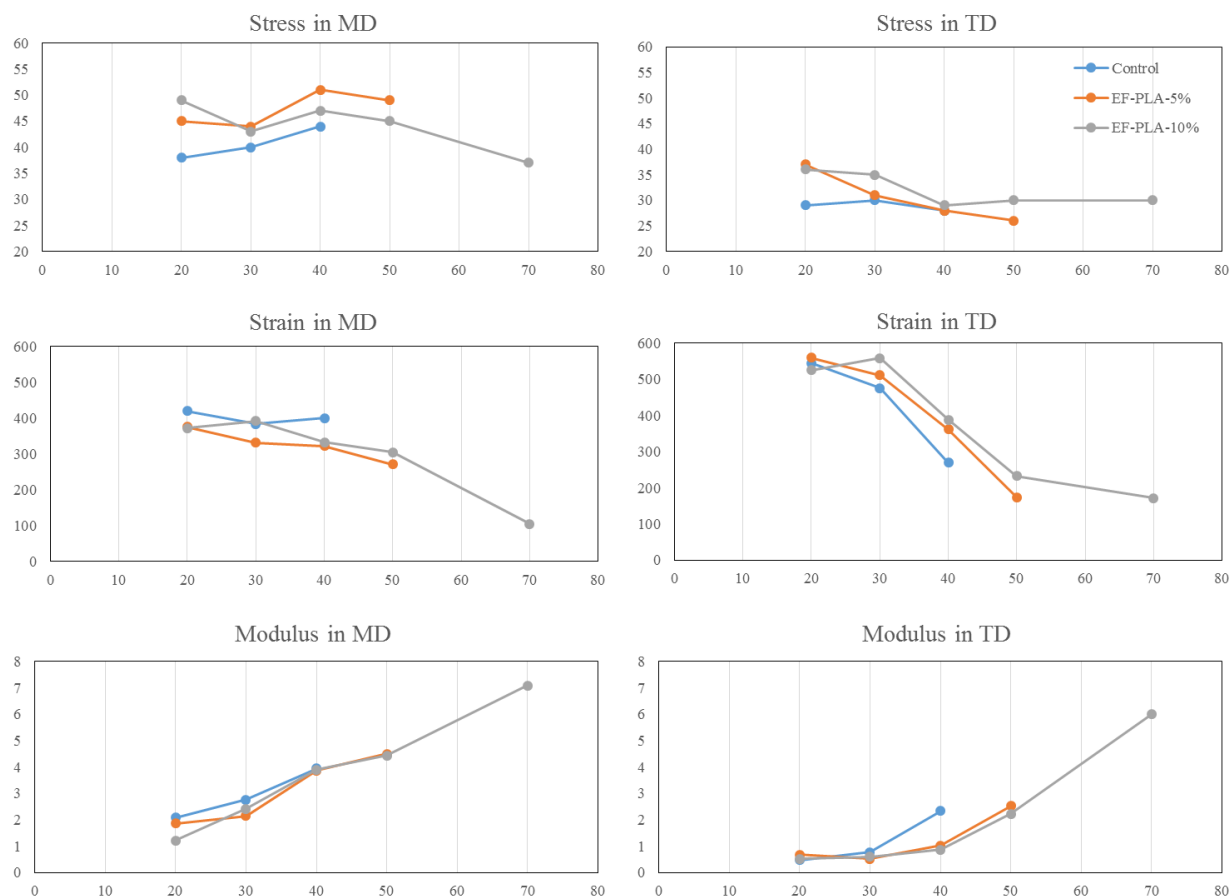


Figure 3.4: Tensile properties of modified and unmodified PLA/PBAT films.

3.3.6 Thermal Properties of Films

The films were analyzed with DSC to determine any effects that EF-PLA modification had on crystallinity and crystallization behavior, and the results are shown in **Table 3.3**. No significant trend was observed for T_g and T_c of PLA and PBAT in the films, however T_m and crystallinity

(X%) were affected by the reactive modifiers. The control films showed a lower melting temperature (T_m) than the EF-PLA modified films, potentially indicating that the crystallites in the control films were smaller.⁵³ When EF-PLA is reactively blended into the film, there is a drastic decrease in PLA crystallinity along with an increase in PBAT crystallinity. The incorporation of the high molecular weight branched PLA structure makes it difficult for PLA to crystallize, hence lower PLA crystallinity is observed. The higher PBAT crystallinity in the modified films could be due to the formation of larger crystallites rather than more crystallites, which would coincide with the increase in T_m .

Even amongst samples modified with EF-PLA there is a slight difference in the crystallinity depending on the EF-PLA modifier used. The samples created with EF-PLA-10% have slightly higher crystallinities than those created with EF-PLA-5% due to the molecular weight difference of these materials. EF-PLA-10% is lower molecular weight than EF-PLA-5% and therefore is capable of more and quicker crystallization. This trend occurs for both the crystallinity of PBAT and PLA in the films.

Table 3.3: Thermal properties of modified and unmodified PLA/PBAT films

Film Sample	T_{m,PBAT}	X_{% ,PBAT}	X_{% ,PLA}
<i>20% PLA Control</i>	120.6	3.8	2.6
<i>20% PLA (EF-PLA-5%)</i>	123.8	5.4	0.0
<i>20% PLA (EF-PLA-10%)</i>	124.0	6.3	0.0
<i>30% PLA Control</i>	110.6	2.9	5.8
<i>30% PLA (EF-PLA-5%)</i>	123.3	5.3	0.2
<i>30% PLA (EF-PLA-10%)</i>	122.3	6.1	0.2
<i>40% PLA Control</i>	109.3	3.4	11.0
<i>40% PLA (EF-PLA-5%)</i>	123.0	4.8	0.3
<i>40% PLA (EF-PLA-10%)</i>	122.0	5.0	0.5
<i>50% PLA (EF-PLA-5%)</i>	123.0	2.9	1.3
<i>50% PLA (EF-PLA-10%)</i>	120.5	4.2	1.5
<i>70% PLA (EF-PLA-10%)</i>	-	0.0	9.6

3.4 Comparison to Common Industrial Modifier

It has become common practice in industry to use epoxy functionalized rheology modifiers for PLA blown films. Often this is done either through direct blending of a material like MEP into PLA or modifying PLA with the reactive masterbatch CesaExtend (Industrial Modifier) sold by Clariant. However, due to its extremely high MEP content (~30 wt%), the Industrial Modifier essentially functions as direct blending with MEP. For the molecular weights of the PLA and MEP used in this study, 30 wt% MEP in PLA correlates to 89.8 mol% MEP. Therefore the majority of the MEP molecules will be completely unreacted and the Industrial Modifier essentially functions as direct blending of MEP. In previous work, from Chapter 2, it was concluded that modifying PLA with EF-PLA is a much more effective and efficient method at enhancing the rheological behavior of PLA compared to direct blending with MEP. Thus creating a PLA more suitable for blown film applications. In this section, the use of EF-PLA as a rheological modifier and compatibilizer is compared to the Industrial Modifier in the production of blown films. The total

MEP content in all films was held constant at 1 wt%, however depending on the modifier used, the distribution of the MEP is very different. The modifiers and films were analyzed looking at molecular weight and remaining epoxide reactivity to give reasons for the differing mechanical properties.

3.4.1 Molecular Weight Comparison

The Industrial Modifier contains a large amount of MEP (~30 wt%); therefore the majority of it is completely unreacted and not chemically combined with PLA to yield high molecular weight branched structures. Without these high molecular weight branched structures the Industrial Modifier exhibits a lower M_w than both EF-PLA reactive modifiers, as seen in **Table 3.4**. The large fraction of unreacted MEP is seen in the elution curves as a bimodal distribution, which results in the large PDI.

Table 3.4: Molecular weight comparison of reactive modifiers

	M_w [10^3]	M_n [10^3]	PDI
EF-PLA-5%	300	170	1.76
EF-PLA-10%	210	120	1.75
Industrial Modifier*	180	6	28.81

*A bimodal distribution was observed

The molecular weight differences of the reactive modifiers leads to molecular weight differences for the blown films, shown in **Figure 3.5**. Earlier, the conclusion was made that the differences in M_w for the films are due to the creation of ultra-high molecular weight

species. Since EF-PLA-5% starts with more of these species, further reaction results in even more giving it the highest M_w . For this same reason, the films made with the Industrial Modifier have a lower M_w than both EF-PLA modified films. Since the majority of the MEP in the Industrial Modifier is unreacted, very few if any of these ultra-high molecular weight species are created, resulting in fewer branched polymers. Also due to this, the M_n is lower and PDI is higher than the EF-PLA films.

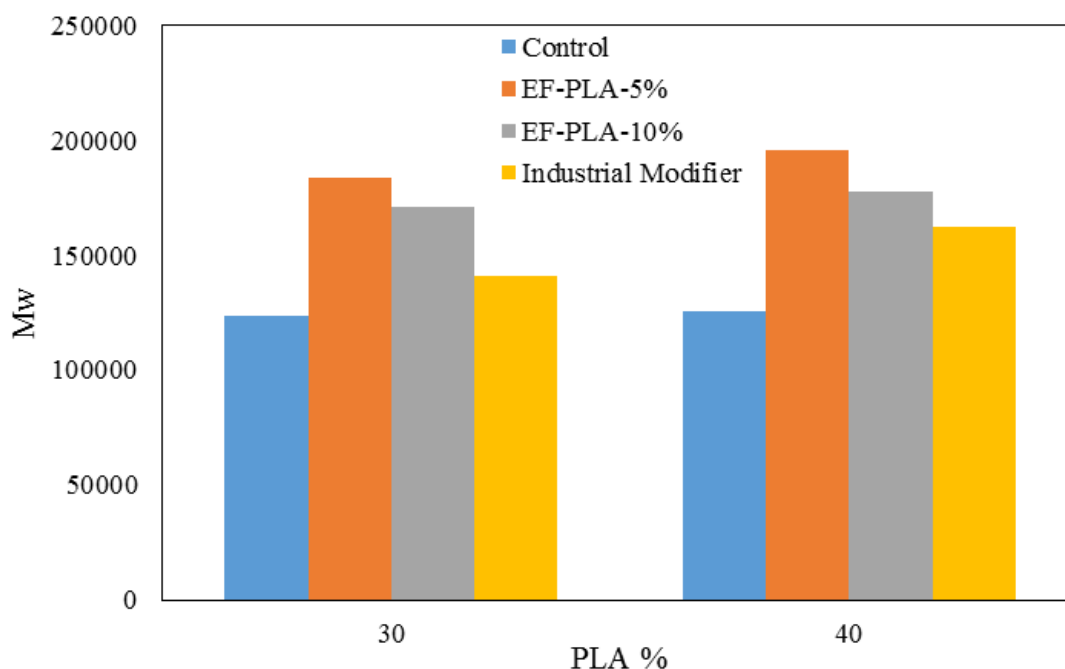


Figure 3.5: Weight average molecular weight of films from the different modifiers.

3.4.2 Epoxide Reactivity Comparison

The Industrial Modifier has a dramatically higher epoxide content (4.56%) compared to the EF-PLA-5% (0.30%) and EF-PLA-10% (0.95%) modifiers. This means the MEP incorporated into the films from the Industrial Modifier has a much lower extent of reaction prior to film blowing. The residual epoxide content of the modified films is shown in **Figure 3.6** as a percent

increase compared to the EF-PLA-5% modified films. It's clear to see that the films with the Industrial Modifier have a much higher residual epoxide content than either of the EF-PLA modifiers. This is a function of how the MEP gets distributed into the PLA during the processing of the reactive blend. The Industrial Modifier has a high MEP content (~30 wt%) which on a molar basis correlates to the modifier being ~90 mol% MEP. Therefore, the Industrial Modifier is mostly virgin, unreacted MEP, on a molar basis. When the Industrial Modifier is used in film blowing, its total extent of reaction is much lower since the starting material is mostly unreacted. This inefficient use of the MEP reactivity is the reason for the higher epoxide content as well as the lower molecular weights after film blowing.

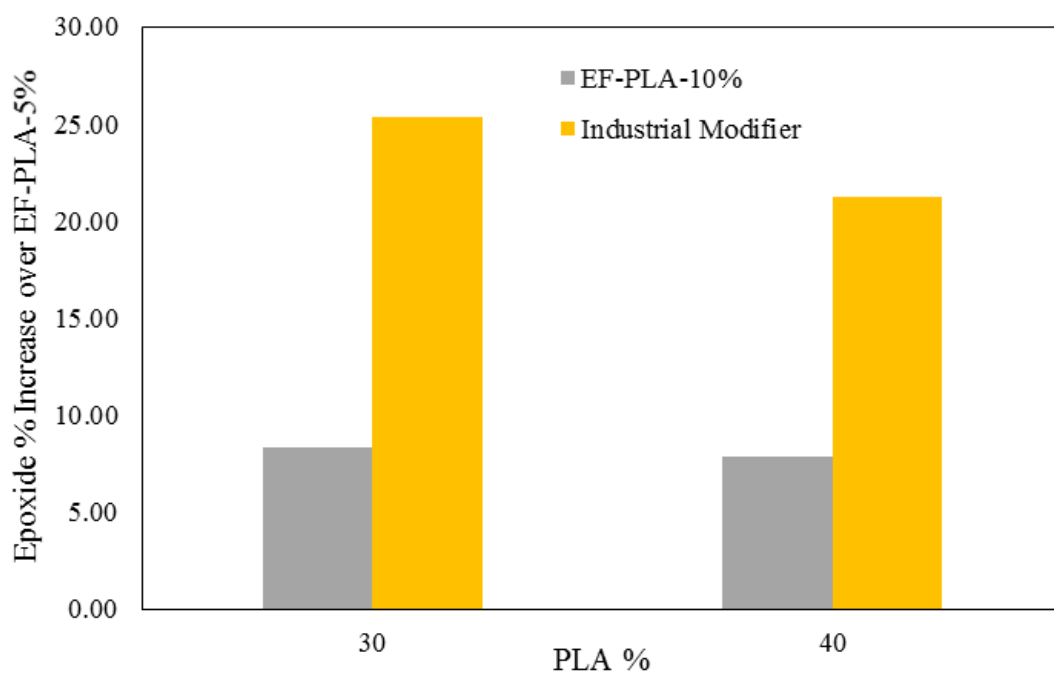


Figure 3.6: Residual epoxide content of the modified films for the various reactive modifiers as a percentage increase compared to EF-PLA-5%.

3.4.3 Mechanical Property Comparison

All of the reactive modifiers had a positive effect on the mechanical performance of the films, especially dart properties. Just as the control films experienced a significant drop in dart performance once the PLA content was increased to 40%, the Industrial Modifier films also showed a drop though not as significant (**Figure 3.7**). In the control films this was due to incompatibility and the onset of the formation of a continuous PLA phase. The Industrial Modifier did improve compatibility of the films resulting in better dart, but not to the extent of the EF-PLA modifiers. This resulted in the films showing a 41% drop in dart performance compared to the 17% decrease of the EF-PLA films. This can be attributed to the lesser reaction of the MEP in the films, resulting in less of a compatibilization effect.

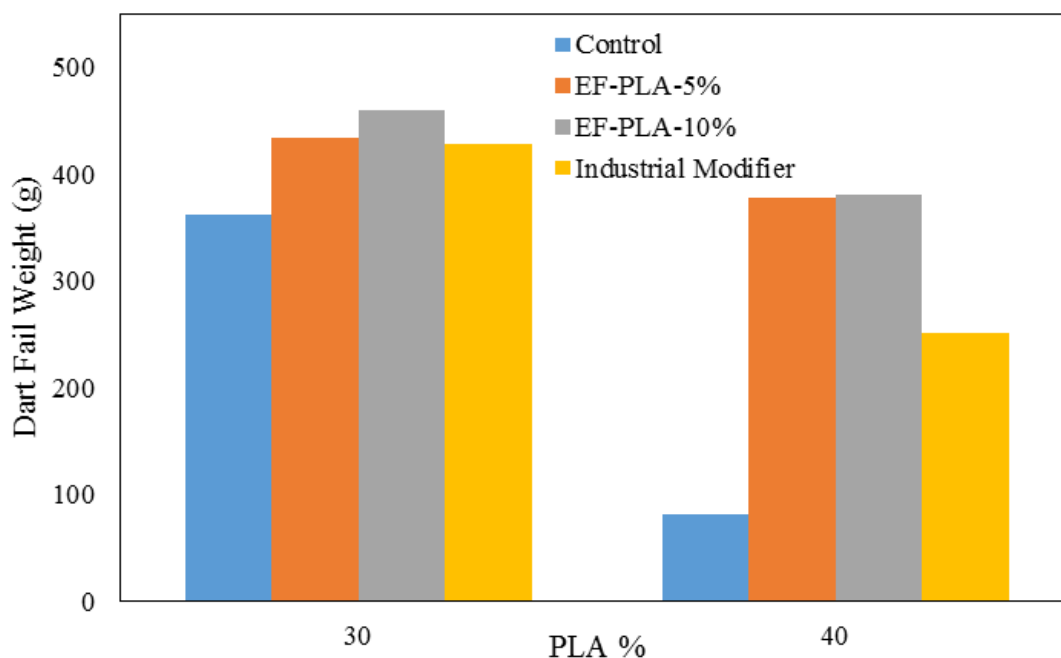


Figure 3.7: Dart failure weight comparison of the modified films.

As discussed previously, the TD modulus appears to inversely correlate to the dart performance of the films as the PLA content is increased. This trend holds true for the Industrial Modifier samples and can be seen in **Figure 3.8**. Between 30 and 40% PLA, the Industrial Modifier films TD modulus increased by 45% which corresponds to the 41% decrease in dart properties for these films.

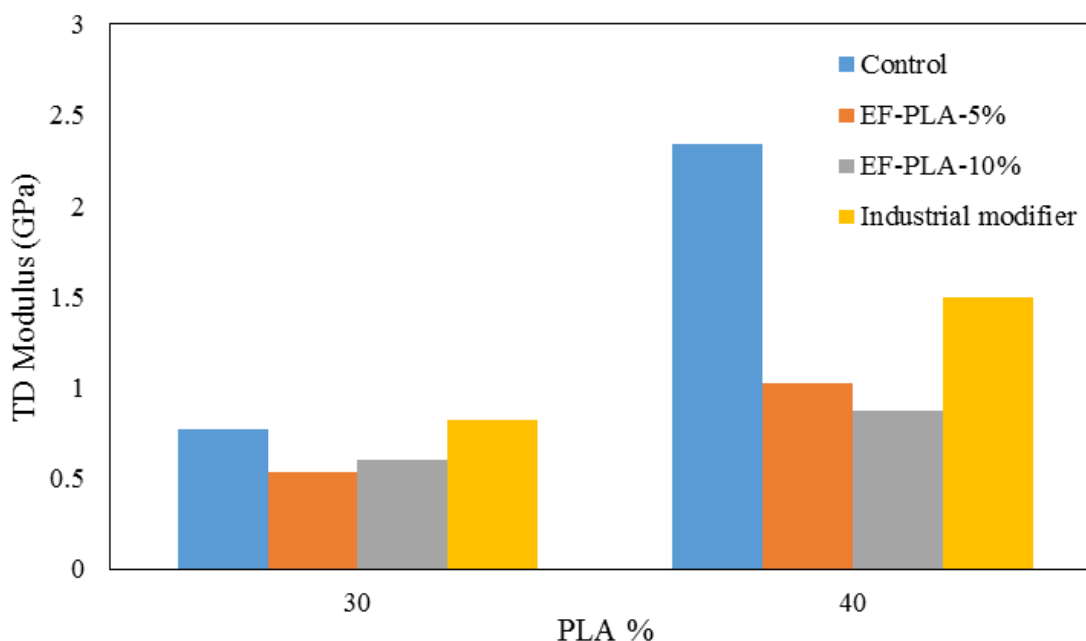


Figure 3.8: Comparison of the transverse moduli of the blown films.

3.5 Conclusion

Modification of the PLA/PBAT films with EF-PLA reactive modifiers resulted in films with superior physical and mechanical properties. The rheological and compatibilization enhancement allowed for films of higher PLA content being efficiently produced without bubble instability and tearing compared to control films. No significant difference in film properties was observed for the two EF-PLA reactive modifiers, however the higher epoxy content of EF-PLA-10% resulted in improved compatibility and processability at high PLA concentrations. An added

benefit of the EF-PLA-10% modifier is that since it is more reactive, less modifier is needed making it more economical. The increase in compatibilization resulted in improved dart performance especially at higher PLA content where the control films experienced a significant decrease in properties. This was due to the change in morphology from a continuous ductile PBAT phase, to the brittle PLA phase coupled with phase incompatibility. Addition of EF-PLA reactive modifiers provided for better and more stable dispersion of the two phases with a more diffused and compatibilized interface. In comparison with a common Industrial Modifier, EF-PLA more effectively uses its reactivity to produce films with superior mechanical properties, again most notably at high PLA content (40%).

Chapter 4 – Synthesis and Reactivity of Siloxane Polymers and Copolymers Containing Multiple Epoxy Functional Groups

4.1 Introduction

Epoxides are highly reactive functional groups making them excellent reactive modifiers. Carbon backbone polymers containing multiple epoxy groups have been reported extensively in literature and have found commercial applicability. These epoxy functionalized polymers have been used to increase molecular weight and rheological properties of polymers through chain extension via epoxide ring opening reactions.^{18–21,24,25,41,54} This process also allows for the compatibilization of otherwise immiscible polymer blends and upcycling of biopolymers.^{55,56} However, to our knowledge, there are no reports on the synthesis and utility of silicone backbone polymers containing multiple epoxy functional groups.

A siloxane backbone polymer can provide for increased flexibility and improved rheological properties as well as better thermal stability and wear properties over that of typical carbon based polymers.^{57–59} Epoxy functionalized siloxanes have the benefit of having improved cure times and enhanced durability over standard siloxane coatings.⁶⁰ However, the only commercially available epoxide functionalized siloxanes are end group difunctional or multifunctional epoxy silicones available as lower molecular weight oligomers.⁶¹ Currently, all cationic polymerization methods rely on polymerization through ring-opening, which only allows for end group functionality and therefore limited epoxide functionality and reactivity.⁶² An epoxy functionalized siloxane could see many potential uses combining the reactivity of the epoxide with

the flexibility and hydrophobicity of the siloxane backbone. This could make these resultant polymers excellent reactive modifiers for enhancement of polyesters and traditional epoxy resins.

The paper describes the homo- and co-polymerization of epoxy functionalized silane monomers through a hydrolysis and condensation polymerization pathway. In the copolymers, poly(dimethyl siloxane) was used as inert segments to create an epoxy functionalized polymer of controllable molecular weight, rheology, and epoxide functionality without opening the oxirane ring. To study the reactivity of the epoxy functionalized siloxanes as a potential reactive modifier, a model compound study involving common functional groups was conducted with selected acid catalysts.

4.2 Experimental

4.2.1 Materials

(3-Glycidoxypentyl)methyl-dimethoxysilane (ES) and silanol terminated polydimethylsiloxane (OH-PDMS) were purchased from Gelest Inc. (PA, USA). ES was kept in a nitrogen environment to deter hydrolysis by atmospheric moisture. The OH-PDMS had a viscosity of 25 cSt and an average molecular weight of ~550 g/mol. The stearic acid, polyethylene glycol (PEG – 4000 g/mol), hexamethyldisiloxane (HMDSO), and titanium isopropoxide (TTIP) was obtained from Sigma Aldrich (MO, USA). Nitric acid (HNO_3) (67-70%) was acquired from EMD Millipore (MA, USA). All reagents were used as received unless specified otherwise.

4.2.2 Epoxy Poly(siloxane) Homopolymer Polymerization

In a 250 mL round bottom flask, 15 g (3-Glycidoxypentyl)methyl-dimethoxysilane (ES), 1.1 g hexamethyldisiloxane (HMDSO), a drop of 12 molar KOH solution, and 2.75 g of water were added together with a Teflon coated magnetic stir bar and allowed to stir for 24 hours to ensure full hydrolysis of the methoxy groups of ES. A small sample was then taken from the flask to verify that no epoxide rings had opened during the hydrolysis procedure and to establish a starting viscosity before proceeding to condensation polymerization.

The round bottom flask with fully hydrolyzed reactants was placed into an oil bath and attached to a cold water condenser. Under constant stirring, the temperature was raised to 80°C and vacuum was applied to pull out the excess water and methanol formed during hydrolysis. The removal of water was used to drive the polymerization forward, as the silanol terminated reactants condense to form siloxane linkages, thereby giving off water as a product. Viscosity measurements were taken periodically to determine progress of reaction. Once the reaction was completed, as verified with FTIR-ATR and viscosity measurements, a piece of dry ice was added to neutralize any remaining KOH catalyst. Samples of the final polymer were taken for FTIR, ¹H NMR, and epoxy content titrations.

4.2.3 Epoxy Poly(siloxane) and PDMS Copolymer Polymerization

Utilizing the same procedure for the hydrolysis and condensation polymerization stated above with the EPS homopolymer, silanol terminated polydimethylsiloxane (OH-PDMS) was added in with ES to create an EPS copolymer. The OH-PDMS is incorporated to act as an inert section of the copolymer, allowing for the control of epoxide functionality and molecular weight.

A general EPS copolymer reaction included in a 250mL round bottom flask, 12.01g ES, 22.8g OH-PDMS, 2.3g HMDSO, a drop of 12 molar KOH solution, and 2g of water added together with a Teflon coated magnetic stir bar and allowed to stir for 24 hours to fully hydrolyze. The ratio of the reactants allows for an average molecular weight of approximately 5000 g/mol with an average epoxide functionality of 5 epoxides per EPS chain. The hydrolyzed monomers were then polymerized using the same procedure as with the EPS homopolymer and characterized in the same manner. EPS copolymers with molecular weights of 7500 and 10000 g/mol with the same functionality per polymer chain were also created.

4.2.4 Characterization

4.2.4.1 *Fourier Transform Infrared Spectroscopy*

Fourier transform infrared (FTIR) spectroscopy was used to monitor the extent of the polycondensation reaction as well as characterize the final polymer. The spectra was recorded on a Shimadzu FTIR (IRAffinity-1, Shimadzu Co., Tokyo, Japan) equipped with a single reflection MIRacle ATR system (PIKE Technologies, WI, USA). The reaction progress was monitored by observing the loss of the -OH peak at 3400cm^{-1} and the growth of the Si-O-Si peak at 1100 cm^{-1} .

4.2.4.2 *Viscosity*

Viscosity measurements were taken using a Brookfield digital viscometer (DV-E, Brookfield Engineering, MA, USA) equipped with a Thermosel heating attachment held constant at 80°C using with Spindle 27. The viscosity was measured throughout the course of the polycondensation reaction as another method of monitoring extent of reaction. The increase in viscosity as a function of reaction time indicates polymer being formed and an end to the reaction

is seen as a plateau is reached. Room temperature viscosity measurements were taken for the various EPS copolymers created for comparison.

4.2.4.3 Nuclear Magnetic Resonance

¹H NMR spectra were recorded on a 500 MHz NMR spectrometer (Varian Unity Plus, Varian Associates Inc., CA, USA) using deuterated chloroform (CDCl₃) as the solvent. Samples were tested pre- and post-polymerization to characterize the poly(siloxane)s produced.

4.2.4.4 Epoxy Content Titrations

Epoxy content titrations were done to determine the quantity of reactive epoxy groups present in the EPS polymers. The procedure used is outlined in ASTM D1652-11: Standard Test Method for Epoxy Content of Epoxy Resins.⁵² In this method, the titration is done using a perchloric acid solution in the presence of an excess of tetraethylammonium bromide. The combination of perchloric acid and tetraethylammonium bromide generates hydrogen bromide in situ, which with the quaternary ammonium halide rapidly opens the oxirane ring. The epoxide weight percentage, E, is determined by the equation:

$$E = F \times \frac{V}{W_e}, \textbf{Equation 4.1}$$

where F is the perchloric acid solution reagent factor, determined through standardization with potassium hydrogen phthalate, V is the volume of the perchloric acid solution needed to reach the equivalence point, and W_e is the weight of the sample used in grams.

4.2.5 Model Compound Reactivity Study

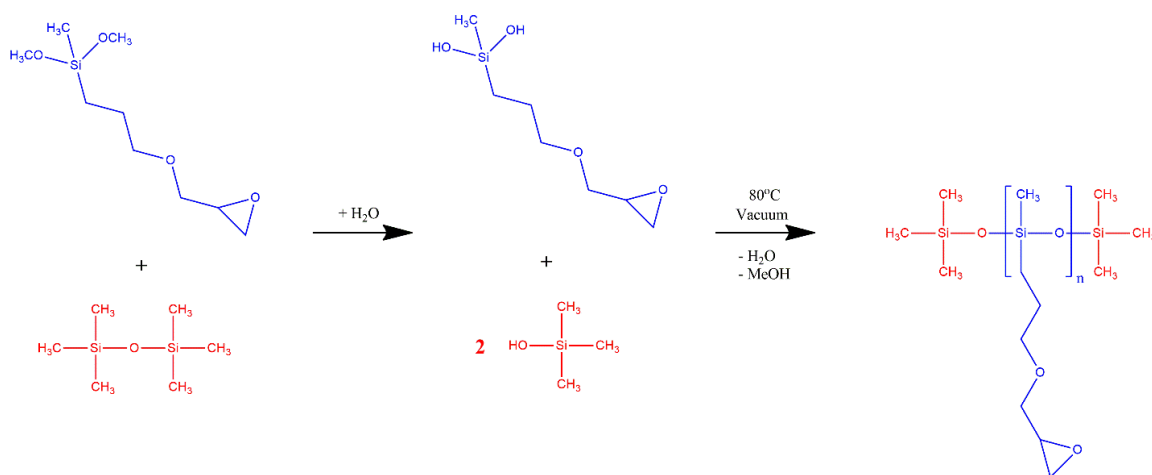
The model compound reactions were monitored using a Differential Scanning Calorimeter (DSC; Q20, TA Instruments, DE, USA). Stearic acid and PEG were used as the model compounds because they contain terminal carboxylic acid and terminal hydroxyl groups, respectively. This makes them excellent compounds for modeling the reaction of EPS with a polyester. The model compounds were premixed with the EPS samples in a 1:1 weight ratio with a catalyst added at a concentration of 1 wt%. Samples of these mixtures were sealed in an aluminum hermetic pan and heated from room temperature to 250°C at 3°C/min in the furnace of the DSC. The heat flow from the exothermic reaction of the epoxide ring opening was recorded.

4.3 Results and Discussion

4.3.1 Poly(siloxane) Homopolymer Containing Multiple Epoxy Groups

A procedural schematic of the EPS homopolymer polycondensation reaction is shown in **Schematic 4.1**. In the first step, involving reactant hydrolysis, the methoxy groups of ES hydrolyze to form silanol functionality and methanol is given off as a byproduct. When the HMDSO is hydrolyzed, the molecule splits into two silanol functionalized molecules. This allows for one HMDSO molecule to function as two end-caps. When heat and vacuum are applied, water and methanol are pulled out of the system. As the silanol groups condense, water is given off and therefore removal of water drives the polymerization forward. This continues until a HMDSO end-capping molecule condenses onto the polymer chain ending its reactivity. HMDSO serves as a polymerization terminating agent for the EPS polymers to control molecular weight by creating an -O-Si-(CH₃)₃ end cap. A 10:1 molar ratio of ES to HMDSO was used which would result in an

average degree of polymerization of 10, assuming complete reaction. This results in a theoretical molecular weight of 1900 g/mol for the EPS homopolymer. Therefore, the ratio of ES to HMDSO is the deciding factor on average molecular weight and other properties for the EPS homopolymer.



Schematic 4.1: Preparation of EPS homopolymer from ES monomer.

4.3.1.1 Viscosity Measurements of Homopolymer Reaction

The condensation polymerization of the EPS homopolymer was monitored by periodically removing a sample and measuring its viscosity. The increase in viscosity as a function of time is indicative of the polymerization occurring due to an increase in the average molecular weight of the mixture as well as the removal of dilutants. This trend can be seen in **Figure 4.1**. It can be seen from this data that the viscosity increased in two steps during the reaction before leveling off at an equilibrium viscosity at the end of reaction. This type of rapid increase followed by a plateau is typical of condensation polymerization. However, since this reaction is driven forward by removal of methanol and water, a two-step increase is observed. Removal of methanol and water

results in an increase in the viscosity, and promotes the polymerization as shown by the increased viscosity.

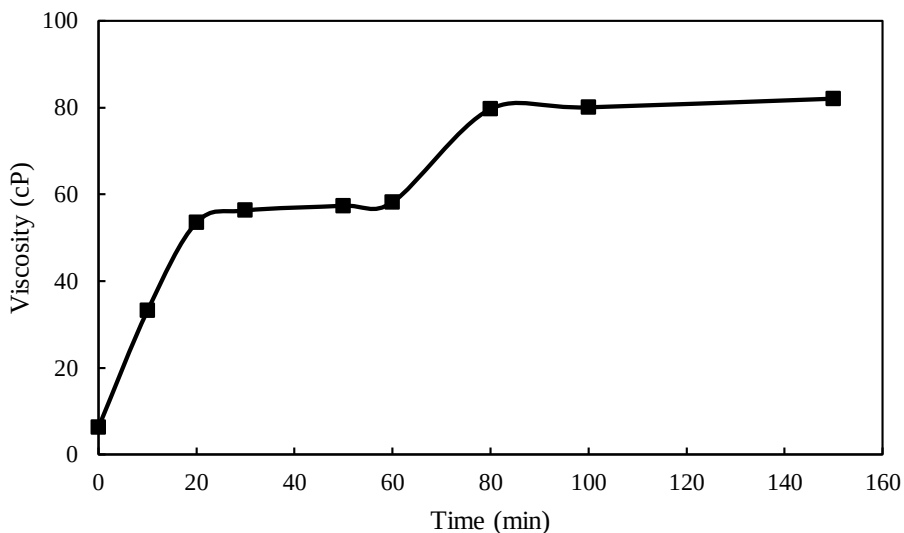


Figure 4.1: Viscosity of EPS homopolymer as a function of polycondensation reaction time.

4.3.1.2 FTIR Spectroscopy

Figure 4.2 shows the FTIR spectra of the EPS homopolymer mixture after hydrolysis (the pre-condensate) and the polymer formed following the polycondensation reaction. In the pre-condensate product, the broad peak centered around 3400 cm^{-1} is due to the presence of -OH groups from water and the silanol functionality. This comes from the hydrolysis of the methoxy groups of ES. The grouping of peaks around $2900\text{-}3000\text{ cm}^{-1}$ and the sharp peak at 1260 cm^{-1} are representative of an epoxy group.⁶³ A small, but noticeable peak corresponding to Si-O-Si linkage around 1100 cm^{-1} is seen prior to condensation indicating the presence of oligomers formed during the hydrolysis step. The disappearance of the broad -OH peak indicates removal of water with concomitant formation of Si-O-Si linkages. This is confirmed by an increase of the Si-O-Si peak.

The epoxy signals at 2900-3000 cm^{-1} and 1260 cm^{-1} wave numbers suggests that the epoxy ring remains intact through the polymerization process.

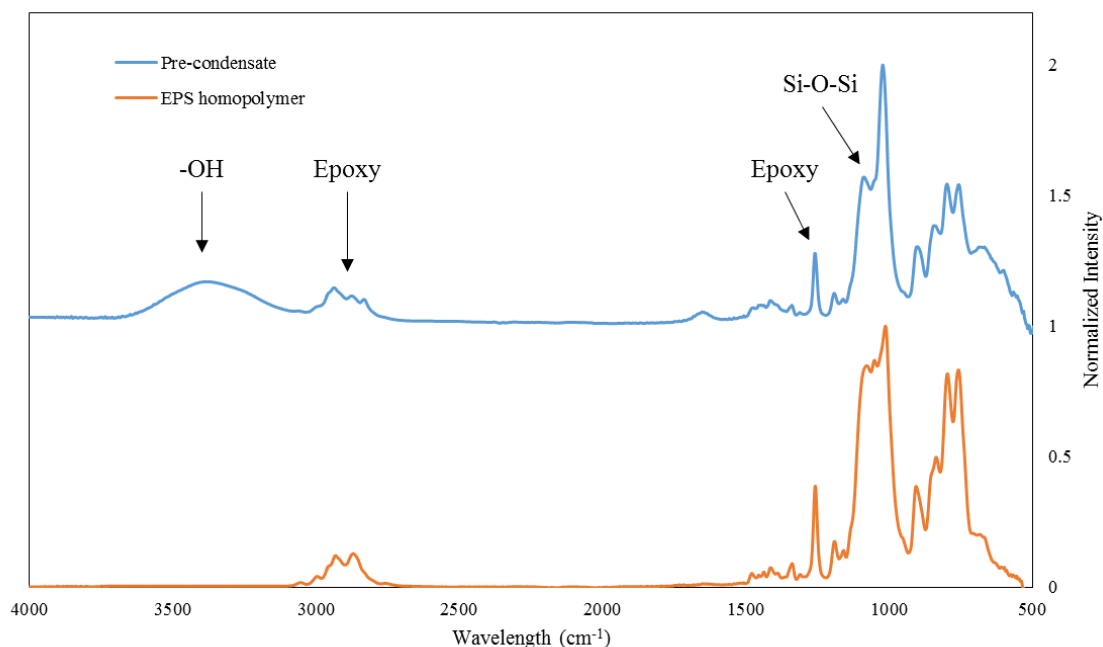


Figure 4.2: FTIR spectra of the EPS homopolymer pre-condensation mixture and final polymer.

4.3.1.3 Epoxy Content Titrations

Table 4.1 provides the experimental and theoretical epoxy wt% of the pre-condensate mixture and the end polymer product. The theoretical epoxy wt% of ES is 19.54% based on 43 g/mol for an epoxy ring (mass of epoxy group in the silane (43 g/mol) / total molar mass of silane (220 g/mol)). The experimental data matches the theoretical calculations, proving that no loss of epoxy functionality occurred during the polycondensation reaction. The final polymer has a higher

epoxy wt% compared to the pre-condensate due to the change in mass since water and methanol is removed during the reaction.

Table 4.1: Comparison of experimental and theoretical epoxy contents of the pre-condensate mixture and the end polymer product

Pre-condensate		End Polymer
15.30 %	<i>Experimental Epoxy wt%</i>	23.93 %
15.55 %	<i>Theoretical Epoxy wt%</i>	24.71 %

4.3.1.4 ^1H NMR

Figure 4.3 shows the ^1H NMR spectra of the ES monomer and the EPS homopolymer. The peaks at roughly 2.6, 2.8, and 3.1 ppm correspond to the protons of the epoxy ring, while the tall sharp peak at approximately 0.1 ppm is from the methyl group attached to silicon. The methylene protons (**c**) attached to the epoxy ring appear at different chemical shifts (2.6 and 3.1 ppm) due to shielding by the oxygen of the epoxy ring. The methine proton (**b**) of the epoxy appears at 2.8 ppm. The integration for the peak of interest are shown above each peak based on the methyl protons (**a**) of silicon as reference. The integration values showing the ratio of the protons **a:b:c** as 3:1:2 is in agreement with the structure shown and having the epoxy ring intact. As expected, both the ES monomer and EPS homopolymer show the same NMR patterns.

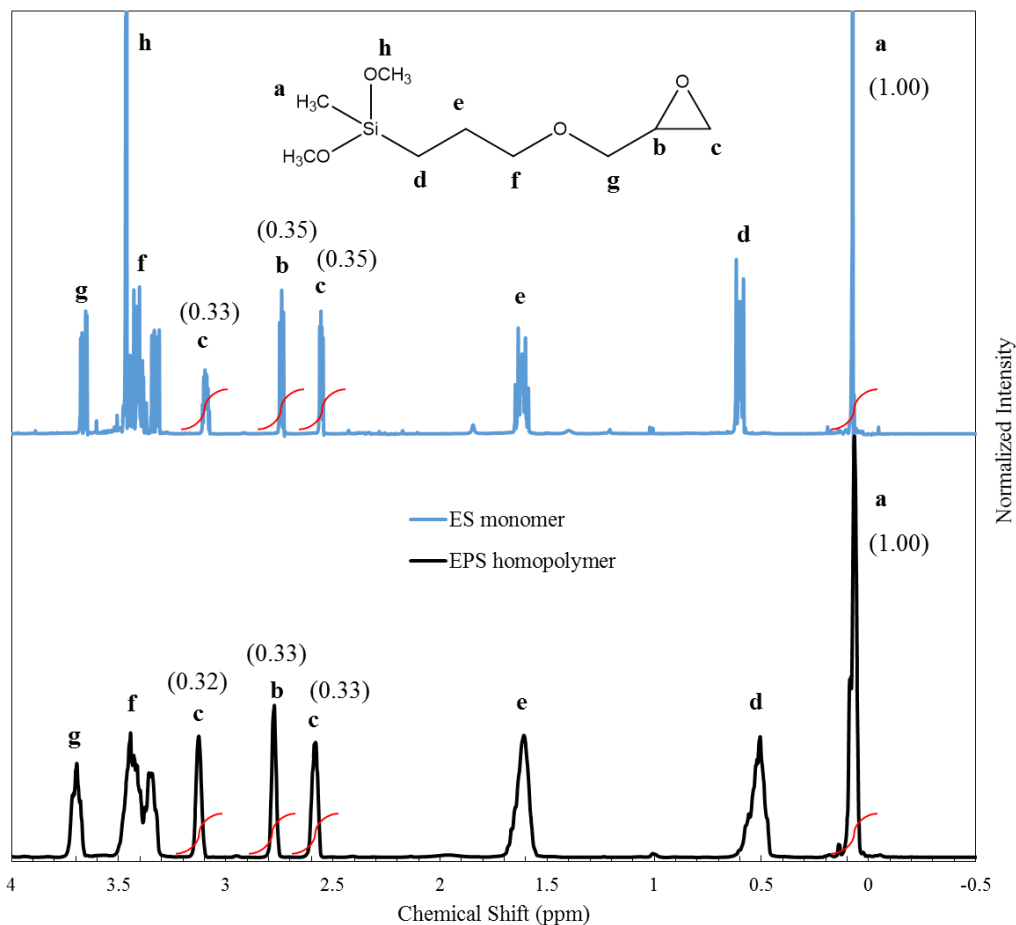
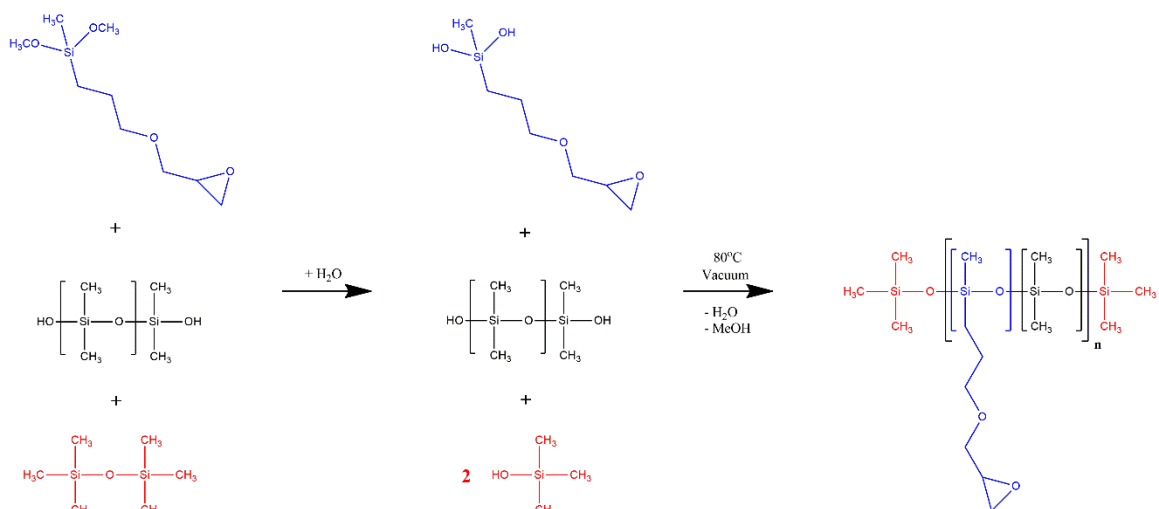


Figure 4.3: ^1H NMR spectra of ES monomer and EPS homopolymer reaction materials.

4.3.2 Epoxy Poly(siloxane) Copolymer with PDMS

The ES monomer was polymerized with HMDSO and low molecular weight silanol-terminated PDMS to create the EPS copolymers (**Schematic 4.2**). The addition of the OH-PDMS allowed tailoring molecular weight, rheological properties, and epoxy functionality per polymer chain. The EPS copolymer synthesis goes through the same steps as the homopolymer synthesis but with OH-PDMS added in. The silanol groups of OH-PDMS will condense with the silanol groups of the hydrolyzed ES and the HMDSO forming the polymer.



Schematic 4.2: Preparation of EPS copolymer from ES and OH-PDMS.

4.3.2.1 Viscosity Measurements of Copolymer Reaction

Figure 4.4 shows the viscosity of the polycondensation product as a function of the reaction time for the EPS copolymer with a theoretical molecular weight of 5000 g/mol. The viscosity trend for the EPS copolymer follows the same trend seen for the EPS homopolymer. However, there are two observable differences when comparing the viscosity versus time data for the homopolymer and the copolymer. Firstly, the copolymer polycondensation is a faster reaction. This is because one of the reactants, the OH-PDMS, is already a short chain polymer and the polymerization requires fewer silanols condensing compared to the synthesis of the homopolymer. Less condensing reactions results in less water needing to be removed for the reaction. Secondly, the EPS copolymer has a lower viscosity compared to the EPS homopolymer even though it has a higher molecular weight. This is because the EPS homopolymer has a pendent chain coming off of every silicon atom on its backbone, creating a densely branched polymer. This provides many more opportunities for chain entanglements resulting in a higher viscosity. The copolymer

structure has pendent chains separated by segments of PDMS which results in fewer chain entanglements resulting in a polymer with lower viscosity, even at higher molecular weights. Using this synthetic approach, copolymers having a wide range of epoxy functionality (# pendent chains per polymer), molecular weights, and range of viscosities can be synthesized.

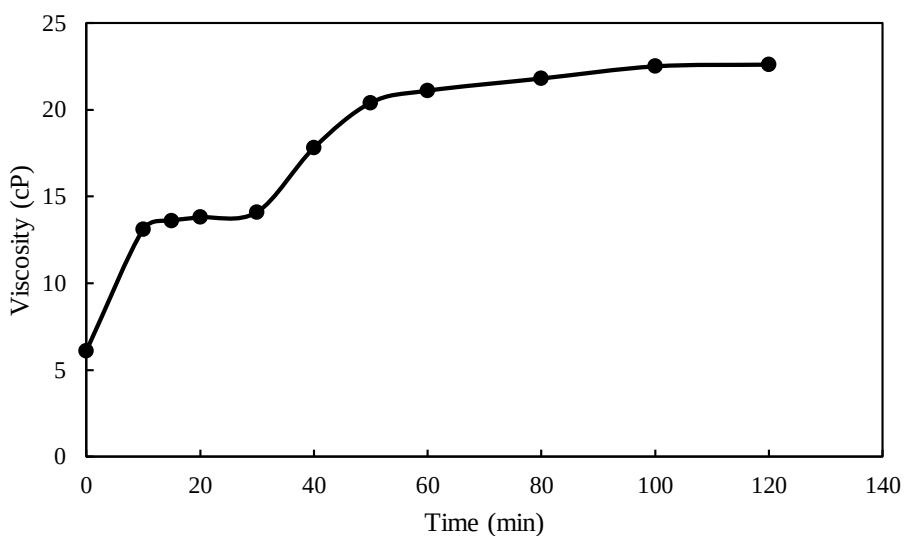


Figure 4.4: Viscosity of EPS copolymer (5000 g/mol) as a function of polycondensation reaction time.

4.3.2.2 Characterization of EPS Copolymers

Three different EPS copolymers were produced to show the material can provide a wide range of properties, as shown in **Table 4.2**. All of the copolymers synthesized have an average functionality of 5 epoxy groups per polymer chain. Therefore, the differences in molecular weight are due to higher amounts of inert PDMS incorporated in the polymer. This results in a higher

viscosity as well as a lower epoxide content. However, at the same molecular weight the epoxide content could still be varied greatly by adjusting the epoxy functionality per polymer chain.

Table 4.2: Material characterization of the EPS copolymers of various molecular weights.

Theoretical copolymer molecular weight (g/mol)	Viscosity (cP)	Epoxide Content (wt%)
5000	46.7	8.25
7500	780	3.48
10000	1380	2.75

*All polymers contain an average of 5 epoxy groups/polymer chain.

This hydrolysis and polycondensation reaction pathway is an effective approach to creating EPS polymers in a one-pot synthesis. Both the EPS homopolymer and copolymers can be created with good control over functionality and viscosity, without loss of the epoxide group's reactivity.

4.3.3 Model Compound Reactivity Study

Epoxide functionality is highly reactive and is capable of reaction with many other functional groups. In this research we choose to model the reactivity of the EPS homo- and copolymers with the hydroxyl and carboxylic acid functionalities. Utilizing these reactions, the EPS polymers could be used as reactive modifiers for polyesters. Various acid catalysts were used, and the reaction was monitored via DSC. The exothermic signal given off by the oxirane ring opening reaction was measured with the DSC, and temperature ranges for these reactions was determined.

Stearic acid and a low molecular weight poly(ethylene glycol) (PEG) were used as the model compounds to represent the carboxyl and hydroxyl functional groups, respectively. Nitric acid (HNO_3) and titanium isopropoxide (TTIP) were used as the acid catalysts for the ring opening reaction.

An example output from the DSC can be seen in **Figure 4.5**. This figure shows the EPS homopolymer's reaction with stearic acid. The endothermic peak at $\sim 70^\circ\text{C}$ is due to the melting of the stearic acid as the mixture is heated. All three samples show a broad exothermic peak from the reaction of the epoxy group with the carboxylic acid functionality. The enhancing effect of the catalysts can be seen when compared to the sample with no catalyst, as the no catalyst sample reacts at a much higher temperature. It is clear that the TTIP catalyst does a more effective job than HNO_3 at facilitating this reaction as seen by a lower reaction temperature. The other negative of the HNO_3 catalyst is its propensity to degrade the compounds in the reaction due to its strong acidic character. This is seen in some of the DSC exotherms as “noisy” data and unsteady baselines. Not only is TTIP a more effective catalyst in terms of reaction, but as a Lewis Acid it will not lead to unwanted degradation.

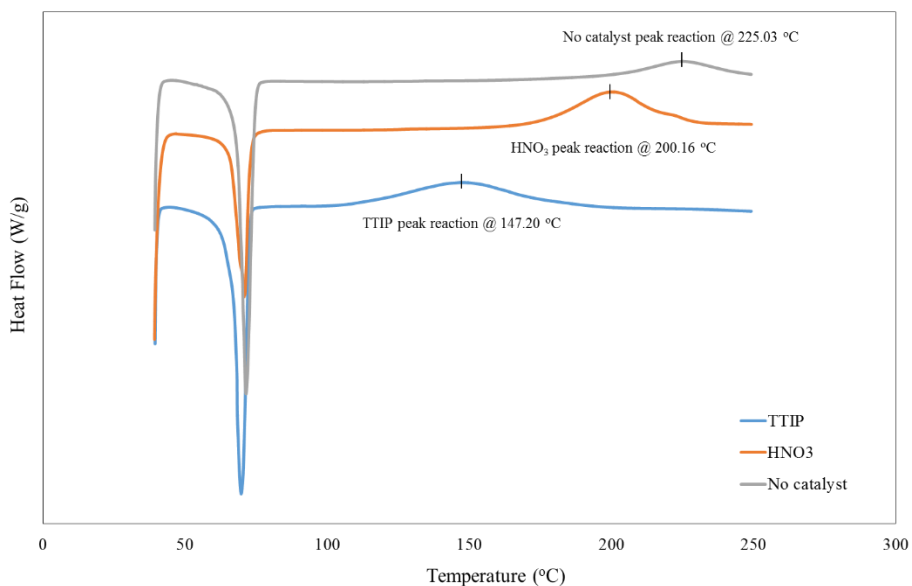


Figure 4.5: DSC exotherms for the model compound reactivity study of EPS homopolymer with stearic acid.

The remaining results of the model compound study comparing the epoxide reactivity with carboxyl and hydroxyl functional groups can be seen in **Table 4.3**. Very little to no reactivity difference was observed between the EPS homo- and co-polymers, showing that the presence of PDMS throughout the siloxane backbone has no effect on the epoxide's reactivity. Another thing of note is the difference in reactivity between stearic acid and PEG. Many of the PEG model compound reactions with both EPS polymers resulted in no exothermic signal. This is due to the role of the acid catalyst in opening an epoxy. In such reactions, acid catalysts donate a hydrogen to help facilitate the ring opening from a nucleophile. Of the two functional groups, a carboxyl is more nucleophilic than a hydroxyl group, making it more effective at opening the epoxy ring.

Table 4.3: Reaction temperatures of EPS polymers with model compounds as measured in DSC

Sample	Peak Reaction Temperature (°C)	Reaction Onset Temperature (°C)
<i>EPS Homopolymer</i>		
+ Stearic Acid	225.0	204.2
+ Stearic Acid/HNO ₃	200.2	175.2
+ Stearic Acid/TTIP	147.2	111.6
+ PEG	*	*
+ PEG/HNO ₃	199.3	175.3
+ PEG/TTIP	*	*
<i>EPS Copolymer</i>		
+ Stearic Acid	>250	230.7
+ Stearic Acid/HNO ₃	197.2	173.3
+ Stearic Acid/TTIP	149.4	114.7
+ PEG	*	*
+ PEG/HNO ₃	199.9	177.3
+ PEG/TTIP	*	*

*No reaction was seen up to 250°C

4.4 Conclusion

A one-pot synthesis reaction was used to create poly(siloxanes) containing multiple epoxy groups with control over molecular weight and epoxy functionality following hydrolysis and condensation steps. An EPS homopolymer and copolymers with PDMS have been synthesized. The copolymer allows for tailoring of molecular weight, rheological properties, and epoxy functionality through insertion of inert PDMS segments. Viscosity measurements, FTIR, ¹H NMR, and epoxy content titrations confirmed a poly(siloxane) structure containing multiple epoxy groups. The model compounds, stearic acid and PEG, were used to look at this new polymer's reactivity with hydroxyl and carboxyl functionalities using two different acid catalysts. The Lewis Acid, TTIP, is more effective at catalyzing the reaction without degradation as well as preferentially reacting with the carboxyl functionality.

Chapter 5 – Moisture Curable Toughened Poly(lactide) Utilizing Vinyltrimethoxysilane Based Crosslinks

5.1 Introduction

Poly(lactide) (PLA) is receiving much attention in the polymer materials space because it is produced from renewable resources and is biodegradable/compostable. Thanks to the commercialization processing improvements of PLA producing companies like NatureWorks, LLC, its cost is around \$1/lb, making it an intriguing cost-competitive alternative to traditional petroleum based plastics.³⁵ However, PLA possesses certain inherent polymer properties such as low impact toughness⁶⁴, poor heat⁶⁵ and hydrolytic stability⁶⁶, and weak melt strength³⁶ that have prevented it from more wide scale commercial use.

Compared to poly(styrene), PLA has very similar mechanical properties such as tensile strength and modulus, as well as similar brittleness and low impact strength.⁶⁷ These limitations of poly(styrene) led to the development of modified high-impact polymers and copolymers (ex. ABS, HIPS) to further its commercial viability. Now in recent years, the toughening of PLA has undergone the same level of interest in effort to develop a toughened PLA. The typical methods of this include plasticization, copolymerization, and melt blending.

Some research has been done utilizing vinyl functionality to graft reactive groups onto PLA's backbone, making it more susceptible to modification. The introduction of new functional groups onto PLA allows for the creation of new materials, with potentially increased properties due to the incorporation of new reactive chemistries. While many different functionalities have been grafted onto PLA, including acrylic acid⁶⁸ and acrylamides⁶⁹, the most popular method of PLA melt grafting is with maleic anhydride. This grafting is typically done using reactive

extrusion (REX) processing making it cost-competitive and commercially scalable. Maleic anhydride grafted PLA polymers (MA-*g*-PLA) have been used as compatibilizers for native⁷⁰ and thermoplastic starches⁷¹ where they have promoted strong interfacial adhesion and better dispersion for these biocomposites. Other researchers have used MA-*g*-PLA as a reactive intermediary to graft more flexible compounds such as poly(ethylene glycol)⁷² and citrate⁷³ onto PLA to increase its toughness.

PLA can also be toughened by introducing an appropriate level of crosslinking into the material. The two common procedures to crosslink thermoplastic polymers are copolymerization with a multifunctional monomer and introducing reactive compounds onto the polymer backbone. Such reactive compounds include the vinyl functionalities previously described, followed by additional crosslinking steps. An example of the copolymerization route is with tetrafunctional spiro-bis-dimethylene-carbonate.⁷⁴ Copolymerizing with L-lactide at 0.2-0.3 mol% resulted in increases in both tensile and impact toughness. The improvement in impact toughness was attributed to increased network strength due to the presence of not only chemical crosslinks but also physical crosslinks. However this copolymerization process requires polymerization of the materials from monomers, instead of the more cost effective method of modifying a homopolymer through grafting/functionalization. Crosslinking through the grafting of a reactive compound route has been commonly done with triallyl isocyanurate (TAIC). This has been performed both in the melt via free radical initiation⁷⁵ and crosslinking prefabricated samples via radiation curing.⁷⁶ TAIC is a highly reactive material making it difficult to control the extent of grafting. And while crosslinking is an effective method of increasing impact toughness, it typically results in a loss in ductility and therefore decrease in tensile toughness.

Vinylalkoxysilane grafting appears to be an excellent combination of the two methods. The vinyl functionality can be easily incorporated onto the PLA backbone via free radical grafting in the melt phase, while the alkoxysilane functionality is capable of forming crosslinks through moisture curing. This procedure was first introduced by Dow Corning for the crosslinking of polyolefins and termed the SioPlas method.⁷⁷ This two-step method of free radical grafting followed by moisture cured crosslinking increases the chemical and thermal resistance of the polyolefins, while also increasing the crack propagation and impact resistance.⁷⁸ However, this method still does result in a loss in ductility. Han *et al.* reported a study adopting this SioPlas method to PLA in which an improvement in thermal stability, hydrolysis resistance, and strength/stiffness properties occurred.⁷⁹ The crosslinked PLA showed an increase in tensile strength and modulus along with a decrease in ductility/elongation, similar to SioPlas. In addition, they only achieved very low grafting efficiency (max of 37%). This study used a hot water crosslinking step, which Rahmat et al. recently showed leads to excessive hydrolytic degradation of PLA.⁸⁰ At long crosslinking times, hydrolytic degradation becomes the dominant mechanism leading to network defects, causing loose gel structures.

In this chapter, improvements to the REX processing are discussed in detail and their effects on the grafting efficiency of VTMOs onto PLA are reported. The improvements result in drastically better grafting efficiency and therefore less VTMO is needed. After process optimization, a silanol-terminated poly(dimethylsiloxane) (OH-PDMS) was added into the system to aid in the crosslinking. This resulted in longer and more flexible crosslinks being formed which had a large positive impact on mechanical properties. Crosslinking was done without the previously used hot water bath to prevent excessive hydrolytic degradation. Tensile and impact properties were determined and the siloxane crosslinking effect was examined.

5.2 Experimental

5.2.1 Materials

PLA resin pellets (3051D) with a molecular weight of ~150,000 and 8% meso-lactide content were purchased from NatureWorks LLC (NE, USA). Vinyltrimethoxysilane (VTMOS) and 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101) were obtained from Sigma-Aldrich (WI, USA). The silanol terminated polydimethylsiloxane (OH-PDMS) was from Gelest and possessed a molecular weight of ~550 g/mol.

5.2.2 Compounding and Sample Preparation

The PLA resin pellets were dried for 24 hours in a 70°C oven to remove moisture. This is crucial for PLA in extrusion processes because it has a tendency to hydrolytically degrade as a result of back-biting and intermolecular transesterification reactions.¹² The VTMOS grafting process was carried out using a ZSK 30mm co-rotating twin screw extruder (Werner Pfleiderer, NJ, USA) with an L/D ratio of 30. The dried PLA pellets were premixed with the required amounts of VTMOS, OH-PMDS, and Luperox before being fed into the hopper using a gravimetric feeder. All samples were compounded at a throughput of 6 kg/hr, cooled in a water bath, and then pelletized. The pellets were tumbled in a bin with absorbent towels to remove the surface moisture. Some moisture was retained in the sample to promote hydrolysis of the methoxy groups and promote the crosslinking chemistry during downstream processing. The screw speed and temperature profile for all compounding were 125 rpm and 120, 140, 160, 170, 170, 165°C, respectively. It is necessary for the first temperature zone to be 120°C or lower to prevent flash evaporation of the VTMOS in the hopper. Previously, Han, et al.⁷⁹ used an initial feed zone

temperature of 170°C and noted very low grafting, even though large percentages were used. This could be because a large amount of it did not even enter the extruder due to flash evaporation as soon as it entered the hopper. This same study used a screw speed of 60 rpm which is rather slow and results in poor mixing. Poor mixing leads to slower reactions, which is another potential reason for the low grafting percentages.

Tensile and impact test specimens were compression molded using a Carver Laboratory Press (IN, USA), immediately after tumble-drying of the pellets. Immediate processing was done to ensure that the crosslinking reaction had not started prior to sample fabrication. The platen were heated to 180°C and the filled mold was pressed at a minimum of 10 ton for 3 minutes. Cooling water was then turned on to cool the platen. The mold was removed when the temperature reached below 40°C, or approximately 10 minutes. After removal from the mold, the specimens were placed into a 50°C oven for 3 days to pull off any residual water and subsequently drive the condensation reaction forward to form the siloxane crosslinks. In the past, this crosslinking step was done by placing the samples in hot water for up to 20 hours, which led to significant degradation of the PLA.⁸⁰ Test specimens were stored in a zip-top bag with as much air removed as possible and were allowed to rest for 2 weeks prior to mechanical testing.

5.2.3 Percent Grafting Determination

The grafting percent of VTMOs onto PLA was measured immediately after compounding and then again prior to mechanical testing using two different techniques, TGA and proton NMR. In the TGA method, the amount of free or ungrafted VTMOs can be determined by isothermally holding the sample above the boiling point of VTMOs (123°C), for 20 minutes. At this temperature, the free VTMOs evaporates and the weight loss represents the un-grafted VTMOs.

Also at this temperature, PLA begins to slightly decompose as seen by a gradual negative slope in the weight percent versus time graph. To correct for this, the slope of the line in the 18-20 minute range is extrapolated back to time zero and is used for determining the percent grafting. The slope is calculated at the end of the isotherm since all free VTMOs has been removed and a steady slope is reached. The extrapolated time zero weight % is the grafted VTMOs and PLA percentage in the sample. Therefore the weight % difference from the extrapolated and starting values, is due to the loss of the ungrafted VTMOs.

Proton NMR was also used to establish percent grafting. The ratio of the vinyl to methoxy proton integrations from neat VTMOs was compared to that of the reacted material. Neat VTMOs shows an integration ratio of 1:3 for vinyl to methoxy protons. So as the VTMOs grafts onto PLA through the reaction of the vinyl group, the signal corresponding to this vinyl group decreases. This results in a decrease in the vinyl to methoxy proton integration ratio. Therefore percent grafting can be calculated with NMR by:

$$\% \text{ Grafting} = \frac{[v:m]_{neat} - [v:m]_{exp}}{[v:m]_{neat}} \times 100, \text{Equation 5.1}$$

Where $[v:m]_{neat}$ and $[v:m]_{exp}$ are the integration ratios corresponding to the vinyl and methoxy groups of VTMOs for the pure/neat material and the experimentally reacted materials, respectively. For the pure material, this in theory should be 1:3, however in practice it is typically slightly higher due to the hydrolysis of some methoxy groups.

NMR was primarily used to verify the grafting percentage determinations obtained by TGA. The grafting percentages calculated by TGA and NMR showed less than 5% statistical variation. Therefore it was concluded that TGA can accurately determine VTMOs grafting efficiency, and was then used as the primary method to determine grafting.

5.2.4 Mechanical Testing

The tensile properties of the siloxane crosslinked samples were tested using a United Testing Systems (CA, USA) SFM-20 load frame with a 1000 lb load cell. The dog-bone shaped specimens had a 2 inch gage length and cross-sectional dimensions of 0.5 x 0.125 inches. The testing rate used was 0.2 in/min, which resulted in most failures occurring between 30-120 seconds. A minimum of 5 replicates were tested for each compound.

The notched IZOD impact properties were determined using a TMI pendulum impact tester (Testing Machines, Inc., DE, USA), following ASTM D256 utilizing a 1 ft-lb pendulum. The specimens had cross-sectional dimensions of 0.5 x 0.125 inches, and the notch was 0.1 inch deep. After notching, the specimens were allowed to rest at least 24 hours prior to impact testing. A minimum of 5 replicates were impact tested for each sample set.

5.2.5 Morphology

The morphologies of the siloxane crosslinked samples were studied using a JEOL 6610V (Japan Electron Optics Laboratories, Japan) Scanning Electron Microscope (SEM). The fractured surfaces following tensile and impact testing were analyzed after coating with osmium.

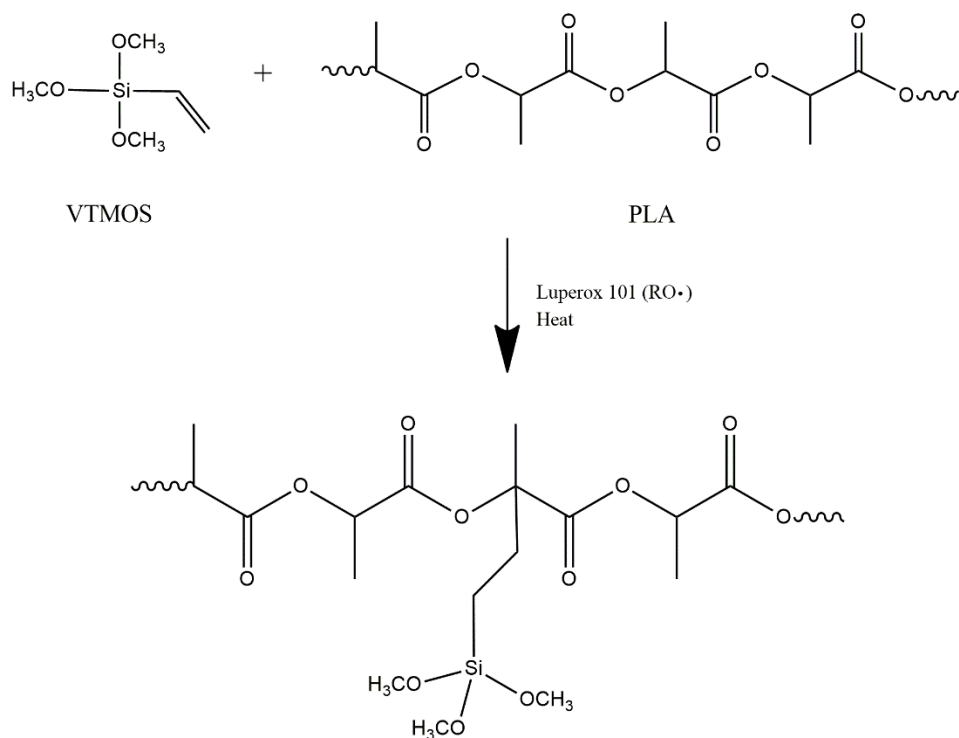
5.3 Results and Discussion

5.3.1 Determination of VT MOS Grafting

The previous study by Han, et al.⁷⁹ showed that VT MOS can be grafted onto the backbone of PLA using a free radical initiator through reactive extrusion (REX) processing. However, with the processing conditions used, very low grafting percentages resulted. Due to this low grafting efficiency, these researchers used high concentrations of VT MOS, up to 8 wt%. This VT MOS concentration results in a molar ratio of ~117 VT MOS per PLA chain, which is excessive and could lead to an extremely high crosslink density as well as a dramatic increase in the cost of the final material. Therefore, the initial portion of this study was to optimize the process to give enhanced grafting efficiency for our materials while using lower concentrations of VT MOS, and thereby reducing costs.

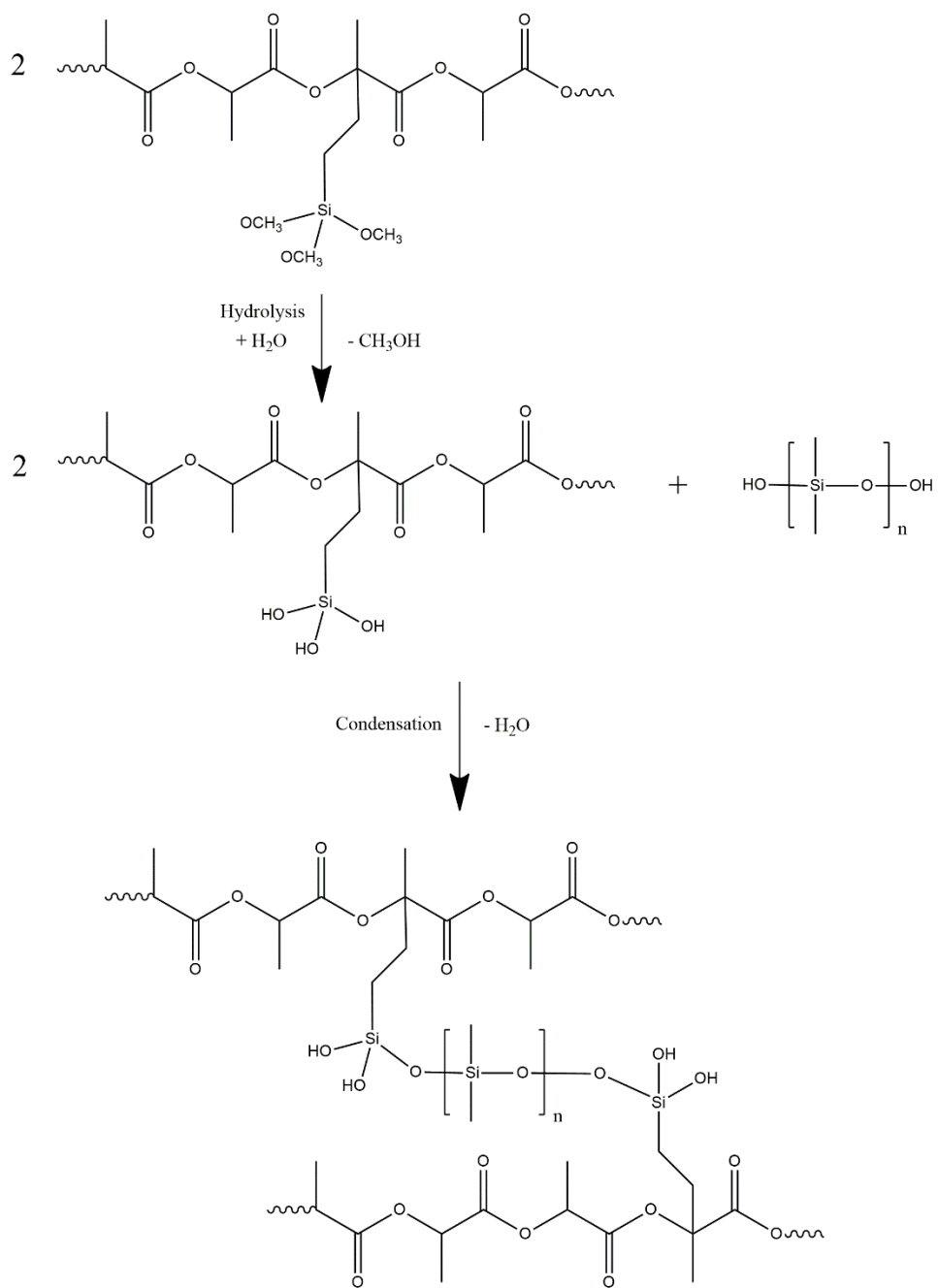
In attempt to increase the grafting efficiency, a lower VT MOS concentration (0.5 and 1.0 wt%), a lower feed zone temperature (starting at 120°C – so no VT MOS loss due to evaporation), and higher screw speed (125 rpm) were used. Initially a higher free radical initiator (Luperox) concentration was also used (0.5 wt%), however this resulted in a rigid and highly brittle thermoset material (incapable of dissolving in solvent). This was caused by an unwanted additional reaction of Si – O – C linkages formed through the methoxy groups and PLA during extrusion. This two sided reaction resulted in the formation of the thermoset. Reducing the Luperox concentration to 0.25 and 0.1 wt% yielded products with slightly lower grafting efficiencies of 87.49 and 82.91%, respectively. However, this reaction was without the unwanted Si – O – C linkages responsible for the formation of a rigid thermoset. Both samples were fully dissolvable in solvent, indicating that no crosslinking occurred through REX, but rather the grafting was done solely via the vinyl attachment onto PLA.

The mechanism for the vinyl attachment of VT MOS onto the PLA backbone is shown in **Schematic 5.1**. This mechanism for melt free radical grafting utilizing vinyl functionality is well accepted and has been used to incorporate many different chemical species onto PLA. The first step is the thermal decomposition of a free radical initiator (Luperox) resulting in the production of radicals. The generated radical abstracts hydrogen from the α -carbon, creating radicals on the PLA chain. This hydrogen abstraction of PLA was first shown by Avella et al. in the reaction with butyl acrylate.⁸¹ The PLA radicals are then capable of coupling with radicals on the vinyl group of VT MOS, as shown below. A potential side reaction involves the PLA radicals coupling with another material, the initiator radical, hydrogen, or another polymer radical, potentially leading to an unwanted result such as β -scission, which is noted by a molecular weight decrease in processing. The vinyl grafting efficiency was determined by NMR using the decrease in the vinyl to methoxy proton integration ratio as well as a slight change in the ratio of the PLA peaks corresponding to the methyl hydrogens and the hydrogen on the C-backbone. These two components prove that VT MOS is grafted onto the PLA backbone as described in Schematic 5.1.



Schematic 5.1: A schematic mechanism for the free radical initiated grafting of VTMOs on PLA.

Following VTMOs grafting, a moisture induced crosslinking of the grafted polymers can occur. First the methoxy groups of VTMOs readily hydrolyze in the presence of water, forming silanol functionality ($\text{Si}-\text{OH}$). The silanols condense to form siloxane linkages leading to the formation of crosslinked compounds. These short siloxane linkages from the coupling of two VTMOs molecules are not flexible enough to impart any toughening benefit. In fact, just crosslinking PLA with VTMOs yields a material with less ductility. Therefore, in an effort to lengthen the siloxane linkages and create a true toughening effect, a silanol functionalized PDMS (OH-PDMS) was incorporated to take part in the condensation portion of the crosslinking reaction. This hydrolysis and condensation crosslinking reaction is shown in **Schematic 5.2**.



Schematic 5.2: A mechanism showing the hydrolysis of the methoxy groups and the condensation resulting in siloxane crosslinked PLA.

After fabrication of test specimens and the following moisture cure, samples were again analyzed to determine grafting efficiency and for the formation of gels. Over this crosslinking period, the compounds experienced very little change in grafting of VTMOs and some samples showed a slight increase. This increase in grafting can be explained by some of the free, or unreacted VTMOs being incorporated in the crosslinking reaction thereby becoming part of the crosslinked material. A few of the samples showed a decrease in grafting which can be attributed to the weight loss of methanol during testing, which is created through the hydrolysis step. VTMOs can also migrate to the surface and evaporate instead of crosslinking. The grafting percentages for the compounds after REX and after the crosslinking period are shown in **Table 5.1**. For the VTMOs only samples, the higher Luperox concentration results in slightly higher grafting. With the addition of OH-PDMS, the opposite trend occurs where 0.1% Luperox results in higher grafting. The other trend to notice is that there was lower grafting efficiency for the 0.5 wt% VTMOs samples compared to the 1 wt% VTMOs samples. This is probably due to small losses of VTMOs in processing due to evaporation, where when using less material, the small losses result in larger percentages.

Table 5.1: Determination of percent VTMOs grafting following REX processing and after two week crosslinking period

%VTMOs	%OH-PDMS	%Luperox	% Graft _{initial}	% Graft _{2 weeks}
0.5	1	0.1	78.2	70.5
0.5	1	0.25	66.1	75.1
0.5	3	0.1	63.5	50.3
0.5	3	0.25	63.7	73.1
1	1	0.1	89.5	83.6
1	1	0.25	86.3	86.5
1	3	0.1	79.3	77.8
1	3	0.25	76.4	79.8
1	0	0.1	82.9	79.9
1	0	0.25	87.5	86.8

After the moisture curing step, the compounds were again placed in solvent to dissolve. All of the samples experienced gel-swell rather than dissolving. This indicates that the siloxane crosslinking had in fact occurred through the hydrolysis and condensation steps shown. The REX procedure used was shown to be effective in its ability to enhance VTMOs grafting efficiency onto PLA compared to previous reports.

5.3.2 Mechanical Properties

The tensile properties of neat and REX modified PLA samples are shown in **Table 5.2**. It should first be mentioned that the mechanical properties experimentally determined for neat PLA are comparable to the properties reported by NatureWorks in their technical data sheet. As mentioned earlier, crosslinking PLA with only VTMOs results in a decrease in ductility. This was observed in our results as the test specimens showed an increased modulus coupled with a loss in elongation. This is due to the formation of a crosslinked network where the crosslinks are short, and rather stiff in nature. As OH-PDMS is added and incorporates in the crosslinking, the siloxane crosslinks become longer and much more flexible due to the physical characteristics of this bond compared to a carbon-carbon bond. With an increase in OH-PDMS content, an increase in elongation is experienced along with a slight reduction in yield stress. In fact, the neat PLA and VTMOs only specimens did not show a true yield stress, but rather an increase in stress until fracture. When OH-PDMS is incorporated, a true yielding is experienced and examples of such samples are shown in **Figure 5.1**.

Table 5.2: Tensile properties of the siloxane crosslinked PLA samples
(a minimum of 5 specimens were tested for each sample set)

%VTMOS	%OH- PDMS	%Luperox	<i>E</i> (ksi)	σ_y (ksi)	ϵ_f (%)
0.5	1	0.1	4.93	7.93	3.07
0.5	1	0.25	4.72	7.98	5.94
0.5	3	0.1	5.33	6.52	9.97
0.5	3	0.25	4.45	6.6	4.45
1	1	0.1	4.97	8.03	3.59
1	1	0.25	4.83	7.71	4.05
1	3	0.1	5.38	6.59	3.24
1	3	0.25	5.05	6.57	4.49
1	0	0.1	5.41	8.51	2.4
1	0	0.25	5.02	8.11	1.92
0	0	0	3.8	8.51	2.93

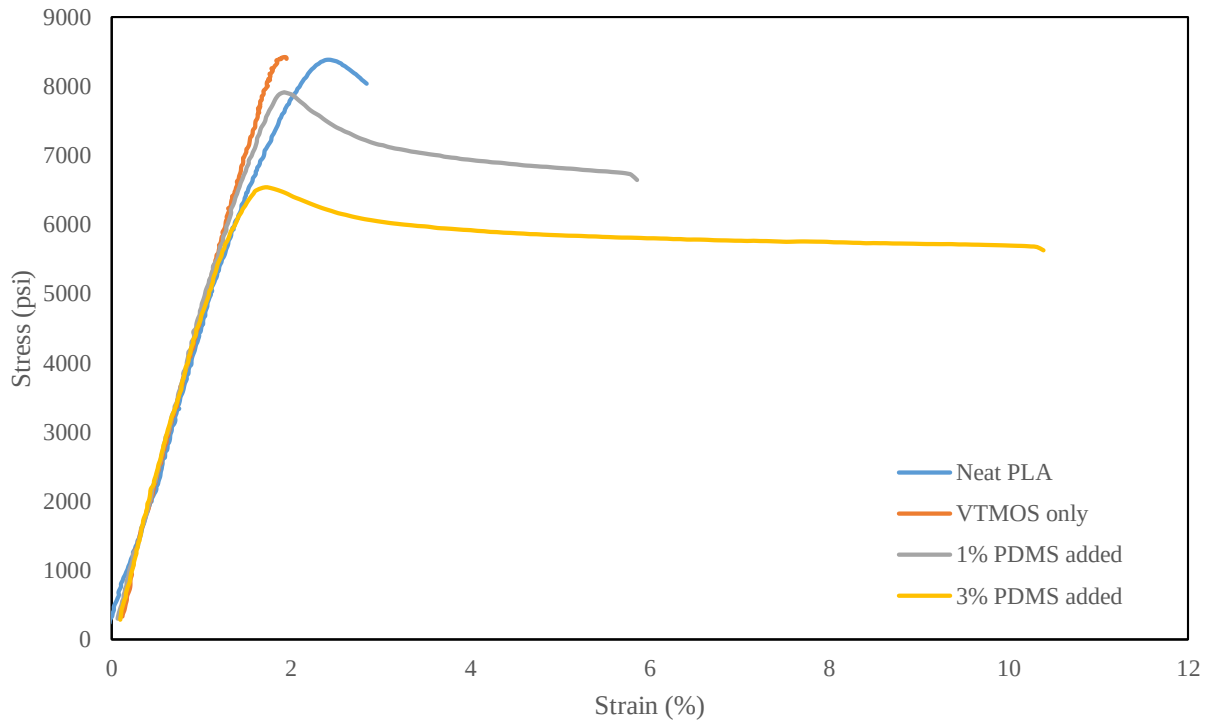


Figure 5.1: Representative stress-strain curves of neat PLA, VTMOS crosslinked PLA, and crosslinked samples incorporating 1% and 3% OH-PDMS.

From Figure 5.1 it is clear to see that by incorporating OH-PDMS, much higher elongations to failure are experienced. However, the very unique result from this modification is that the elongation was increased without reduction in moduli of the specimens. In fact, the crosslinked samples with OH-PDMS showed a significantly higher modulus than neat PLA. This is caused by crosslinking a stiff material with a very ductile polymer. The crosslinked structure initially provides rigidity, raising the modulus. Yet these ductile crosslinks are capable of stretching under the applied load until they reach their limit, where the PLA then fails. This explains why even with increased elongation, a brittle failure was still observed. All tensile specimens showed a flat and smooth fracture surface, indicating a brittle fracture. The OH-PDMS crosslinked samples are both stiffer and more ductile in comparison to neat PLA, resulting a significant increase in the tensile toughness, as seen by the area under the curves. The addition of OH-PDMS does result in a slight reduction in ultimate stress, but with the increases in elongation and modulus, an increase in toughness is still experienced.

Another thing of note is how the crosslink density affects the tensile properties. Assuming 80% grafting efficiency, 0.5 wt% and 1 wt% of VTMOs results in ~4 and ~8 VTMOs groups grafting onto each PLA chain, respectively. Therefore these samples experience different crosslink densities. The lower crosslink density samples (0.5 wt% VTMOs) show higher elongations to failure, while the high crosslink density samples have a higher modulus. This fits with theory and is what would be expected when dealing with crosslinked samples. The higher amount of crosslinks in a specific area result in the material not being able to stretch and deform as much, coincidentally resulting in a higher modulus. However, regardless of the VTMOs content in the samples, a significant increase in tensile toughness was observed with the presence of OH-PDMS due to increases in both elongation to failure and modulus compared to neat PLA.

IZOD Impact testing also showed a significant increase in toughness (~25%) for the modified samples. However there was no discernible trend based on VTMOs, OH-PDMS, or Luperox concentrations, as seen in **Table 5.3**. It appears that with such a dynamic and fast fracture, the extent of crosslinking (VTMOs concentration) and the crosslink length (OH-PDMS concentration) has no direct effect. But rather, a siloxane crosslinked sample of any nature shows approximately a 25% increase in impact toughness over neat PLA. The quick fracture likely doesn't allow for the longer siloxane linkages to stretch and absorb more energy, yielding a higher toughness as is seen with higher OH-PDMS concentrations in tensile testing. But rather the presence of these siloxane crosslinks is enough to increase the impact toughness compared to neat PLA.

Table 5.3: Notched IZOD impact toughness of siloxane crosslinked samples compared to neat PLA

%VTMOs	%OH-PDMS	%Luperox	Impact Energy [ft-lb / in]	% Increase vs Neat PLA
0.5	1	0.1	0.504	22.6
0.5	1	0.25	0.522	27.0
0.5	3	0.1	0.512	24.6
0.5	3	0.25	0.515	25.3
1	1	0.1	0.519	26.3
1	1	0.25	0.519	26.3
1	3	0.1	0.518	26.0
1	3	0.25	0.479	16.5
1	0	0.1	0.504	22.6
1	0	0.25	0.525	27.7
0	0	0	0.411	0

5.3.3 Morphology

The tested samples were analyzed using SEM to determine if the siloxane crosslinks affected the morphology of the fractured surfaces. **Figure 5.2** shows the fractured surfaces of select samples following tensile testing. The neat PLA sample in Figure 5.2a shows an extremely rough surface in comparison to the others which are just VTMO crosslinked (Figure 5.2b) and containing both VTMO and OH-PDMS crosslinking (Figure 5.2c). This extremely rough surface corresponds to the brittle fracture experienced by the neat PLA samples during testing. Not only do the siloxane crosslinked samples exhibit a smoother fracture surface but they show siloxane pullout. In these samples, small holes (black circles) of where the siloxane was pulled out are visible along with the analogous opposite, the stretched siloxane (white circles). The sample containing OH-PDMS shows the presence of long white strands which are most likely the long siloxane linkages from the PDMS polymers.

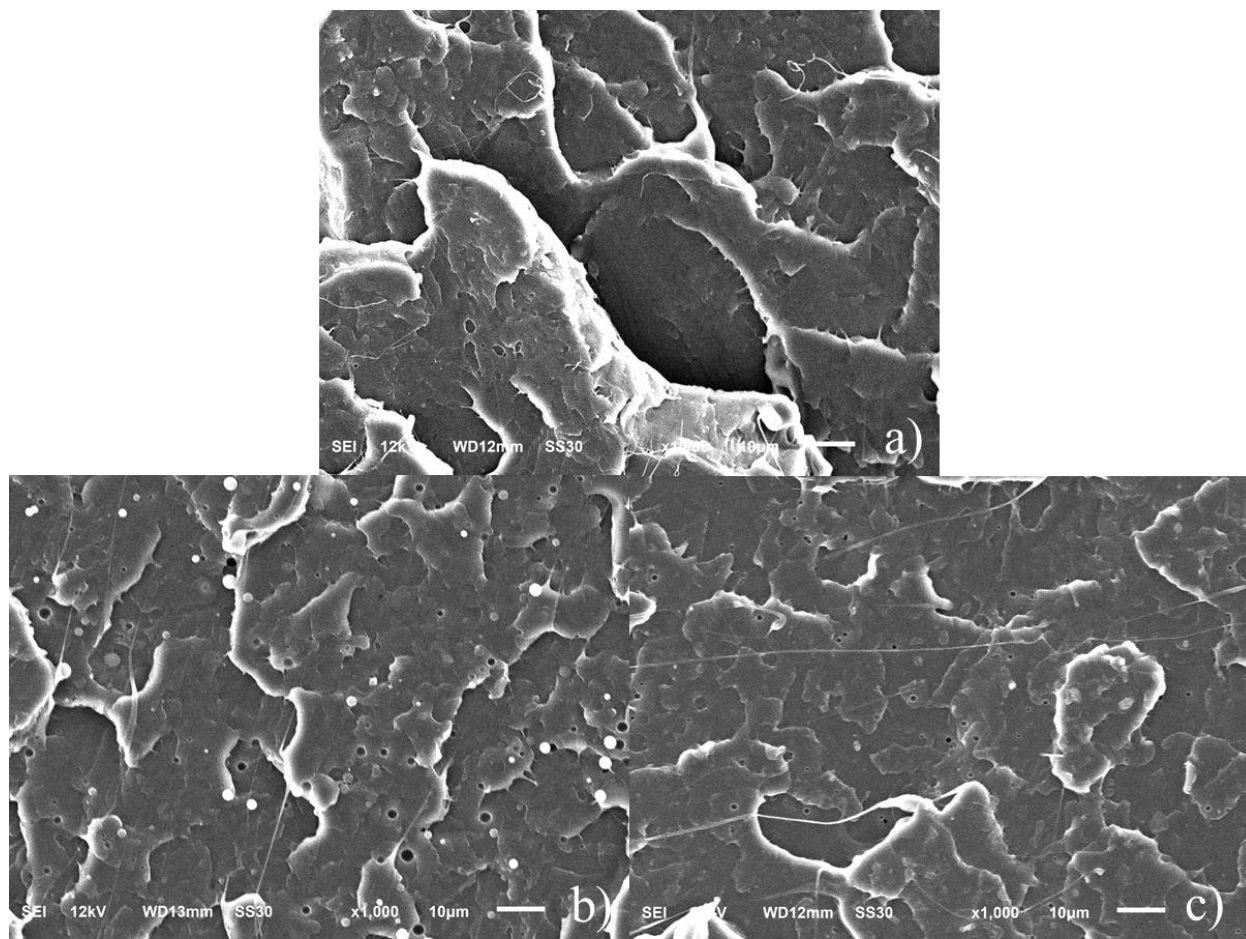


Figure 5.2: SEM micrographs of the tensile fractured surfaces of a) neat PLA, b) 1% VTMOs – 0.25% Luperox, and c) 0.5% VTMOs – 3% OH-PDMS – 0.1 % Luperox samples.

The morphologies of the impact test samples are shown in **Figure 5.3**. All of the fractured surfaces exhibited a rippled pattern morphology, seen by the vertical columns in the figure. The crosslinked samples show more visual connectivity of the raised sections of the surface, which are from the crosslinking. For the sample with OH-PDMS, the same long linkages are visible as seen in the tensile samples, due to the longer siloxane crosslinks. This added connectivity and ability to deform prior to fracture is the cause of the increase in impact energy.

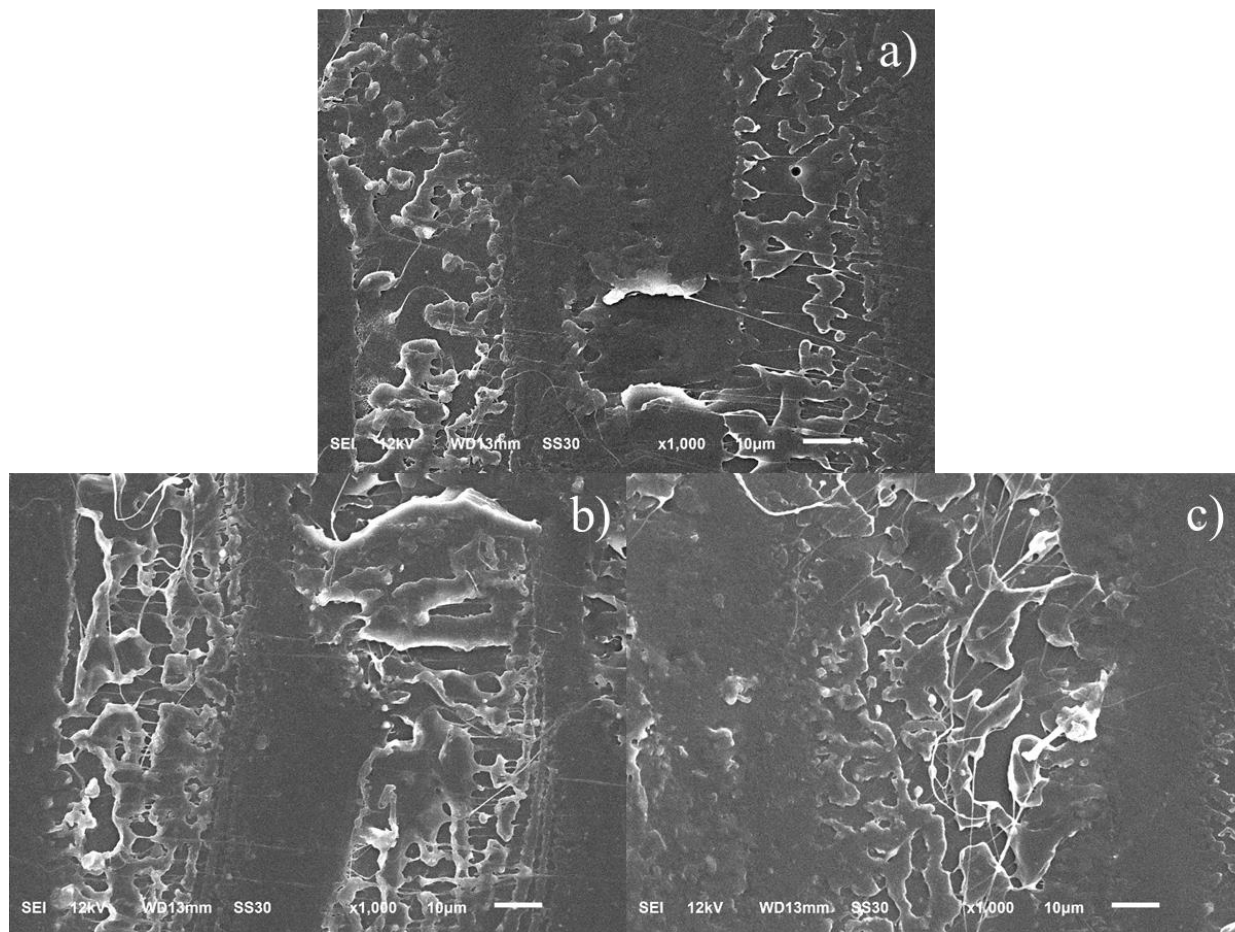


Figure 5.3: SEM micrographs of the impact test fracture surfaces of a) neat PLA, b) 1% VTMOs – 0.25% Luperox, and c) 1% VTMOs – 1% OH-PDMS – 0.1% Luperox samples.

5.4 Conclusion

VTMOs was grafted onto PLA using REX processing and moisture cured to form a siloxane crosslinked PLA material. Process improvements compared to a previous study resulted in greater than a two fold increase in grafting efficiency of VTMOs onto the PLA backbone. This resulted in less VTMOs used, lowering the cost of the final product. OH-PDMS was added to lengthen the siloxane crosslinks, resulting in improved tensile toughness. The samples crosslinked with only VTMOs showed improvements in modulus, strength, and impact properties with a

decrease in ductility, as previously reported. However, by incorporating OH-PDMS into the crosslinking reaction, not only did an increase in modulus and impact toughness occur compared to neat PLA, but increased elongation to failure was observed resulting in the improvement in tensile toughness. SEM of the fractured surfaces showed the presence of the stretched siloxane crosslinks for the impact samples and siloxane pullout for the tensile samples. This enhanced ability for the material to deform and absorb energy gives reason for the increase in toughness.

Chapter 6 – Poly(lactide) – Poly(dimethylsiloxane) Block Copolymers From Reactive Extrusion Processing for Toughening Applications

6.1 Introduction

There has been a rise in awareness and use of bioplastics due to environmental and sustainability concerns that arise from conventional petroleum derived polymer materials. This has driven both academia and the polymer industry to improve existing biobased polymers.⁸² Poly(lactide) (PLA) is one of the most popular bioplastics to date and advances in processing technologies make it an economically sound alternative to petroleum derived polymers. It has shown good performance in the packaging, textile, and automotive industries as the push for more eco-friendly alternatives for traditional plastic products continues.^{35,37} PLA is advantageous as it can be made from a variety of biomass feedstocks such as corn, sugar cane, and potentially methane in the future.⁸³

However, in the case of using PLA directly for packaging or consumer use, the brittle mechanical properties have hindered its widespread application despite its high strength and modulus.⁸⁴ Just as the inherent brittleness of poly(styrene) led to the development of engineered copolymers and blends for improved toughness, PLA toughening has become an area of focus. It is of both industrial and academic interests to improve the toughness of PLA through a variety of mechanisms. Many strategies have been reported in literature including plasticization^{85–87}, melt-blending^{88,89}, stereochemical/crystallinity effects^{90–93}, and copolymerization. Copolymers can form many different physical structures including linear random, block, and graft copolymers. The ability to combine materials with different properties into a wide variety of differing structure

makes copolymerization an excellent method to obtain material properties that are not possible by either of the homopolymers.

Random copolymers are an excellent way of imparting ductility and a toughening effect to PLA. This procedure involves two different monomeric units polymerizing together forming a random repeating pattern. A common biodegradable polymer copolymerized with PLA is poly(ϵ -caprolactone) (PCL). Its low T_g of -60°C can impart a great deal of ductility to the resultant copolymers. Varying PLA and PCL ratios from 80/20 to 40/60, Hiljanen-Vainio et al. created copolymers behaving like tough thermoplastics to weak elastomers.⁹⁴ It was also shown the ring-opening polymerization temperature has an effect on the mechanical properties of the copolymers created.⁹⁵ Higher polymerization temperatures led to a more random distribution of monomers, yielding copolymers with decreased strength properties and higher elongation than those processed at lower temperatures. However, issues with scaling these processes prevent polymerization from monomers being cost effective commercially as of now.

Block copolymers on the other hand can be created from existing PLA polymers and “connected” with more ductile materials, creating a more economical method of copolymerization. Block copolymers are polymers that contain sections or “blocks” of one type of polymer connected to block(s) of another polymer. The number of blocks in the copolymer determines how a block copolymer is named. Two block sections and three block sections are termed diblock and triblock copolymers, respectively. Block copolymers are an excellent method to enhance the properties of a homopolymer. For example, Martello et al. produced sustainable PLA and poly(ϵ -decalactone) block copolymers to function as thermoplastic elastomers. A triblock with a molecular weight of 170,000 g/mol with a PLA volume fraction of 21% exhibited a max stress of ~ 4 MPa and a strain to failure of over 1500%.⁹⁶

Previous studies have used silicone rubbers to improve impact strength and toughness of PLA, though the majority of these involve crosslinking mechanisms.^{79,97} Silicones as modifying materials for PLA and other biobased materials has garnered very little attention in literature. Typically biobased materials, PLA included, are susceptible to thermal and hydrolytic/moisture degradation, and in the case of PLA is brittle. The interest in using silicones in copolymers is due to the interesting inherent properties that they possess. Due to the siloxane (-Si-O-Si-) backbone they usually exhibit very high flexibility, very low T_g (for PDMS $\sim -120^\circ\text{C}$), good thermal and oxidative stability, and very low surface tension values making them hydrophobic.⁵⁸ Because of the unique properties of silicones, they are an interesting material for property enhancement of PLA. PLA-PDMS di- and tri-block copolymers have been produced with a PDMS content range of 25-64 wt%, resulting in up to a 60% increase in strain to failure.⁹⁸ However, the copolymers use as an impact additive into neat PLA resulted in blends with significant improvement in tensile strength and strain to failure compared to the copolymers alone.

This chapter describes the investigation of the controlled breakdown and resultant copolymerization of PLA with aminopropyl-terminated PDMS (NH-PDMS) in the presence of Tin(II) 2-ethylhexanoate as a catalyst in a reactive extrusion process. Processing conditions and catalyst content were varied to study their effects on molecular weight, NH-PDMS reactivity, and the breakdown of PLA through the process. Various molecular weights of the NH-PDMS were used at different loadings to study the reactivity and the resultant mechanical properties of these copolymers. A brief discussion on block copolymer equilibrium phase behavior is included to explain the mechanical performance trends.

6.2 Experimental

6.2.1 Materials

The grade of poly(lactide) (PLA) used in this study was 3051D from NatureWorks LLC. (MN, USA), with a weight average molecular weight of $\sim 130,000$ g/mol and a meso-lactide content of $\sim 8\%$. Three different molecular weights (1000, 5000, and 30000 g/mol) of a diaminopropyl-polydimethylsiloxane (NH-PDMS) were used. The NH-PDMS materials were purchased from Gelest (PA, USA). The catalyst tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) and dichloromethane were obtained from Sigma-Aldrich (WI, USA).

6.2.2 Block Copolymer Synthesis

The copolymerization procedure involves the controlled breakdown of PLA followed by reaction with NH-PDMS, building the molecular weight back up through the formation of a block copolymer. This was all done through an efficient reactive extrusion (REX) process. Prior to REX, the PLA pellets were dried in a 70°C oven for 24 hours. Removing as much moisture from the material as possible is critical because PLA can easily hydrolytically degrade through transesterification and back-biting reactions, resulting in a decrease in mechanical properties.¹² Ensuring minimal moisture can prevent any excessive or unwanted breakdown of the PLA during processing. The reaction was carried out in a ZSK-30 co-rotating twin screw extruder with a screw diameter of 30mm and an L/D ratio of 42 from Century Extrusion (MI, USA). The dried PLA pellets were premixed with the NH-PDMS and $\text{Sn}(\text{Oct})_2$ before being fed into the extruder. The resultant polymer melt strand was cooled in a water bath and then pelletized. These pellets were

then again dried before further use. The screw speed and temperature profile for all compounding was 125 rpm and 140-150-160-160-160-170-170-170-160°C, respectively.

6.2.3 Sample Purification and Characterization

The polymer after REX is a combination of both copolymer and some residual unreacted NH-PDMS, which could act as a plasticizer. To purify the samples and determine reaction extent, a solvent wash procedure was used. First the dried pellets were dissolved in dichloromethane. The copolymer, neat PLA, and NH-PDMS are all fully soluble in this solvent. After dissolving, the solution was poured into a large excess of methanol. This causes the copolymers and neat PLA to precipitate out of solution, while the unreacted NH-PDMS remains suspended. The precipitated polymer was then filtered out and this wash process was performed a minimum of three times per sample. A control mixture of PLA and NH-PDMS showed that all of the free (or unreacted) NH-PDMS gets removed from the filtered product.

6.2.3.1 ^1H NMR

Proton NMR was used as a method of determining the extent of reaction for the NH-PDMS in the copolymerization. By determining the PLA to NH-PDMS ratios from both the unpurified product following REX and the purified product allows for the percent reacted to be calculated. NH-PDMS shows a strong and distinct peak ~ 0.2 ppm corresponding to the hydrogen of the methyl groups off of silicon. PLA exhibits a distinct peak corresponding to its methyl group at ~ 1.6 ppm. The change in the ratio of these can be used to calculate the percent of remaining NH-PDMS, or the reacted NH-PDMS, after the purification process based on the equation below.

$$\% \text{ Reacted} = \left[1 - \frac{IR_{pur.} - IR_{REX}}{IR_{pur.}} \right] \times 100\% , \textbf{Equation 6.1}$$

Where IR_{REX} is the integral ratio of PLA to NH-PDMS following the REX copolymerization and $IR_{pur.}$ is the integral ratio after the purification steps. This calculation determines the percentage of the NH-PDMS used in the REX processing that was incorporated into a block copolymer and that which remained unreacted and functions as a plasticizer.

6.2.3.2 Gel Permeation Chromatography

The molecular weight characteristics of the copolymers were determined by gel-permeation chromatography (GPC). Tetrahydrofuran was used as the mobile phase at a rate of 0.500 mL/min at 40°C. The intensity as a function of elution time was measured by a Refractive Index Detector (RID-10A, Shimadzu, Japan) using a Styragel column from Waters Corporation (MA, USA). Monodisperse polystyrene standards were used as a reference in the molecular weight calculations.

6.2.3.3 Tensile Properties

The tensile bar specimens were injection molded using a DSM micro-injection molding system. The sample pellets were melted in a DSM Micro 15cc Compounder (Vertical, corotating twin screw microextruder) at a temperature of 190°C and a screw speed of 100 rpm. After melting,

~1 minute, the polymer melt was then directly transferred to a Daga Micro Injector with a barrel temperature of 190°C and a mold temperature of 50°C. The tensile specimens were allowed to cool in the mold for around 15 seconds prior to being removed.

The tensile testing was completed using an Instron (MA, USA) mechanical testing fixture model 5565P6021 with a 5 kN load cell. The rate of grip separation used was 12.5 mm/min as per ASTM D882 for materials with a percent elongation at break of less than 20.⁵⁰ A minimum of 6 tensile specimens were tested for each material composition to ensure accurate results.

6.3 Results and Discussion

6.3.1 Processing Effects

REX can be a time efficient reaction method, however small changes in the processing conditions can have a large impact on the resultant materials. The first aspect of this study was to determine the ideal REX processing conditions for this reaction to occur. For all samples, the temperature profile and screw speed were held constant as mentioned above. However, the catalyst concentration and torque, adjusted by feed rate - a function of residence time, were changed and the resulting NH-PDMS reaction and molecular weight characteristics of the materials were experimentally determined.

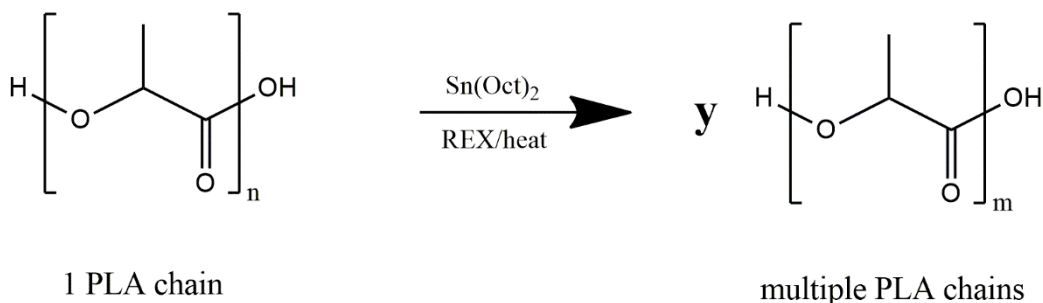
Table 6.1 below shows the NH-PDMS reactivity and molecular weight characteristics of the resulting materials as a function of processing parameters. The NH-PDMS used for this portion of the study was the 5000 g/mol material, and this was kept consistent. The first section of the table shows all of the “control” samples. This includes neat PLA with two different catalyst concentrations and a PLA/NH-PDMS mixture without any catalyst, all processed with consistent

torque values (residence time). For the neat PLA experiments, increasing catalyst concentration results in a larger reduction in both weight and number average molecular weights and an increase in the polydispersity (PDI). As the catalyst concentration is increased for PLA at high temperatures, chain scission and depolymerization increases resulting in the lower molecular weight values observed.⁹⁹ A diagram of this concept is shown in **Schematic 6.1**. Therefore, the higher catalyst sample experiences more PLA breakdown and results in a lower molecular weight. When PLA and NH-PDMS undergo REX without any catalyst, very low (~3%) NH-PDMS reaction is observed and without the large decrease in molecular weights. Without catalyst and the breakdown of PLA during processing there are many fewer chain ends, and therefore less functional groups on the PLA chains for the NH-PDMS to react with. This coupled with slower reaction speeds for the lack of catalyst contribute to only observing 3% reaction.

The PLA and catalyst only control samples show that there is dramatic breakdown of the PLA during REX processing when in the presence of catalyst. Without catalyst there is not dramatic breakdown, however the NH-PDMS only control sample shows that there is only a negligible amount of reaction of the NH-PDMS without catalyst. Therefore, for the copolymer samples which have both catalyst and NH-PDMS the fact that there is both NH-PDMS reaction and high molecular weights signifies that a block copolymer was formed. The PLA will breakdown in the presence of catalyst, yet the catalyst also helps the NH-PDMS react with the newly created carboxyl groups of PLA. This reaction of NH-PDMS is what builds back up the molecular weight of the resultant copolymers. This reaction also leads to the higher polydispersity observed.

Table 6.1: REX processing effects on block copolymer synthesis

Sample		Torque	Residence Time	NH-PDMS Reaction	M _w	M _n	PDI
PDMS%	cat. %						
0	0.1	35		-	68000	34000	2.01
0	0.2	35		-	50000	23000	2.13
3	0	35		3	122000	68000	1.79
3	0.1	50	~1.5 min	55.7	121000	61000	1.99
3	0.1	35	~2 min	62.7	133000	73000	1.82
3	0.1	25	~2.5 min	71.2	81000	40000	2.03
3	0.2	35	~2 min	60.0	95000	49000	1.94
3	0.2	25	~2.5 min	73.4	64000	32000	2.01

**Schematic 6.1:** Diagram showing PLA chain scission when in the presence of catalyst and elevated temperatures like in REX processing.

Previous work in our group has shown that PLA in the presence of a high Sn(Oct)₂ catalyst concentration and temperature can lead to thermal depolymerization yielding lactide.⁹⁹ However this was done at higher temperatures, longer times, and with higher catalyst concentrations than used in this REX processing. **Figure 6.1** shows the ¹H NMR spectra of PLA processed with REX

in the presence of just catalyst. The doublets marked **a** and **b**, relate to the methyl groups of PLA. The **c** marker at 1.5 ppm would correspond to lactide if it were in the system. From this analysis it is clear to see that there is a negligible amount of lactide formed during processing. The thing of note is the presence of the **b** doublet corresponding to the methyl groups at the end of the polymer chains. In a typical NMR spectra of a high molecular weight PLA, **b** is negligible due to the low number of end groups. This spectra shows that there is an increase in the methyl units near end groups. This lead to the conclusion that the diagram in Schematic 1, indicating the creation of many low molecular weight polymers from the starting PLA, is correct. This short time period and low catalyst concentration results in chain scission of the polymer rather than depolymerization.

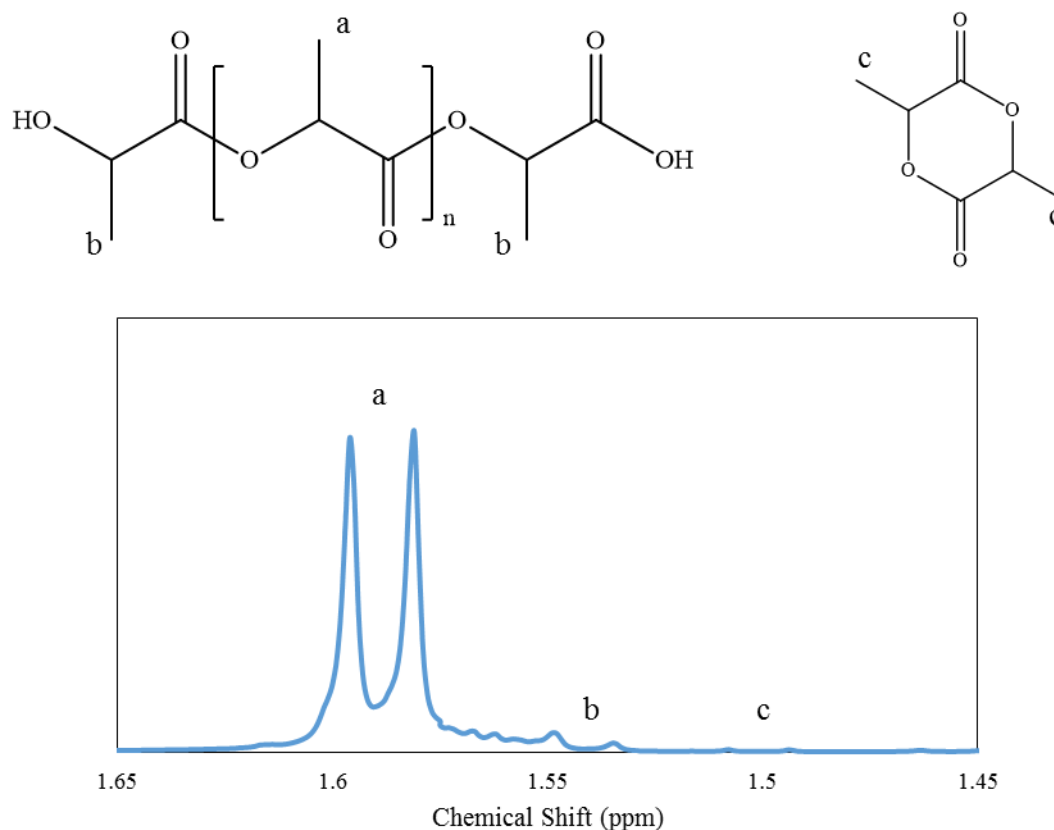
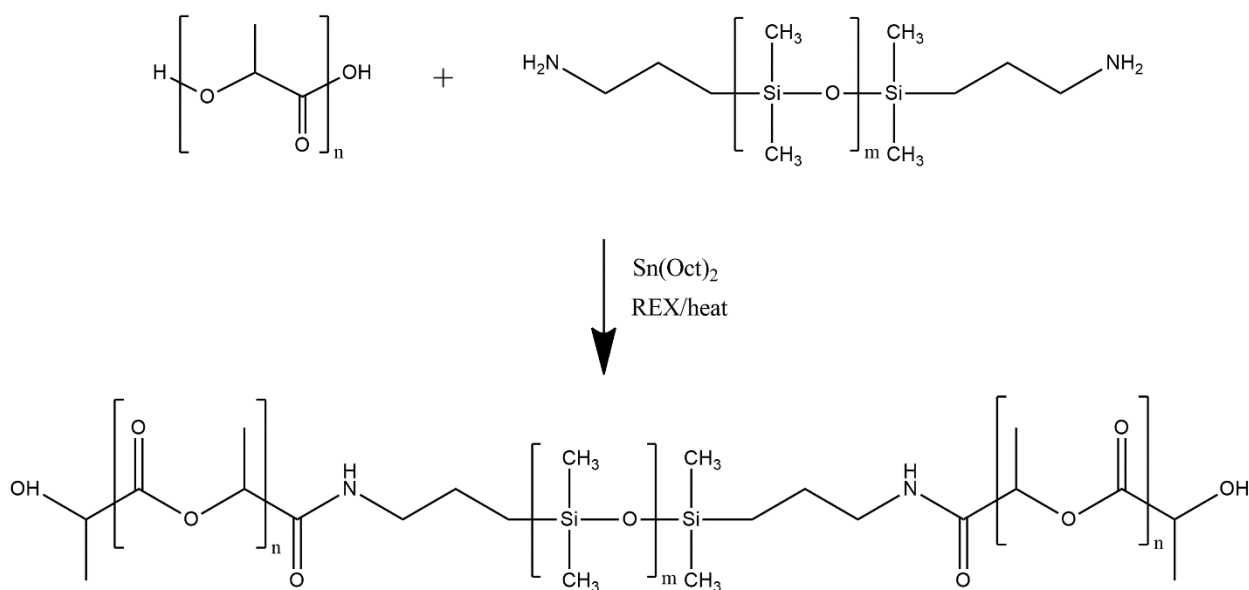


Figure 6.1: ^1H NMR spectra of PLA processed with just catalyst.

The remainder of the samples in the table vary both the catalyst concentration and the torque/residence time the polymer is in the extruder. **Schematic 6.2** shows a triblock copolymer created from this reaction. If both amine groups of NH-PDMS react then a triblock is formed. If only one group reacts then a diblock will be created. For the unreacted NH-PDMS, neither of its amine groups react with PLA so these do not create a block copolymer. With increasing residence time, for both catalyst concentrations, the NH-PDMS reaction percentage increased. Residence times ranging from 1.5, to 2, to 2.5 minutes resulted in roughly 50, 60, and 70% reaction, respectively. The increase in NH-PDMS reactivity for the 50 and 60% reacted samples also

resulted in an increase in molecular weight. However, the 2 minute residence time showed the maximum molecular weights produced while residence times longer than this resulted in a molecular weight decrease. Even though there was an increase in the NH-PDMS reactivity, the longer residence time results in more hydrolytic breakdown of PLA so that a decrease in molecular weight is observed. This excessive hydrolytic breakdown is also noted by an increase in the PDI for the samples due to the more significant decrease in M_n caused by the formation of these small polymer chains.



Schematic 6.2: A molecular representation of the formation of a PLA-PDMS-PLA triblock copolymer.

As with the PLA controls, increasing the catalyst concentration resulted in a decrease in the molecular weight characteristics. Catalyst concentration did not show any significant effect on the NH-PDMS reactivity, however it did lead to further breakdown. Based on the results of

this brief discussion, the preferred processing conditions that were used for the remainder of this study are 0.1% catalyst and 35% torque corresponding to ~2 minute residence time.

6.3.2 Copolymer Synthesis

Using the previously determined preferred processing conditions, both the PDMS concentration and molecular weights were experimentally altered to study the various copolymers formed. The reactivity of NH-PDMS and the molecular weight characteristics are presented in **Table 6.2**. With increasing NH-PDMS content, a reduction in its reaction percentage was observed. Even at the low weight percentages used in this study, this can be explained on the basis of molar percentage. For example, 3 wt% of 1000 g/mol NH-PDMS mixed with PLA results in 80.1 mol% due to the large molecular weight difference. Even if we make the assumption that the PLA gets broken down and the molecular weight becomes $\frac{1}{4}$ of the original polymer length, this results in 50 mol% of the NH-PDMS. The maximum number of copolymer blocks from this processing is a triblock, though the copolymers formed are a combination of di- and tri-block. Based on this, only 33 mol% of NH-PDMS could be incorporated into the copolymers. So unless PLA gets further broken down, a decrease in reaction amount is expected when the NH-PDMS content is increased. The lower reactivity also led to a reduction in the molecular weight of the copolymers, with an increase in the PDI.

As the molecular weight of the NH-PDMS was increased, the reaction percentage increased as well. Again this can be explained by molar ratios. When the molecular weight was increased there were fewer moles of NH-PDMS at the same wt% loading. Therefore a higher percentage of them are able to react, and the rise in reactivity was observed.

Table 6.2: Reactivity and molecular weight characteristics of PLA – PDMS block copolymers

Sample		<i>NH-PDMS</i> <i>Reaction</i>	M_w	M_n	<i>PDI</i>
<i>NH-PDMS MW</i> (g/mol)	<i>PDMS %</i>				
1000	3	65.9	100000	55000	1.80
1000	5	47.0	88000	48000	1.84
5000	3	62.7	133000	73000	1.82
5000	5	53.5	117000	56000	2.11
30000	3	70.3	101000	48000	2.10
30000	5	52.1	86000	44000	1.96
30000	7	56.8	98000	49000	2.00

6.3.3 Tensile Properties

The addition of a flexible component to brittle PLA should impart a toughening effect. Along with this increased toughness, a reduction in modulus and yield stress and an increase in strain to failure is expected. **Table 6.3** shows the tensile properties of the various samples tested. For the most part the properties were exactly as expected. Increasing the NH-PDMS content resulted in a decrease in the modulus and yield stress, while the strain to failure increased. The minimal decrease in strength properties coupled with the significant rise in strain/elongation results in materials with much improved tensile toughness.

Table 6.3: Tensile properties of PLA – PDMS block copolymers compared to neat PLA

NH-PDMS MW [g/mol]	NH-PDMS [%]	Modulus [GPa]	Yield Stress [MPa]	Strain at Break [%]	% Strain Improvement
PLA 3051D		1.57	66.9	8.76	-
1000	3	1.43	61.7	10.10	15.19
1000	5	1.39	55.4	10.82	23.47
5000	3	1.56	63.8	11.39	29.96
5000	5	1.47	59.4	12.89	47.06
30000	3	1.46	59.4	13.13	49.86
30000	5	1.38	57.6	14.27	62.86
30000	7	1.37	52.5	12.86	46.69

However, the copolymer with 7% NH-PDMS (30,000 g/mol) shows slightly different behavior for strain at break. This is shown graphically in **Figure 6.2**. From the figure it is clear to see that with increasing NH-PDMS content and molecular weight, an increase in the strain improvement compared to neat PLA is observed. This holds true for all three molecular weights at 3 and 5 wt% NH-PDMS. But the 30,000 g/mol NH-PDMS sample at 7 wt%, shows a decrease in the strain improvement compared to the trend. Again, what is expected based on the assumption of normal mixing is increasing NH-PDMS content will result in increasing strain. The dramatic change in the trend experienced indicates that some physical change is occurring, most likely a different morphology is observed for the copolymer with higher (7%) NH-PDMS content.

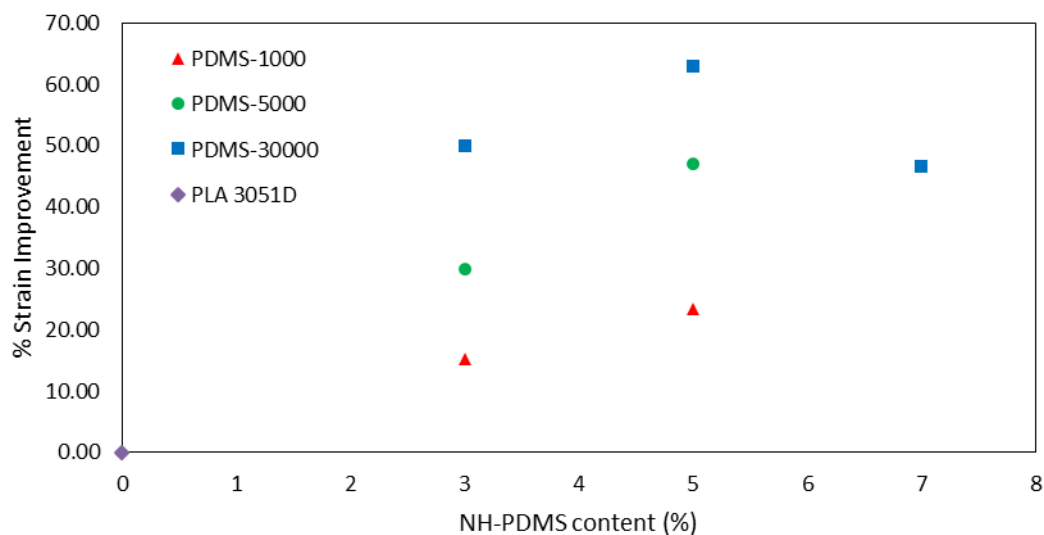


Figure 6.2: Percent improvement of strain to failure of block copolymers compared to neat PLA, as a function of NH-PDMS content.

6.3.4 Block Copolymer Equilibrium Phase Behavior

This deviation of properties from the trend can hopefully be explained via the phase behavior of block copolymers as described by self-consistent field theory (SCFT). Over the last few decades, SCFT has been used to predict the phase behavior and morphology of AB_n block copolymers and the theory has been very successful in describing the experimental equilibrium phase behavior.^{100–102} Typically phase diagrams are created for specific block copolymer types (ex. diblock, triblock, star, etc...) predicting the morphology of the resultant copolymer as a function of volume fraction of block B and χN (the Flory-Huggins interaction parameter for the polymers multiplied by the degree of polymerization). The morphology is predicted by minimizing the overall free energy of the system to find an equilibrium state of a block copolymer. A phase diagram for symmetric ABA triblock copolymers is shown below in **Figure 6.3**.¹⁰³ The

phase diagram shows two major sections, the disordered phase below the arced line and multiple ordered phases above. The disordered phase will not show any phase separation but will rather be a homogeneous mixture of the copolymers. In the ordered structures, there will be phase separation of the two polymers comprising the copolymer and the relative volume fractions and molecular weights play a factor into determining the structure of the dispersed phases (ex. spherical, cylindrical, gyroid, etc...). For the order structures at lowest volume fractions a spherical dispersed phase is observed, whereas a more even 50:50 volume fraction typically results in a lamellar morphology.

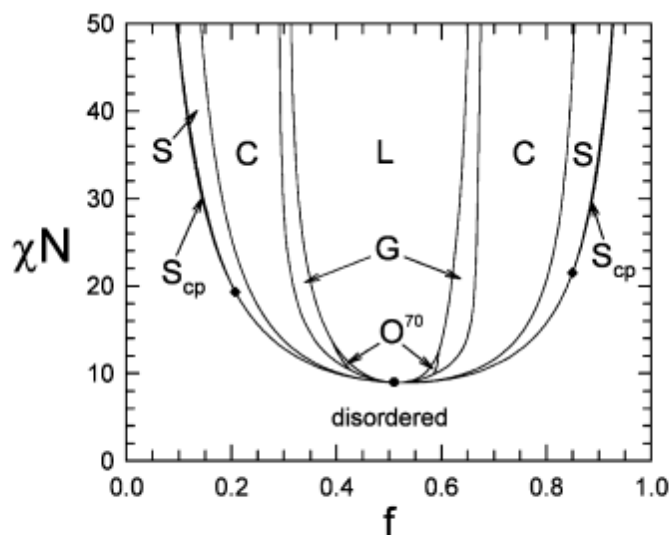


Figure 6.3: Phase diagram for symmetric ABA triblock copolymers, showing the stability regions of the ordered lamellar (L), cylindrical (C), bcc spherical (S), hcp spherical (S_{cp}), gyroid (G), and $Fddd$ (O^{70}). Here N is the degree of polymerization of the diblocks formed by snipping the triblocks in half. Figure copied without permission from Matsen, Mark W. "Effect of architecture on the phase behavior of AB-type block copolymer melts." *Macromolecules* 45.4 (2012): 2161-2165.¹⁰³

The phase diagram for triblock copolymers predicts that at $\chi N = 50$, the disordered state will transform into a dispersed spherical phase at $\sim 10\%$ volume fraction. Meaning a triblock copolymer with a χN of 50 will be in a disordered state and have no dispersed phase below a volume fraction of 10%. The PLA-PDMS block copolymers described in this study all have volume fraction below critical value for $\chi N = 50$ copolymers. However, the high molecular weight of these copolymers and the extremely high χ value for PLA and PDMS ($\chi_{\text{PLA-PDMS}} = 0.94$ at 298K – determined by Hildebrand solubility parameters¹⁰⁴) gives χN values for these copolymers that are above the y-axis of this phase diagram. For the 30,000 g/mol NH-PDMS copolymers, the M_n values are around 50,000 g/mol. Therefore based on the repeat unit weights of PLA and PDMS and a χ value of 0.94, the χN for these block copolymers is around 322. An expanded phase diagram would need to be created to accurately predict equilibrium phase behavior of these copolymers. However this high value of χN makes the math to create the phase diagram very difficult, this is the primary reason why the phase diagrams in literature only typically go up to $\chi N = 100$ as a max. It should also be noted that at high χN values (>100), the disordered to ordered phase lines are vertical lines. Therefore based on the behavior to the above phase diagram and extending the phase lines vertically, it seems plausible that the samples with 5 and 7% NH-PDMS could show different morphology and phase behavior based on SCFT. The low NH-PDMS samples (3 and 5%) would exhibit a disordered phase behavior and increasing NH-PDMS content to 7% could lead to the formation of spherical domains. This morphological difference would have an impact on the mechanical properties of these copolymers and explain the deviation from the trend for the strain to failure data.

6.4 Conclusion and Future Work

REX was used as a fast and efficient method of producing PLA-PDMS block copolymers through a controlled breakdown of PLA before reaction with NH-PDMS forming the copolymers. Adjusting the catalyst concentration and residence time in the extruder had a large effect on both the extent of PLA breakdown and the reactivity of the NH-PDMS. Increasing each results in further breakdown and further NH-PDMS reactivity. However these are competing reactions, one breaking down the polymer and one building it back up. Because of this, the lower catalyst concentration and medium residence time were used for the remainder of the project as this combination resulted in the highest overall molecular weight of the copolymers. A variety of copolymers were produced with varying NH-PDMS molecular weight and concentrations. The low molecular weight NH-PDMS showed the lowest reactivity as the molar ratio compared to PLA prevented any high level of reaction. Conversely, the highest molecular weight NH-PDMS exhibited the highest NH-PDMS reactivity. The higher molecular weight NH-PDMS also led to the greatest improvement in toughness compared to neat PLA. Even at the same wt% loadings, the longer siloxane chains resulted in enhanced ductility compared to the low molecular weight NH-PDMS. This led to a >60% increase in strain compared to neat PLA with only a marginal loss in modulus and yield stress. SCFT has been well studied as a method to determine block copolymer equilibrium phase behavior. At low NH-PDMS loadings, a disordered phase is expected. SCFT is discussed to explain the tensile strain decrease at highest NH-PDMS loading, and is attributed to the formation of spherical PDMS domains.

Further work is needed to complete this study. The purpose of this chapter is to discuss the REX copolymerization of PLA-PDMS block copolymers with a general characterization of the new materials. The end goal of the project is to use these block copolymers as impact modifiers

into neat PLA. As already discussed, previous work by Hazer et al.⁹⁸ showed incorporating PLA-PDMS block copolymers as modifiers into neat PLA results in a significant improvement in toughening over the copolymers alone. If this is the case for this study, then the scalable and efficient copolymerization route discussed can provide for a more cost effective method of PLA toughening.

Chapter 7 – Increasing Heat Deflection Temperature and Decreasing Cycle Time of Poly(lactide) Injection Molded Materials

7.1 Introduction

In the food industry, plastic products such as packaging, utensils, and beverage cups made from non-biodegradable materials such as polyethylene, polypropylene, and polystyrene are difficult to recycle because of food contamination and are generally thrown away. Being both biodegradable and recognized as safe for contact with food, PLA is an excellent alternative to replace these traditional petroleum based plastics. However many of these food applications require high temperature use (**Figure 7.1**), where PLA is limited by its low Heat Deflection Temperature (HDT), typically $\sim 55^{\circ}\text{C}$.¹⁰⁵ HDT is a measurement of the temperature at which a polymer part loses its dimensional stability, as measured by a specified sample deflection under a specified load while heating. Essentially above this temperature, the polymers lose their integrity and become too “gummy” for use.

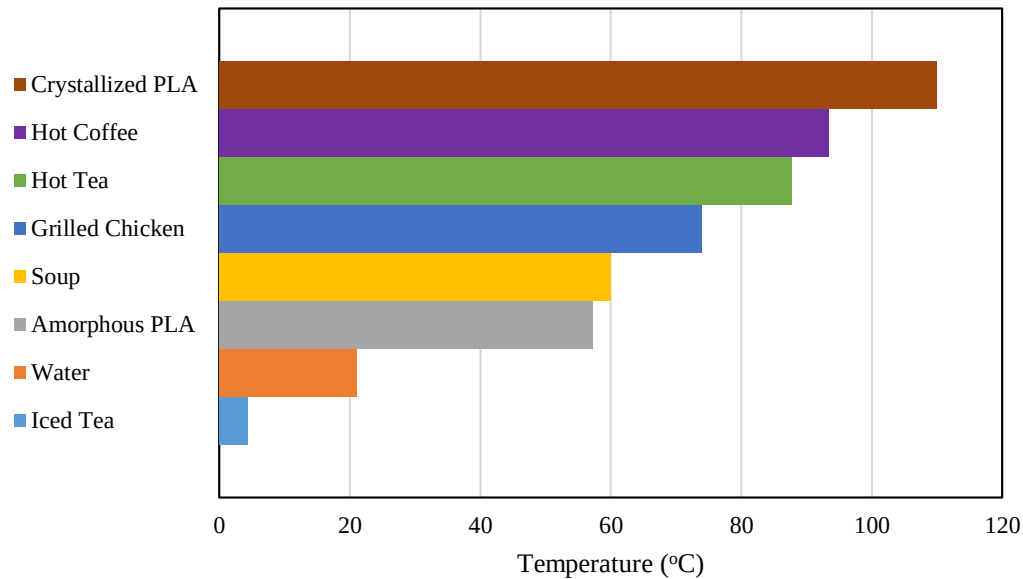


Figure 7.1: Serving temperatures of various foods compared to the typical HDT of PLA.

As an example, this can cause PLA cutlery to soften when exposed to high temperatures such as hot coffee or cutting grilled chicken. This is due to the loss of mechanical properties attributed to the amorphous phase being above its T_g . If the cutlery possessed enough crystallinity then this sudden drop in mechanical properties at T_g would not be seen. Since PLA has a melting temperature in the range of 150 – 180°C (depending on the monomeric makeup), with enough crystallinity it can boost the high temperature strength as the crystalline regions maintain their mechanical properties until T_m . The problem is that most commercial PLA resins have slow crystallization rates and only low crystallization is achievable, resulting in most injection molded products having low levels of crystallinity and being mostly amorphous. Therefore, increasing the degree of crystallization is critical and necessary for improved high temperature mechanical performance.

As previously mentioned, the isomeric makeup of the PLA has a large effect on properties of the polymer, such as T_m and its ability to crystallize.¹⁰⁶ This is caused by irregularities (most

prevalent - meso-lactide) being introduced into the polymer chain, which affects crystallization and therefore the overall performance/behavior of the material. A pure P(L)LA can be used for these injection molding applications to create a product that possesses higher degrees of crystallinity than typical PLA polymers. However, until recently this was not a commercially abundant material. Even now, the cost of this pure P(L)LA polymer is significantly more expensive due to the additional purification steps required to remove D- and meso-lactide prior to polymerization.

The more common approach used is to increase the rate and extent of crystallization by introducing nucleating agents, which lower the energy barrier needed for crystallization. These additives act as the nucleus or core of the crystallites that get formed. Typical nucleating agents such as talc¹⁰⁷ and clays¹⁰⁸ have shown high temperature improvements.

An additional factor affecting the crystallization is the molecular weight of the polymers. Typically a polymer of lower molecular weight will have a higher rate of crystallization. This is due to its increased chain mobility from more free volume which is from the presence of more end groups. Typically lower molecular weight materials also possess a lower viscosity which enhances chain mobility. A more mobile polymer chain can align itself easier, resulting in an enhanced ability to crystallize.¹⁰⁹ While this phenomenon regarding crystallization and molecular weight is generally accepted, few studies have been reported taking advantage of this effect.

The purpose of this study was to determine the effect of crystallization on the high temperature properties of various PLA grades and to test the performance of different nucleating agents at enhancing the crystallization rates. The PLA grades possessed different molecular weight characteristics and meso-lactide content, and their affects were studied. Various injection molding conditions (mold temperature and hold time) were used in order to obtain a sample with

sufficient high temperature mechanical properties while bringing the cycle time of processing to a minimum. The degree of crystallization was correlated with the HDT of these injection molded samples. An elevated temperature mold was utilized to incorporate additional crystallinity into the molded bars without a post-annealing step.

7.2 Experimental

7.2.1 Materials

Various injection molding grades of PLA (3001D, 3051D, and 3251D) were obtained from NatureWorks LLC (NE, USA). The talc grade ABT2500, with an average particle size of 2.3 micron was kindly supplied by Specialty Minerals (PA,USA). The LAK-301 nucleating agent, or dimethyl 5-sulfoisophthalic acid potassium salt (**Figure 7.2**), was supplied by Takemoto (Japan) and had an average particle size of 10 micron.

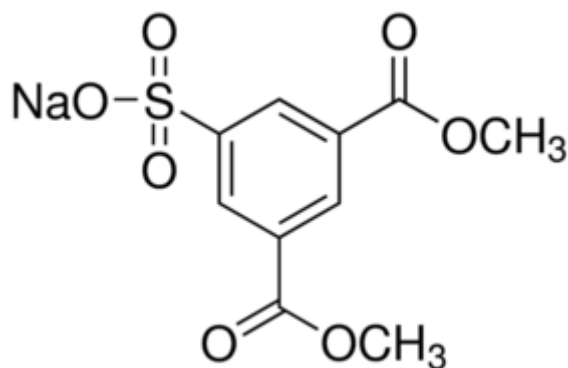


Figure 7.2: Molecular structure of LAK-301 nucleating agent.

7.2.2 Compounding

The PLA resin pellets were dried for 24 hours at 75°C prior to compounding to remove moisture. PLA, talc, and LAK-301 were all fed into a 30 mm ZSK twin screw extruder from

Werner Pfleiderer (NJ, USA), with an L/D ratio of 30, using separate gravimetric feeders. The total throughput for compounding was kept constant at 6 kg/hr. For samples containing talc as a nucleating agent, its weight percentage in the compound was held constant at 20%. The temperature profile of the extruder for all compounding was 140, 160, 170, 170, 170, and 165°C and the screw speed was held at 125 rpm. The compounded melt strand was cooled in a water bath and then pelletized and dried before further use.

7.2.3 Injection Molding of Sample Bars

Standard tensile bars were molded from the dried compounded pellets in a 75 ton Milacron (OH, USA) Injection Molding machine equipped with an oil heater. Molding was done with both a room and high temperature (100°C) mold. Various hold times in the mold were used to determine its effect on material properties. For the high temperature molding, the holding time was originally set to 180 seconds, and then the cycle time was minimized. An elevated temperature mold was used in effort to impart more crystallization into the parts prior to ejection, cutting out the post-annealing step typical used.

7.2.4 Characterization Methods

The molecular weight of the neat PLA resins were determined by gel permeation chromatography (GPC), equipped with a refractive index detector (Shimadzu, Japan, RID-10A) and a combination of three Styragel columns (Waters Co., Israel). Tetrahydrofuran was used as the mobile phase at a flow rate of 0.500 mL/min at 40°C. Monodisperse polystyrene standards were used as reference for the molecular weight calculations.

Thermal properties of the polymer samples were analyzed using a Q20 Differential Scanning Calorimeter (DSC) from TA Instruments (DE, USA). Meso-lactide content of the various PLA grades was determined by the melting enthalpy peak from the second heating ramp as described by the equation later. DSC was also used to study the crystallization kinetics. After the first heating ramp to clear the thermal history of the sample, the temperature was quenched (50°C/min) to 100°C and then held isothermally for 10 minutes. When heat flow is analyzed with respect to time, a clear crystallization peak can be seen. The time from the start of the isothermal hold to the crystallization peak and to the finish were recorded. After the isothermal hold was completed, the temperature was increased to measure the melting enthalpy and determine the overall crystallinity obtained.

The gage section of the injection molded sample bars were tested for HDT following ASTM D648 utilizing a Dynamic Mechanical Analyzer (DMA) from TA Instruments. The three point bending method applies steady pressure on the sample as the temperature is slowly ramped and deformation is recorded, allowing for the determination of HDT. To be deemed as useable for high temperature food applications, a HDT greater than 100°C needed as that exceeds common food/drink temperatures.

7.3 Results and Discussion

7.3.1 Analysis of Neat PLA Resins

The molecular weights of the various PLA grades were determined by GPC and the normalized intensity versus retention time (**Figure 7.3**) and molecular weight characteristics (**Table 7.1**) are shown below.

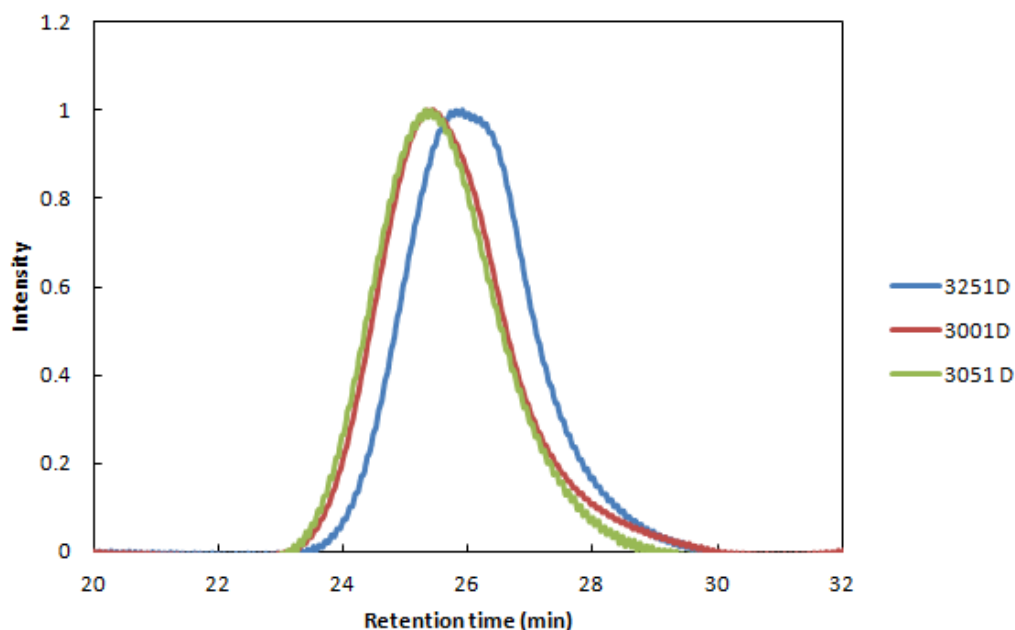


Figure 7.3: GPC spectra of the various PLA grades.

Table 7.1: Molecular weight characteristics of PLA grades

Grade	3001 D	3051 D	3251 D
M_w	97000	99000	77000
M_n	7000	72000	5800
PDI	1.38	1.36	1.33

PLA grades 3001D and 3051D are similar in molecular weight, while 3251D is lower (~80%) in comparison. However, all the grades showed a similar polydispersity index indicating similar molecular weight distribution. An important aspect of this study is to compare how the molecular weight of the polymer affects the crystallization rate. Since all grades show similar molecular weight distributions we are testing molecular weight and can rule out factors such as low molecular weight fractions or the presence of monomers.

In addition to molecular weight effects, the effects due to meso-lactide content are also of interest. It has been previously reported by our group¹⁰ that as the meso-lactide content in PLA is increased, the melting temperature of the resulting polymer decreases, to the point that an amorphous polymer is obtained. An empirical equation in this study has been well adapted to describe such a relation:

$$T_m = 175 - 300 * w_{meso} , \textbf{Equation 7.1}$$

where T_m (°C) is the peak melting temperature and w_{meso} is the weight fraction of meso-lactide in the polymer. The melting temperatures of the PLA grades studied were determined by DSC and meso-lactide content was calculated (**Table 7.2**) according to the equation above.

Table 7.2: Meso-lactide content determination based on DSC properties

Grade	3001 D	3051 D	3251 D
T_m [°C]	170	151	171
T_g [°C]	55-57	55-57	55-57
Meso-lactide [%]*	1.5	8	1.5

*Calculated from empirical equation

The data shows a much lower melting temperature for 3051D compared to the other two grades, which corresponds to a higher meso-lactide content in the polymer, close to 8%. The other grades have meso-lactide contents of ~1.5%, which should result in these grades having a faster crystallization rate and higher overall extent of crystallization. Ideally, a pure P(L)LA would perform the best for this purpose, however the additional purification steps results in a more

expensive material. Only within the last 1-2 years has a pure P(L)LA been available on a commercial scale.

7.3.2 Crystallization Kinetics of PLA Compounds

In injection molding, a polymer melt is pushed into an empty mold via a single screw extruder. Typically the mold is kept at room temperature, and when the part has sufficiently cooled (as noticed by part shrinkage) it is removed. However, this process usually results in very low amounts of crystallinity, leading to poor high temperature mechanical properties. If high crystallinity is required an additional annealing step is typically used. This process can be streamlined by using an elevated temperature mold and allowing the part to crystallize prior to removal. In this case, the shrinkage required for removal is due to the formation of dense crystalline regions. Ideally, the mold temperature would be held at the crystallization temperature, or T_c , of the material (typically $\sim 100^\circ\text{C}$ for PLA).

Rapidly cooling the polymer from its molten state and holding isothermally in a DSC acts as a simulation of the injection molding process. Using an isothermal hold at 100°C , this elevated temperature mold process can be simulated. This allows for a way to quantify the rate of crystallization and maximum crystallinity achievable for an injection molded part from the various compounds. The time needed to reach maximum achievable crystallinity as well as the time to the peak rate of crystallization was monitored and are shown below in **Table 7.3** for the different compounds.

Table 7.3: DSC study of crystallization behavior of compounded resins

Compound	T _c [°C]	Crystallinity [%]	Time to Complete Crystallization [min]	Time to Peak Crystallization [min]
3001D/Talc	90.3	59.8	1.7	0.6
3051D/Talc	103.8	28.6	3.4	1.0
3251D/Talc	90.2	51.8	1.5	0.4
3001D/Talc/LAK-301	124.6	36.6	0.9	0.1
3051D/Talc/LAK-301	105.3	26.5	5.7	2.6
3251D/Talc/LAK-301	123.5	39.1	1.5	0.1

The nucleating agents act as catalysts to start the formation of crystallites, which results in a faster rate of crystallization. It can be clearly observed that the compounds prepared from the PLA grades with the lowest meso-lactide content showed both faster rates of crystallization as well as a higher achievable degree of crystallinity. In fact, 3001D and 3251D with talc required only half of the time to reach complete crystallization compared to 3051D, which contains ~8% meso-lactide content. The overall degree of crystallinity of the compounds follows a similar trend where the grades with less meso-lactide content achieve higher crystallinity. Grade 3001D showed the highest value, of almost 60% whereas 3051D possessed only ~30%. When the 3001D and 3251D compounds with talc are compared (similar meso-lactide content), the molecular weight effects can be observed. The lower molecular weight grade (3251D) showed a faster rate of crystallization but also a lower overall crystallinity. This fits with polymer theory, as the shorter chains can rearrange themselves easier, resulting in a higher rate of crystallization, and the creation of smaller crystallites, leading to the slightly lower overall crystallinity. The smaller crystallites occur because chain ends act as impurities in a crystallite and a lower molecular weight polymer has

more chain ends, therefore smaller crystals are formed. The effects of molecular weight are much less significant than the effect due to the meso-lactide content.

The addition of talc as a nucleating agent enhanced both the crystallization rate and the overall crystallinity hopefully leading to an improvement in HDT. However, the time necessary for high degrees of crystallinity, and therefore high HDT, are still too long for commercial scale injection molded products. In effort to boost this rate, the nucleating agent LAK-301 was used in conjunction with talc to look for a synergistic effect on nucleation. The talc content was kept consistent at 20%, where it also functions as a filler, and LAK-301 was added at 1 wt%.

Incorporating LAK-301 resulted in an increase in the crystallization temperature of the compounds when cooling from the melt. This allowed for crystallization of the polymer to begin earlier while being cooled, resulting in faster crystallization. The most significant improvement is seen in the time to peak crystallization, which is due to the shape of the crystallization curve. Rather than the peak having a symmetric, almost Gaussian shape (as in the case of PLA/talc), these compounds with the inclusion of LAK-301 exhibited skewed behavior. The majority of the crystallization happened almost immediately and then the rate dropped off as it moved towards complete crystallization. This explains why the peak crystallization time is drastically different than for just talc, while the time to complete crystallization is similar. This most likely is caused by the increase in the crystallization temperature, allowing for crystallization to start sooner, even prior to reaching the isothermal temperature. The combination of LAK-301 with talc shows a synergistic effect on improving the nucleation in this study.

This enhanced, or synergistic, nucleating effect can be due to the formation of different crystal structures depending on which material nucleates the crystal growth. Typically, PLA exhibits two different crystal structures, denoted α and β . α -PLA has a pseudo-orthrhombic unit

cell while β -PLA has a orthorhombic unit cell. Because of this small difference, α -PLA has a T_m approximately 5-10°C higher.⁹¹ The talc and LAK-301 nucleated PLA exhibited this dual- T_m phenomenon, shown in **Figure 7.4**. When only talc is used as the nucleating agent, only one T_m is observed. This dual structure crystal growth led to a faster crystallization rate but also led to lower overall crystallinity.

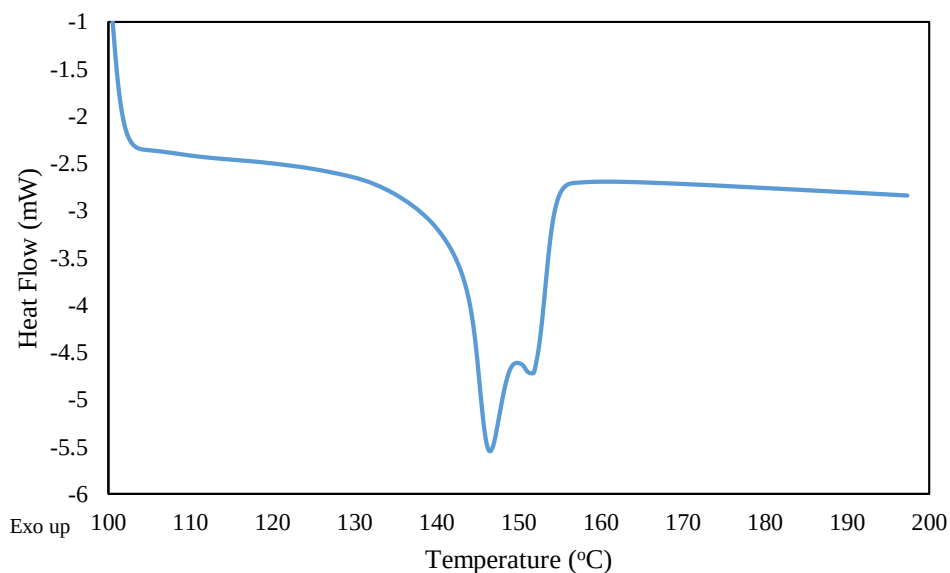


Figure 7.4: Dual melting peak of 3051D PLA nucleated with both LAK-301 and talc following isothermal crystallization in DSC.

7.3.3 Crystallinity and HDT Analysis of Injection Molded Bars

As discussed previously, when the temperature is above the T_g of a polymer, only the crystalline phase imparts rigidity and strength whereas the amorphous phase now has the ability to flow. Therefore for improved high temperature properties, more crystallinity is necessary. Although some degree of crystallization can be achieved using a room temperature mold, the cooling rate is generally too high for PLA to obtain a sufficient crystallinity. Due to this, both a

room and elevated temperature (100°C) mold was used. For a sample to be successfully removed from the mold it must possess a certain level of strength and shrinkage either by cooling below its T_g or by an increase in crystallinity. Initially the parts were held in the mold for 180 seconds to ensure high crystallinity, and then the hold time was decreased until the part was no longer able to eject in order to find a minimum cycle time of processing. After production, HDT and crystallinity were determined by DMA and DSC respectively.

It should be noted that none of the PLA grades processed with the room temperature mold were capable of reaching high enough crystallinity to result in an elevated HDT. The low meso-lactide content grades were able to reach ~25% crystallinity, but this was not enough to see an improvement in HDT. Again, this is how most commercial injection molded products are made; therefore for high temperature applications an additional annealing step is necessary. It can be seen in **Table 7.4** that the PLA/talc compounds containing 3001D and 3251D, showed a high degree of crystallinity which resulted in a high HDT value when the mold was at 100°C. These samples showed an HDT higher than 130°C which is sufficient for most applications for PLA resins. On the other hand, the 3051D sample was not able to crystallize enough in the mold to be removed with the same hold time. Without enough crystallinity in the 3051D sample at an elevated temperature, the part did not possess the mechanical strength or the shrinkage necessary to be effectively removed from the mold. Therefore, the part remained soft and gummy and deformed while being taken out of the mold.

Table 7.4: Effect of mold temperature on the crystallinity and HDT of PLA/Talc compounds

PLA grade	Mold Temperature	X%	HDT[°C]
3051 D	RT	3.0	54.1
3051 D	100 C	**	**
3001 D	RT	25.3	54.4
3001 D	100 C	58.6	130.1
3251 D	RT	25.1	54.1
3251 D	100 C	48.6	138.0

** Sample failed to be removed from the mold.

After observing that 3001D and 3251D samples were able to crystallize enough in the elevated temperature mold with the three minute hold time, the annealing time was decreased. For each compound the goal was to find the minimum cycle time, the shortest amount of time needed to create a product. For both 3001D and 3251D, this minimum time occurred at 150 seconds of hold time.

Even with the addition of LAK-301, the 3051D compound was not capable of crystallizing enough to be removed from the mold. Just as with the talc only samples, the other PLA grades were able to crystallize enough in the three minute annealing time, so then the cycle time was minimized. The annealing (hold) time and its effect on crystallinity and HDT is shown in **Table 7.5**. The minimum hold time needed for the bars to be effectively kicked out of the mold for both low meso-PLA grades was 60 seconds. A hold time of 45 seconds was also tried; however the parts had not crystallized enough to be removed. All of the sample bars with 3001D annealed 60 seconds or longer achieved roughly the same degree of crystallinity (~42%), and this resulted in HDT of greater than 100°C for all samples. This is less than half of the time needed for a HDT

greater than 100°C as compared to using only talc as a nucleating agent. The 3251D sample also possessed crystallinity greater than 40% for all annealing times over 60 seconds. However, the 60 second annealing time sample showed a lower HDT (97°C) compared to 3001D. This is most likely a molecular weight effect. A lower molecular weight usually results in lower mechanical properties like modulus and strength, and therefore with a similar amount of crystallinity a lower HDT is observed. For annealing times of 90 seconds and higher though, an HDT of over 100°C is seen. Therefore the concluded minimum time of annealing would be somewhere between 60-90 seconds for 3251D. This is still approximately less than half of the time necessary for the PLA/talc compounds as the addition of LAK-301 provided a synergistic nucleating effect in increasing the crystallization rate. Thus allowing for the efficient production of high temperature PLA products through a one-step, elevated temperature mold, injection molding process.

Table 7.5: Effect of anneal time on the HDT of the PLA/Talc/LAK-301 injection molded bars

Anneal Time (s)	3001D		3251D	
	X%	HDT [°C]	X%	HDT [°C]
60	41.7	113.2	41.4	97.0
90	42.8	129.7	45.2	112.1
105	42.3	130+	47.1	130+

*With 45 second anneal time, bars could not be removed from the mold

7.4 Conclusion

The crystallization rate of various PLA grades was increased through the incorporation of nucleating agents. With the addition of both talc and LAK-301 as nucleating agents in these compounds, the crystallization rate and overall degree of crystallinity achieved was faster and higher than either of the nucleating agents alone. This synergistic benefit was attributed to the

growth of differing crystal structures, as seen by a dual- T_m melting peak following DSC analysis. DSC was used to monitor the crystallization and crystallization rate while acting as a simulation of an injection molding process used to create high temperature PLA products. High levels of crystallinity are needed in these products to exhibit HDT greater than 100°C, making the materials more suitable for many food applications. The meso-lactide content of the PLA played a significant role in the ability of the compounds to crystallize rapidly as well as to a high degree. Because of this, the 3051D compounds could not crystallize enough in an elevated temperature mold to allow for the removal of the part during annealing times under 180 seconds. Molecular weight played a much smaller effect on crystallization. A lower molecular weight resulted in a slightly faster crystallization rate when measured using DSC, however no benefit was seen when injection molding. 3001D compounds showed fast crystallization and good HDT thanks to its low meso-lactide content and higher molecular weight compared to 3251D. This PLA grade allowed for a fast one-step injection molding process for high temperature PLA products which don't require an additional annealing step. These samples could be processed with the shortest cycle time (60s – less than half the time of just talc) while still having sufficient high temperature mechanical properties.

Concluding Remarks

There has been a large increase in the amount of focus and research going into biobased and biodegradable/compostable plastics. A lot of this drive is from industry, as they are looking to make “greener” products. This enhanced awareness has led to the growth of PLA, however the neat polymer has certain inherently weak properties holding it back. In this thesis, I have discussed various methods of which I have tried to enhance rheological properties, toughness, and high temperature performance of PLA through cost-effective processing techniques. For large scale growth, and commercial acceptance of bioplastics the cost and performance must be similar if not better than our traditional petroleum based plastics. While PLA is already of similar cost, its performance in many aspects must continue to be improved.

I firmly believe that there will come a time when our world’s oil stores start to dry up. Our current life style and transportation methods rely heavily on oil-based products. In fact, ~70% of oil consumption in the United States is directed into fuels for transportation. This is the life blood of our country’s infrastructure creating gasoline, diesel, and jet fuels allowing transportation to occur. However, less than 3% of total oil is converted into plastics. And when oil production begins to slow, these plastics may not be the best use of the remaining precious oil our planet has to provide. It is for this situation that we must have an established bioplastics industry ready to fill the shoes that have been dominated by petroleum based products in the past. As of now, the low cost of PLA compared to other commercial bioplastics makes it the most promising polymer for this situation.

This might happen 10 years from now, and it might happen 50 years from now, it might not even happen in my lifetime. But if PLA does find its way into a substantial commercial role

in the future, I am happy to have played my part in enhancing its properties and preparing it for such a situation.

APPENDIX

The article (**Figure A1**) on the following page was written by the National Science Foundation (NSF) highlighting the rheological enhancement of PLA for blown film applications described in Chapters 2 and 3. This was published in the AIChE journal: Chemical Engineering Progress in 2014. The NSF selected this project to showcase commercially successful NSF SBIR projects, and this recognition is greatly appreciated.



Greening the Packaging Industry

Globalization has changed the landscape of global manufacturing and supply chains, creating huge opportunities for more efficient production of goods and services, but also significant sustainability issues. One such challenge is the waste of packaging materials throughout the supply chain. Manufacturers have made progress toward end-of-life product strategies by developing biodegradable and compostable packaging materials. But what about the beginning-of-life strategies — designing packaging materials that start from plant-based feedstock rather than fossil carbon? In other words, can plant-based carbon sequestered from CO₂ in the environment be incorporated into packaging materials?

Northern Technologies International Corp. (NTIC), a small business headquartered in Circle Pines, MN, has developed biodegradable, compostable, and, for the first time, bio-based, polylactide (PLA) for blown plastic packaging films and end products.

Conventional PLA resins have several drawbacks that have limited their commercial success. PLA is a brittle polymer with poor flexibility and impact properties. Its glass transition temperature is around 50°C,



▲ When placed in a composting environment, a biodegradable-compostable bag made with the epoxy-modified PLA degrades in six weeks. Image courtesy of NTIC.

making it unsuitable for applications that require heat resistance (e.g., disposable hot-food containers). Its crystallization rate is too slow and its cycle time too long for molding applications. And, because of its poor melt strength and integrity, it is difficult to form thin films out of PLA.

To address these issues, NTIC developed an innovative reactive-extrusion process to synthesize epoxy-modified PLA molecules through transesterification and coupling chemistries. The new epoxy-functionalized PLA molecule can be reactively blended with regular PLA resin and other biodegradable polyester resins, such as poly(butylene adipate-co-terephthalate) (PBAT), to achieve properties not found in traditional PLA resins — strain hardening properties for blown-film applications, as well as improved processability, heat resistance, and impact resistance.

The epoxy modification not only improves the rheology of the PLA resin, but also functions as a surfactant to aid in blending the PLA with other biodegradable polyesters, which would otherwise phase separate. The resin can also be blended with fillers, modifiers, and additives to confer additional desired properties.

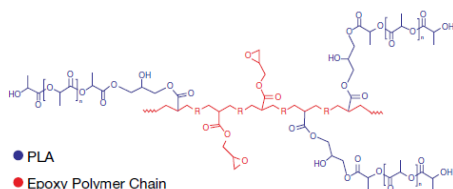
NTIC developed the functionalized PLA technology in collaboration with Ramani Narayan's

Biobased Materials Research Group at Michigan State Univ., with support from the Small Business Innovation Research Program of the National Science Foundation. The company has successfully commercialized its innovation in bio-based and biodegradable-compostable specialty packaging films, coated paper/paperboard products, and cutlery.

With its 100% bio-based carbon content, every kilogram of PLA effectively recycles 1.83 kg of CO₂ from the environment, i.e., the CO₂ is incorporated into the polymer molecule through plant-biomass photosynthesis. The functionalized PLA products are completely biodegradable in industrial composting systems and offer an environmentally responsible end-of-life option: microorganisms present in the composting environment readily utilize PLA and completely remove it safely and efficaciously.

Building upon the initial commercial success of its injection-molded, bio-based and biodegradable-compostable cutlery, NTIC has now successfully introduced its sustainable packaging films into the marketplace. The company currently supplies biodegradable-compostable bags to global companies such as Levi Strauss & Co. About 76,000 m.t./yr of plastic packaging resins are used for packaging 5 billion garments in South Asia alone, translating to about \$200 million in economic value.

This technology was funded through the NSF Small Business Innovation Research Program.



▲ NTIC has designed new bio-based PLA resins that are modified with epoxy polymer chains. Depending on the application, the ratio of PLA to epoxy can be changed. The resin shown here is composed of one epoxy polymer chain for every three PLA chains. Image courtesy of NTIC.

This article was prepared by the National Science Foundation in partnership with CEP.

Figure A1: CEP article written about the work presented in chapters 2 and 3.

Below is a brief explanation (with examples) of the code used to create the PLA – MEP simulation used in Chapter 2 to describe the formation of EF-PLA.

Figure A2 shows the probability and molecular weight simulation data for a sample containing 4 wt% MEP, in this situation the molar % of PLA is higher than MEP. Therefore based on the assumptions described in Chapter 2, it is assumed that all MEP molecules react. It can be seen here that the probability of an unreacted MEP molecule after reaction is zero.

	A	B	C	D	E	F	G	H	I
1				wt%	mol	mol %			
2			PLA %:	96	0.00096	0.620061			
3			MEP %:	4	0.000588235	0.379939			
4	MEP MW				0.001548235				
5	6800		PLA MW:	100000					
6									
7	# epoxides can react: (0-7)			5					
8									
9		Species	MW		Relative Prob.	Freq.			
10		MEP (M)	6800		0	0			
11		PLA (P)	100000		0.204103343	0.103839			
12		MP ¹	106800		0.471170813	0.239711			
13		MP ²	206800		0.43823182	0.222953			
14		MP ³	306800		0.362307158	0.184326			
15		MP ⁴	406800		0.280815579	0.142867			
16		MP ⁵	506800		0.208947276	0.106303			
17		MP ⁶	0		0	0			
18		MP ⁷	0		0	0			
19								Mn	250635.9
20								Mw	325585.9
21					1.96557599	1		MWD	1.29904
22									

Figure A2: Example simulation table when molar % of PLA is greater than MEP.

Figure A3 shows the same data as above except for the situation where the molar % of MEP is greater than that of PLA. In this case, the assumption that all PLA polymers react is made. It can therefore be seen that the probability of remaining unreacted PLA following processing is zero.

	A	B	C	D	E	F	G	H	I
1				wt%	mol	mol %			
2			PLA %:	93	0.00093	0.474632			
3			MEP %:	7	0.001029412	0.525368			
4	MEP MW				0.001959412				
5	6800		PLA MW:	100000					
6									
7	# epoxides can react: (0-7)			5					
8									
9		Species	MW		Relative Prob.	Freq.			
10		MEP (M)	6800		0.124355454	0.096571			
11		PLA (P)	100000		0	0			
12		MP ¹	106800		0.450551531	0.349887			
13		MP ²	206800		0.320769426	0.249102			
14		MP ³	306800		0.202996682	0.157642			
15		MP ⁴	406800		0.120435963	0.093528			
16		MP ⁵	506800		0.06859535	0.053269			
17		MP ⁶	0		0	0			
18		MP ⁷	0		0	0			
19								Mn	202947.6
20								Mw	288973.1
21					1.287704406	1		MWD	1.423881
22									

Figure A3: Example simulation table when molar % of MEP is greater than PLA.

The shaded cells are the only cells which need entered data. Note that the PLA molecular weight entered into the program is the molecular weight of neat PLA run through the extruder, therefore this value is lower than the neat/unprocessed PLA data. Shown below is the code used to populate the values in the simulation.

$$\mathbf{D2} = 100 - \mathbf{D3}$$

$$\mathbf{E2} = \mathbf{D2} / \mathbf{D5}$$

$$\mathbf{E3} = \mathbf{D3} / \mathbf{A5}$$

$$\mathbf{E4} = \mathbf{E2} + \mathbf{E3}$$

$$\mathbf{F2} = \mathbf{E2} / \mathbf{E4}$$

$$\mathbf{F3} = \mathbf{E3} / \mathbf{E4}$$

$$\mathbf{C10} = \mathbf{\$A\$5}$$

$$\mathbf{E10} = \text{IF}(\mathbf{F3} > \mathbf{F2}, (\mathbf{E12} + \mathbf{E13} + \mathbf{E14} + \mathbf{E15} + \mathbf{E16}) * ((\mathbf{F3} - \mathbf{F2}) / \mathbf{F2}), 0)$$

$$\mathbf{F10} = \mathbf{E10} / \mathbf{E21}$$

$$\mathbf{C11} = \mathbf{D5}$$

$$\mathbf{E11} = \text{IF}(\mathbf{F3} > \mathbf{F2}, 0, (\mathbf{\$F\$2} - \mathbf{F3}) * (1 - ((1 * (\mathbf{E12} > 0) + 2 * (\mathbf{E13} > 0) + 3 * (\mathbf{E14} > 0) + 4 * (\mathbf{E15} > 0) + 5 * (\mathbf{E16} > 0) + 6 * (\mathbf{E17} > 0) + 7 * (\mathbf{E18} > 0) + 8 * (\mathbf{E19} > 0) + 9 * (\mathbf{E19} > 0)) / 100)))$$

$$\mathbf{F11} = \mathbf{E11} / \mathbf{\$E\$21}$$

$$\mathbf{C12} = (\mathbf{\$D\$7} > 0) * (\mathbf{\$D\$5} + \mathbf{\$A\$5})$$

$$\mathbf{E12} = (\mathbf{C12} > 0) * \text{IF}(\mathbf{F3} > \mathbf{F2}, 2 * \mathbf{F2}^2, 2 * \mathbf{\$F\$3} * \mathbf{\$F\$2})$$

$$\mathbf{F12} = \mathbf{E12} / \mathbf{\$E\$21}$$

$$\mathbf{C13} = (\mathbf{\$D\$7} > 1) * (2 * \mathbf{\$D\$5} + \mathbf{\$A\$5})$$

$$\mathbf{E13} = (\mathbf{C13} > 0) * \text{IF}(\mathbf{F3} > \mathbf{F2}, 3 * \mathbf{F2}^3, 3 * \mathbf{\$F\$3} * \mathbf{\$F\$2}^2)$$

$$\mathbf{F13} = \mathbf{E13} / \mathbf{\$E\$21}$$

$$\mathbf{C14} = (\mathbf{\$D\$7} > 2) * (3 * \mathbf{\$D\$5} + \mathbf{\$A\$5})$$

$$\mathbf{E14} = (\mathbf{C14} > 0) * \text{IF}(\mathbf{F3} > \mathbf{F2}, 4 * \mathbf{F2}^4, 4 * \mathbf{\$F\$3} * \mathbf{\$F\$2}^3)$$

$$\mathbf{F14} = \mathbf{E14} / \mathbf{\$E\$21}$$

$$\mathbf{C15} = (\mathbf{\$D\$7} > 3) * (4 * \mathbf{\$D\$5} + \mathbf{\$A\$5})$$

$$\mathbf{E15} = (\mathbf{C15} > 0) * \text{IF}(\mathbf{F3} > \mathbf{F2}, 5 * \mathbf{F2}^5, 5 * \mathbf{\$F\$3} * \mathbf{\$F\$2}^4)$$

$$\mathbf{F15} = \mathbf{E15}/\mathbf{\$E\$21}$$

$$\mathbf{C16} = (\mathbf{\$D\$7}>4)*(\mathbf{5*\$D\$5+\$A\$5})$$

$$\mathbf{E16} = (\mathbf{C16}>0)*\mathbf{IF(F3>F2,6*F2^6,6*\$F\$3*\$F\$2^5)}$$

$$\mathbf{F16} = \mathbf{E16}/\mathbf{\$E\$21}$$

$$\mathbf{C17} = (\mathbf{\$D\$7}>5)*(\mathbf{6*\$D\$5+\$A\$5})$$

$$\mathbf{E17} = (\mathbf{C17}>0)*\mathbf{IF(F4>F3,6*F3^6,6*\$F\$3*\$F\$2^5)}$$

$$\mathbf{F17} = \mathbf{E17}/\mathbf{\$E\$21}$$

$$\mathbf{C18} = (\mathbf{\$D\$7}>6)*(\mathbf{7*\$D\$5+\$A\$5})$$

$$\mathbf{E18} = (\mathbf{C18}>0)*\mathbf{IF(F5>F4,6*F4^6,6*\$F\$3*\$F\$2^5)}$$

$$\mathbf{F18} = \mathbf{E18}/\mathbf{\$E\$21}$$

$$\mathbf{E21} = \mathbf{SUM(E10:E18)}$$

$$\mathbf{F21} = \mathbf{SUM(F10:F18)}$$

$$\mathbf{I19} = (\mathbf{C10*F10+C11*F11+C12*F12+C13*F13+C14*F14+C15*F15+C16*F16+C17*F17+C18*F18+C19*F19+C20*F20})$$

$$\mathbf{I20} = (\mathbf{C10^2*F10+C11^2*F11+C12^2*F12+C13^2*F13+C14^2*F14+C15^2*F15+C16^2*F16+C17^2*F17+C18^2*F18+C19^2*F19+C20^2*F20})/(\mathbf{C10*F10+C11*F11+C12*F12+C13*F13+C14*F14+C15*F15+C16*F16+C17*F17+C18*F18+C19*F19+C20*F20})$$

$$\mathbf{I21} = \mathbf{I20/I19}$$

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