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DEVELOPMENT OF POLYLACTIC ACID-BASED MATERIALS THROUGH REACTIVE MODIFICATION

By

Alison Camille Fowlks

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Materials Science and Engineering

ABSTRACT

DEVELOPMENT OF POLYLACTIC ACID-BASED MATERIALS THROUGH REACTIVE MODIFICATION

By

Alison Camille Fowlks

Polylactic acid (PLA)-based systems have shown to be of great potential for the development of materials requiring biobased content, biodegradation, and sufficient properties. The efforts in this study are directed toward addressing the current research need to overcome some of the inherent drawbacks of PLA. To meet this need, reactive extrusion was employed to develop new materials based on PLA by grafting, compounding, and polymer blending.

In the first part of this work, maleic anhydride (MA) was grafted onto PLA by reactive extrusion. Two structurally different peroxides were used to initiate grafting and results were reported on the basis of grafting, molecular weight, and thermal behavior. An inverse relationship between degree of grafting and molecular weight was established. It was also found that, regardless of peroxide type, there is an optimum peroxid-to-MA ratio of 0.5:2 that promotes maximum grafting, beyond which degradation reactions become predominant. Overall, it was found that the maleated copolymer (MAPLA) could be used as an interfacial modifier in PLA-based composites. Therefore, MAPLA was incorporated into PLA-talc composites in varying concentrations. The influence of the MAPLA addition on the mechanical and thermal behavior was investigated. When added in an optimum concentration, MAPLA improved the tensile strength and crystallization of the composite. Furthermore, microscopic observation confirmed the compatibilization effect of MAPLA in PLA-talc composites.

Vinyltrimethoxysilane was free-radically grafted onto the backbone of PLA and subsequently moisture crosslinked. The effects of monomer, initiator, and catalyst concentration on the degree of crosslinking and the mechanical and thermal properties were investigated. The presence of a small amount of catalyst showed to be a major contributor to the crosslinking formation in the time frame investigated, shown by an increase in gel content and decrease in crystallinity. Furthermore, thermogravimetric analysis helped to establish a correlation between crosslinking density and thermal decomposition—providing conclusive evidence of improved thermal stability as a result of the crosslinking reaction. The mechanical properties indicated that the crosslinked PLA was developed without embrittlement or a reduction in tensile strength.

In the final section of this work a blend comprising of PLA and PBAT was reactively compatibilized via an *in situ* transesterification reaction and blown films were produced. The compatibilized films demonstrated enhanced properties compared to those of the physical blends. The most significant improvements were observed in the composition where PBAT was the majority phase, PLA was the minor phase, and catalyst was added in low concentration. Morphological observation confirmed interaction between polymer phases by improved dispersion and significant reduction in domain size which inferred the formation of an interfacial copolymer. Dedicated to

My Parents

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Chapter 1

INTRODUCTION

RATIONALE

Over the last century, a vast array of synthetic polymers was introduced and has since been incorporated into essentially all aspects of modern society. The development of these materials, derived from petroleum resources, has played a central role in transforming daily life,¹ replacing many natural materials in an unprecedented range of applications. Several characteristics and qualities of plastics account for their utility and ubiquitous presence in society; among these are their convenience, versatility, low cost, low weight, and high strength.² Additionally, the once-thought notion of an abundant supply of petroleum-based monomers as basicbuilding blocks contributed to their unrelenting growth. Likewise, their durability and resistance to degradation made them all the more attractive.³ However, this non-degradability is what prevents their disposal in safe and ecologically sound ways.⁴ Although some of these materials are recyclable, it is not always economically, nor energetically viable to do so and, as a result, they end up in landfills occupying valuable space. According to a 2006 study by the Environmental Protection Agency,⁵ each year, over 14 million tons of plastic waste is generated by the United States, of which only 7 percent is recycled.⁶ This underscores the importance of sustainability and the development of biobased materials.

This concept of sustainability can be envisioned by a basic understanding of the dynamics of the global carbon cycle.⁷ The amount of carbon in the atmosphere, which exists as carbon dioxide, is kept in balance by arth's natural cycles, and it, with the addition of water and sunlight energy, promotes bioorganic growth through photosynthesis. Over geological time frames this biomass is fossilized into petroleum, natural gas, and coal—the raw materials used in the production of polymers, chemicals, and fuels.⁸ Once consumed, these fossil resource-derived products release carbon back into the atmosphere at a much greater rate than that at which it is being consumed. This imbalance leads to a surplus of atmospheric carbon content, which has been declared to as the primary cause of global warming.

In a sustainable system, bio-organics are used in the direct production of polymers, chemicals, and fuels. This can help to mitigate the impact of petroleum-based materials on the rising carbon content in the atmosphere. These biobased products, at the end of their life, release the same amount of carbon dioxide that is required for their growth, therefore helping to equalize the

rate of consumption and emisson.⁸ The production of petroleum-based plastics not only results in a disruption of the global carbon cycle caused by a surplus of greenhouse gases in the atmosphere,^{9,10} but also contributes to our nation's dependence on foreign oil. This realization is becoming a major concern as oil prices continue to rise and societal demands for a clean and healthy environment move to center stage. With economical and environmental threats continuing to surface, greater impetus is focused on new technological advancements. Materials are being sought to decrease the dependence on imported oil, to reduce carbon dioxide emissions, and to generate more economic opportunity by presenting entirely new value-added pathways for agriculture and industry allowing for major gains in farm income and rural development in the United States.

The rekindled interest of plastics derived from biological precursors has been at the forefront of research objectives for the past 30 years. Now more than ever, with an increased demand,¹¹ efforts are continuously being made by the United States government to regulate the consumption of fossil fuels and to promote the use of annually renewable resources. This has stimulated the urgent development of materials from biobased feedstocks.^{12,13} According to a market study by Rapra Technology,¹⁴ the global consumption of biobased and synthetic biodegradable polymers is expected to increase by nearly 20 percent between the years 2005 and 2010. A major step in this direction was seen in early 2006, when federal agencies began complying with federal procurement programs set forth by the 2002 Farm Security and Rural Investment Act to establish biobased

preference programs.¹⁵ Many US cities have even begun to place bans on polystyrene for food packaging and plasticware. Regulations such as these have compelled plastic manufacturers to incorporate the concepts of sustainability, industrial ecology, biodegradability, and recyclability into their considerations for materials design and selection with the aim of producing commercially valuable and environmentally friendly polymers. The expectation is for the biobased plastics market to reach 3 billion pounds or more in the next two years.¹³ Such an innovation would boost the economics of energy crops and biomass for biobased polymer and biofuel production, with the long term goal of one day displacing many of the 280 million gallons of oil currently consumed annually with a renewable source.¹⁶

For the reasons outlined above, there is an emerging market for biobased, biodegradable polymers that can be disposed of safely and efficiently. This market, driven by rising oil prices and growing health and environmental concerns, has placed precedence on developing materials from renewable feedstocks such as corn, sugar beets, sugar cane, wheat, rice, and sweet potatoes.¹⁷ Although, development of numerous novel biobased polymers is currently underway, economic and engineering barriers may encumber their success. One of the major issues faced with overcoming these barriers is meeting the performance requirements of conventionally used plastics. Research and development of novel materials and improvements upon existing biobased polymers are needed to enable competition on a comparable price and

performance level and is crucial for the successful implementation of biobased products into a variety of plastics niche markets.¹⁸

Many biobased plastics, including cellulose-based polymers, polylactic acid. polyhydroxyalkanoates, and starch-based polymers, are increasingly being investigated.¹⁹ In this work, of particular interest is polylactic acid (PLA). PLA has been receiving considerable attention lately and is viewed by many as part of the solution to addressing the market need for biobased materials.^{19,20} This is partly due to its increasing abundance, but also because it is easily recovered from plants, relatively inexpensive, and holds great potential to be modified and incorporated into polymeric blends and composites with good end uses. The combination of good physical and mechanical properties along with its biocompatibility has deemed PLA a key player in the biomedical arena, with applications ranging from drug delivery systems and arterial grafts to implants. fracture fixation, and bioresorbable sutures.²¹ Recent advances, including the reduction in cost of lactide monomer production and new technological advancements, have permitted PLA to be introduced into a broader array of commercial applications.²²⁻²⁴ This is especially true in the biodegradable commodity polymer industry such as in the packaging field with single-use, disposable items and in agricultural mulch film production. However, PLA's full potential has yet to be exploited. The commercial success of PLA is a function of its utilization and its utilization relies on its ability to compete with petroleumbased products by overcoming its inherent drawbacks.

SCOPE OF THE STUDY

PLA is a polymer that has many properties superior to those of other biobased polymers currently in commerce. On the basis of economic and environmental considerations, the use of PLA presents a major opportunity for the development of new biobased products that can be implemented into existing plastics applications. However, some drawbacks of PLA, namely its low heat distortion temperature, low melt strength, and brittle behavior, have limited its use and therefore have incited the desire for improvement. In order for emerging technologies based on PLA to be forwarded, much needed research remains and a deeper understanding of PLA is necessary and the ways in which it can be modified. Thus, the specific goal of this work is to develop new PLA-based materials through compounding, blending, and grafting to help to overcome some of the current challenges faced by PLA. With the underlying objectives met, the range of applications to which PLA is suited can be greatly expanded.

STRUCTURE OF THE DISSERTATION

The efforts in this study have been directed toward addressing the current research need of PLA by various methods of reactive modification to develop new materials based on PLA. In the paragraphs that follow are descriptions of the contents of each chapter.

Chapter 2 provides the necessary background of PLA as it pertains to the nature of this work, beginning by introducing some of the basic concepts related to PLA: its chemical structure, polymerization, and stereochemical differences, and how they relate to its properties. Processing of PLA and degradation

mechanisms are also described. Details of the experimental methods adopted in this work are presented in Chapter 3.

The subsequent chapters discuss research pertaining to specific projects. The first project, which is detailed in Chapter 4, concerns the modification of PLA by the grafting of maleic anhydride (MA) onto its backbone. A study of the impact of peroxide type on the resultant properties of the maleated product was undertaken. Specific attention was focused on minimizing degradation while maximizing MA grafting yield. Achieving a balance between grafting efficiency and molecular weight enables MAPLA to be used as an interfacial modifier in PLA-matrix composites, as exemplified in Chapter 5. Chapter 5 specifically deals with evaluating the potential of the MAPLA as an interfacial modifier in PLA-talc composites. The purpose of this work was to investigate the mechanical, thermal, and microstructural properties and to identify a relationship between microscopic cause and macroscopic effect in the composites.

Chapter 6 introduces the concept of silane grafting to post-polymerized PLA. The goal was to use reactive extrusion to achieve radical melt functionalization of an organo functional silane onto PLA followed by the moisture-induced crosslinking of the silicon moieties. The aim was to evaluate the crosslinking efficiency and to characterize the resultant crosslinked polymers on the basis of mechanical considerations, thermal properties, and molecular characteristics.

The final project, in Chapter 7, involves the reactive compatibilization of PLA with a synthetically-derived biodegradable polymer, PBAT. The objective

was to use a transesterification catalyst to promote sufficient compatibilization of the two polyesters, followed by the production of blown film. The degree of compatibilization was assessed by investigating the thermal, mechanical, and morphological properties. Finally, Chapter 8 concludes the work with a summary of the findings and recommendations for future work.

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Chapter 2

POLYLACTIC ACID BACKGROUND

Polylactic acid (PLA) is a biodegradable, aliphatic polyester derived from the simplest alpha-hydroxy acid, lactic acid (2-hydroxy propionic acid).^{1,2} The monomer lactic acid was first isolated from sour milk by Carl Scheele in 1780^{3,4} and produced on the commercial level in the late 1800s for food, cosmetic, pharmaceutical, and agricultural applications.²

Lactic acid can be obtained by the bacterial fermentation of carbohydrates (corn or potato starch; cane or beet sugar; and cheese whey) or by chemical synthesis. From an economic point of view, the latter is not practical; therefore, the former is the preferred route.^{5,6} Lactic acid exists in two optically active configurations, namely as L(+) and D(-) isomers. Both isomeric types are produced in bacterial systems; however, only the L(+) isomer, which is easily assimilated during metabolism, is produced in mammalian species.²

From a polymer standpoint, lactic acid was of no practical use until it was later solidified by self-esterification to produce low molecular weight dimers and oligomers. In 1932, Carothers' pioneering research led to the production of a low molecular weight polyester from lactic acid. Then, in 1954 DuPont patented a process that yielded a high-molecular weight PLA from the cyclic dimer of lactic acid, lactide. This process entails a two-step method, which will be discussed in the forthcoming section.⁷

Due to its chiral nature, lactide exists as three stereoisomers: D-lactide, Llactide, and D,L-lactide (meso-lactide), corresponding to D-lactic acid, L-lactic acid and combinations thereof, respectively. Each of the lactic acid isomers and their lactide monomer structures are shown in Figure 2.1. L-lactide and D-lactide are chiral enantiomers and have a diastereometric relationship with the achiral meso lactide.⁵ PLA can be polymerized from any combination of the three lactide isomers, producing random copolymers whose stereochemistry is dependent upon the feedstock type, temperatures, and catalysts used during production.^{2,8,9,10}



Figure 2.1: Schematic illustration of the stereochemically different lactic acid monomers and their corresponding cyclic dimer lactide monomers

PLA Synthesis

The synthesis of PLA for polymer applications is a multistep process. The production of PLA is performed by either batch or continuous processes and may proceed by a number of routes. In the simplest route, a basic stepwise condensation polymerization produces lactic acid consisting of mainly lactyl units. The method shown in Figure 2.2 can produce one of or both D- and L-lactyl units in varying ratios. This direct polycondensation method is an equilibrium reaction; therefore, water must be removed to drive the reaction to the right. In addition, high temperatures and long reaction times are required. The resulting polymer is

a glassy, brittle, low molecular weight PLA with substandard mechanical properties. In order to obtain a PLA polymer with useful end properties via this direct route, chain extenders must be added to increase the molecular weight.⁹ The chain extenders used in PLA are usually bifunctional low-molecular weight compounds that increase the molecular weight of polymers in a fast and convenient extrusion reaction. Though the use of chain extenders do contribute to additional costs,^{11,12} one major advantage is that most chain extending agents do not produce byproducts, which could contaminate the resulting polymer.¹³



Figure 2.2: Synthesis of low molecular weight PLA via a condensation polymerization reaction

Alternate routes are often taken to obtain a higher molecular weight PLA and are shown in Figure 2.3. One such method is through an azeotropic dehydration polymerization step involving first, a polycondensation reaction. Then, an azeotropic mixture of water and solvent are removed from the polymer mixture.¹⁴ Because this method requires the use of organic solvents and entails a time-consuming melt/solid polycondensation step, it is used infrequently.¹⁵

The most common, yet more costly method of synthesizing high molecular weight PLA proceeds via the ring opening polymerization of the lactide dimer.¹⁶ Variations of this method have been patented by Cargill¹⁷ Camelot Technologies,¹⁸ and Ecological Chemical Products.¹⁹ Each of which allows for a controlled chemistry, therefore controllable and reproducible properties, which in turn broaden the applications of PLA. In this method a naturally occurring L-lactic acid, D-lactic acid, or mixture thereof is polymerized to yield a low molecular weight PLA prepolymer, which is then catalytically depolymerized through an intramolecular transesterification reaction to produce the dehydrated form of the cyclic diester lactide. This diester lactide can be present in any of the three stereoforms. The six-member lactide is ring-opened with a metal catalyst containing tin or aluminum derivatives. The most preferred catalysts used to yield high molecular weight PLA are Lewis acid catalysts, such as stannous 2ethylhexanoate. The polymerization proceeds by a coordination-insertion mechanism. During the reaction the Sn(II) atoms are not covalently bound to the growing polymer chain at any stage of the polymerization.²⁰ Because of this, more than one chain may be activated.



Figure 2.3: Synthesis of high molecular weight PLA via azeotropic condensation, chain extension, and ring-opening polymerization

PLA Properties

Like that of many polymers, the physical properties of PLA are dependent upon a number of factors, the most important being the stereochemical makeup of the polymer backbone, which can be controlled by the polymerization of the Land D- enatiomeric isomers. The ratio of its stereoisomers directly influences the kinetics of crystallization, mechanical properties, and processing conditions.²¹ Of particular importance is the effect the optical composition has on the crystallization behavior of PLA. By adjusting the initial distribution of lactides, PLA can be made either semicrystalline or amorphous. Semi-crystalline PLA polymers are formed by the syndiotactic arrangement of lactic acid by the polymerization of pure L,L-lactide or D,D-lactide. Polymerization of the meso-monomer produces an atactic chain because the combination of L- and D-lactide disrupts the stereoregularity of the polymer, inhibiting crystallization, resulting in an amorphous material.²²

The stereochemical composition of PLA also determines the melting temperature, rate of crystallization, and extent of crystallization. For example, a stereochemically pure PLA produced from L-lactide (PLLA) has an equilibrium melting temperature of approximately 207°C and a glass transition near 60°C.²¹ However, its maximum practical melting temperature is 180°C with an enthalpy of melting of 40-50 J/g.^{11,23} Copolymerizing L-lactide with meso-lactide or D-lactide can yield polymers that melt at temperatures as low as 130°C. This is because the addition of meso-lactide or D-lactide disrupts the stacking order of the L-lactide chains; it also reduces the obtainable level of crystallinity and the rate of crystallization, but does not significantly affect the glass transition temperature.²⁴ An interesting phenomenon found in equimolar mixtures of L-lactide and D-lactide is the formation of a stereocomplex. This racemic crystalline mixture possesses a melting temperature of 230°C, which is approximately 50°C higher than either homopolymer.²⁵

Crystallizable PLA can be crystallized by the incorporation of nucleating agents, by strain induction, and by annealing at temperatures between 75°C and

the melting temperature.²⁴ It was found that annealing these crystallizable polymers tend to yield two distinct melting peaks. The origin of multiple melting has been the focus of many researchers' work. Many theories to explain the occurrence of multiple peaks can be found in the literature. In the case of PLA, it has been reported that multiple melting is a result of crystal lamellar rearrangement during crystallization, with the lower temperature endotherm corresponding to the melting of the original crystallites and the higher one to their subsequent reforming into more perfect, higher melting crystals.²⁴ Additional studies have determined that the occurrence of double melting endotherms is strongly dependent on the heating rate.^{28,29} Because PLA crystallizes very slowly, lower heating rates allow more time for thorough crystallization, usually resulting in the display of multiple melting endotherms. It is important to note that the total heat of fusion remains unchanged with variations in heating rate because the degree of crystallinity does not change during reorganization.³⁰ It does, however, change with the incorporation of nucleating agents, including talc, which have been shown to effectively increase the nucleation density thereby enhancing the rate and degree of crystallization.²¹

The stereochemical makeup of PLA, along with its crystalline orientation and molecular weight, also affects the mechanical properties of the polymer. Table 2.1 shows the mechanical properties of PLLA and PDLA. As shown, crystallized PLA polymerized solely with L-lactide has higher tensile and impact properties than a PLA polymer comprising of D- and L-lactide because of its ability to crystallize and its higher molecular weight. Annealed L-PLA exhibits the highest mechanical and thermal properties of the three. This is because of enhanced chain stereoregularity and crosslinking of the crystalline domains, which lead to respective increases in the tensile and impact strengths.¹

		Annealed	
	L-PLA	L-PLA	D,L-PLA
Tensile strength (Mpa)	59	66	44
Elongation at break (%)	7	4	5.4
Modulus of elasticity (MPa)	3750	4150	3900
Yield strength (MPa)	70	70	53
Flexural strength (MPa)	106	119	88
Unnotched Izod impact strength (J/m)	195	350	150
Notched Izod impact strength (J/m)	26	66	18
Rockwell hardness	88	88	76
Heat distortion temperature (°C)	55	61	50
Vicat penetration (°C)	59	165	52

Table 2.1: Mechanical Properties of PLA²

Among the other properties of PLA, some of the properties that make it attractive in packaging applications are its good crease-retention, crimp, and heat sealability properties, and excellent resistance to oil. It also acts as a good barrier to flavors and aromas.²¹

PLA Biodegradation

Biodegradable polymers in this context are those "which can be disposed of in bioactive environments and degrade by the enzymatic action of microorganisms"³¹ and one that can be "converted safely into carbon dioxide, biomass and water." ³² Polymer degradation mostly occurs through macromolecular chain scission. In the environment, a variety of chemical, physical, and biological processes play a role in the degradation of polymers.³²
Therefore, different degradation mechanisms may be involved, including thermal activation, hydrolysis, biological activity (enzymes), oxidation, photolysis, or radiolysis. These mechanisms can occur in combination or in isolation, alongside other dependent factors such as pH, phase, temperature, exposure, mechanical stress, and biological activity that affect the polymer degradation process. In addition, the properties of a polymer are important and can alter the process.³³ Some of the properties affecting degradation consist of polymer diffusivity, porosity, morphology, crosslinking, purity, and chemical reactivity.¹¹

The primary method by which PLA biodegrades is hydrolysis and has been studied both in-vivo and in vitro.³⁴⁻³⁷ Typically, degradation in PLA is autocatalyzed by carboxylic end-groups, resulting in the random non-enzymatic chain scission of the ester linkages. This eventually produces monomeric lactic acid and leads to a reduction in molecular weight with the associated catastrophic loss in mechanical strength.³⁸ Next, the molecular integrity of the chain deteriorates. As the molecular weight approaches very low values (M_n~10,000-40,000 g/mol), microorganisms consume the remaining oligomers, converting them into carbon dioxide and water. ^{1,24,38} The degree and rate of hydrolysis are dependent upon a variety of factors including time, temperature, moisture, molecular weight, low molecular weight impurities, monomer ratio, crystallinity, and residual catalyst concentrations,² all of which can lower the degradation temperature and promote a faster rate of degradation.

Polylactic Acid Processing

The rheological characteristics of PLA permit it to be processed by most conventional modes of polymer processing, including extrusion, injection molding, blow molding, and fiber spinning.²¹ Film production, however, has been shown to be quite difficult due to the low melt strength and instability at elevated temperatures. Nevertheless, by controlling polymer composition and the addition of stabilizing agents, PLA can be cast into films ranging in thicknesses of 8 μ m to 510 μ m using standard film casting equipment.³⁸

The processing conditions, (residence time, temperature, and mechanical shear rate) as well as any moisture present in the polymer, govern the properties of the resultant polymer. Being an aliphatic polyester, the main disadvantage of PLA is its susceptibility to molecular weight loss due to thermal degradation at temperatures above its melting point, making the window for processing fairly narrow. It has been postulated that thermal degradation in PLA results not only from hydrolysis. but also from intramolecular and intermolecular transesterification, oxidative main chain scission, zipper-like depolymerization, and pyrolytic elimination.¹ Each of these reactions has been reported to be influenced by a number of parameters, including moisture, molecular weight, end-groups, residual catalysts, and hydrolyzed monomers.¹³

PLA Limitations

PLA has shown to possess some very interesting properties, while some are already sufficient, others present an opportunity for improvement through

modification. As mentioned previously, PLA is an aliphatic polyester and because of its structure it degrades readily, which in some cases may cause unpredictable performance. High temperature applications of unmodified PLA are nearly impossible owing to its low glass transition temperature and low heat distortion temperature. In addition, its low melting point prevents it from displacing many commodity plastics. Many packaging applications of PLA are limited by its brittle behavior and low melt elasticity, both of which prevent it from being blown into film. PLA's water transmissibility rate is very high, increasing its ability to undergo molecular fragmentation by hydrolysis. Many of these drawbacks prevent the more widespread commercial acceptance and have recently been major topics of ongoing research, some of which will be discussed in the forthcoming sections.

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Chapter 3

EXPERIMENTAL TECHNIQUES

REACTIVE EXTRUSION

Reactive extrusion is a processing technique that offers the potential to produce innovative materials in a relatively simple and cost effective manner. Using an extruder as a continuous melt reactor for the production or the modification of polymers was developed in the mid-1960s,¹ however, it has recently experienced a dynamic growth in materials innovation and has become the dominant route for polymer blending and compounding as many polymer companies are moving away from classical reaction vessels.^{2,3,4} From the standpoint of polymer modification and blending, the use of reactive extrusion proves to be the most efficient means of polymer processing, exemplified by the following advantages:^{4,5}

• The ability for chemical reactions to take place in the absence of solvents, therefore, solvent removal or a recycling infrastructure is unnecessary

- Precisely controlled residence time distributions and temperature profiles
- The ability to combine several processes such as mixing, reacting, and shaping all into one step
- Processing of high viscosity polymers
- Improved surface/volume ratio leading to higher reaction rates

In principle, reactive extrusion consists of creating conditions for specific chemical reactions between components during mechanical blending. It is often performed by the introduction of either a reactive third component with appropriate functional groups or a catalyst. As a result of the process, the chemical reaction takes place within the extruder. This process has proven to be an attractive route to carry out variety of reactions including: ^{3,6,7,8,9}

- Bulk polymerization to produce high molecular weight polymers prepared
 from monomers or oligomers
- Grafting reactions for incorporation of side chains along the polymer chain
- Copolymerization through coupling of multiple polymers
- Functionalization of polymers to introduce functional end-groups onto the polymer chain, providing improved chemical or thermal stability, mechanical, morphological, or optical properties
- Controlled molecular weight degradation in which higher molecular weight polymers are reduced to lower weight through exposure of shear, high temperature, and a free radical generator
- Promotion of a reaction by catalysis

In this work, reactive extrusion was employed in the development of PLA-based polymers through grafting, compounding, and blending. The extruder used was a Century ZSK-30 twin-screw co-rotating extruder consisting of a screw diameter of 30 mm and a length-to-diameter ratio of 42. The system was equipped with an extruder driver with a speed control gearbox and an Accurate single-screw feeder. The specific conditions of each extrusion run are detailed in its corresponding chapters.

TITRIMETRIC ANALYSIS

Titration is a chemical analysis technique commonly used to determine the concentration of an unknown reagent using a standard amount of a known reagent. By knowledge of simple acid-base chemistry, the quantity of acidic or basic groups in a substance can be determined. There are a variety of titrations types. The technique employed in this work uses a visual pH indicator whereby the endpoint of reaction can be identified by a color change, denoting the equivalence point. The volume corresponding to this point can then be related to the amount of the unknown reagent using a balanced chemical reaction. The grafting yield of reactive monomers can be quantified using a calibration curve. Comparison of the results can provide valuable information on the optimum parameters for maximum grafting efficiency.

In this work, titration was employed to quantify the amount of maleic anhydride grafted onto the PLA backbone (as will be discussed in Chapter 4). In the titration, 1 g of purified, dried MAPLA was dissolved in a 100 mL

chloroform:methanol (3:2 v/v) solution. The carboxylic acid concentration was determined by a direct alkali titration using 0.1 N potassium hydroxide in methanol, which had been standardized against a solution of potassium hydrogen phthalate. The solution was titrated using 1 wt% phenolphthalein as an indicator. The grafted polymer was completely soluble and did not precipitate during titration. The percentage of MA grafting was calculated using Equation 3.1 and verified by utilization of a linear regression calibration curve (y=0.9675x–0.288; $R^2 = 0.9996$) constructed by using a known amount of reagents. Each sample was tested in triplicate and average values were reported.

% MA grafting =
$$\frac{N_{KOH}V_{KOH}}{M_{sample}} \times 98.06 \times 100$$
 (3.1)

 N_{KOH} and V_{KOH} are the normality (mole/equivalent) and volume (in mL) of KOH solution, respectively. M_{sample} is the mass (in grams) of the maleated sample.

GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC measures the molecular weight and molecular weight distribution of a polymer as compared to that of a known standard. In the procedure, a polymer is dissolved in a solvent and injected through a series of columns consisting of tightly packed porous polymer beads. As the polymer molecules travel down the column, the smaller solute particles are able to diffuse into the holes of the porous polymer. The larger polymer solutes can only enter a fraction of the holes, if any, and are therefore only slightly retarded as they traverse the length of the column and hence have a faster elution time. The molecular weight moments (M_n and M_w) are calculated and used to study of the effect of grafting, crosslinking, and processing on the molecular characteristics of the polymer. Furthermore, the distribution as given by the polydispersity index (M_w/M_n) can provide information on polymer chain scission, branching, and crosslinking.

Molecular weight measurements of all PLA-based samples were carried out in a Waters GPC system equipped with an isocratic 1515 HPLC pump (flow rate = 1 mL/min), a 2414 refractive index detector, and a 717 autosampler. Samples were dissolved in tetrahydrofuran in concentrations of 2 mg/mL. Molecular weights (M_n and M_w) and molecular weight distributions (M_w/M_n) were calculated using a universal calibration curve constructed with polystyrene standards.

THERMAL CHARACTERIZATION

Thermal analysis techniques are used to measure the changes in a material as a function of temperature. Techniques such as differential scanning calorimetry, thermal gravimetric analysis, and dynamic mechanical analysis are used to study transitions representing characteristic chemical reactions. The results obtained can help to understand material behavior during polymer modification, manufacturing processes, and process optimization, while enabling improvement in material properties. Given the relative importance of the employed thermal analysis techniques, an introduction will be provided in the following sections to provide some background and appropriate terminology for the technical discussions that will follow.

Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical tool used to study the thermal transitions based on chemical or physical characteristics. The technique involves the heating of a sample and reference pan at the same rate over a specific temperature range. The heat differential that is formed by increasing the temperature is measured and plotted as a function of temperature. When the sample undergoes a physical transformation, the process is either exothermic or endothermic and is displayed as a DSC thermogram. From the curve, the heat capacities, melt enthalpies, transition temperatures, and chemical reactions can be measured and can provide information regarding crystallization, kinetic processes, and phase transitions.¹⁰ In the context of this work, a TA instrument 2920 differential scanning calorimeter was used to identify the thermal transitions (T_g, T_m, T_c) and assess the changes taking place. Of particular importance are the effects of modifications on the crystallization behavior of PLA. The crystallinity, χ_c , of the materials can be calculated according to Equation 3.2.

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^o \times \phi_{PLA}} \times 100 \%$$
(3.2)

where ΔH_m is the enthalpy of fusion (in J/g) and ΔH_m^o is the enthalpy of fusion of a PLA crystal of infinite size, whose reported value is 93.7 J/g. ϕ_{PLA} is the weight fraction of PLA in the sample.

Thermogravimetric Analysis (TGA)

TGA provides information on a material's thermal stability and its fraction of volatile components by permitting analysis of desorption, degradation, and decomposition processes under a controlled atmosphere. In TGA experiments, a sample is heated and the changes in weight that occur are measured. The measurement is normally carried out in air or in an inert atmosphere and the weight is recorded as a function of increasing time or temperature.¹¹

The main application of TGA in this work was to determine the decomposition temperatures of the grafted and crosslinked PLA to assess the effect of the modification on the thermal stability of the polymer. In each of the projects of this study, a high resolution thermogravimetric analyzer TGA 2950 from TA instruments was used to determine the change in weight of the sample due to decomposition. The sample was heated from 25°C to 500°C at the heating rate of 25°C/min. The balance and the samples were purged with nitrogen gas at rates of 40 ml/min and 60 ml/min, respectively.

Dynamic Mechanial Analysis (DMA)

Dynamic mechanical behavior of materials provides a deeper understanding of molecular relaxation mechanisms and their relationship with microstructure. DMA is a technique used to assess the changes in the viscoelastic response of materials over a spectrum of temperature, time, or frequency. In polymer blends and composites, dynamic mechanical tests are very sensitive tools for the determination of thermal transitions.

Unlike perfectly elastic materials, polymers including PLA are viscoelastic and have characteristics of both viscous liquids and elastic solids. In DMA tests, an oscillating force is applied to a sample at a particular frequency, ω and the displacement, ε is measured.¹² Upon deformation, some of the energy is stored (elasticity) and some of it is dissipated as heat (damping).¹³ The stress and strain for viscoelastic materials are shown by Equation 3.2 and Equation 3.3, respectively.

$$\sigma = \sigma_o \sin(\omega t + \delta) \tag{3.2}$$

$$\varepsilon = \varepsilon_0 \sin(\omega t + \delta)$$
 (3.3)

Where ε_o is the initial strain, σ_o is the initial stress, and δ is the relative angular displacement of the stress and strain. From the deformation, it is possible to measure the stiffness, which can be expressed as an in-phase component and out-of-phase component corresponding to its storage (E') and loss moduli (E"), respectively. Thus, it is possible to define a complex modulus, E* as:

$$E^* = \frac{\sigma(t)}{\varepsilon(t)} = E' + iE'' \tag{3.4}$$

The two moduli are measured simultaneously and their ratio, tan δ , is the loss factor representing the ratio of the energy dissipated to the energy stored. ¹⁴

$$\tan \delta = \frac{E''}{E'} \tag{3.5}$$

All of these components can be determined from DMA and infers details of the polymer structure. In this study, a TA 2980 DMA was used to characterize the changes in properties that take place as a result of crystallinity, molecular aggregation, and phase separation in modified PLA, composites, and blends. For the injection molded products, measurements were run on rectangular bars with approximate dimensions of 57 mm x 3 mm x 12.7 mm using a dual-cantilever bending clamp at a frequency of 1 Hz and a heating rate of 10°C/min over a temperature range of 24°C to 140°C. All measurements were performed and properties were reported in accordance with ASTM D 4065.

For the blown films, specimens were cut along the longitudinal direction having dimensions of 30 mm x 6.45 mm x 0.1 mm and mounted in a tension clamp. All films (except that of neat PLA) were heated from -50°C to 140°C at a rate of 2°C/min. Tests were run at an amplitude of 50 μ m and a frequency of 1 Hz. For both the injection molded bars and the blown film specimens, the storage moduli (E'), loss moduli (E"), and tan δ (E"/E") were recorded as functions of temperature.

MECHANICAL CHARACTERIZATION

The mechanical behavior involves studying the deformation of a material by applied forces. Determination of these properties helps to derive relationships between the mechanical behavior and the chemical or molecular structure of polymers, which can, in turn help to predict and improve the performance of materials.¹⁵

Tensile Testing

The tensile strength of a material is a measure of the ability of a material to withstand stress under a tensile load. During the test, a tensile specimen is loaded between two mechanical grips and an axial pull is exerted on the sample at a fixed speed. The extension is continuously measured as the applied force or load increases. Strain is calculated as the ratio of the change in length to the initial specimen length (Equation 3.6).

$$\varepsilon = \frac{\Delta l}{l_0},\tag{3.6}$$

where l_0 is the initial length and Δl is the change in length of the specimen as a result of testing.

The stress is plotted as a function of strain and the final stress-strain curve, such as the one depicted in Figure 3.1, can help to predict the performance of materials.



Figure 3.1: Schematic diagram representing a typical tensile test of a material showing the stress-strain relationship

The relationship between the applied force and the elongation is linear. In this linear region, the curve obeys Hooke's Law (Equation 3.7), where the ratio of stress to strain is a constant and:

$$\sigma = E\varepsilon \tag{3.7}$$

E is the slope of the line in this region where stress (σ) is proportional to strain (ε) and is called the Modulus of Elasticity. The maximum load that can be sustained by the specimen in tension corresponds to the tensile strength, as denoted by σ_{uts} in Figure 3.1.

In this work, the tensile behavior of modified PLA was determined using a United Testing System (UTS) Mechanical Tester (Model SFM-20) fitted with a load cell with a maximum of 1000 lbs (for tensile bars) or 100 lbs (for blown film specimens). Prior to testing, specimens were conditioned at 25°C and 50% relative humidity for at least 40 hours. The crosshead speed was set at 0.5 in/min. As will be discussed in the forthcoming sections, the tensile behavior of materials can be drastically affected by the coupling of two or more phases and thus will be used to provide a correlation between interfacial adhesion and mechanical behavior.

Impact Testing

Impact tests determine the toughness of a material under high impact velocity conditions. Specifically, notched Izod impact tests measure a material's resistance to impact by determining the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Each Izod specimen is notched to a specific radius to prevent deformation of the specimen upon impact. A weighted pendulum is released, swinging through the path where the sample is fixed. As the sample breaks, energy is absorbed by the sample. The height the pendulum attains after impact is measured by an indicator on a fixed

scale which reads in joules (ft-lb). The impact strength is then calculated by the loss of momentum in the pendulum while breaking the sample off at the notch.¹⁶

Impact strength can be related to results obtained from tensile tests in that the area under a stress-strain curve is proportional to the energy required to break the material. Under the condition that the test is performed at a high enough rate, the area under the curve is equal to the impact strength of the material. In many applications, impact strength is a critical measure of service life. In this work, the Izod impact strength of the PLA-talc composites was measured using a Testing Machines Inc. (TMI) 43-02-01 monitor/impact machine. Rectangular specimens cut from Type I tensile bars were notched and conditioned, according to the ASTM D256 standard.

MELT FLOW INDEX (MFI)

The MFI of a material is a measure of the rate of extrusion of molten polymers through an orifice of specific dimensions at prescribed conditions. The melt flow rate of a polymer is an empirically defined property, which is affected by the physical properties of the polymer, including molecular structure as well as the measurement conditions.¹⁷ Though determining the melt flow rate of a polymer is not a direct measure of any intrinsic polymer property, it does correlate, to a certain extent, to the molecular weight and molecular weight distributions of some polymers.¹⁸ As follows, it can be used to differentiate between grades of a specific polymer, or in this context, to determine the relative extent of degradation and/or crosslinking of a polymer as a result of modification

and processing. A more degraded polymer or a material with fewer crosslinks has a higher melt flow index as a result of reduced molecular weight and in turn could result in poorer physical and/or mechanical properties. For the VTMOS-grafted samples, experiments were carried out using a RayRan Melt Flow Indexer. All tests were run in accordance with ASTM D1238-90b. The pelletized samples were melted at 190°C and driven through a capillary die using a 2.16 kg weight attached to a piston. The mass (in grams) of the extrudate was measured at 30 second intervals and the MFI was calculated accordingly.

GEL CONTENT AND SWELL RATIO

Gelation

The determination of gelation is used to verify the existence of crosslinking in a polymer. The formation of gel occurs abruptly at the onset of crosslinking. It is an infinite network of polymer entanglements produced by sufficiently high crosslink concentrations. The gel content of a polymer is a measure of the insoluble portion of a polymer and can be determined using Equation 3.8:

% Gel content =
$$\frac{w_f}{w_i}$$
 (3.8)

where w_f and w_i are the final and initial sample weights, respectively.

Degree of Swelling

The swelling ratio of a crosslinked polymer can be measured by the amount of solvent uptake in the polymer network. Generally, it is defined "as a

system consisting of a polymer network swollen with solvent"¹⁹ and can be related directly to the degree of chain crosslinking by Equation 3.9:

$$DS = \left[\left(W_s - W_g \right) / W_g \right] \left(\frac{\rho_p}{\rho_{solvent}} \right)$$
(3.9)

where W_g is the average weight of the dry gel component in the crosslinked sample and W_s is the weight of the gel component swollen at room temperature for 48 hours in methylene chloride. ρ_p and $\rho_{solvent}$ are the densities of the polymer and solvent, respectively.

ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM)

SEM is a technique used to observe the surface morphology and composition of a material. From this, polymer compatibility can be determined, since the appearance of multiple phases would clearly show whether or not components are miscible. An SEM image is formed when an electron gun generates a primary electron beam, which under vacuum follows a vertical path through the microscope. The beam travels through electromagnetic fields and lenses to a sample where it generates secondary electrons, backscattered electrons, and x-rays. Secondary electrons are produced by the interaction between the primary beam and the sample. They are emitted from a very shallow region of the material and collected using an Everhart-Thornley detector, which then conveys the signal to an amplifier to modulate the intensity of the screen displaying the surface image. Secondary electrons can only come from the top

few nanometers of the material, making them topography-sensitive. Thus, contrast evolves from the surface properties of the sample.²⁰

In contrast, backscattered electrons are primary beam electrons that have been scattered by the sample nuclei and escape from the surface of the sample. Their escape depth is greater (at least 1 μ m) than that of secondary electrons, thus providing compositional contrast. Backscattered electron microscopy coupled with x-ray microanalysis is an excellent method to determine chemical composition.²¹

SEM is often used to observe fracture surfaces, etched surfaces, and extracted samples of polymer blends and composites to study adhesion phenomena and the nature of the corresponding phases, which is an important part of investigating the structure-property relationships of materials. In this context, SEM is used to determine surface properties and particulate dispersion in PLA-talc composites, as the images can provide valuable information on the mode of failure and interesting physical properties of the material, including mechanical behavior and interfacial characteristics. However, small, dispersed, and well-adhered phases are often not visible in the SEM because they do not provide sufficient contrast.

Transmission Electron Microscopy (TEM)

TEM is also a microscopic technique used to study the morphology of a material and has the ability to detect very small phase sizes (0.2 nm). Similar to an SEM, a "light source" at the top of the microscope emits the electrons that travel through a vacuum in the column of the microscope. Using electromagnetic

lenses, the electron beam is magnified and focused into a very thin beam. Unlike in SEM, the electron beam travels through the ultrathin specimen. Depending on the density of the material present, some of the electrons are scattered, while others are absorbed. At the bottom of the microscope the unscattered electrons reach a fluorescent screen, which give rise to an image of the specimen with its components displayed in varied darknesses according to their density. However, in most cases, if the phases do not have atomic number differences, they must be stained in order to produce adequate contrast.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS also called ESCA (electron spectroscopy for chemical analysis) is a solid-state spectroscopic technique that allows a surface of a material to be analyzed quantitatively by measuring the elemental composition, empirical formula, chemical state, and electronic state of the elements that exist within a material. The principle of XPS is such that a sample is irradiated with x-ray photons that are absorbed, causing the emission of photoelectrons. The photoelectrons have kinetic energies E_{kin} , given by:²²

$$E_{kin} = hv - E_b - F \tag{3.10}$$

where hv is the energy of the photon, E_b is the binding energy of the atomic orbital from which the electron originates, and F is the work function of the spectrometer. Each element gives rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. Therefore, the presence of certain elements is signified by the presence of peaks at particular energies, with their intensities corresponding to the concentration of the element within the sampled region.²³ XPS can be used to determine the elemental composition of a sample, but only on the surface. The mean free path for the photoelectrons and the Auger electrons is relatively short, meaning that the emitted electrons in the solid can only travel from a certain depth, thus making XPS a very surface sensitive analytical method with a maximum sampling depth of approximately 10 nm.²⁴

In the VTMOS-grafted samples XPS spectra were obtained using a Perkin Elmer Phi 5400 ESCA system with a magnesium K α x-ray source. Samples were analyzed at pressures between 10⁻⁹ and 10⁻⁸ torr with a pass energy of 29.35 eV and a take-off angle of 45°. The spot size was approximately 250 μ m².

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

FTIR is a chemical analytical technique used to determine sample composition. In FTIR, a sample is excited by infrared radiation, which is absorbed into the material and converted into energy causing bonds to stretch, contract, and bend.²⁵ Each chemical functional group absorbs infrared radiation in a specific wavenumber range, and as a result, produces a spectrum with bands corresponding to the wavenumbers that can be correlated to a chemical structure to identify the functional groups in a sample.

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Chapter 4

EFFECT OF PEROXIDE ON THE MALEATION OF POLYLACTIC ACID

INTRODUCTION

Polymer compounding is a well established route leading to the development of new polymeric-based materials and is attracting more and more attention because of their expanded applications. Its continued growth is driven by the ability to easily achieve tailored properties and cost reduction over traditional unfilled polymers. Recently, federal bylaws and increased environmental concerns have encouraged the development of these materials from renewable resources. In view of this, biobased polymers, particularly polylactic acid (PLA) used as composite matrices, have become of recent commercial interest. These materials have been experiencing rapid growth in a number of industries, with the expectation of replacing some petroleum-based plastics. Nevertheless, this expectation cannot be met without overcoming some

of the technical hurdles associated with the development of PLA-based composites.

A major hurdle is the incompatibility between phases. PLA is a hydrophobic polymer, whereas most fillers are hydrophilic. This chemical dissimilarity makes interfacial adhesion in a physical blend impossible, preventing necessary stress transfer from one phase to the other, resulting in poor performance. Thus, in order to fully maximize the reinforcement effect of the filler, the requirement of sufficient interfacial bonding must be met. Considerable efforts to improve the physical and mechanical properties of multiphase PLA-based materials have garnered some success by the addition of compatibilizers.¹⁻³

Compatibilizers are intermediate components that are preferentially situated at the interface of two phases. Their use is based on a rather straightforward concept. In general, they are multi-functional, bearing distinct segments, each of which has an affinity to one of the phases. Once added to the system, their role is essentially to create a bridge between the incompatible phases through chemical or physical bonding. The result is a reduction in interfacial tension, enhanced adhesion, and improved dispersion of the filler.

In many cases compatibilizers are produced from polymers that are grafted or functionalized with reactive molecules, which enable them to interact with the functional groups of one or both phases. It is common for the functionalization of a polymer to be performed via a reactive extrusion method,

which combines the chemical modification step with the processing step into a single process.^{4,5}

Several functional monomers that have been used in melt grafting reactions include isocyanates, amines, carboxylic acids, epoxides, oxazolines, and combinations thereof; however, the most commonly used is maleic anhydride (MA). MA is a polar monomer that has been extensively studied and shown to be an effective mode to improve the adhesion between two or more phases. From a commercial standpoint, it is the most important and oftentimes the monomer of choice, primarily because of its low cost, its high reactivity, and the relative ease with which it can be grafted onto polymers in an extruder.⁶ This ease stems from the dual reactivity that MA possesses, resulting from the free radical reactivity of the double bond and functional reactivity through the cyclic anhydride.

The maleation of PLA involves the grafting of MA onto the PLA backbone in the presence of an organic peroxide. Having long been performed in the modification polymers, particularly polyolefins⁷, and more recently in biodegradable polyesters⁸⁻¹⁰, the maleation of polymers can lower the interfacial tension between components to effectively transmit the applied forces from one constituent to another leading to blends and composites with useful end properties.¹¹⁻¹⁴

The concept of grafting MA onto PLA was first introduced in our group by Carlson et al.^{15,16} and was investigated as a matrix material in starch-filled composites. Studies conducted on the morphology of the resultant materials

revealed a substantial improvement in adhesion between MAPLA and starch. Not long after, other researchers followed suit with respect to the development of MAPLA-starch blends.¹⁷ They expounded upon Carlson's work by investigating the mechanical behavior and interphase thicknesses of starch-filled MAPLA. Enhanced adhesion was reported, as evidenced by improvements in mechanical properties and microstructural analyses. Various other studies have since been performed, most of which confirm property improvements and increased adhesion in MAPLA-based composites and blends.¹⁸⁻²²

The literature infers that the mechanism, concentration, resultant properties, and location of MA grafting are dependent upon several variables including: grafting technique, reaction conditions, and initiator type and concentration, making it difficult to pinpoint optimal conditions for this process. In the present study, MA was free-radically grafted onto a PLA backbone by reactive extrusion. Two structurally different peroxides were used to initiate the reaction. The effects of varying the concentrations of the peroxides were examined. The MA content was also varied. The effects of the variations were studied by molecular and thermal analyses to determine the optimal concentrations of monomer and initiator to be utilized for future use as an interfacial modifier in PLA-based composites.

EXPERIMENTAL

Materials

PLA (Nature Works 3051D) was obtained from Cargill Dow (Minneapolis, MN). Maleic anhydride (MA) (Figure 4.1) was purchased from Sigma-Aldrich

Chemical Company. Two peroxides, 2, 5-dimethyl-2, 5-di-(*tert*-butylperoxy) hexane (L101) (Figure 4.2) and 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (T301) (Figure 4.3), were supplied by Akzo Nobel. Both were used as received.



Figure 4.1: Structure of maleic anhydride (MA)







Figure 4.3: Structure of 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (T301)

Methods

Maleic Anhydride Grafting

MA grafting was performed according to a modified experimental protocol by Carlson et al.¹⁶ Prior to extruding, the PLA was dried overnight in an oven at 80°C to remove excess moisture. The dried PLA pellets were combined with varying amounts of MA and peroxide (L101 or T301). The peroxide concentration employed was varied between 0% and 0.5% while the MA concentration was held constant at 2%. Likewise, the MA concentration was varied between 1% and 3% at a constant 0.5% peroxide concentration. Each mixture was manually tumble-mixed before being introduced into a Century ZSK-30 twin-screw corotating extruder using a mechanical feeder set at a feed rate of 150 rpm. The extruder screws have a diameter of 30 mm, with an L/D ratio of 40. Previous studies by Carlson et al.¹⁶ and Nabar et al.²³ concerning MA grafting onto polyesters confirmed that temperature has an insignificant effect on the grafting yield. Therefore, only one processing temperature range was employed for each peroxide type corresponding to a half-life of 1 minute.

L101initiated samples: 25/90/145/175/175/175/175/175/175/170

T301initiated samples: 25/90/165/190/190/190/190/190/185

For all samples, the extruder screw speed was maintained at 100 rpm and a continuous flow of nitrogen was purged throughout the extruder. Unreacted MA and excess moisture were removed by applying vacuum at the vent port. The extrudate was cooled in a water bath and pelletized downstream.

Fourier Transform Infrared Spectroscopy

FTIR spectra were recorded using a Perkin Elmer 2000 FTIR Spectrometer. Thin films were obtained by dissolving MAPLA samples in dichloromethane and solvent casting onto a glass disc. The films were dried overnight under vacuum to remove any unreacted maleic anhydride and to transform any diacid into the cyclic anhydride form. The samples were scanned from 4000 to 400 cm⁻¹

Titration

The grafting yield was determined by titrimetric analysis according to a slight modification of a procedure presented by Nabar.²³ Each sample was dried

at 80°C under a vacuum to evaporate any unreacted MA. The grafted sample was then dissolved in 100 mL of chloroform and 1 mL of hydrochloric acid (1M) was added to hydrolyze the anhydride groups. The solution was stirred vigorously for 30 minutes. The grafted polymer was selectively recovered by precipitation into methanol, followed by filtration, then drying at 80°C. 1 g of purified, dried MAPLA was dissolved in a 100 mL chloroform:methanol (3:2 v/v) solution. The carboxylic acid concentration was determined by a direct alkali titration using 0.1N potassium hydroxide in methanol, which had been standardized against a solution of potassium hydrogen phthalate. The solution was titrated using 1% phenolphthalein as an indicator. The grafted polymer was completely soluble and did not precipitate during titration. The percentage of MA grafting was calculated using Equation 4.1 and verified by utilization of a linear regression calibration curve (y=0.9675x-0.288; $R^2 = 0.9996$) constructed by using a known amount of reagents. Each sample was tested in triplicate and average values were reported.

% MA grafting =
$$\frac{N_{KOH}V_{KOH}}{M_{sample}} \times 98.06 \times 100$$
 (4.1)

where N_{KOH} and V_{KOH} are the normality (mole/equivalent) and volume (in mL) of KOH solution, respectively. M_{sample} is the mass (in grams) of the maleated sample.

Gel Permeation Chromatography (GPC) Molecular weight measurements of PLA and MAPLA were carried out in a Waters GPC system equipped with an isocratic 1515 HPLC pump (flow rate = 1 mL/min), a 2414 refractive index detector and a 717 autosampler. Samples were dissolved in tetrahydrofuran in concentrations of 2 mg/mL. Molecular weights (M_n and M_w) and molecular weight distributions (M_w/M_n) were calculated using a universal calibration curve constructed with polystyrene standards.

Differential Scanning Calorimetry (DSC)

The melting (T_m), glass transition (T_g), and crystallization (T_c) temperatures, along with the enthalpies of fusion (Δ H) of the maleated PLA specimens were investigated using differential scanning calorimetry (DSC). The samples were heated to 200°C at 20°C/min and held for 5 minutes to erase any thermal history. The samples were then cooled to -30°C at a rate of -5°C/min to observe crystallization behavior, then reheated to 220°C at 5°C/min. Crystallization and melting temperatures were obtained from the cooling and second heating scans, respectively. The degrees of crystallinity of the composites were calculated according to Equation 3.1.

Thermal Gravimetric Analysis (TGA)

A high resolution thermogravimetric analyzer TGA 2950 from TA instruments was used to determine the change in weight of the sample due to decomposition. The sample was heated from 25°C to 500°C at the heating rate of 25°C/min. The balance and the samples were purged with nitrogen gas at rates of 40 ml/min and 60 ml/min, respectively.

Statistical Analysis

Statistical analysis was performed using *SPSS* for Windows. Thermal and data were compared by two-way analysis of variance (*ANOVA*) and a Tukey post-Hoc test. The mean differences were significant at the 0.05 level ($p \le 0.05$).

RESULTS AND DISCUSSION

MA Grafting Reaction

The functionalization of PLA by MA is discussed in the current section. The effect of the reaction conditions as well as the initiator type and concentration must be taken into consideration to ensure successful grafting. Selection of a suitable peroxide for grafting MA onto PLA should involve consideration of the following:

- Low toxicity
- Low volatility
- Appropriate half-life
- High hydrogen abstraction ability

In addition to satisfying the above criteria, L101 was selected as an initiator because of its known ability to induce successful grafting of MA on a variety of polymers as reported in the literature.^{24,25} T301 is a peroxide that is quite well established in the modification of polypropylene, yet relatively new and unexplored peroxide in terms of being incorporated in polyesters and polymer grafting. It is a cyclic tri-functional initiator that potentially holds benefits over conventionally used peroxides. It was chosen in this project because, upon

decomposition, it produces a diradical (shown in Figure 4.4) which, like many other multi-functional peroxides, may have the ability to produce a higher molecular weight polymer than those of a lower functionality. Another advantage is its potential ability to impart branching in the polymer leading to improved melt strength of PLA.²⁶



Figure 4.4: Proposed decomposition reaction of T301

The proposed reaction is illustrated in Figure 4.5. In the schematic, it is shown that the mechanism proceeds via two steps. In the first step, the organic peroxide undergoes homolytic rupture producing either a diradical or multiple monoradicals, depending on the peroxide type. Then, a hydrogen atom from the PLA chain is abstracted by a radical attack resulting in a PLA chain radical. In order for the desired grafting reaction to occur, the macroradical reacts with MA, which is then grafted onto the polymer backbone and forms a branched macroradical. This macroradical can then either react with additional MA monomers or undergo transfer with a hydrogen atom on its chain or another PLA chain to form a new macroradical. This process continues until grafting is terminated by recombination.



Figure 4.5: Proposed reaction for grafting MA onto PLA

Aside from grafting, the PLA chain radical faces two possible side reactions: crosslinking and chain scission.¹⁶ In the former, after the PLA radical reacts with MA by an addition reaction and is grafted onto the polymer chain, the radical then propagates to form a longer MA grafted pendant. This reaction is undesirable in MA grafting because it consumes the reactive sites, preventing desired grafting reactions from occurring. In the latter reaction, after the monomer addition, the skeletal bonds of PLA are broken and the radical is transferred to a fragmented chain end. Excessive chain scission leads to lower molecular weight and poor performance in the resultant material. The probability of each side reaction depends on both the nature of the macroradical and the nature of the polymer backbone.
Although unlikely to occur, an additional side reaction that becomes relevant in any system involving MA and free radicals together is the controversial homopolymerization of MA versus grafting of MA. Although this work will not delve into the specifics of kinetics of polymerization, it is helpful to address some of the issues pertinent to MA grafting. Conflicting reports by Russell ²⁷ and Gaylord ²⁸ have spurred much uncertainty of the occurrence of MA homopolymerization in a variety of systems. Others²⁹ have investigated the thermodynamics of the possible reaction on the basis of the ceiling temperature which homopolymerization precluded of maleic anhvdride at temperaturesexceeding 160°C. Furthermore, calculation of reaction ratios provided evidence that at high reaction temperatures, the reaction favors hydrogen abstraction over homopolymerization of MA by primary radicals. Thus, for grafting of MA onto PLA in the present work, analyses were conducted based on the assumption that homopolymerization would not occur under the prescribed conditions.

Proof of MA Grafting by Fourier Transform Infrared Spectroscopy (FTIR)

The grafting of MA onto PLA using T301 has been attested by FTIR. The spectra of pure PLA and MAPLA are shown in Figure 4.6. The spectral region containing the main differences between MAPLA and PLA is highlighted in the inset plot. Comparison of the spectra within this region reveals a doublet containing bands at 1759 cm⁻¹ and 1771 cm⁻¹ in the MAPLA sample, where only one absorption band was observed in that region for PLA at 1755 cm⁻¹ corresponding to its ester group. The doublet in the MAPLA sample is a result of

the overlapping of two absorption bands. The band located at 1759 cm⁻¹ is associated with the carbonyl stretching of the ester group in PLA. The peak at 1771 cm⁻¹ can be assigned to grafted anhydride because five-member cyclic anhydrides characteristically exhibit an intense absorption band between 1770 cm⁻¹ and 1792 cm⁻¹ due to symmetric C=O stretching, thus confirming the grafting of MA onto PLA.



Figure 4.6: FTIR spectra of PLA and MAPLA initiated with T301 verifying MA grafting

Grafting Efficiency and Molecular Weight

In the use of multifunctional polymers for reactive compatibilization, the degree of functionalization influences the extent of reaction at the interface, which, in turn, affects the properties of the resultant multiphase system. The molecular weight of the compatibilizer is also of prime importance because it is

directly proportional to the viscosity of the matrix material, which is a key factor in the compatibilization reaction and morphological development. The molecular characteristics and grafting yields of the maleated samples initiated with L101 and T301 were determined. The molecular weights, their distributions, and the grafting yields were all affected by the MA concentration as well as the initiator type and concentration. The extent to which they were affected will be discussed in the forthcoming sections.

Effect of Initiator Concentration on the Grafting Yield of MAPLA

Table 4.1 shows the molecular characteristics as obtained from Gel Permeation Chromatography (GPC) as well as the grafting yields as functions of initiator concentration.

MA %	Initiator (%)	M _n (g/mol)	M _w (g/mol)	M _w /M _n	Graft Yield (%)
0*	0	105938 ± 4715 ^a	140756 ± 7020 ^a	1.33 ± 0.13 ^a	
0**	0	96491 ± 1005 ^b	133238 ± 5250 ^a	1.38 ± 0.07 ^a	
2	0	94805 ± 3718 ^b	134119 ± 2007 ^a	1.41±0.08 ^a	0.01±0.00 ^a
2 ated	0.1	89105 ± 1962^{b}	126997 ± 549^{b}	1.43±0.04 ^a	0.13±0.02 ^b
-initia	0.25	$\textbf{72922} \pm \textbf{6205}^{\textbf{C}}$	110787 ± 3431 ^c	1.52±0.19 ^a	0.19±0.00 ^c
L101	0.5	21525 ± 3802 ^d	32546 ± 9331^{d}	1.51±0.85 ^a	1.49±0.05 ^d
2 ted	0.1	117808 ± 1525 ^e	143721 ± 14330 ^a	1.22±0.14 ^a	0.37±0.02 ^e
-initia	0.25	94192 ± 1626 ^f	116827 ± 17236 ^{bc}	1.24±0.21 ^a	0.40±0.00 ^e
T301	0.5	60080 ± 3330 ^b	85930 ± 14678 ^e	1.43±0.34 ^a	0.70±0.00 ^f

Table 4.1: Molecular Weight Data and Grafting Yield as a Function of Initiator Concentration

*Neat PLA; **Extruded PLA

The effect of initiator concentration on the grafting of MA onto PLA is shown in Figure 4.7. The initiator concentration was varied from 0% to 0.5%, while the MA concentration was held constant at 2%. As was expected, for both initiators an increase in initiator concentration resulted in an increase in MA graft yield. The increased degree of grafting can be attributed to an increase in the number of radicals formed upon the thermal decomposition of the initiator. The greater the amount of free radicals, the more chain-transfer to polymer, leading to a higher grafting.

In addition to the concentration of initiator, initiator type also played a role in the degree of grafting. Comparison of the grafting yields with respect to peroxide type shows that the samples initiated with L101 displayed much higher grafting than those initiated with T301. In the L101-initiated samples, a 1.5% MA grafting yield was seen, while in the T301-initiated samples, a maximum of 0.7% MA was obtained. It is interesting to note that at low initiator concentrations, the opposite trend was seen, and the T301-initiated samples had higher grafting than the L101-initiated samples. This discrepancy can be explained by consideration of the structures of the peroxides. Upon thermal decomposition, T301 being a cyclic, multifunctional initiator generates a radical with two reactive sites, unlike L101, which produces multiple monoradicals. This means that there are fewer T301 radicals that are able to partake in the grafting reactions. On the other hand, the excess diradicals of T301 at higher initiator concentrations may favor crosslinking or branching as opposed to the desired grafting reactions.



Figure 4.7: Effect of initiator concentration on MA grafting yield at 2% MA loading

Effect of Initiator Concentration on the Molecular Weight of MAPLA

In the samples prepared with constant MA concentration, increasing the initiator concentration yielded higher grafting, but it also led to a decline in molecular weight, as illustrated in Figure 4.8. In other words, the grafting yield was found to be inversely proportional to the molecular weight. The aliphatic nature of PLA makes it quite susceptible to hydrolysis during thermal processing, which is why its molecular weight was determined both before and after extrusion. However, no significant changes were observed between the neat and the extruded polymer. Thus, ruling out the high temperatures and mechanical shear as the sole cause of degradation.

As is well known, molecular weight changes in polymers due to the addition of peroxides are generally associated with chain scission, branching, or crosslinking reactions. When branching or crosslinking are the dominant reactions, the molecular weight typically increases, but, when chain scission dominates, the polymer undergoes degradation, lowering its molecular weight.



Figure 4.8: Effect of initiator concentration on the number average molecular weight of MAPLA at 2% MA loading

The reason for such degradation in the L101 samples is attributed to the increased concentrations of initiator, which gave rise to a greater number of propagating macroradicals, allowing chain scission to take place alongside grafting. This evidently caused the reduction in molecular weight. Conversely, in the T301 samples, though chain scission may have occurred, branching or light crosslinking appeared to dominate at low degrees of T301, shown by a relatively constant molecular weight. At a T301 concentration of 0.5%, a sudden decrease in molecular weight was seen and attributed to the simultaneous occurrence of grafting, chain scission, and crosslinking in the system. A small reduction in molecular weight is not uncommon in MA grafting and is not necessarily a negative consequence for compatibilizing agents. The surface area of the interface is, in part, controlled by the molecular weight of reactive polymers. Due

to their lower viscosities, lower molecular weight polymers are able to diffuse faster to the interphase of a multi-component system, where they can preferentially locate to form the interfacial region to improve adhesion. Nonetheless, there is a limit below which the molecular weight will have adverse effects due to the compatibilizer seeping from the interface and mixing with the bulk polymer.³⁰ These results indicate that an optimum amount of initiator should be used to achieve maximum grafting of MA with a minimum molecular weight reduction.

Effect of MA Concentration on the Grafting Yield of MA

Table 4.2 lists the molecular characteristics and grafting yield of MAPLA obtained as functions of MA concentration. The MA concentration was increased from 0% to 3% as the initiator concentration remained at 0.5%.

	MA %	L101 %	M _n (g/mol)	M _w (g/mol)	M _w /M _n	Grafting Yield (%)
	0*	0	105938±4715 ^a	140756±7020 ^a	1.33 ± 0.13 ^a	
	0**	0	96491±1005 ^b	133238±5250 ^a	1.38 ± 0.07^{a}	
ß	0	0.5	94715±4297 ^b	133169±11225 ^a	1.41 ± 0.17 ^a	
nitiat	1	0.5	74802±12694 ^c	103975±22076 ^a	1.39 ± 0.45 ^a	0.15±0.03 ^a
101-i	2	0.5	21525±3802 ^d	32546±9331 ^b	1.51 ± 0.85 ^a	1.49±0.05 ^b
	3	0.5	16062±414 ^e	23776±1833 ^b	1.48 ± 0.16 ^a	0.74±0.01 ^c
ated	0	0.5	113116±492 ^f	140591±27636 ^a	1.24 ± 0.25 ^a	
-initia	1	0.5	87496±8976 ^b	126051±27669 ^a	1.44 ± 0.52 ^a	0.44±0.05 ^d
301.	2	0.5	$60080 \pm 3330^{\circ}$	85930±14678 ^a	1.43 ± 0.34 ^a	0.70±0.00 ^e
Ϋ́.	3	0.5	86776 ± 195 ^b	108843 ± 5576 ^a	1.25 ± 0.07 ^a	0.41±0.01 ^d

Table 4.2: Molecular Weight Data and Grafting Yield as a Function of MA Concentration

Neat PLA, Extruded PLA

Figure 4.9 presents the MA grafting yield as a function of MA concentration. The effect of MA concentration on the grafting is much more complex than the effect of initiator concentration. For both L101 and T301 initiated samples, it was observed that at lower MA amounts the graft content considerably increased with an increase in monomer concentration and reached a maximum at 2%; thereafter, it decreased with increasing MA concentration.



Figure 4.9: Effect of MA loading on the MA grafting yield at 0.5% initiator concentration

This effect is similar to results presented by Mani et al.⁸ on the MA grafting onto polybutylene succinate, who suggested that there is an optimum monomer concentration or MA-to-peroxide ratio to promote grafting, beyond which the grafting efficiency decreases. This is apparently the case in the current system as well. At lower MA loadings, the PLA macroradicals reacted directly with MA. As the MA concentration was increased, termination reactions became prominent and the grafting content decreased. This suggests evidence of competition between MA and the PLA chains to react with primary radicals generated by peroxide decomposition.

Effect of MA Concentration on the Molecular Weight of MAPLA

The effect of MA concentration on the number average molecular weight is shown in Figure 4.10. Without any MA added, both T301- and L101-initiated samples retained the molecular weight of the neat polymer. The reason for this retention could be related to the light crosslinking reactions that may have taken place or to the deactivation of any residual catalyst in PLA by the peroxides, preventing hydrolysis.³¹ In this case, the former is expected to have occurred; the reason for which will be explained in a subsequent section. In the samples containing MA, the molecular weight decreased as MA concentration was increased because of hydrolysis. At higher MA concentrations, however, the molecular weights in the L101-initiated samples began to level off after 2% MA, whereas the T301-initiated samples experienced a slight increase in molecular weight at 3% MA. Because grafting is inversely related to the molecular weight, both the leveling and the ascent in molecular weight in the L101- and T301initiated samples--respectively--can be ascribed to the increase in grafting reactions. The differences observed between the T301- and L101-initiated samples can, again, be related to the structural differences of the corresponding peroxides in this system.



Figure 4.10: Effect of MA loading on the number average molecular weight at 0.5% initiator concentration

Thermal Stability of MAPLA

L101-Initiated Samples

Figure 4.11 displays the thermograms of the maleated samples initiated with varying L101 contents. Each of the samples shows a one-step decomposition profile. Thermogravimetric analyses of the samples show the decomposition temperatures to be lower for the maleated polymers than those of the neat PLA, implying that MA grafting yielded products of lower thermal stability. Although there are no implications of a causative relationship, the decreasing trend in thermal stability correlates well with the molecular weight data. More free radicals in the system promote both chain scission and the formation of less thermally stable polymer chains. Correspondingly, the presence of MA in the system also impacted the thermal stability as shown in Figure 4.12. As expected, the sample prepared with only peroxide was the forerunner in terms

of thermal stability due to the fact that the L101 can cause crosslinking, which will inherently increase the decomposition temperature because of fewer end groups. Upon addition of MA however, the thermal stability decreased and continued to decrease as MA concentration was further increased. The decline in decomposition temperatures can be related to the presence of MA – as the number of hydroxyl and carboxyl groups increased, so did the ease of thermal decomposition.



Figure 4.11: Effect of L101 on the thermal stability of PLA prepared with 2% MA





T301-Initiated Samples

Similar to the L101-initiated samples, the thermogravimetric data for the T301-initiated samples show reduced degradation temperatures as both initiator and MA concentration are increased. In Figure 4.13 the only sample that displayed improved thermal stability is the one without MA, confirming that T301 also may lead to crosslinking of the polymer chains.



Figure 4.13: Effect of MA concentration on the thermal stability of PLA prepared with 0.5% T301

At a constant MA concentration (Figure 4.14), the sample initiated with 0.1% T301 had the highest thermal stability, lending to the assumption that while working alongside crosslinking reactions, chain scission became more predominant as the initiator concentration increased. Overall, the thermogravimetric data, in conjunction with the previously discussed molecular weight data, clearly confirm the fact that molecular weight is correlated with thermal stability, showing that the lower molecular weight samples are less thermally stable.



Figure 4.14: Effect of T301 concentration on the thermal stability of PLA prepared with 2% MA

Differential Scanning Calorimetry

DSC was performed on the MAPLA samples to investigate the effect of maleation on the thermal behavior of PLA. Thermal properties of the maleated samples as functions of L101 are shown in Tables 4.3. A reduction in the glass transition temperature was seen; however, no statistically significant changes ($p \ge 0.05$) were observed in the melting temperature of the sample extruded with MA in the absence of L101. The crystallinity also increased two-fold – from 16% in the extruded polymer to nearly 35%. This is due to the increasing acid groups induced by the MA addition acting as plasticizers for the bulk polymer. This increased chain mobility and permitted the ease of chain stacking.

By comparing the DSC results of the maleated and unreacted samples, it was observed that a small amount of peroxide had no effect on the glass transition, crystallization, or melting temperatures ($p \ge 0.05$). However, in the samples initiated with a greater amount of L101, the temperatures slightly decreased while the crystallinity increased, which was due to the increased molecular motion of the lower molecular weight grafted samples.

% MA	% L101	T _g (°C)	T _c (°C)	T _{m,1} (°C)	T _{m,2} (°C)	%χm
0	0	58.1±1.0 ^a	106.9±3.1 ^a	146.5±1.5 ^a	153.7±1.2 ^a	16.1±1.1 ^a
2	0	51.5±0.7 ^b	101.5±2.6 ^a	140.0±0.9 ^b	150.1±0.6 ^b	34.7±4.6 ^b
2	0.1	56.9±2.6 ^a	112.1±1.8 ^a	147.7±0.6 ^a	154.5±0.3 ^a	22.8±1.2 ^C
2	0.25	55.9±1.2 ^a	107.3±1.4 ^a	146.5±0.9 ^a	154.5±1.0 ^a	28.7±0.3 ^b
2	0.5	51.9±0.3 ^b	110.5±4.3 ^a	140.8±2.5 ^b	144.6±2.6 ^c	30.8±1.5 ^b

Table 4.3: DSC Data of L101-initiated MAPLA with Varying L101 Concentrations

Different letters within the same column represent significant differences at the 95% confidence level.

The DSC data for the maleated sample in the absence of MA are shown in Table 4.4. It is shown that the addition of L101 increased the crystallinity of PLA. As discussed previously, the molecular weight of this sample remained fairly high and the thermal stability was improved. Therefore, under the assumption that branching had occurred concurrently with grafting it was expected that the polymer would have a lesser degree of crystallinity.¹⁵ However, this was not the case. The increased crystalline fraction could be a result of microgel particles acting as nucleating agents in the bulk polymer promoting crystallization. In the sample prepared using 1% MA, the T_c was 11% higher and experienced a 15% increase in crystallinity compared to the pure extruded polymer. In the 2% MA sample, a decrease in the melting and glass transition temperatures was observed with a slight increase in crystallinity. From the information presented in

the previous section, it should be recalled that this sample had the highest grafting percentage. The 2% MA sample also corresponds to that which had the lowest number average molecular weight, which accounts for the increased chain mobility and consequently lower glass transition and melting temperatures and a higher crystallinity. At 3% MA, the glass transition and melting temperatures were equal to those of the 1% MA sample, but the higher MA concentration induced a higher crystalline fraction due to the severe degradation of the polymer chains.

% MA	% L101	T _g (°C)	T _c (°C)	T _{m,1} (°C)	T _{m,2} (°C)	%χm
0	0	58.1±1.0 ^a	106.9±3.1 ^a	146.5±1.5 ^a	153.7±1.2 ^a	16.1±1.1 ^a
0	0.5	58.1±2.4 ^a	102.5±1.8 ^ª	144.3±0.8 ^a	152.5±1.4 ^a	22.7±0.3 ^b
1	0.5	57.3±2.1 ^ª	114.2±1.6 ^b	146.4±0.4 ^a	150.8±0.6 ^a	26.1±0.7 ^C
2	0.5	51.9±0.3 ^b	110.5±4.3 ^b	140.8±2.5 ^b	144.6±2.6 ^b	30.8±1.5 ^d
3	0.5	54.8±1.2 ^a	108.1±1.7 ^{ab}	146.8±2.3 ^a	154.4±0.9 ^a	40.4±1.2 ^e

Table 4.4: DSC Data of L101-initiated MAPLA with Varying MA Concentrations

Different letters within the same column represent significant differences at the 95% confidence level.

The effect of T301 concentration on the thermal behavior is shown in Table 4.5. In the absence of MA, the 0.5% T301 sample, like the 0.5% L101 sample also experienced a sudden increase in crystallinity compared to the unmodified PLA and is also attributed to the formation of microgels that nucleate PLA, leading to an increase in crystallinity. Of the maleated samples, that which was prepared with 2% MA and 0.5% T301 showed significant differences from the others, with twice the crystalline content than the other samples with lesser amounts of T301. This increase corresponds to increased polymer degradation resulting from MA grafting.

% MA	% T301	T _g (⁰C)	T _c (°C)	T _{m,1} (°C)	T _{m,2} (°C)	%χm
0	0	58.1±1.0 ^a	106.9±3.1 ^a	146.5±1.5 ^a	153.7±1.2 ^a	16.1±1.1 ^a
2	0	51.5±0.7 ^b	101.5±2.6 ^a	140.0±0.9 ^b	150.1±0.6 ^b	34.7±4.6 ^b
2	0.1	58.2±0.9 ^a	113.8±1.3 ^b	144.2±0.4 ^a	154.2±0.6 ^a	13.9±1.2 ^a
2	0.25	57.0±2.1 ^a	119.8±4.4 ^b	149.1±2.3 ^a	154.7±1.8 ^a	12.9±3.3 ^a
2	0.5	55.7±0.4 ^a	115.6±2.6 ^b	144.9±1.9 ^a	154.1±0.9 ^a	25.7±2.0 ^c

Table 4.5: DSC Data of T301-initiated MAPLA with Varying T301 Concentrations

Different letters within the same column represent significant differences at the 95% confidence level.

DSC results of the samples maleated with a constant concentration of T301 are shown in Table 4.6. As is evident, no significant changes were observed in the temperatures or the crystallinities as a result of maleation, fueling the assumption that the initial concentration of radicals has more of an influence than MA in terms of what dictates the molecular behavior of the polymer chains in this system.

% MA	% T301	T _g (°C)	T _c (°C)	T _{m1} (°C)	T _{m2} (°C)	%χm
0	0	58.1±1.0 ^a	106.9±3.1 ^a	146.5±1.5 ^a	153.7±1.2 ^a	16.1±1.1 ^a
0	0.5	57.9±0.6 ^a	107.3±1.7 ^a	146.1±0.4 ^a	153.6±0.6 ^a	35.4±3.7 ^b
1	0.5	58.5±1.5 ^a	119.2±3.2 ^b	149.0±2.5 ^a	155.0±1.9 ^a	22.4±0.7 ^c
2	0.5	55.7±0.4 ^a	115.6±2.6 ^b	144.9±1.9 ^a	154.1±0.9 ^a	25.7±2.0 ^c
3	0.5	57.1±0.7 ^a	120.3±08 ^b	149.2±1.3 ^a	154.9±2.0 ^a	28.1±0.3 ^c

Table 4.6: DSC Data of T301-initiated MAPLA with Varying MA Concentrations

Different letters within the same column represent significant differences at the 95% confidence level.

CONCLUSIONS

MA was successfully grafted onto PLA through reactive extrusion and the products were characterized on the basis of molecular weight, graft yield, mechanical properties, and thermal stability. Two different peroxides T301 and L101 were used to initiate grafting and the chemistry of peroxide initiation was elucidated. Results on the basis of grafting, molecular weight, and thermal behavior were compared. The results revealed that the samples that were initiated with L101 resulted in a higher overall grafting efficiency, while those initiated with T301 underwent the least degradation. The differences were attributed to the structural differences of the peroxides. Correspondingly, an inverse relationship between the degree of grafting and molecular weight was established. It was also found that regardless of peroxide type, there is an optimum ratio of peroxide to MA (0.5:2) that promotes maximum grafting, beyond which degradation reactions become predominant. The DSC results indicate that the crystallinities of the samples were in accord with the molecular weight measurements, with the exception of the samples containing only peroxide. In those samples the increase in crystallinity was attributed to microgel particles acting as nucleating agents. Thermogravimetric data revealed that the thermal stability of the samples, for the most part, decreased with the degree of maleation and the samples initiated with T301 being more thermally stable overall. Moreover, it was concluded that there must be a balance between grafting and degradation reactions in MAPLA polymers for their use as effective interfacial modifiers. Furthermore, an optimum MAPLA composition with a high enough molecular weight with sufficient grafting can be used to promote adhesion between different phases in composites and blends, as will be seen in Chapter 5.

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Chapter 5

MALEATED POLYLACTIC ACID (MAPLA) AS AN INTERFACIAL MODIFIER IN PLA-TALC COMPOSITES

INTRODUCTION

PLA-based composites are becoming increasingly important, providing the advantage that one can, in principle, tailor properties to be suitable for specific applications. Whether organic or inorganic in nature, fillers can be either fibrous or particulate, all of which have been incorporated into PLA with the aim of driving down costs and increasing performance capabilities.¹ Natural fillers have been receiving the most interest.² An example of this is work by Oksman et al.³, in which the mechanical properties of a flax fiber-reinforced triacetin-plasticized PLA were studied and the results were compared to those of polypropylene (PP)-flax composites. In that work, promising mechanical properties were reported – a 50%higher tensile strength of PLA with the addition of fibers, as compared with

that of the PP-based composites. In an attempt to overcome the brittle behavior of the composite a plasticizer was added. Resultantly, an increase in elongation at break was found, though at the expense of the tensile strength and modulus. Furthermore, in their study of the morphology, it was concluded that an optimization of the adhesion at the interface must be met in order to further improve the mechanical properties. In another study on the thermal and mechanical behavior. Serizawa et al.⁴ produced kenaf reinforced PLA-matrix composites and found that the addition of kenaf fibers increased the crystallization, thus resulting in significant increases in heat distortion temperature and modulus. However, no improvement in impact strength was seen with kenaf fibers used as-received. Nevertheless, by eliminating the crushed fibers and using only the longer fibers in conjunction with a single-screw extruder (as opposed to a twin-screw extruder), the impact strength was improved, supporting the well-known theory that composite behavior is very much influenced by the type of fiber used and by the processing conditions employed. In a study by Huda⁵, the incorporation of wood fibers into PLA improved the mechanical and thermomechanical properties. Generally, it has been the consensus that the use of natural fibers can provide a tremendous increase in both the tensile strength and modulus, however, only few reports show significant improvement in the elongation at break or impact properties without the use of a plasticizer.

In order to increase the thermal resistance of PLA, researchers have incorporated into it, starch,⁶ clay,⁷ carbon fibers,⁸ and glass fibers,⁹ each with the

aim of increasing crystallization. Ke and Sun⁶ studied the crystallization kinetics of the PLA/starch composites at varying isothermal crystallization temperatures and found that the starch addition was effective in increasing the crystallization rate. Mohamed et al.¹⁰ blended PLA with wheat gluten and studied the thermal characteristics of the composites. They found that the gluten addition led to decreased crystallization, which they attributed to a high degree of interaction between PLA and gluten.

Urayama and coworkers¹¹ studied the effects of particle-type and whiskertype fillers on the thermal and mechanical properties of PLA. The fillers of interest were calcium silicate, potassium titanate, and aluminum borate, none of which had any significant effect on the glass transition and melting temperatures. However, the composites did show decreased crystallization temperatures as compared with the neat polymer. Mechanical data showed that, in general, the whisker-type filler is much more effective than the particle-type with respect to matrix reinforcement, with the highest tensile strength being associated with the potassium titanate and aluminum borate whiskers.

A number of inert fillers, such as talc and calcium carbonate, have also made their way into PLA-matrix composites for similar reasons as those outlined above, as well as to reduce cost and improve mechanical properties. Thakur et al.¹² found that talc can act as a nucleating agent for PLA and increases the number of spherulites during crystallization. Kolstad¹³ confirmed this finding and concluded that the addition of 6% talc gave a 500-fold increase in the nucleation density. Huda et al.¹⁴ incorporated as much as 30% talc into PLA and reported a

decrease in tensile strength, but a 92 % increase in tensile modulus. In that work, the heat distortion temperature was reported to have increased by 24 degrees.

As found in the literature, a number of researchers have produced PLAbased composites with desirable properties, however, the most important issue still must be addressed-the compatibility between the matrix and the filler. Based on a review of the published literature, it is clearly indicated that a simple uncompatibilized mixture of PLA and filler, regardless of filler type, is insufficient to produce composites with good end properties. In fact in many cases, simple admixing can deteriorate the existing properties of the matrix material as any addition can disrupt the homogeneity and act as a stress concentrator. Furthermore, the nonpolar nature of PLA makes it difficult to react with reinforcements containing polar moieties such as fibers, talc, and starch and assuch, composites with these reinforcements display poor dispersion, a lack of adhesion, and reduced properties. This presents a major disadvantage to PLA matrix composites provided that they are unable to reach their full performance potential. Consequently, the use of coupling agents or compatibilizers is essential to introduce chemical bonding across the filler/matrix interface.

Substantial experimental effort has been made in an attempt to improve the phase interaction in PLA-based composites by reactive compatibilization. This is typically done by modifying either one or both of the composite constituents by grafting or by the incorporation of a third component – a coupling agent that acts to reduce the interfacial tension between the phases and improves the dispersion of the filler in PLA.

A well-known compatibilizer, maleic anhydride-grafted PLA (MAPLA), as mentioned in Chapter 4, can be used as an interfacial agent in many composite systems. When added into a mixture, it can preferentially reside at the interface to act as a bridge between binary phases to improve the interfacial adhesion, which results in a finer dispersion and more stable morphology.¹⁵

The use of MAPLA has been exploited in PLA composites reinforced with inorganic and natural fillers alike. Plackett¹⁶, for example, studied the use of MAPLA in PLA-based composites separately filled with wood fiber, nanoclay, and jute fiber mat. He showed enhanced adhesion in the PLA/wood fiber system, but no improvement in the latter two. Other PLA-based composites filled with cellulose powder, corn starch, and wood flour have been compatibilized with MAPLA and were reported to have shown improvements in the tensile behavior and morphology.¹⁷ Petersson et al.¹⁸ reported improved phase interaction and mechanical properties from using MAPLA as a compatibilizer in layered-silicate nanocomposites.

Based on the published literature, MAPLA has been shown to be an effective method to compatibilize PLA-based composites compounded with various fillers, however, no studies have been performed on the coupling effect in a talc filled system. In this work, talc was chosen as the filler not only because of its low cost, but also because of its known nucleating effects in PLA. Its structure is a trioctahedral phyllosilicate with the simplified molecular formula, $Mg_3Si_4O_{10}(OH)_2$. Although talc comprises mainly of a hydrophobic face, its edge surface is composed of approximately 10% hydroxyl groups, which are available

for reacting with hydrophilic moieties, such as maleic anhydride to form covalent bonds.¹⁹ Thus, this project aims at investigating the effect of maleic anhydride functionalized PLA (containing 0.7% MA) as an interfacial modifier in PLA-talc composites. The concentration of MAPLA was varied from 3 to 10% and the composites were studied on the basis of mechanical, thermal, and morphological properties. In the sections that follow, basic theory of composites and interfacial phenomena will be discussed as it pertains to the context of this work.

THEORETICAL BACKGROUND

Broadly defined, polymer-matrix composites are materials having two or more constituents of different phases: (1) the polymer matrix and (2) the reinforcing species.²⁰ The main functions of the polymer matrix are to hold the reinforcements together in the desired orientation and location, and to transfer the distributive stresses.²¹ The second phase, the reinforcement, can be classified into two groups: fibrous and particulate. Fibrous fillers are characterized by their large aspect ratios, whereas particulate fillers can be spherical, cubic, tetragonal, or any other shape. The geometry of the filler has great bearing on the strengthening mechanism.²² While both types of fillers share the stress load with the matrix, the particle type does so to a lesser extent and is not known to generally strengthen the material. Particulate fillers do, however, stiffen the matrix and improve resistance to creep and oxidation. In general, properties of composites are determined by:²³

- The properties of the filler
- The properties of the polymer matrix

- The volume fraction and volume fraction distribution
- The interaction between the matrix and the filler
- The orientation of the fillers in the composite

Rule of Mixtures

Knowledge of the relative proportions of a composite's constituents along with their respective material properties is sufficient to predict the mechanical behavior of the composite. A widely used model for predicting the ultimate strength and modulus of the composite in tensile loading is the rule of mixtures. The upper-bound approximation (Equations 5.1 and 5.2) is based on the assumption that the matrix and reinforcement are parallel elements:^{24,25}

$$\sigma_c = \sigma_m (1 - V_f) + k_\sigma \sigma_f V_f \tag{5.1}$$

$$E_c = E_m(1 - V_f) + k_E E_f V_f$$
 (5.2)

Under the assumption that the matrix and the filler are arranged in series, the lower bound approximation of the strength and modulus can be estimated by Equation 5.3 and Equation 5.4:²⁵

$$\sigma_c = \frac{1}{(1 - V_f)/\sigma_m + k_\sigma V_f / \sigma_f}$$
(5.3)

$$E_c = \frac{1}{(1 - V_f) / E_m + k_E V_f / E_f}$$
(5.4)

where σ_c , σ_m , and σ_f are the tensile strengths of the composite, matrix, and filler, respectively. E_c , E_m and E_f are the respective Young's moduli of the composite, matrix, and filler. V_f is the volume fraction of the filler and k_σ and k_E are constants corresponding to the type of filler and its interaction with the polymer matrix.

Adhesion Theory

It is necessary to understand that the mechanical performance of a composite is not only a function of the individual components, but also relies on the ability to effectively transfer stress through the bond and its distribution throughout the interface.²⁶ The interface is of utmost importance in realizing the degree to which a composite's potential strength is met and maintained. In order for a composite system to obtain its full potential, strong adhesion at the interface must exist. While the specifics of adhesion are not the focus of this work, an elucidation of the various coupling mechanisms will be helpful in understanding the complex nature of adhesion in the development of composite materials. The adhesion between the matrix and reinforcement is what dictates the ultimate performance, as the level of adhesion is directly correlated to resultant properties. Lacking sufficient adhesion at the interface prevents the necessary stress transfer between the components. Having an adhesion that is too strong, on the other hand, limits the energy absorption mechanisms by causing all of the energy to be focused on a small region of polymer, promoting the ease of crack propagation and premature brittle failure under stress.²⁷ Therefore, an optimum adhesion level is necessary at the interface for sufficient mechanical properties. There are five primary mechanisms in studying the principles of adhesion²⁸:

- Adsorption and wetting
- Interdiffusion

- Electrostatic attraction
- Chemical bonding
- Mechanical interlocking

These five mechanisms (whether in isolation or in combination) play a significant role in the adhesion in composite materials as well as those which have relevance to composite materials will be further discussed in the following subsection.

Adsorption and Wetting

Thermodynamics provide the basis for the adsorption theory in the study of filler-matrix surface energetics. Under the assumption of thermodynamic equilibrium, the following equation was proposed by Young to describe the relationship between the solid surface free energy and the liquid surface free energy (Equation 5.5): ²⁹

$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV} \cos\theta \tag{5.5}$$

where θ is the angle between the liquid and solid surfaces and γ_{SV} , γ_{LV} , and γ_{LS} are the free energies of the solid-vapor, liquid-vapor, and the liquid-solid interfaces, respectively. The precondition for achieving adhesion is wetting. In order to effectively wet a substrate, the surface energy of the substrate must exceed that of the liquid resin. Additionally, the resin must initially be of low viscosity and form a contact angle less than 90° (Figure 5.1).³⁰



Figure 5.1: Schematic diagram of a contact angle and its surface tension components.

Liquids that form contact angles greater than 90° are called non-wetting liquids. However, if a droplet is not formed, i.e. the contact angle is 0° , spontaneous wetting occurs and Equation 5.5 will not hold true. Rather, the equilibrium reaction can be written as Equation 5.6:

$$\gamma_{LV} \leq \gamma_{SV} - \gamma_{LS} \tag{5.6}$$

This inequality further implies that in order for spontaneous wetting and spreading to occur the liquid free energy must be lower than that of the substrate.²⁷

After wetting is achieved the next essential step to acheive an effective interphase is the adhesion, which is also governed by the surface energy and interfacial tension of each of the multiple phases. Adhesion at the interface allows stress to be transferred across the surfaces of the multiple phases, which is important to improve physical and mechanical properties of the composite system. The work of adhesion, W_a , is the maximum force exerted when the two adhering materials are separated. If only secondary forces are acting, then the work of adhesion can be expressed by the classical Dupre equation: ³⁰

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \tag{5.7}$$

Combining Equations 5.5 and 5.7 gives the Young-Dupre equation (Equation 5.8):

$$W_a = \gamma_{LV} \left(1 + \cos \theta \right) \tag{5.8}$$

When θ = 0, the work of adhesion is at a maximum and the following relationship exists between the surface energies:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \tag{5.9}$$

This equation implies that in order to have sufficient adhesion, much like for adequate wetting, the surface energy of the solid must exceed that of the liquid. Although these thermodynamic relationships are derived for use in equilibrium conditions, the knowledge of these mechanisms can help to understand wetting and spreading in compatibilizing polymer composites.

Chemical Bonding

Another type of bonding that is relevant to this work and must be considered is chemical bonding, which invokes the formation of covalent, ionic, or hydrogen bonds across the interface (Figure 5.2). Although chemical bonding is perhaps the most understood theory in adhesion principles, in many cases chemical bonds cannot form between the components due to their dissimilar chemical moieties, therefore, the use of coupling agents must be employed. Coupling agents contain chemical functional groups that will coreact with the surface of the filler as well as with the matrix. Theoretically, if this occurs, the coupling agent can act as a vehicle to bond the matrix and filler with a chain of primary bonds and, in theory, produce the strongest type of interfacial bonding.³⁰



Figure 5.2: Schematic diagram of chemical bonding between interfaces

Mechanical Interlocking

The oldest theory of adhesion is the mechanical interlocking theory, which states that good adhesion occurs only when an adhesive penetrates into the pores, holes, crevices, and other irregularities of the adhered surface of a substrate, and locks mechanically to the substrate (as shown in the schematic in Figure 5.3). However, this method has not been considered to be a viable mechanism of adhesion in polymer composites. ³¹



Figure 5.3: Schematic diagram of mechanical interlocking

Interdiffusion

The interdiffusion theory involves the diffusion across the bond interface to produce entanglement of polymer chain molecules. It is believed that the molecular chains interpenetrate at the interface where the adhesive and surfaces being bonded meet as shown in Figure 5.4. In essence, the two surfaces become interlocked at a molecular level and, therefore, become one. This theory pertains

exclusively to the bonding of polymers and has relative applicability composite applications.



Figure 5.4: Schematic diagram of interdiffusion adhesion mechanism

EXPERIMENTAL

Materials

PLA (3051D) was obtained from NatureWorks. Talc (Artic Mist) was supplied by Luzenac America, Inc., having a median diameter of 2 microns. Prior to extruding, the PLA and talc were separately dried overnight in an oven at 80°C to remove excess moisture. MAPLA (containing 0.7% grafted MA), which was previously obtained and characterized by methods outlined in Chapter 4,^{32,33} was also dried for 24 hours and used.

Methods

Compounding PLA/Talc Composites

PLA/talc composites were compounded using a Century ZSK-30 twinscrew co-rotating extruder. PLA pellets were pre-mixed with 40% talc and varying amounts of MAPLA. The MAPLA was incorporated by replacing 3%, 5%, and 10% of the PLA matrix. After mixing, the components were fed into the extruder at 100 rpm and extruded under the conditions listed in Table 5.1. The extruded strands were collected, pelletized, and dried at 80°C for 24 hours before further processing.

 Table 5.1: Extrusion Conditions for Compounding PLA/Talc Composites

Zone	1	2	3	4	5	6	7	8	9	Die
Temperature (°C)	25	95	145	165	175	180	180	180	175	170
Motor speed (rpm): 100										
Feeder speed (rpm): 150										

Injection Molding

The dried extruded pellets were injection molded into tensile bars using a Cincinnati Milacron VSX85 model equipped with an ASTM type IV mold (16.51 x 1.191 x 0.318 cm). The samples were processed under the conditions shown in Table 5.2.

Table 5.2: Injection Molding Temperatures for PLA and PLA/Talc Composites

Temperature (°C)									
Sample	Zone 1	Zone 2	Zone 3	Nozzle	Mold				
PLA	210	202	199	196	24				
MAPLA	182	177	177	171	24				
PLA/Talc (60:40)	212	210	210	205	24				
PLA/MAPLA/Talc (57:3:40)	212	210	210	205	24				
PLA/MAPLA/Talc (55:5:40)	212	210	210	205	24				
PLA/MAPLATalc (50:10:40)	212	210	210	205	24				

Differential Scanning Calorimetry

The melting and crystallization behavior of the PLA-talc composites were investigated using differential scanning calorimetry (DSC). The samples were heated to 200°C at 20°C/min and held for 5 minutes to erase any thermal history. The samples were then cooled to -30°C at a rate of -3°C/min to observe crystallization behavior, then reheated to 220°C at 3°C/min. Crystallization and melting temperatures were obtained from the cooling and second heating scans, respectively. The degree of crystallinity of each composite was calculated according to Equation 5.1:

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^o \times \phi_{PLA}} \times 100 \%$$
 (5.1)

where ΔH_m is the enthalpy of fusion (in J/g) and ΔH_m^o is the enthalpy of fusion of a PLA crystal of infinite size, whose reported value is 93.7 J/g. ϕ_{PLA} is the weight fraction of PLA within the sample, accounting for the talc and MAPLA addition.

Mechanical Properties

A United Testing System (UTS) Mechanical Testing Apparatus (Model SFM-20) fitted with a 1000 lb load cell was used to determine tensile properties of the samples. Prior to testing, the tensile bars were conditioned at 25°C in 50% relative humidity for at least 40 hours per the ASTM D638 standard.³⁴ The crosshead speed was set at 0.5 in/min. At least five specimens were tested and the average values were reported. The Izod impact strength was measured using a Testing Machines Inc. (TMI) 43-02-01 monitor/impact machine. Rectangular specimens cut from Type I tensile bars were notched and conditioned

appropriately according to the ASTM D256 standard.³⁵ Reported values were taken as the average five specimen measurements.

Thermo-mechanical Properties

Dynamic mechanical analysis (DMA) was performed to investigate the storage modulus, loss modulus, and tan delta values as a function of temperature for the PLA/talc composites. Measurements were run on rectangular bars with dimensions of $57 \times 3 \times 12.7$ mm using a TA 2980 DMA equipped with a dual-cantilever bending clamp at a frequency of 1 Hz and a heating rate of 10° C/min over a temperature range of 24° C to 140° C. All measurements were performed and properties were reported in accordance with ASTM D 4065.³⁶

Heat distortion temperatures (HDT) of the composites were also determined using DMA according to ASTM D648³⁷. Using a three-point bending clamp on rectangular specimens with dimensions of 12 x 12 x 3 mm, each specimen was heated from 25°C to 150°C at a rate of 2°C/min. The temperature at which the test bar was deflected by 0.10 inches was recorded as the HDT.

Scanning Electron Microscopy

Examination of the composite microstructure was carried out using two separate scanning electron microscopy (SEM) techniques. For the first technique, injection molded specimens were cut into rectangular sections, mounted in epoxy, and polished. Each specimen was coated with osmium then imaged using the backscattered electron imaging mode at an accelerating voltage of 12 kV and a working distance of 15 mm.
The second technique was performed on the tensile fracture surfaces. The samples were dried overnight to remove any sorbed water before being mounted onto an aluminum stub and sputter-coated with a thin layer (21 nm) of gold. Micrographs were obtained using secondary electrons at an accelerating voltage of 15 kV and a working distance of 15 mm.

Statistical Analysis

Statistical analysis was performed using SPSS for Windows. Data were compared by one-way analysis of variance (ANOVA) and a Tukey post- ANOVA test. The mean values were considered significant at the 0.05 level ($p \le 0.05$).

RESULTS AND DISCUSSION

Proposed Reaction Mechanism

It has been proposed that the maleated PLA will react with the talc through an esterification reaction. In Figure 5.5, this reaction is shown to occur between the anhydride group on the functionalized PLA and the hydroxyl groups on the edge surface of the talc particle resulting in the formation of a monoester on the surface of the talc particle.





The molecular weight of a polymer is known to significantly affect its surface tension. In general, surface tension decreases as molecular weight decreases.³⁸ Presumably, the lower molecular weight of MAPLA would enable good wetting during processing, allowing MAPLA polymers/oligomers to coalesce at the interface of the PLA and talc, creating an interphase. This thin region is believed to be responsible for stronger interaction between the phases, as evidenced by the improvements properties that will be discussed in the subsequent sections.

Differential Scanning Calorimetry

Table 5.3 summarizes the impact that the addition of talc and MAPLA has on the glass transition, melting, and crystallization temperatures, as well as the crystallinity of PLA. The talc, alone, increased the crystallinity of the PLA in the system from 16% to 26%. This increase in crystalline fraction is in agreement with the well known nucleating effect of mineral particles in semicrystalline materials.^{39,40} In investigating the efficacy of an interfacial modification induced by a coupling agent, it is important to examine the effect that it has on the glass transition temperature. The incorporation of MAPLA into the composite resulted in no significant changes in the T_g nor did it have any major effect on the melting temperatures. (Figure 5.6). However, the addition of both talc and MAPLA did show an increase in crystallinity ($p \le 0.05$) when compared to the unfilled polymer. In the composites, the higher crystallization temperatures (measured upon cooling) suggests the ability of the polymer to crystallize sooner and to a greater extent as shown in Figure 5.7. According to Feng⁴¹, in order to fully

understand the effect of a maleated coupling agent on the melting and crystallization behavior of a composite, two factors must be considered. The first is that MAPLA is of lower molecular weight and may have a lubricating effect on the PLA matrix. The second consideration is of the covalent and acid-base interactions induced between the anhydride on the MAPLA and the hydroxyl groups on the talc. Good interaction between the two functional groups could possibly restrict the mobility of the molecules, thus, the grafted MAPLA could disrupt the regularity of the PLA chain and hinder crystallization. Alternatively, the low molecular weight of MAPLA could promote chain movement and favor crystallization. In this case the latter is believed to have occurred. The crystalline fraction increased progressively with the level of MAPLA. The MAPLA contributed to more freely moving polymer chains and the enhanced chain mobility permitting higher molecular orientation and better filler dispersion, which in turn led to increased crystallization activity.⁴²

Sample	T _g (⁰C)	T _c (°C)	T _{m,1} (°C)	T _{m,2} (°C)	χ(%)
PLA	58.1±1.0 ^a	106.9±3.1 ^a	146.5±1.5 ^a	153.7±1.2 ^a	16.1±1.1 ^a
MAPLA	55.7±0.4 ^b	115.6±2.6 ^b	144.9±1.9 ^a	154.1±0.9 ^b	25.7±2.0 ^b
PLA/Talc (60:40)	56.7±0.7 ^{ab}	101.8±0.2 ^c	147.7±0.7 ^a	154.6±0.9 ^b	25.5±1.1 ^b
PLA/MAPLA/ Talc (57:3:40)	56.3±0.3 ^{ab}	103.8±0.6 ^a	147.0±0.2 ^a	153.8±1.6 ^b	27.3±1.0 ^b
PLA/MAPLA/ Talc (55:5:40)	54.6±0.6 ^b	107.4±1.0 ^a	147.8±0.9 ^a	154.7±0.4 ^b	30.0±0.6 ^c
PLA/MAPLA/ Talc (50:10:40)	53.6±0.5 ^b	109.9±1.5 ^a	148.0±1.3 ^a	154.9±0.5 ^b	32.9±0.2 ^d

Table 5.3: Melting, Crystallization, and Glass Transition Temperatures for PLA/Talc Composites

Different letters within the same column represent significant differences at the 95% confidence level.



Figure 5.6: DSC thermograms of PLA/talc composites revealing the effect of MAPLA on the melting behavior



Figure 5.7: DSC thermograms of PLA/talc composites revealing the effect of MAPLA on the crystallization temperature

Mechanical Properties

As was evidenced by an increase in crystallinity of PLA in the composite, the incorporation of talc influences gradual structural changes in the system. In this way, the interactivity between composite components, combined with the addition of MAPLA and factors such as orientation and dispersion of talc, can affect the properties of the composites. Thus, the mechanical behavior of the composites was investigated to study the extent of interaction between PLA and talc with varying amounts of MAPLA. The effects of the interfacial phenomena on various parameters, namely, the tensile strength, elongation at break, and Young's modulus are presented in Table 5.4.

Generally, the incorporation of a filler into a matrix may increase or decrease the tensile strength of the resulting composite, depending on the filler shape. Particulate fillers, such as talc tend to decrease the strength of the composites due to their lower ability to support stresses transferred from the polymer matrix. Interestingly, in this case the sole addition of talc had no significant effect on the tensile strength. Adding MAPLA, however, increased the tensile strength from 60 MPa for the unmodified composite to 66 MPa at 3% MAPLA up to 72 MPa at 5% MAPLA, at which the tensile strength reached a maximum; beyond which it dramatically dropped to 24 MPa. From this, it may be inferred that increasing the amount of anhydride groups in the system increases the number of the acid-base interactions and the degree of hydrogen bonding. which leads to a stronger interaction between the filler and the matrix. With excess amounts of anhydride groups, however, the coupling effects of MAPLA could have been counteracted by hydrolysis of the bulk polymer caused by theincreased amount of end groups which could have contributed to the decline in tensile strength.

In all of the composites, the most prominent physical effect of the talc was observed to be the stiffening effect. This is because the Young's modulus of talc (170 GPa) ⁴³ is significantly higher than that of PLA and also because of the enhanced crystallization of the composites. The Young's modulus values increased up to an MAPLA content of 3% and remained fairly constant thereafter. This increase is most likely associated with talc particles being more dispersed throughout the PLA in the samples with compatibilizer. Increased stiffness could

also be an indication of efficient stress transfer from polymer matrix to filler as a result of increased interaction.¹⁴ The tensile behavior can be correlated with the thermal results in that the degree of crystallinity can, in general, have an appreciable effect on the mechanical properties as it affects the extent of intermolecular secondary bonding. While the crystalline content, due to the presence of talc, caused an increase in the strength and modulus of the composites, it also made it brittle, accounting for the drop in elongation.

Sample	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
PLA	58.7 ± 2.2^{a}	3.6 ± 0.2^{a}	4.3 ± 1.0^{a}
MAPLA	60.2 ± 2.1 ^a	4.0 ± 0.2^{a}	3.9 ± 0.8 ^a
PLA/Talc (60:40)	59.6 ± 2.2 ^a	7.0 ± 0.4^{b}	1.1 ± 0.2 ^b
PLA/MAPLA/Talc (57:3:40)	66.0 ± 3.1 ^b	10.1 ± 0.1 ^c	0.9 ± 0.1 ^b
PLA/MAPLA/Talc (55:5:40)	72.4 ± 1.8 ^c	11.1 ± 1.9 ^c	1.5 ± 0.1 ^c
PLA/MAPLA/Talc (55:10:40)	24.1 ± 2.3 ^d	11.4 ± 1.7 ^C	0.3 ± 0.1 ^d

 Table 5.4: Tensile Properties of PLA/Talc Composites

Different letters within the same column represent significant differences at the 95% confidence level.

Moreover, the tensile behavior of the composites suggests that the MAPLA sufficiently improved the wettability of the filler with the polymer, which led to improved adhesion at the interface. In addition, the results show that only a small amount of MAPLA is needed to act as an interfacial modifier to enhance the properties, as was seen by the sudden decrease in tensile strength with MAPLA content. This confirms the existence of a critical amount of MAPLA, which has an ultimate effect on the macroscopic properties of the composite. In this work, the goal of the interfacial agent was to bridge the surfaces of talc and PLA by providing sufficient interfacial adhesion. However, too much interfacial agent was seen to have an adverse reaction, lending to the formation of an interphase that is too thick, limiting interfacial interactions. Therefore, it was postulated that there exists an optimum saturation level of MAPLA that provides the most favorable interactions across the interface of the PLA and talc.^{39,44}

Figure 5.8 illustrates the effect of the addition of MAPLA on the notched lzod impact strengths of the PLA/talc composites. Different factors contribute to differences in the impact strength of the composites, such as particle size, filler rigidity and its concentration, aspect ratio of filler, interaction between components and matrix phase, nucleation, orientation, and consequent structural changes in the matrix.⁴⁵ The highest impact strengths were seen for the neat polymer and for the composite without MAPLA whose impact strengths were virtually identical ($p \ge 0.05$). These results are notwithstanding reports indicating that the impact strengths of particulate-filled brittle polymers are typically lower than the neat matrix.⁴⁶

Owing to the proposed chemical reaction between MA and talc and the resulting adhesion at their interface, higher values of notched impact strength of composites with MAPLA were expected. However, the impact strength was lower for all of the specimens containing MAPLA, with no significant differences among them ($p \ge 0.05$). Conflicting data have been reported as to whether increased adhesion improves or worsens the material's resistance to impact.^{47,48} In the

case of this work, a plausible explanation for the decrease associated with the addition of compatibilizer is that the MAPLA induced a stronger interfacial bond which prevented adequate crack diverting. Because of this, the composite may not have been allowed to absorb a substantial amount of energy and caused the composite to exhibit brittle behavior.



Figure 5.8: Impact properties of PLA/talc composites

Thermomechanical Properties

The heat distortion temperature (HDT) or softening temperature is the maximum temperature at which a material can support a sufficient load. A semicrystalline polymer's HDT is very sensitive to the physical properties of a polymer, the amount of filler used, and the type of filler. For example, the crystallinity of the polymer and the glass transition temperature play a very important role in the heat distortion temperature. Typically, the use of inorganic fillers, especially those possessing a platelet structure, improve the heat resistance of polymers because the filler can prevent deformation of the molded composite while promoting crystallization of the polymer near the surface of the

filler.⁴ The addition of talc and MAPLA increased the crystallinity of PLA, thus, was expected to result in an increase in the HDT of PLA. However, neither the incorporation of talc nor the addition of 3% or 5% MAPLA had any impact on the HDT as shown in Table 5.5. Nevertheless, when 10% MAPLA was added the HDT dropped to 50°C from 58°C, that which was seen for the uncompatibilized composite. Since a material's HDT is directly related to its T_g, the decrease in the HDT of the composites containing 10% MAPLA corresponds to the decrease in T_g that was observed from the DSC data. A reasonable explanation for these results is that when there is better adhesion at the interface there is better wettability of the matrix, binding it to the talc platelets. This, in turn, means higher load transfer efficiency between the filler and the matrix, making it more difficult to withstand distortion upon heating.

Sample name	HDT (°C)
Neat PLA	56.8±2.0 ^a
PLA/Talc (60:40)	58.1±0.3 ^a
PLA/MAPLA/Talc (57:3:40)	55.4±0.3 ^a
PLA/MAPLA/Talc (55:5:40)	55.0±0.0 ^a
PLA/MAPLA/Talc (50:10:40)	50.4±0.1 ^b

Table 5.5: Heat Distortion Temperatures of PLA/Talc Composites

Different letters represent significant differences at the 95% confidence level.

To further investigate the effect that MAPLA has on the filler-matrix interactions, DMA was also used to study the response of the composite to periodic forces. Such experiments enabled the mechanical damping and elastic

modulus to be measured simultaneously.⁴⁹ In doing so, it was possible to obtain valuable information on the relaxation mechanisms correlated to the microstructure of a material. The peaks shown in the loss modulus (G'') and loss factor (tan δ) curves are related to the molecular motion of the polymer⁵⁰ and the storage modulus (G') curve provides information on the elastic behavior.

Figure 5.9 shows representative curves of the storage moduli (E') of PLA and its composites as a function of temperature. Consideration over the entire temperature span shows that all of the specimens followed an identical trend. The curves of the composites and the PLA each showed significant decreases in modulus in the range of 65-75°C. This temperature range correlates to the region where the molecules underwent a transition from being glassy to rubbery and there was minimal contribution of stiffness to the matrix.⁵¹ At temperatures below this transition the incorporation of talc in the PLA matrix increased the elastic component of the system. This was expected since most inorganic fillers, including talc, have moduli at least one order of magnitude higher than most polymers. The progressive increase of E' within the low-temperature region with MAPLA is indicative of the reinforcement effect, which allows effective stress transfer from the PLA matrix to the talc filler, leading to a higher number of PLAtalc interactions and an increase in the load-bearing capabilities⁵² Consideration of E' at the glass transition temperatures (the respective inflection points of the curves) gives insight into the relationship between the storage modulus and the compatibilization effect. The highest modulus value corresponds to the 5% MAPLA system, followed by 10% MAPLA, 3% MAPLA, 0% MAPLA, and lastly

PLA. The increase in storage modulus can be attributed to enhanced interfacial adhesion. Beyond the glass transition region another plateau region is apparent. This recovery of E' is an effect typical of cold crystallization of the amorphous regions in the polymer, a phenomenon commonly seen in PLA.⁵³



Figure 5.9: Storage modulus curves of PLA and PLA/talc composites

Figure 5.10 shows curves representing the tan δ trends as functions of temperature for PLA and its talc-filled composites. Tan δ is defined as the ratio of the loss modulus to the storage modulus (E"/E'). It is sensitive to the balance of heat dissipated and energy stored and can be used to detect thermochemical relaxations. The tan δ peaks remained at nearly the same temperatures for all of the composites except for that containing 10% MAPLA, which shifted to a lower temperature. This correlates with the previously discussed concept of the

plasticization effect of high MAPLA concentrations. Peak intensities were affected by both the presence of talc and the compatibilization effect. Talc reduced the mobility of the polymer chains, resulting in lower tan δ values. The MAPLA addition also decreased the tan δ values accordingly.



Figure 5.10: Tan δ curves of PLA and PLA/talc composites

For the compatibilized composites, it is possible to observe a correlation between the intensity of the tan δ peak and the interfacial adhesion. All of the curves displayed a similar tendency until a temperature of about 80°C was reached, at which the 10% MAPLA curve showed a small shoulder. This effect could imply that at 10% of MAPLA the existence of a third component, rather than an interfacial additive in a two-phase system.³⁹

The loss modulus curves, E", are shown in Figure 5.11. The temperatures denoting the maxima of the loss modulus curves are representative of the glass transition temperatures due to the motions associated with unrestricted amorphous PLA. From the figure it can be seen that the Tg value for the composite containing 3% MAPLA shifted to a slightly higher temperature, the Tg of the 10% MAPLA system shifted to a lower temperature, while the 5% MAPLA system remained the same as the neat polymer. This suggests that 5% MAPLA may be a more efficient compatibilizer than the other concentrations. It should be noted, however, that the T_gs obtained from DMA are quite different from those obtained from the DSC thermograms and may even show a slight contradiction. This discrepancy can be attributed to a difference in chain mobility as a result of different experimental conditions. The kinetics of the glass transition, the heating rate, and the loading frequency each has some impact on the molecular mobility. Therefore, DMA is a more sensitive tool than DSC in determining the thermal transitions of polymers.54

Furthermore, the peak heights of the loss modulus curves are associated with the damping of the material and are related to the energy converted into heat upon deformation. The composites had higher loss moduli than PLA because the presence of talc disrupts the polymer bulk, as the mineral particles are coated by the amorphous phase. The addition of MAPLA at the interface further increased the loss modulus values. The highest peak corresponds to the 5% MAPLA composite, followed by the 10% MAPLA composite, the 3% MAPLA

composite, and finally the unmodified composite. Furthermore, a pronounced broadening was seen in the loss moduli of the compatibilized composites, bringing about a transition region with high damping over a temperature range a few times greater than that of the unfilled polymer. The broadening effect as well as the increase in the E" can be attributed to a combination of the high surface area of the fillers and the strong interaction between PLA and talc. It is possible that the stronger interaction resulted in the partial immobilization of the polymer chains due to adsorption of polymer on the talc surface. The restriction of the polymer chains induced by talc caused a change in density of the packing of the polymer and increased the loss modulus.



Figure 5.11: Loss modulus curves of PLA and PLA/talc composites

Composite Microstructure

The morphology and microstructure of composite materials play a significant role in the prediction of macroscopic properties. The composite microstructure was examined using backscattered electrons to effectively observe the size, dispersion, and orientation of the talc particles within the PLA matrix. Unlike secondary electrons, backscattered electrons are primary beam electrons that have been elastically scattered by nuclei and are strongly dependent on the average atomic number of the sample. The backscattered electron images of the polished samples clearly show contrast based on the local chemical composition of the material. Talc, having a higher average atomic number than PLA, is revealed as white particles in the micrographs denoted by the arrows in Figures 5.12 through 5.15. In the sample that contains no MAPLA (Figure 5.12) large talc agglomerates are present. The talc particles are relatively unevenly distributed and show no orientation. This configuration is as opposed to that seen in the samples that contain MAPLA (Figures 5.13 through 5.15), all of which display talc particles that are more evenly dispersed within the matrix and exhibit axial orientation.



Figure 5.12: Backscattered electron image of PLA-talc composite containing no MAPLA



Figure 5.13: Backscattered electron image of PLA-talc composite containing 3% MAPLA



Figure 5.14: Backscattered electron image of PLA-talc composite containing 5% MAPLA



Figure 5.15: Backscattered electron image of PLA-talc composite containing 10% MAPLA

Fracture surface analysis

Postmortem investigation of the PLA-talc composite fracture surfaces provided significant insight into fracture mechanisms and morphological changes that led to changes in fracture behavior. The microstructures of the composites were correlated with their fracture surfaces to help elucidate the mode of failure. Each of the composites' topographical micrographs was examined to lend evidence to the assertion of improved interfacial adhesion with added MAPLA. Although all of the composites demonstrated brittle behavior due to the inherent brittle nature of PLA, one of two failure mechanisms was shown to be dominant—(1) failure of the PLA matrix or (2) debonding via platelet pull-out. The micrograph of the composite without added MAPLA displays typical characteristics of an incompatible composite (Figure 5.16). In it, a large number of voids appear resulting from talc platelet debonding. The distinct edges of the talc particles with no polymer adhered to the surface indicate behavior representative of a multi-component system in which there is little or no adhesion at the interface.

In the composite containing 3% MAPLA, shown in Figure 5.17, it can be seen that many of the talc particles are imbedded within the polymer matrix. Less distinction is seen between talc and PLA. Fewer cavities and edges are present around the talc particles and the talc platelets are coated with PLA, which indicates an increase in adhesion. In addition, the talc platelets are more imbedded within the polymer, which causes the talc particles to appear smaller than in the uncompatibilized composite.

In Figure 5.18, the fracture surface of the composite with 5% MAPLA shows a very different morphology from the other composites, one that is quite distinctive of a ductile failure. The morphology of this specimen shows significant localized deformation of the PLA matrix in the form of fibrils. It is also evident that the talc particles are more deeply lodged within the matrix and that failure occurs within the polymer, as shown by the deformation of the PLA rather than by debonding at the interface. This suggests better wetting of the talc by the PLA in this system. These observations substantiate the higher mechanical properties that were exhibited in this sample, since stronger adhesion permits an applied load to be effectively transferred from the matrix to filler.

The 10% MAPLA system, in Figure 5.19, shows behavior characteristic of a brittle material. In materials that undergo brittle fracture there is rapid crack propagation and very little plastic deformation, yielding a flat surface. It was also interesting that throughout this particular sample composition. two microstructures were apparent: a very flat surface and one in which multiple voids were present. This is likely caused by the high concentration of MAPLA exceeding its solubility limit in PLA, resulting in a heterogeneous microstructure and acting as a detriment to the mechanical behavior. It is necessary to note that it was this composition which displayed the poorest tensile strength and the lowest elongation at break. The brittle behavior exhibited by this composite is most likely due to either excess interfacial adhesion between talc and PLA, preventing safe debonding of the constituent phases, or to increased degradation of the composite due to excess MAPLA which lowered the molecular weight of the polymer. These electron micrographs further conirm the existence of a critical value of MAPLA which is necessary to improve the adhesion in PLA/talc composites.



Figure 5.16: Secondary electron SEM micrograph of PLA-talc composite with no added MAPLA indicating little or no adhesion between talc and PLA as evidenced by platelet pull-out



Figure 5.17: Secondary electron SEM micrograph of PLA-talc composite containing 3% MAPLA denoting slight to moderate adhesion between talc and PLA



Figure 5.18: Secondary electron SEM micrograph of PLA-talc composite containing 5% MAPLA revealing enhanced adhesion and a more ductile fracture



Figure 5.19: Secondary electron SEM micrograph of PLA-talc composite containing 10% MAPLA displaying a flat surface texture, indicating brittle composite failure in the PLA matrix

CONCLUSIONS

MAPLA was used as an interfacial modifier in PLA-talc composites. Investigation of the thermal, mechanical, and morphological properties provided experimental evidence of increased adhesion at the interface. These data indicate the existence of a critical value, beyond which no more improvements occurred as reflected by a sudden decrease in tensile strength. Microstructural observation of the composites revealed the modes of failure and the dispersion of the talc particles with the matrix, both of which were in accordance with the mechanical properties analyses.

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Chapter 6

REACTIVE MODIFICATION OF POLYLACTIC ACID BY SILANE GRAFTING AND CROSSLINKING REACTIONS

INTRODUCTION

PLA has become a polymer of increasing commercial interest and is the biobased material of choice for many, owing to its good physical and mechanical properties. In spite of its many advantages, some drawbacks have hindered its growing success in a number of industrial markets. One major limitation of PLA is its processing instability which is generated by the thermal, oxidative, and hydrolytic degradation that occurs during processing. This results in a breakdown of chain integrity and a reduction in molecular weight, both of which have detrimental effects on the rheological properties of the melt and the mechanical properties of the product. This, together with PLA's inherent low melt strength, has motivated considerable research efforts to overcome these shortcomings.

Most of such efforts have been focused on increasing the molecular weight and melt viscosity of PLA, many of which involved the introduction of functional additives to link multiple chains together, but these have been performed with little success.²⁻⁶ In other efforts common chain extenders, such as boric acid and lactone compounds, have been employed. However, these have proven ineffective in PLA-based polymers.⁷ Consequently, crosslinking has been deemed a well-suited approach to increase the molecular weight of PLA and improve upon some of the properties that continue to plague its widespread usage.

Crosslinking is an important process in polymer technology that involves the formation of a three-dimensional network of polymer chains through covalent or ionic bonding. The incorporation of crosslinks within a polymer can provide substantial improvements in its properties. Oftentimes crosslinked polymers find use in applications that require good thermal and dimensional stability, chemical resistance, and electrical properties.

Figure 6.1 shows a schematic illustration of the structural differences between a crosslinked polymer network and a linear polymer. The links between the polymer chains in the crosslinked network add important features to the polymer. They allow a semicrystalline polymer, such as PLA, to exhibit mechanical properties characteristic of a thermoplastic below its melting temperature. In addition, they permit the polymer to resist flow and exhibit the mechanical properties of a rubber when heated above its melting temperature.⁸ With this in mind, crosslinking PLA may not only improve its high temperature

properties, but it might also improve its melt strength and enhance its molecular weight to compensate for the degradation associated with thermal processing.⁹⁻²²

This project introduces the concept of silane grafting and crosslinking to post-polymerized PLA. A sequential series of experiments was performed to monitor the effects of various parameters, such as concentrations of silane, peroxide, and catalyst, with an intention to explore the structure-property relationships related to crosslinking. The specific objectives are the following: (1) the use of reactive extrusion to achieve radical melt functionalization of an organofunctional silane; (2) the moisture-induced crosslinking of the silanol moieties that are attached to the polymer chain; and (3) evaluation of the crosslinking reaction and the characterization of the resultant crosslinked polymers on the basis of gel content, mechanical behavior, and thermal properties, in order to understand how the crosslinked structure affects the properties of PLA.





In the paragraphs that follow, an introduction to polymer crosslinking including types and mechanisms, as well as a review of past work with particular regard to PLA, will be given. In addition, a brief theoretical background as it pertains to the nature of this work will be provided.

PLA Crosslinking Background

The effects of crosslinking on the properties of PLA have been well studied. The most reported and undoubtedly the most preferred route, according to the literature, is associated with peroxide-induced radical reactions in which peroxides are incorporated into PLA via extrusion processes. In this method, the role of the peroxide is two-fold: (1) to stabilize PLA by deactivating the residual catalysts that promote thermal degradation and (2) to introduce free radicals that can be linked together by coupling reactions.²³ This multi-step process is done by, first, the generation of free radicals induced by the thermal decomposition of a peroxide. These free radicals are then capable of extracting hydrogen atoms from the polymer backbone and transferring the free radical site to the PLA chains containing active radicals can undergo bimolecular recombination to produce a crosslinked PLA network.

In the crosslinking of PLA via the peroxide-generated radical technique, one of the most important factors that must be considered is the peroxide type and whether it is capable of abstracting hydrogen from PLA. Additionally, the peroxide's half-life and the extruder's residence time play critical roles in the degree of peroxide decomposition, rate of cure, and the ultimate extent of crosslinking. Various peroxide types have been investigated and results have been presented on the optimum stabilization and crosslinking effects in PLA. For

example. Sodergard et al.²³ found that when dialkyl peroxides having no carbonyl groups were used, such as dicumyl peroxide (DCP), the results yielded PLA with improved elongation at break and reduced crystallization rates, yet with increased rates of hydrolytic degradation. Nevertheless, when peroxides containing carbonyl groups were used the opposite was seen and the hydrolytic activity of PLA was stabilized. Nijienhuis et al.⁹ also noted that DCP resulted in the degradation of PLA and that the decomposition products induced a plasticization effect on the polymer. Other researchers, including Carlson et al.²⁴, have shown Luperox 101, a difunctional di-tertiary alkyl peroxide, to be guite effective in inducing free radical branching and crosslinking of PLA. Peroxide decomposition rates and molecular weights were studied by Takamura et al.¹ who assessed various peroxides based on crosslinking efficacy in terms of free radical efficiency and hydrogen abstraction ability. Their results pointed toward using peroxides with higher decomposition rates to obtain a higher degree crosslinking. This is because the formation of more radicals leads to a higher probability of crosslinking, allowing it to predominate over chain scission.²⁵ Based on these results, the main difficulty with using peroxide to crosslink PLA lies in the nature of the radical reactions. Often a surplus of radicals in PLA causes it to be more susceptible to chain scission, giving rise to a greater number of oligomers. The increased number of hydroxyl and carboxylic end groups promote thermal decomposition, resulting in lower molecular weight and decreased properties.²⁴

Similar to peroxide-induced crosslinking is the irradiation of polymers to form a network structure. This technique, first introduced in the 1950s,²⁶ has been proven to be effective for the grafting, crosslinking, and degradation of many polymers, typically polyolefins. However, in recent years, it has also been utilized in polyesters.^{9,13,14,27,28} In this technique, the formation of macroradicals is based on hydrogen expulsion via irradiation by gamma or electron beams, yielding macroradicals that can combine with adjacent chains to form three-dimensional networks by carbon-carbon linkages.

Expensive equipment and the necessary high voltages coupled with difficulty producing sections with even irradiation represent the major limitations of this technique. Furthermore, in PLA, the direct exposure to gamma-ray or electron beams through ionization results in degradation at low irradiation doses and embrittlement at higher irradiation doses.^{9,29} Consequently, the use polyfunctional monomers (PFMs) as crosslinking agents in combination with irradiation has been investigated to combat the issues with degradation with some success. PFMs are very reactive and their ability to react with PLA can be utilized to form a crosslinked structure. According to Nagasawa et al.³⁰, 3% of triallyl isocyanurate (TAIC) is effective in producing crosslinked PLA, manifested by a thermal stability exceeding 200°C. The increase in thermal stability was attributed to the cyclic unit in TAIC and the large three-dimensional network that it produces. Other researchers, including Jin et al.³¹, Mitomo et al.¹⁴, and Quynh et al.³², confirmed these findings, reporting the use of TAIC to result in high gel contents and improved thermal stability of PLA.

Silane Crosslinking

The crosslinking technique of interest in this work is silane crosslinking using organic silicon compounds. Limited evidence exists in the published literature of silane crosslinking in aliphatic polyesters and no studies have been reported on silane-crosslinked post-polymerized PLA. In general, this method entails grafting an organofunctional silane onto a polymer backbone and subsequently crosslinking in a moisture-rich atmosphere.

Organofunctional silanes are bifunctional. Bound to the central silicon atom are two different functional groups, an organofunctional group and a silicofunctional group. The organofunctional group is strongly attached to the silicon atom by a highly unreactive carbon chain. The silicofunctional groups-those which are directly bound to the silicon atom, are hydrolyzable with relative ease.³³ Upon hydrolysis to silanol groups, the silicofunctional groups may react with the hydroxyl groups of an inorganic or organic material or by condensation to form stable siloxane linkages, which are then responsible for the formation of the resultant network structure. The higher bond energy associated with the Si-Si bonds induced by silane crosslinking leads to much less thermal degradation by chain scission when compared to free-radical crosslinking (C-C) bonds. Therefore, a major advantage of silane crosslinking is the ability to yield products with much higher thermal stability than peroxide or irradiation crosslinked materials.

The concept of silane crosslinking was first introduced in the late 1960s, when Dow Corning patented a two-step crosslinking method using organic peroxides and vinyl silanes to improve the high temperature properties, chemical
resistance, and mechanical properties of polyethylene, all without the high investment costs of irradiation equipment and the risk of pre-curing.³⁴ This technology, based on organic silicon chemistry, was first established in an attempt to improve the properties of polyethylene in cable insulations and hot water pipes, but has since been expanded to other applications. The process, known as SioPlas technology, involves the peroxide initiated melt grafting of vinyl silane onto a polyethylene backbone and then crosslinking in the presence of water.³⁵ Crosslinking will occur spontaneously at ambient conditions, however, it is a very slow process, which is why a masterbatch of a suitable catalyst is typically used prior to the condensation step to accelerate cure.

Another technique, similar to the SioPlas method, is the Monosil technique, which was patented by Maillefer and BICC.³⁶ Using this one-step approach, polyethylene pellets, an antioxidant, and peroxide are combined into a high-shear extruder. Next, meter-fed silane and catalyst are pumped into the melt to ensure crosslinking during processing, eliminating the need for multiple steps. The resultant products obtained from the Monosil process are comparable to those produced from SioPlas technology.

With the advent of SioPlas and Monosil technologies, silane crosslinking has been an ever-growing field. This technology has been fully exploited in polyethylene³⁷⁻⁴⁵ and has expanded to other polymers such as polyvinyl chloride ^{46,47}, polypropylene⁴⁸⁻⁵¹, and polyethylene-octene⁵². However, as was previously mentioned, the modification of PLA by the grafting of an organofunctional silane and the subsequent crosslinking has yet to be explored as an avenue for

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increasing the molecular weight, enhancing the melt strength, and improving the hydrolytic stability of PLA or any other aliphatic polyester.

Network Theory

The formation of a crosslinked material begins by the branching of linear chains, followed by their linking together into a network whose molecular weight diverges to infinity. This irreversible transformation of a linear polymer into a thermoset material is known as gelation and the point at which it occurs is defined as the gel point. It is at this critical point beyond which the polymer loses its ability to flow. Once a polymer is completely crosslinked it is not readily thermally processable and is insoluble.

Chemical crosslinks in a polymer at the molecular level are manifested by macroscopic effects, such as changes in molecular weight, mechanical behavior, crystallization kinetics, melting, and glass transition behavior, as well as differences in thermal stability. The extent to which these properties are affected is governed by both the properties of the constituent monomers and by the crosslink density.⁵³ The crosslinking density is defined as the number of crosslinks in a unit volume of a polymer network and can be correlated with the distance between crosslinking points by Equation 6.1: ⁹

$$v = \frac{\rho}{M_c},\tag{6.1}$$

where v is the crosslink density, ρ is the density of the polymer, and M_c is the molecular weight between crosslinks. As a general rule, the greater the crosslink density, the tighter the mesh size, and the more apparent are the property

changes. Topological constraints, such as polymer loops and entanglements, also play a role in altering the properties, but are effective only if the minimum crosslink density is such that it prevents the chains from uncoiling.⁵⁴ The determination of crosslink density can be achieved by a number of methods. One method is by measurement of the swelling equilibrium. When a crosslinked polymer is immersed in a good solvent, rather than dissolving the polymer, the solvent molecules diffuse into the network, solvating the polymer chains. This breaks the intermolecular forces and the network swells. An elastic retractive force is generated by the polymer opposing deformation and establishing equilibrium between the solvation forces that drive the chains apart and the elastic forces of the network that hold the chains together.⁵⁵⁻⁵⁷ This equilibrium can be characterized by the steady-state swelling ratio. Given the direct correlation with the crosslink density, swelling ratio determination is a simple and cost-effective tool to characterize crosslinked polymer networks. The steadystate swelling ratio can be described using Equation 6.2:

$$v_2 = \frac{1}{1 + Q\frac{\rho_r}{\rho_1}}$$
(6.2)

where $v_2 = V_0/V$ (V_0 is the volume of the uncrosslinked network and V is the volume of the crosslinked network). Q is the swelling value defined as the weight ratio of the crosslinked polymer before and after immersion in the solvent, ρ_T and ρ_1 are the densities of the polymer and the solvent, respectively. The number of

crosslinked monomer units per main chain in the absence of solvent can then be defined mathematically by J.P. Flory's equation (Equation 6.3)⁵⁶:

$$v_x = -\frac{\ln(1-v_2) + v_2 + \chi_1 v_2^2}{\Phi_1 (v_2^{1/3} - v_2/2)}$$
(6.3)

Where v_x is the crosslink density, v_2 is defined above, χ_1 is the Flory interaction parameter, and Φ_1 is the molar volume of the solvent. Knowledge of the Flory interaction parameter permits the crosslink density to be calculated. The molecular weight between crosslinks, M_c , can then be determined by Equation 6.4:

$$M_c = \frac{1}{\overline{v}v_x}, \qquad (6.4)$$

where v_x was previously defined as the crosslink density and \overline{v} is the specific volume of the polymer.

EXPERIMENTAL

Materials

PLA (3051D) was obtained from Natureworks. The silane used in this work was vinyltrimethoxysilane (VTMOS) (Figure 6.2) and was purchased from Gelest. The free-radical initiator, 2, 5-dimethyl-2, 5-di-(*tert*-butylperoxy) hexane (L101) (Figure 6.3) and the catalyst, dibutyltin dilaurate (DBTDL) (Figure 6.4) were obtained from Sigma. All reagents were used as received.



Figure 6.2: Structure of vinyl trimethoxysilane (VTMOS)



Figure 6.3: Structure of 2, 5-dimethyl-2, 5-di-(*tert*-butylperoxy) hexane (L101)



Figure 6.4: Structure of dibutyltin dilaurate (DBTDL)

Methods

Preparation of PLA-g-VTMOS

In the first step, VTMOS was grafted onto PLA by a free-radical reaction. Solutions of 0.1% L101 with varying VTMOS percentages (0.5% to 3%) and of 3% VTMOS with varying L101 (0.05% to 0.5%) were prepared. Sample compositions are tabulated in Table 6.1. The mixtures were then manually combined with the PLA pellets to ensure even coating before being introduced into the feeder of a Century ZSK-30 twin-screw extruder. The polymers were extruded according to the processing conditions in Table 6.2. The extrudate was cooled through a water bath and pelletized downstream. Selected samples were subsequently dried and combined with varying amounts of DBTDL and reextruded under the same extrusion conditions. Following extrusion, the samples were dried and stored in a desiccator prior to further processing by injection molding according to the conditions in Table 6.3.

	without catalys	<u>t catalyst</u>			
L101 (⁴	%) V1	VTMOS (%)			
0.1		0			
0.1		0.5			
0.1		1			
0.1		3			
0.1		5			
0.05		3			
0.2		3			
0.5		3			
	with catalyst				
L101 (%)	VTMOS (%)	DBTDL (%)			
0.1	0	0.05			
0.1	0.5	0.05			
0.1	1	0.05			
0.1	3	0.05			
0.1	5	0.05			
0.05	3	0.05			
0.2	3	0.05			
0.5	3	0.05			
0.2	3	0.1			
0.2	3	0.2			

Table 6.1: VTMOS Grafting Sample Compositions

Table 6.2: Extrusion Processing Conditions for VTMOS Grafting

Zone:	1	2	3	4	5	6	7	8	9	Die
Temperature: (°C)	25	95	145	175	180	180	180	180	175	170
Motor speed: (rpm)	100									

		T	emperatu	ire (°C)	
Sample	Zone 1	Zone 2	Zone 3	Nozzle	Mold
VTMOS-g-PLA	210	202	199	196	24

Table 6.3: Injection Molding Processing Conditions for VTMOS Grafting

Moisture Crosslinking

Moisture crosslinking was performed on the injection molded articles. Since the rate of crosslinking depends on the rate of water diffusion into the polymer specimens of the same shape and thickness were used. Crosslinking of the catalyzed and uncatalyzed specimens was carried out in a moisture saturated chamber at room temperature over a 28-day period. Crosslinking properties were determined at varying curing time intervals of 1 day, 7 days, 14 days, 21 days, and 28 days. After crosslinking, all samples were dried and conditioned for further characterization.

Melt Flow Index (MFI)

The melt flow rate was used to investigate the degree of crosslinking of PLA. Experiments were carried out using a RayRan Melt Flow Indexer. All tests were run in accordance with ASTM D1238-90b. The pelletized samples were melted at 190°C and driven through a capillary die using a 2.16 kg weight attached to a piston. The mass (in grams) of the extrudate was measured at 30 second intervals and the MFI was calculated accordingly.

Gel Content and Degree of Swelling

The gel content of the crosslinked polymers was determined by Soxhlet extraction using methylene chloride as the solvent. First, 2 grams of the dried

sample were introduced into a cellulose thimble and extracted over a period of 24 hours. After extraction, the residual polymer was dried to constant weight. The gel content was calculated as the percentage ratio of the final weight of the polymer to its initial weight using Equation 3.8. Gel contents of at least three specimens of each sample were determined and the average was reported. The degree of crosslinking was determined by calculation of the swelling ratio, which was evaluated by weighing approximately 1 gram of the dried crosslinked polymer, immersing it in 100 mL of methylene chloride for 48 hours, removing and then weighing the gel in its fully swollen state. The gel was later dried to constant weight and the degree of swelling (DS) was calculated using equation 6.5:

$$DS = \left[\left(W_s - W_g \right) / W_g \right] \left(\frac{\rho_p}{\rho_{CHCl_2}} \right), \tag{6.5}$$

where W_g is the average weight of the dry gel component in the crosslinked sample, W_s is the weight of the gel component swollen at room temperature for 48 hours in methylene chloride, and ρ_p and ρ_{CHCl_2} are the densities of PLA and methylene chloride, respectively.

Differential Scanning Calorimetry (DSC)

The melting and crystallization behavior of both the crosslinked and uncrosslinked polymers were investigated by DSC analysis using a TA Instruments 2920 DSC machine operated under nitrogen. The samples were heated to 220°C at 20°C/min and held for 5 minutes to erase any thermal history. The samples were then cooled to -30°C at a rate of -5°/min, then reheated to

27 ť Ī ľ Cſ ba an χ. 54 at ta C 220°C at 5°C/min. Crystallization and melting temperatures were obtained from the cooling and second heating scans, respectively.

Thermal Gravimetric Analysis (TGA)

A high resolution thermogravimetric analyzer TGA 2950 from TA Instruments was used to determine the changes in thermal stability due to crosslinking. Each sample was heated from 20°C to 500°C at 25°C/min. The balance and the samples were purged with nitrogen gas at rates of 40 ml/min and 60 ml/min, respectively.

X-ray Photoelectric Spectroscopy (XPS)

XPS spectra of crosslinked PLA were obtained using A Perkin Elmer Phi 5400 ESCA system with a magnesium K α X-ray source. Samples were analyzed at pressures between 10⁻⁹ and 10⁻⁸ torr with a pass energy of 29.35 eV and a take-off angle of 45°. The spot size was approximately 250 μ m². Atomic concentrations were determined using previously determined sensitivity factors. All peaks were referenced to the signature C1s peak for adventitious carbon at 284.6 eV.

Statistical Analysis

Statistical analysis was performed using *SPSS* software for Windows. Data were compared by two-way analysis of variance (*ANOVA*). A Tukey post-Hoc test was used to test multiple comparisons. For each analysis the mean difference was found significant at the 0.05 confidence level ($p \le 0.05$).

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RESULTS AND DISCUSSION

Proposed Reaction Mechanism

A schematic illustration detailing the proposed mechanism for silane grafting is illustrated in Figure 6.5. A two-step reaction is necessary to attain the desired functionalized product. It is expected that L101 undergoes thermallyinduced decomposition in the first step, forming peroxide radicals under the extrusion conditions. The peroxide radical is then able to react with the PLA chain and undergo radical transference to form a PLA macroradical. This PLA macroradical breaks the silane unsaturation, enabling grafting onto the PLA backbone. This reaction is followed by another radical transfer forming a VTMOS grafted macroradical, which can react with other molecules of PLA to continue the reaction until the chain terminates by chain transfer to polymer. The resultant arafted polymer contains alkoxyl mojeties that can easily be hydrolyzed to silanol groups, which are capable of reacting with polymers or fillers containing hydroxyl groups or by condensation to form a crosslinked network. The latter, as shown in Figure 6.6, will be the focus in the context of this work. The moisture crosslinking reaction of the grafted silane is comprised of, first hydrolysis of the alkoxysilanes to silanol groups, which when combined can condense to siloxane groups. Thus, what follows is the formation of a network of PLA chains tied together by stabilized siloxane linkages.

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Figure 6.5: Proposed reaction of VTMOS grafting onto PLA



Figure 6.6: Proposed reaction of moisture crosslinking in VTMOS-grafted PLA

Role of the Catalyst

The moisture crosslinking reactions take place spontaneously in the presence of water, however, the process is very slow, making the aid of a suitable catalyst of practical importance. Organotin catalysts are commonly employed in silane grafting reactions to expedite the crosslinking process. In this study, DBTDL was incorporated during the second extrusion pass. The exact mechanism by which DBTDL accelerates the process is not fully understood, but it is believed to be broken down to yield dibutyltin laurate hydroxide and lauric acid (Figure 6.7). The reaction products are what are believed to act as the actual "catalyst", whose overall role is to reduce the activation energy to accelerate hydrolysis of the alkoxysilane groups to silanols followed by their condensation to siloxane.^{33,58}



Figure 6.7 Expected mechanism of DBTDL reaction³³

Effect of Silane Concentration on the Degree of Crosslinking

The degree of crosslinking was determined by measuring the gel content of the grafted polymers. Figure 6.8 depicts the effect of silane concentration on the samples prepared in the presence and absence of catalyst measured after the maximum crosslinking period. The concentration of silane was varied from 0% to 3%, while the concentration of peroxide and catalyst were kept constant at 0.1% and 0.05%, respectively.

A greater degree of VTMOS grafting was expected to ensue more crosslinking, and hence, a higher gel content. As both curves in Figure 6.8 indicate, increasing the VTMOS content indeed induced a rapid increase in the degree of crosslinking at low VTMOS concentrations. At higher VTMOS concentrations, the curves gradually leveled off to a constant value. This is prime indication that the addition of VTMOS beyond a certain amount has very little effect on the gel content. This is attributed to the possible homopolymerization of the VTMOS resulting in long molecular chains of monomers, which would then reduce the effective grafting yield of silane onto PLA.⁵⁹ As expected, the

catalyzed samples performed better than the uncatalyzed samples. The maximum gel contents were nearly 70% in the presence of catalyst and approximately 58% in the absence of catalyst.



Figure 6.8: Effect of VTMOS concentration on the gel content of samples prepared with 0.1% L101 after 28 days of crosslinking

Effect of Initiator Concentration on Gel Content

Figure 6.9 shows the influence of initiator concentration on the gel contents in the catalyzed and uncatalyzed samples when VTMOS was held constant at 3% and measured at the end of the 28day period. With increasing initiator concentration similar trends were observed in the gelation behavior for both sets of samples. The gel content was observed to initially increase sharply with increasing initiator content, inferring a high rate of gel formation. Thereafter, the rate decreased as the achievable gel content of 79% was reached at 0.2% L101 and maintained upon further L101 addition. The initial increase in gel content is due to primary free radicals generated by peroxide decomposition

either favoring chain combination or inducing more sites for grafting. Consequently, more crosslinking would occur. At higher L101 concentrations no further increase in gel content was seen in the range of the examined concentration. This indicates that the maximum attainable amount of gel had been achieved in both sets of samples in the cure period. Overall, these curves show that the initiator had more influence on the gel formation than did the VTMOS concentration, as evidenced by the difference in gel contents in the two sets of experiments.



Figure 6.9: Effect of L101 concentration on the gel content of samples prepared with 3% VTMOS after 28 days of crosslinking

Effect of Catalyst Concentration on Gel Content

The effect of catalyst concentration on the gel content was also studied to identify the optimal catalyst concentration for achieving sufficient crosslinking. The sample composition investigated was that which was prepared with 0.1% L101 and 3% VTMOS. Catalyst concentrations of 0.05%, 0.1%, and 0.2% were

used and the gel contents were measured after 28 days. The relationship between gel content and catalyst concentration is depicted in Figure 6.10. Based on the data, no significant differences were observed in the samples, except for the sample containing 0.2% catalyst in which the insoluble fraction dropped to 49%, an effect which could be attributed to increased degradation of the polymer, producing fragmented polymer chains that are soluble in dichloromethane. These results indicate that at low concentrations and after longer curing times the effect of the catalyst on the gelation is miniscule, therefore, only a small concentration of catalyst is necessary for achieving maximum attainable degree of crosslinking.





Effect of Crosslinking Time on Gel Content

The gel content was measured and plotted as a function of crosslinking time. As Figure 6.11a illustrates, the gel contents of the samples prepared with 0.5% and 1% VTMOS reached a maximum of less than 10% and remained

constant throughout the entire crosslinking period. However, those of the 3% or 5% VTMOS samples increased with crosslinking time until about 21 days, when the values began to level off to nearly 60%. When catalyst was added, as shown in Figure 6.11b, the samples prepared with 3% and 5% VTMOS achieved a higher gel content in a shorter time frame, which gradually increased to approximately 70% at the end of the crosslinking period.

Figure 6.12a shows increasing gel content with increasing L101 concentrations and increasing time. The samples with catalyst in Figure 6.12b illustrate less change in gel content over the crosslinking period. These data imply that the relationship between crosslinking time and gel content is dependent upon whether catalyst was added. In both Figures 6.11 and 6.12, it can be seen that samples with added catalyst achieved the maximum gel content in a shorter time frame than the samples without any catalyst, suggesting that the catalyst addition can increase efficiency of the overall crosslinking process.



Figure 6.11: Effect of crosslinking time and VTMOS concentration on the gel content of crosslinked samples (a) no DBTDL (b) 0.05% DBTDL



Figure 6.12: Effect of crosslinking time and L101 concentration on the gel content of crosslinked samples (a) no DBTDL (b) 0.05% DBTDL

Rate of Crosslinking

The rate of crosslinking of the samples prepared with and without catalyst was calculated based on a method derived by Kelnar and Schatz (Equation 6.6):⁶⁰

$$r(t) = \ln \left[\frac{G_{\alpha} - G_t}{G_{\alpha} - G_0} \right]$$
(6.6)

where G_t is the gel content at time t, G_{α} is the maximum gel content, and G_0 is the initial gel content. A plot of the logarithm of relative gel content as function of crosslinking time is shown in Figure 6.13. The slope of the straight line was taken as the "rate constant", which is shown in Table 6.3. The rate constant for the crosslinking reactions in the absence of DBTBL is slightly lower than that of the sample in the presence of catalyst, which confirms that DBTDL is capable of accelerating the crosslinking reaction.



Figure 6.13:Linear dependence of crosslinking time on the relative gel content of samples prepared in the presence and absence of catalyst

	Rate Constant (min ⁻¹)
No catalyst	0.001
0.05% DBDTL	0.003

 Table 6.3: Crosslinking Rate Constants of Crosslinked Samples

Degree of Swelling

According to network theory, two crosslinks per polymer molecule are sufficient to crosslink a substantial portion of chains and increase the gel content to its maximum. In other words, gel content is not necessarily an accurate measure of the crosslink density, but rather the crosslinking ability. Polymer networks with differing crosslink densities can result in the same degree of gel formation. Therefore, in order to make quantitative inferences of the crosslink density, another property must be considered—the equilibrium swelling ratio (Q). Q is defined as the volume ratio of a gel in its fully swollen state to that in its dry state. In many practical cases, the reciprocal of the swelling ratio (1/Q) is-to a good approximation-directly proportional to the crosslink density. The study of the equilibrium swelling ratio of the crosslinked PLA indicated that the degree of swelling was reduced with increasing L101, implying a tighter crosslinking network, hence a higher crosslinking density. Figure 6.14 illustrates the relationship between 1/Q and varying the initiator concentration after 28 days of curing. Comparison of the swelling ratios with the gel contents shows that more siloxane linkages were formed even after the attainable gel content was achieved.



Figure 6.14: Reciprocal swelling ratio as a function of initiator concentration determined after 28 days of crosslinking

Proof of Grafting by XPS

XPS was used to verify the presence of silicon in the crosslinked samples. Figure 6.15 displays the spectrum of PLA. Figures 6.16 through 6.18 present XPS spectra of the crosslinked PLA prepared with 0.1% L101 and 0.05% DBTDL with varying VTMOS concentrations. Figures 6.16 through 6.18 all reveal that the crosslinked PLA has additional peaks at 103 eV and 154 eV when compared to the unmodified PLA. The peak at 103 eV corresponds to Si2p and that at 154 eV is representative of Si2s. The XPS data confirm the presence of VTMOS grafting/crosslinking in the tested samples.



Figure 6.15: XPS spectrum of extruded PLA



Figure 6.16: XPS spectrum of crosslinked PLA prepared with 0.5% VTMOS



Figure 6.17: XPS spectrum of crosslinked PLA prepared with 1% VTMOS



Figure 6.18: XPS spectrum of crosslinked PLA prepared with 3% VTMOS

Effect of Crosslinking on Melt Flow Behavior

As expected, crosslinking had an appreciable effect on the melt behavior of PLA, as shown by the melt flow index (MFI) data in Table 6.4. The addition of VTMOS decreased polymer flow, eventually to levels where the MFI could not be determined due to the highly crosslinked network. Likewise, increasing the peroxide content also resulted in the greater decrement of MFI, that is, until a L101 concentration of 0.5% was reached, which increased the MFI to a measurable value. It was apparent that there was competition between grafting and chain scission and the increase in flow is believed to be a result of degradation by chain scission. Typically, the addition of excess VTMOS relative to the peroxide content will ensure that grafting prevails over chain scission.³³ However, the melt flow behavior attests that at this L101 concentration, chain scission prevailed in the linear portion of the polymer. In the highly crosslinked samples, including all of those prepared with catalyst, crosslinking reactions were dominant, preventing flow of the polymer even at elevated temperatures.

Sample #	L101 (%)	VTMOS (%)	DBTDL (%)	MFI (g/10min)
1	0	0		13.0 ± 1.7
2 "	0	0		15.8 ± 1.2
3	0.1	0		14.2 ± 1.5
4	0.1	0.5		12.4 ± 2.2
5	0.1	1		10.0 ± 1.1
6	0.1	3		
7 ***	0.1	5		
8	0.05	3		1.7 ± 0.7
9	0.2	3		
10	0.5	3		1.8 ± 0.1
11	0.05	3	0.05	
12	0.1	3	0.05	
13	0.2	3	0.05	
14 ***	0.5	3	0.05	
neat PLA				
		_		

Table 6.4: Melt Flow Index Values for Crosslinked PLA

would not melt at 190°C or 230°C

Thermal Properties

Tables 6.5 and 6.6 show the DSC data of the crosslinked samples as a function of L101 and VTMOS content, respectively. One observation that must be noted is, despite identical heating conditions, the samples that were loaded with 3% VMTOS all displayed only one melting endotherm, while those with lower VTMOS loadings showed two. This indicates the existence of a level of VTMOS, above which significant crosslinking and changes in morphology occur. In this case, that level is 3%. The presence of multiple endotherms is an effect that is often seen in PLA-based polymers and is usually a result of the melting of imperfect, lower melting crystals then their recrystallization into higher-melting, more perfect crystals. The disappearance of the higher temperature endotherm in the 3% VTMOS samples may be attributed to the presence of only one

crystalline "type" due to an increased amorphous phase by the incorporation of crosslinks. This effect may also account for the drop in crystallinity that was seen in these samples. Crosslinks work to impede mobility, preventing chains from ordering into a crystalline structure. As a result, the samples containing more crosslinks have fewer linear chains that are able to crystallize. The samples with a constant peroxide concentration and varying VTMOS concentrations (up to 3% VTMOS) are less crosslinked and therefore have more linear chains excluded from the polymer network. These chains are more likely to recrystallize into different types of crystals, thus explaining the multiple endotherms.

The glass transition, melting, and crystallization temperatures remained fairly constant throughout all sample compositions. The heats of fusion and percent crystallinities of the samples are also shown. The samples with constant VTMOS concentration showed lower crystallinities than that of the neat polymer, while those initiated with a constant amount of L101 experienced no significant change, except for the sample prepared with 3% VTMOS. The lower degree of crystallization suggests that the molecular chains were crosslinked in the amorphous state.³² Those crosslinks act as defect centers to suppress the molecular motion and impede chain folding required for crystallization, hence the decrease in crystallinity and melting enthalpies of the samples.

		Table 6.5: [DSC Data of C	rosslinked F	PLA with Vary	ing Initiator	Concentra	ations	
VTMOS (%)	L101 (%)	Τ _g (°C)	T _{m,1} (°C)	T _{m,2} (°C)	Τ _c (°C)	∆H _{m,1} (J/g)	∆H _{m,2} (J/g)	ΔHc (J/g)	χ%
0	0	58.1±1.0 ^a	146.5±1.5 ^a	153.7±1.2	106.9±3.1 ^ª	7.4±0.3 ^ª	7.7±0.6	21.1±2.4 ^a	16.1±1.1 ^a
S	0.05	57.4±0.9 ^a	148.8±0.4 ^ª	ł	122.3±2.9 ^b	14.1±0.7 ^b	ł	9.0±1.0 ^D	15.5±0.7 ^a
e	0.1	57.9±0.6 ^a	142.0±1.0 ^b	ł	111.7±1.3 ^a	11.4±0.3 ^c	ł	10.2±0.8 ^b	12.6±0.6 ^b
e	0.2	58.3±0.3 ^a	145.4±0.5 ^ª	ł	112.4±0.9 ^a	10.6±1.6 ^c	ł	9.2±0.6 ⁰	11.7±1.1 ^D
С	0.5	58.7±0.7 ^a	143.1±0.2 ^{ab}	ł	113.8±0.6 ^a	9.4±0.7 ^{ac}	ł	8.7±0.3 ^b	10.4±0.5 ^b
	Different	letters within th	le same column r	epresent signi	ficant difference	s at the 95% c	onfidence le	vel.	

MOS Concentrations
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χ%	16.1±1.1 ^a	18.3±1.7 ^a	18.2±0.7 ^a	20.5±0.9 ^ª	12.6±0.6 ^b	
ΔH _c (J/g)	21.1±2.4 ^a	17.0±0.7 ^b	23.6±3.2 ^ª	19.2±1.3 ^{ab}	10.2±0.8 ^C	vel.
ΔHm,2 (J/g)	7.7±0.6 ^a	13.6±1.2 ^b	8.3±0.2 ^a	10.9±0.8 ^C	ł	% confidence le
∆Hm,1 (J/g)	7.4±0.3 ^a	3.6±0.2 ^b	8.7±0.6 ^a	8.1±0.5 ^a	11.4±0.3 ^c	ices at the 95%
Τ _c (°C)	106.9±3.1 ^a	99.6±0.9 ⁰	109.2±0.4 ^ª	107.6±2.1 ^ª	111.7±1.3 ^a	gnificant differer
Tm,2 (°C)	153.7±1.2 ^a	152.8±0.3 ^a	154.6±0.3 ^а	153.5±1.0 ^ª	ł	nn represent siç
Tm,1 (°C)	146.5±1.5 ^a	144.4±1.3 ^a	147.4±0.6 ^a	146.3±0.8 ^ª	142.0±1.0 ^a	the same colur
 رى») (2°)	58.1±1.0 ^a	57.6±0.4 ^ª	57.2±0.9 ^ª	57.8±0.9 ^ª	57.9±0.6 ^ª	nt letters within
L101 (%)	0	0.1	0.1	0.1	0.1	Differe
VTMOS (%)	0	0	0.5	-	ო	

The DSC data of the samples prepared with catalyst are shown in Table 6.7. It was apparent that the addition of catalyst had no major effect on the T_g until the catalyst amount was raised to 0.2%, at which point the T_g decreased to nearly 52°C. At a catalyst concentration of 0.05%, the crystallinity was significantly lower than that of the other samples. Upon further catalyst addition, the degree of crystallinity progressively increased to nearly 24% at a catalyst addition of 0.2%. This, along with the decline in T_g , is attributed to the degradation caused by excess catalyst, with the resulting fragmented chains acting as plasticizers in the polymer bulk.

χ%	12.6±0.6 ^a	2.9±0.7 ^b	17.2±1.5 ^c	23.8±1.4 ^d	
ΔH _c (J/g)	10.2±.8 ^a	2.4±0.6 ^b	8.5±1.3 ^a	11.2±1.6 ^a	nfidence level.
ΔH _m (J/g)	11.4±0.3 ^a	2.7±0.9 ^b	15.6±1.8 ^c	21.6±1.2 ^d	s at the 95% cor
Τ _c (°C)	111.7±1.3 ^a	123.0±0.8 ^b	121.7±0.9 ^b	121.0±1.0 ^b	nificant difference
۳۵°) ۳۵°)	142.0±1.0 ^a	147.9±2.3 ^b	148.0±2.6 ^b	148.6±1.4 ^b	mn represent sigi
د) دن	57.9±0.6 ^a	56.9±1.1 ^a	57.2±0.9 ^a	51.6±0.2 ^b	n the same colu
SnOct ₂ (%)	0	0.05	0.1	0.2	letters withiu
L101 (%)	0.1	0.1	0.1	0.1	Different
VTMOS (%)	e	ო	ო	က	

Table 6.7: DSC Data of Crosslinked PLA with Varying Catalyst Concentrations

Thermal Stability

One of the primary objectives of crosslinking polymers, PLA in particular, is to increase the upper service temperature limit by restricting chain mobility and preventing thermal degradation when heated at or above the crystalline melting temperature. An investigation of the thermal stability of the crosslinked products was performed using TGA. The thermogravimetric results of neat PLA and VTMOS crosslinked PLA, with and without catalyst, are shown in Figures 6.19 and 6.20, respectively. As can be clearly seen from the figures, both catalyzed and uncatalyzed samples display similar trends. All of the crosslinked samples showed improved thermal stability over the neat polymer, with the exception of the sample initiated with 0.5% L101 due to its molecular weight reduction by chain scission. Figure 6.20 shows that the catalyzed samples were only slightly more thermally stable than the uncatalyzed ones. This increase in decomposition temperature could be due to a higher degree of crosslinking in this system, previously shown by increased gel content.



Figure 6.19: TGA traces of crosslinked PLA with varying initiator concentrations



Figure 6.20: TGA traces of crosslinked PLA with varying initiator concentrations prepared with 0.05% catalyst

Improvements in the thermal stability of PLA resulting from crosslinking prompted investigation of the influence of catalyst concentration on the thermal decomposition. While holding constant the initiator and VTMOS concentrations, the catalyst content was increased from 0.05% to 0.2% and the corresponding thermograms are presented in Figure 6.21. An increase in catalyst concentration did not increase the thermal stability as was expected, rather it decreased it significantly. This is most likely a result of the depolymerization of PLA with excess catalyst, providing further evidence that only a small amount of catalyst is necessary for achieving sufficient crosslinking.



Figure 6.21: TGA traces of crosslinked PLA with varying catalyst concentrations at a constant 3% VTMOS and 0.1% L101 loadings.

The TGA data show evidence of correlation between the thermal stability and crosslink density of the crosslinked samples indicating that the crosslinking reaction of VTMOS-grafted PLA could possibly raise its upper limit temperature of application. Similar results have been reported in the literature with other polymer systems.³²

Mechanical Properties

The mechanical behavior of the crosslinked polymers was investigated and is illustrated in Figure 6.22. PLA itself is a fairly brittle polymer with high strength and modulus. Crosslinking was expected to have an effect on the mechanical behavior of PLA because the strength and modulus of semicrystalline polymers are dominated by the hard crystalline regions which are held together by strong forces. With the addition of crosslinks, the polymer is unable to crystallize as easily, weakening the forces holding together the crystalline structure, usually reducing its strength and modulus. In this instance, the tensile strength and modulus remained relatively unchanged as a result of crosslinking. Since PLA remains partially crystalline even after crosslinking, the crystallites in the original polymer are responsible for the lack of any significant changes in the tensile properties.

In most cases, the elongation at break is also affected by crosslinks between chains because they tend to impose a greater restriction on the elongational properties, due to shorter segments in the polymer. This prevents chain entanglements and slippage, thereby resulting in a reduction in elongation at break. Nevertheless, in this work a reduced elongation was not seen. Interestingly, in the 3% VTMOS sample an increase in elongation was seen (from 4.3% to approximately 8%). This particular sample also had the highest gel

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content and the lowest measured crystallinity. It should be noted that in the highly crosslinked samples the properties are mainly governed by the chemically introduced crosslinks and the VTMOS grafted chain ends that are not excluded from the crosslinked network.



Figure 6.22: Mechanical properties of crosslinked PLA prepared with varying VTMOS concentrations and 0.1% L101 with 0.05% catalyst.

CONCLUSIONS

It can be concluded that VTMOS can be effectively grafted onto commercial grade PLA via a free radical initiation and the resultant polymer can successfully undergo moisture crosslinking to form siloxane linkages. Evidence of the presence of silicon moieties in the polymer was provided by XPS analysis. The effects of monomer, initiator, and catalyst concentrations on the reaction products indicated the composition corresponding to the optimum properties and showed that presence of only a small amount of catalyst showed to be a major
contributor to the crosslinking formation in the time frame investigated. Furthermore, thermogravimetric data showed an increase in thermal stability as a result of crosslinking. An investigation of the mechanical properties revealed that this crosslinking technique enabled PLA to retain its mechanical strength without resulting in polymer embrittlement.

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Chapter 7

REACTIVE COMPATIBILIZATION OF POLYLACTIC ACID AND POLYBUTYLENE ADIPATE CO-TEREPHTHLATE

INTRODUCTION

In recent years, increased interest in effectively managing global carbon resources and reducing our carbon footprints has sparked the development of compostable and biobased polymers for single-use and disposable products, specifically for blown film applications. Of the biobased polymers currently on the market, polylactic acid (PLA) is, for many reasons, a very attractive option. Notwithstanding the high strength and stiffness that PLA offers, its high T_g and susceptibility to physical aging render it hard and brittle. This, along with its low melt strength at elevated temperatures cause PLA to fall short of the necessary properties required for blown film manufacturing.

C P ir P 0 le in m pa Sj þ re pi Ot 51 PĮ S 'n ٢U Combining PLA with flexible polymers appears to be the natural solution to combat some of these issues, while extending its range of achievable properties. Polymer blending is a well-established strategy to improve properties of individual polymers and is becoming increasingly important in polymer production. Just as novel polymers are being developed from the polymerization of individual monomer units, the blending of two or more existing polymers can lead to new materials with unique properties. In doing so, properties of the individual components can be retained and combined or modified to collectively meet the various demands of the resulting polymer.¹

Blending polymers with PLA represents alternate routes to develop partially biobased materials with tailored properties, which are intermediate to or synergistically favorable to over the component homopolymers. Various properties of these polymer blends are particularly interesting as they can be related to the interactions between component phases, phase morphology, and processing parameters.

In the following sections, blends that have been produced from PLA and other polymers will be discussed. In addition, theory pertinent to polymer blending will be presented.

PLA-Based Blends

PLA has been blended with numerous different types of polymers (synthetic, organic, miscible, and immiscible) mainly for the reason of improving the ductility of PLA. From the literature, it has been found that only a limited number of polymers are able to form miscible blends with PLA. For example, low

molecular weight polyglycols are miscible with PLA at low concentrations acting as polymeric plasticizers. However, higher concentrations of polyethylene glycol (PEG), according to Sheth et al.², contribute to a decrease in modulus and elongation at break along with lower degradation temperatures. In another work, Nijenhuis et al.³ confirm these results and attributes the increased degradation to the hydrophilic nature of PEG. Polyvinyl acetate (PVAc) is another polymer that shows miscibility with PLA by the detection of a single T_g. Gajria et al.⁴ show that the addition of low concentrations of PVAc (5-30%) can increase the tensile properties to values higher than that of the pure PLA. Furthermore, studies of enzymatic degradation showed that PVAc decreases the rate of degradation of PLA. Because of this, Park and Im⁵ partially hydrolyzed PVAc into poly (vinyl acetate-co-vinyl alcohol) poly (VAc-co-VA) and studied it in blends with PLA, finding that the two polymers were miscible, but only up to 10% poly (VAc-co-VA), after which two distinct T_gs were observed.

Another family of polymers that is reportedly miscible with PLA is methacrylates. Eguiburu et al.⁶ prepared blends of PDLA and PLLA, each with poly (methyl methacrylate) (PMMA) and poly (methyl acrylate) (PMA). The blends containing amorphous PDLA exhibited miscibility over the entire composition interval presenting only one T_9 . On the other hand, the blend systems with semi-crystalline PLLA only presented some degree of miscibility in the melt, undergoing phase separation upon cooling.

Biodegradable PLA-Based Blends

Since PLA is a biodegradable polymer, blending other biodegradable polymers with PLA is a highly desirable means to alleviate some of the environmental concern regarding single-use plastics in disposable product applications. The development of a completely biodegradable blend is important to combat some of the major problems associated with the ultimate disposal of polymeric materials. Therefore, polymers such as thermoplastic starch⁷, collagen⁸, and biodegradable aliphatic polyesters and copolyesters have each been blended with PLA to achieve a polymer blend that is entirely biodegradable. Lee and Lee⁹ developed blends with PLA and polybutylene succinate adipate (PBSA) and reported properties characteristic of an incompatible blend, yielding poor tensile strengths and moduli. The strains at break and impact strengths, however, were favorably affected by the addition of PBSA, even at low concentrations.

Blends of PLA with polyhydroxybutyrate-co-hydroxyvalerate (PHBV) were investigated by Ferreira et al.¹⁰ and lannace et al..¹¹ Although, it was possible for interaction to have occurred between the two phases in both studies, the blends were immiscible as evidenced by discrete phase separation and the presence of multiple glass transitions. In addition, a direct correlation between crystallization temperature and degradation time was established, showing that the crystallinity of the blends decreased in relation to degradation time, while the crystallinity of neat PLA was seen to increase. The reason for this is that the presence of PHBV in the blend disrupted the crystallization of PLA.

Simple blends of PLA and polybutylene adipate co-terephthalate (PBAT), an aromatic, aliphatic polyester based on terephthalic acid, adipic acid, 1,4butanediol, and modular units, have also been studied. Jiang et al. described enhanced elongation and toughness with increased PBAT addition, however, at the expense of the tensile strength and modulus.^{12,13} Also with the addition of PBAT improvements in melt elasticity and viscosity were seen. A patent issued to Cortec, in which blown films were produced, reports tensile strengths up to 6940 psi and elongation values of up to 360% for blends containing 5% PLA and 40% PLA, respectively.¹⁴

One of the most notable polymer blend systems, however, is that comprising of PLA and polycaprolactone (PCL). This polymer pair has received much interest recently, especially in drug delivery systems where the need for a strong, tough biocompatible polymer exists. Miscibility, morphological, and mechanical studies have been performed on these blends and have shown immiscible phases at elevated temperatures¹⁵, along with decreased tensile behavior with PCL addition. Results also showed that the mechanical properties and morphology can be altered by varying the composition, which can be explained by the percolation theory. ¹⁶

However, given that most polymer pairs are intrinsically incompatible and form immiscible blends, their simple melt blending usually results in poor properties. The development of a blend with sufficient properties depends on the ability to control its morphology and interfacial adhesion. By reducing the components' interfacial tensions, one is able to produce an emulsifying effect,

leading to good dispersion of one phase in the other. Likewise, the generation of strong bonds at the interface can, in principle, improve the stress transfer between component phases and result in improved properties. In this respect, extensive studies of the compatibilization of PLA and biodegradable polymers using coupling agents were carried out by several authors. Some employed the use of reactive additives, such as peroxides and catalysts¹⁷⁻¹⁹, while others prepared di- or tri-block copolymers to be utilized as compatibilizers at the interface. Tsuji et al.²⁰ found that a di-block copolymer of lactic acid and caprolactone was miscible with both PLLA and PCL and improved the tensile strength, modulus, and elongation at break. Conversely, in a similar set of experiments on the mechanical behavior, Hiljanen-Vainio et al.²¹ reported that while the copolymer improved processibility and the strain at break, it decreased tensile strength and modulus. Nevertheless, the compatibilizer addition accelerated the degradation of PLLA. Dell'Erba et al.²² studied the thermal and morphological effects of a triblock copolymer on the blend, reporting a reduced domain size, signifying an emulsifying effect on the system.

Although, the blending of PLA and PBAT has been reported¹²⁻¹⁴, no systematic investigation of the properties as they pertain to phase interaction has been performed nor have any studies focused on the compatibility of the system. While PBAT and PLA are both biodegradable polyesters, PBAT is not derived from biobased feedstock. Therefore, blending PLA and PBAT not only can potentially result in a product that performs well, it can also be a practical strategy for imparting biobased content into PBAT. In this project, PLA was

reactively blended with PBAT and blown film was produced. The high ductility and toughness of PBAT permit the blend to be easily processed using standard film blowing apparatuses. The combination of the high strength and stiffness of PLA with the flexibility of PBAT can lead to a polymer capable of being blown into film resulting in synergistic properties, providing that they have sufficient interaction at their interface.

A method to obtain sufficient interaction in a phase-separated polymer blend is to add an interfacial modifier to the blend that can enhance the adhesion between the two phases and improve the properties of the resultant mixture.²³ One type of interfacial modifier that has shown significant promise is a copolymer that consists of the two monomers that comprise the individual homopolymers that are being blended. Additionally, it is well known that two polyesters can undergo a transesterification reaction in which the conversion of one or two esters into one or two other esters proceeds by reacting in the presence of heat and an alcohol, a carboxylic acid, or a catalyst.²⁴ The reaction yields a copolymer, comprising of components of the individual polyesters.

In this work, reactive extrusion was employed to improve the interaction between PLA and PBAT via a transesterification reaction. The focus of this project was on the thermal, mechanical, and morphological properties of PBAT/PLA blown films. The goal was to understand the effects of the coupling reaction on the structure of the blend and how it relates to the overall blend performance.

THEORETICAL BACKGROUND

Basic Thermodynamics of Polymer Blending

As was previously mentioned, not all polymer blends are miscible. In fact, the most polymer blends are completely immiscible or only show partial miscibility. These blends are characterized by a coarse, meta-stable morphology with poor adhesion between phases and poor performance. The best way to understand the basis of polymer blending phenomena is to consider thermodynamics, which ultimately defines miscibility given in terms of Gibbs free energy of mixing, shown in Equation 7.1:²⁵

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \tag{7.1}$$

where H_{mix} is the enthalpy of mixing, S_{mix} is the entropy of mixing, and T is temperature. It is this equation that governs the existence of a miscible or immiscible polymer mixture. To have a system with complete miscibility ΔG_{mix} must be negative, implying that for exothermic reactions spontaneous mixing will occur. For endothermic reactions only high temperatures will provide the driving force for miscibility.

The requirement that the Gibb's free energy be negative is not the only requisite in achieving miscibility because many immiscible blends can also have a value of ΔG_{mix} less than zero. For further understanding, other necessary criteria for complete thermodynamic miscibility will be discussed herein. Considering the Flory-Huggins theory of polymer solutions as it can be applied to polymer mixtures, the Gibbs free energy can be expressed by Equation 7.2:²⁶

$$\Delta G_{mix} = \left(\frac{RTV}{V_r}\right) \left[\left(\frac{\phi_A}{x_A}\right) \ln \phi_A + \left(\frac{\phi_B}{x_B}\right) \ln \phi_B + \chi_{AB} \phi_A \phi_B \right]$$
(7.2)

where V_r is a reference volume, taken as the molar volume of the smallest polymer repeat unit. ϕ_A and ϕ_B are the respective volume fractions of polymers A and B. x_A and x_B are the respective degrees of polymerization of polymers A and B. χ_{AB} is related to the enthalpy of interaction of the polymer repeat units, each having a molar volume of V_r .

By taking the second and third derivatives of ΔG with respect to the respective volume fractions and setting them both to zero (Equation 7.3) one can solve for the conditions of χ_{AB} (Equation 7.4) and the volume fractions (Equations 7.5 and 7.6) for achieving complete thermodynamic miscibility and thermodynamic stability. Meeting these conditions will indicate a homogeneous phase in a binary mixture and ensure against phase segregation. ²⁶

$$\frac{\partial^2 \Delta G_{mix}}{\partial \phi_A^2} = \frac{\partial^3 \Delta G_{mix}}{\partial^3 \phi_A^3} = 0$$
(7.3)

$$(\chi_{AB})_{cr} = \frac{1}{2} \left[\frac{1}{x_A^{1/2}} + \frac{1}{x_B^{1/2}} \right]^2$$
 (7.4)

$$(\phi_A)_{cr} = \frac{x_B^{1/2}}{x_A^{1/2} + x_B^{1/2}}$$
 (7.5)

$$(\phi_A)_{cr} = \frac{x_B^{1/2}}{x_A^{1/2} + x_B^{1/2}}$$
 (7.6)

Miscibility requires polymer mixtures to exhibit a single phase over a range of temperatures, pressures, and compositions and can be best illustrated by a phase diagram. A general view of liquid-liquid phase equilibrium is shown in Figure 7.1 (a) presenting the upper critical solution temperature (UCST) and the lower critical solution temperature (LCST). The UCST is convex upward and associated with the occurrence of an initially homogenous polymer mixture that undergoes phase separation upon lowering of temperature. When a mixture phase separates upon raising the temperature, the critical temperature is referred to as the LCST and is concave upward. Most polymer systems exhibit only an LCST because the polymer mixture generally passes through the glass transition as the temperature is lowered. If a blend is held at a temperature below the LCST, the blend will presumably be frozen in the single phase. At higher temperatures the blend components have increased molecular mobility and tend to dissociate, breaking into separate phases.²⁷

Although both the UCST and the LCST can be used to describe the generalities of thermal phase changes in polymer mixtures, in most polymer mixtures of utmost relevance is the solid-liquid equilibrium behavior as shown in Figure 7.1 (b). In such a system, polymers display two solid phases below the T_g line. At temperatures above the glass transition amorphous and glassy phases exist. Above the T_g line only a liquid mixed phase is present.



Figure 7.1: Phase diagrams showing transition behavior in polymer blends ²⁶

Miscibility Determination

Aside from the thermodynamic requisite of displaying negative Gibb's free energy, physical detection can also provide supplementary evidence of a miscible blend. Preparation of a thin film from miscible amorphous homopolymers should yield no macroscopic heterogeneity and, therefore, result in an apparent transparent material. However, it is important to point out that transparent films can also be formed by amorphous immiscible blends if the refractive indices are equal or if the size of the disperse phase is smaller than the wavelength of light.²⁸ Therefore, turbidity is not sufficient as the sole method for determination of miscibility.

The method that is perhaps the most unequivocal criterion for miscible blends is based on the glass transition temperature (T_q) determination. Phase-

separated blends have multiple T_gs , each characteristic of the respective phases, while miscible blends have a single, composition dependent glass transition temperature that falls at a temperature intermediate of those of the individual homopolymers. Several empirical equations are available that relate T_g with composition. The most common is Fox's relationship (Equation 7.7), which can be used to predict the glass transition temperature of a miscible polymer blend:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$
(7.7)

where w_1 is the mass fraction of the respective polymers and T_g is the glass transition temperature.

Aside from thermal techniques such as differential scanning calorimetry, differential thermal analysis, and dynamic mechanical analysis, electron microscopy can also be used as the existence of multiple phases is a clear indication of immiscibility.²⁸ For practical measures of miscibility detection, multiple methods should be used to ensure reliability.

Polymer Blend Morphology

The properties of immiscible polymer blends depend, to a large extent, on the arrangement of the separate phases. In other words, the morphology of a binary-phase blend governs the overall behavior. Two major morphologies can be distinguished: isolated particles dispersed in a continuous phase matrix and a two phase co-continuous morphology. In the former, the dispersed phase typically corresponds to the lower mass fraction phase and will form isolated droplets in the form of spheres, fibrils, or platelets dispersed in a continuous phase of the higher mass fraction polymer (the matrix). At higher mass fractions of the dispersed polymer phase, the polymer droplets will coalesce and form what is known as a co-continuous structure. In this morphology, two co-existing, continuous and interconnected phases are present throughout the whole blend volume.

In the case of having a dispersed phase within the matrix the properties of the matrix phase will typically dominate. In contrast, in a co-continuous, two-phase morphology the parallel arrangement allows for the properties of the blend to be spatially isotropic; both components tend to contribute simultaneously to the properties of the blend.^{28,29}

Additionally, the morphology of a polymer blend has dependence on a number of parameters, including the polymer molecules, elasticity, interfacial interaction, shear mixing, phase separation kinetics, and most importantly, the melt viscosity of the individual components and the polymer component composition.

White and Min³⁰ studied the effect of viscosity ratio on the phase morphology development during processing. The relationship between the melt viscosity and volume ratio is schematically illustrated in Figure 7.2.



Figure 7.2: Schematic representation of the effect of viscosity ratio and blend composition on the morphology development of a polymer blend

From the figure, it can be deduced that the state of dispersion depends on the concentration and the rheological properties of the individual components. The higher proportion or the less viscous component forms the continuous phase.³¹ The condition for dual phase co-continuity, as asserted by a study authored by Jordhamo, Manson, and Sperling³², is the application of shear to a polymer blend system close to the phase inversion region (the dotted horizontal line in Figure 7.2). The model predicts that phase inversion should occur when the viscosity ratio and the volume ratio are approximately equal i.e., when

$$\frac{\eta_1}{\eta_2} = \frac{\phi_1}{\phi_2}$$
(7.8)

where η_1 and η_2 are the viscosities of phases 1 and 2, respectively, ϕ_1 and ϕ_2 are the respective volume fractions of phases 1 and 2.

Tailored Polymer Blend Properties

A property of a two component polymer mixture can be described by Equation 7.9: ³³

$$P = P_1 C_1 + P_2 C_2 + I P_1 P_2 \tag{7.9}$$

where *P* is a property value and *P*₁ and *P*₂ are the component property values. *C*₁ and *C*₂ are the concentrations of the components and *I* is an interaction coefficient. The relationship between property and composition is illustrated in Figure 7.3. The desired combination of properties results in *I* being equal to zero, and the properties of the blend are a weighted arithmetic average of the component properties. In most instances, blends are incompatible with *I* having a negative value typically due to poor interfacial adhesion. In cases such as these, the blend will display poorer properties than the additive result. Very seldom a positive value of 1 generates a property synergy i.e. the resulting properties. ³³



Figure 7.3: Property-composition relationship in polymer blends

Compatibilized Polymer Blends

As previously mentioned immiscibility dominates polymer blend technology. Nevertheless, this does not mean that immiscible blends cannot provide useful properties. Fortunately, immiscible blends can be compatibilized and such blends cover a much broader scope of polymer mixtures than domiscible polymer blends. Traditionally, compatibility is thought of as a polymer mixture that does not exhibit any gross symptoms of phase separation. More recently a more suitable definition was established to define a compatible system as one which has one phase finely dispersed within the other phase, good adhesion between blend phases, strong resistance to phase coalescence, and possesses a desirable set of properties.³⁴ Consideration of the latter definition will be the basis of compatibility in the context of this work because oftentimes a polymer blend with controlled two-phase morphology is desired because of its ability to preserve the good features of each of the polymer components. In such cases it is possible to still have improved properties by a synergistic effect of the blend components. Compatibilization is essential for improved blend properties usually by achieving the following:

1. Reduction of the interfacial tension, facilitating dispersion

- 2. Stabilization morphology against high stress and strain processing
- 3. Enhancement in adhesion between the phases in the solid state to facilitate stress transfer

The above effects collectively result in a compatibilized product. Having a disparity between surface energies of the respective components will yield poor adhesion and may lead to phase separation and poor dispersion during processing, resulting in brittle behavior. Thus, adhesion is a major issue and must be fully understood in the development of polymer blends and composites alike, as it plays a crucial role in governing the morphology and hence the performance of the overall system.³⁵ Suitably, many of the same principles that apply to the composite adhesion theory discussed in Chapter 5 also apply here. In both blends and composites the key is to develop techniques and processes that will allow careful control over morphology and the interfacial polymer components.

Compatibilization of binary polymer blends is very much inspired by colloidial science. An example of this is the emulsification of two Newtonian liquids in which an emulsifier (surfactant) is added to a hydrophobic/hydrophilic mixture to improve the dispersion of one phase in another and to stabilize the

system. Polymer systems can be thought of in a similar way, where a compatibilizer or coupling agent is analogous to the emulsifier. The addition of a compatibilizer improves the interfacial adhesion between the blend constituents. In both types of systems the compatibilization effectiveness depends on the type of equipment, mixing time, size of the dispersion, relative affinity of compatibilizer to the two polymers, molecular weight of the principal ingredients, the orientation of the emulsifier at the interface, and its ability to stabilize the interface against flocculation and coalescence. ³⁶

In polymer blends the compatibilizer has segments that can specifically interact with each of the main polymeric components. During mixing it will preferentially locate at the interface between the phases and act by lowering the interfacial tension between the components leading to a well dispersed morphology. Various polymer systems are reported to have been compatibilized by a variety of methods, yielding improved properties.³⁷⁻³⁹ Some of such methods include:⁴⁰

- Incorporation of a core-shell copolymer that behaves like a multipurpose compatibilizer
- Addition of block or graft copolymers (non-reactive blending) that are miscible with one or both phases
- Addition of bi-functional polymers with one part miscible with one component and the second with the other component
- Induction of *in situ* grafting (reactive blending) designed to enhance
 domain interactions

Reactive Compatibilization

Of specific interest in this project is the *in situ* formation of a copolymer and its ability to improve the compatibility between immiscible pairs in polymer blends. This commonly used and cost-effective method is arguably the best strategy to produce new, multiphase polymeric materials from existing polymers with superior properties. The copolymer formed at the interface is comparable to a pre-made copolymer that is typically added at the interface of physical polymer blends; it acts to reduce the interfacial tension between the phases, promote adhesion between polymers, and stabilize the phase morphology.³⁶ For the successful execution of this technique four fundamental criteria must be fulfilled:^{36,41}

- 1. Adequate mixing to ensure the necessary distribution and dispersion of one polymer within another
- 2. The presence of proper functional groups in each phase capable of reacting across the polymer-polymer interface
- 3. The ability for reactions to occur in the extruder in the available residence time
- 4. The formation of stable bonds across the interface during processing.

If these criteria are met, the result is a compatible blend whose degree of compatibility is based on experimentally measured properties, some of which will be discussed in the following section.

EXPERIMENTAL

Materials

PLA (4042D) was obtained from Natureworks LLC. PBAT (Ecoflex F BX7011) (Figure 7.4) from BASF with a density of 1.26 g/cm³, a molecular weight of 55,000 g/mol, and a melting temperature of 120°C was also used. Stannous 2-ethylhexanoate (SnOct₂) (Figure 7.5) was purchased from Sigma Aldrich and used as the transesterification catalyst.



Figure 7.4: Structure of poly (butylene adipate co-terephthalate) (PBAT)



Figure 7.5: Structure of stannous 2-ethylhexanoate (SnOct₂)

Methods

Reactive Blending of PLA/PBAT Blends

Prior to extrusion, PLA and PBAT pellets were oven dried at 85°C for 24 hours. PBAT, PLA, and catalyst were weighed and manually tumble-mixed before being fed into the feeder of a Century ZSK-30 twin screw extruder. The compositions of the blends are listed in Table 7.1. The extruder barrel is comprised of nine zones, whose temperatures are presented in Table 7.2. All

polymer blend compositions were extruded at 150 rpm. Upon exiting the die the extrudate was cooled through a waterbath and pelletized downstream. Pellets were collected and oven dried for 48 hours at 65°C.

Blend Composition (wt%)					
PLA	PBAT	SnOct ₂			
30	70	0			
50	50	0			
70	30	0			
30	70	0.05			
50	50	0.05			
70	30	0.05			
30	70	0.10			
50	50	0.10			
70	30	0.10			
30	70	0.50			
50	50	0.50			
70	30	0.50			

Table 7.1: PBAT/PLA Blend Compositions

 Table 7.2: Extrusion Processing Conditions for PBAT/PLA Blends

Temperature (°C)										
Zone	1	2	3	4	5	6	7	8	9	Die
	25	95	160	165	170	180	180	180	170	165

Blown Film Extrusion

The dried extrusion-blended pellets were blown into films using a Killion single-screw blown film extruder with a screw diameter of 25.4 mm and a length-diameter ratio of 25.1. Films were blown through an inner die with a diameter of 50.8 mm and a die gap size of 1.5 mm. The film blowing conditions are shown in Table 7.3.

Temperature (°C)							
Zone 1	Zone 2	Zone 3	Clamp Ring	Adaptor	Die 1	Die 2	
205	205	205	205	202	199	174	

 Table 7.3: Blown Film Processing Conditions for PBAT/PLA Blends

Mechanical Properties

Tensile tests were performed using a UTS Mechanical Testing Apparatus (Model SFM-20) fitted with a 100 lb load cell. Testing was done as per the ASTM D882⁴³ standard on specimens mounted both parallel to the axis of film processing (the machine direction) (MD) and perpendicular to the processing axis (the transverse direction) (TD), with the average of 8 specimens reported. Tear resistance was determined using the trouser test method (ASTM D 1938-02a)⁴⁴ on film specimens approximately 1 mm in thickness.

Differential Scanning Calorimetry (DSC)

Thermal transitions of the blends were measured by means of DSC. Film samples were heated to 200°C at a rate of 30°C/min and held for 5 minutes in a nitrogen atmosphere. With prior thermal history erased the samples were cooled at a rate of 30°C/min then reheated to 200°C at a rate of 5°C/min. Cold crystallization, melting, and glass transition temperatures were obtained from the second heating scan. The degrees of crystallinity of the composites were calculated according to Equation 3.2, using 115 J/g or 93.7 J/g for the respective heats of fusion for PBAT and PLA.

Thermogravimetric Analysis (TGA)

A high resolution thermal gravimetric analyzer (Model 2950) from TA Instruments was used to determine the thermal decomposition temperature of the neat polymers and of the blends. Films were heated from room temperature to 500°C at a heating rate of 10°C/min under a nitrogen atmosphere. The thermal stabilities of the blends were evaluated based on the weight loss percentage versus temperature curves.

Thermo-mechanical Analysis

Dynamic mechanical analysis (DMA) was performed on a TA 2980 DMA. Film specimens were cut along the machine direction having dimensions of 30 mm (length) x 6.45 mm (width) x 0.1 mm (thickness) and mounted in a tension clamp. All films, except for the PLA cast film, were heated from -50°C to 140°C at a rate of 2°C/min. The PLA film was heated from 20°C to 140°C. Tests were run at an amplitude of 50 μ m and a frequency of 1 Hz. Storage modulus (E'), loss modulus (E'), and tan δ (E''/E'') were recorded as a function of temperature.

Gel Permeation Chromatography (GPC)

Molecular weight measurements of the blends were carried out in a Waters GPC system equipped with an isocratic 1515 HPLC pump (flow rate = 1 mL/min), a 2414 refractive index detector, and a 717 autosampler. Samples were dissolved in tetrahydrofuran in concentrations of 2 mg/mL. Molecular weights (M_n and M_w) and molecular weight distributions were calculated using a universal calibration curve constructed with polystyrene standards.

Transmission Electron Microscopy (TEM)

The effects of catalyst concentration on the morphology of the blends were examined using TEM. Using an ultramicrotome, samples were cryogenically sectioned from an extruded pellet in a plane perpendicular to the

extrusion direction. For each sample, a formvar film was used for support and mounted on a copper grid. Sections were examined under a JEOL JEM-100CX II TEM through condenser aperture #1, using objective aperature #2, and an accelerating voltage of 100 kV.

Statistical Analysis

Statistical analysis was performed using SPSS software for Windows. Data were compared using analysis of variance (ANOVA) and a Tukey post-ANOVA test ($p \le 0.05$).

RESULTS AND DISCUSSION

Proposed Transesterification Reaction

A possible transesterification reaction between the PBAT and PLA is depicted in Figure 7.6. The proposed reaction induces the *in situ* formation of a diblock copolymer at the interface between the two phases in the phaseseparated system. The copolymer is expected to act as an interfacial modifier to strengthen the interfacial region between the blend components resulting in improved properties of the blend.



Figure 7.6: Possible transesterification reaction between PLA and PBAT

Mechanical Properties of Blends

Tensile Behavior

The tensile properties of the films are given in Figures 7.7 and 7.8. In the physical blends increasing the PLA content was seen to progressively increase the tensile strength and decrease the elongation in both the machine and transverse directions. This was expected because PLA is stronger and more brittle than PBAT. Upon the addition of catalyst, a noticeable effect was seen in the low PLA composition. In these samples, the tensile strengths of the blends containing a minimal amount of catalyst were enhanced compared to the physical blend. For example, in the blends containing 30% PLA, the addition of 0.05% catalyst gave the most significant increase from 31.3 MPa to 58.4 MPa in

the machine direction and 15.3 MPa to 35.3 MPa in the transverse direction. At higher PLA concentrations, however, the addition of catalyst resulted in no significant change in strength as compared to the physical blends. It was also apparent that the tensile properties began to deteriorate at catalyst levels exceeding this optimum concentration and this was the case for films tested in both the machine and transverse directions.



Figure 7.7: Tensile strength of PBAT/PLA films tested in the machine direction



Figure 7.8: Tensile strength of PBAT/PLA films tested in the transverse direction

The effect of catalyst concentration on the elongation was also examined. Figures 7.9 and 7.10 show that at a low PLA concentration (30%), the SnOct₂ addition resulted in a continuous increase in elongation at break with catalyst in both directions, but particularly in the machine direction. The sample containing 50% PLA showed an increase only with 0.05% SnOct₂. Beyond this catalyst concentration a drastic decrease in elongation at break was observed. The samples containing 70% PLA displayed brittle behavior, characteristic of neat PLA, which further decreased with catalyst addition. It is known that the elongation at break of a blend is sensitive to the strength at the interface between components, reflecting the degree of compatibilization. Thus, the improved elongation is an indication of a stronger bond between components. The lack of improvement at high PLA concentrations suggests minimal mixing in this composition range; otherwise, the PBAT phase would have had a toughening effect on the PLA rather than increasing the brittleness.



Figure 7.9: Elongation at break of PBAT/PLA films tested in the machine direction



Figure 7.10: Elongation at break of PBAT/PLA films tested in the transverse direction

Not only are the mechanical properties of the films dependent on the intermolecular forces, chain stiffness, and molecular symmetry of the individual polymers, they also depend on the orientation of the films. It was observed that the mechanical properties of the films tested in the machine direction were slightly higher than those tested in the transverse direction. Blown films are typically anisotropically oriented, with their molecular chain axis lying in the plane parallel to the processing direction. The alignment due to the blown film processing dominated the film's properties and can be explained by realizing that, parallel to the orientation (in the machine direction), stresses are exerted largely on the primary bonds of the polymer chain, while in the transverse direction, forces are applied to the weaker secondary bonds between polymer chains.⁴⁵

Orientation also played a role in the elongation at break of the blends. The samples containing a low PLA content showed greater elongations at break in the direction perpendicular to the direction of orientation, which is the opposite of what was observed in the tensile behavior. This can be best explained by the re-orientation that takes place among the molecules that occurs as a perpendicular stress is applied. The molecules first disorient; then, when stress is applied they re-orient themselves in the direction of the applied stress. This, consequently results in an elongation at break characteristic of an elongation ensuing from the parallel direction, combined with that associated with the disorientation and reorientation of the molecules. ⁴⁵

Tear Strength

Plots of tear resistance versus blend composition for films tested in both the machine direction (MD) and the transverse direction (TD) are shown in Figure 7.11 and Figure 7.12, respectively. In both directions the tear resistance of the blends increased with increasing SnOct₂ content for films with 30% PLA. However, the overall tear strength in the TD was greater than the corresponding tear strength in the MD. Clearly, this behavior is plausible due to the formation of chemical or physical linkages between the two polyesters. These linkages may have resulted in a network structure and thus, induced increased tear strength in the transverse direction all while restricting chain movement in the longitudinal direction.⁴⁶

Furthermore, the superior tear strength of the catalyzed blends can be attributed to increased compatibilization. Li and Wong⁴⁷ showed that, in general, tear resistance increases as the degree of transesterification increases, but decreases with a decline in molecular weight. Therefore, optimal tear strength may be achieved with conditions that favor a balance between a high degree of transesterification and minimal degradation.⁴⁷


Figure 7.11: Tear resistance of PBAT/PLA films tested in the machine direction



Figure 7.12: Tear resistance of PBAT/PLA films tested in the transverse direction

It is important to note that with regard to the mechanical properties, the effects of transesterification are dependent upon the composition of the blend. It relies on whether PBAT or PLA makes up the major phase. When PLA is the minor component, the tensile strength, tear strength, and elongation at break values of the blends prepared with catalyst show improved properties over those of the physical blends. This is because this composition is more suitable for resistance to failure due to the blend morphology, which will be discussed in a subsequent section. Conversely, for the blends in which PLA was the major component, the catalyst addition had an adverse effect on the properties. This could be due to the catalyst-induced degradation of PLA or to poor mixing during the reaction, causing dramatic embrittlement and lower tear properties. On the basis of mechanical property analysis, there appears to be more association between the polymer phases when PBAT was the majority phase.

Molecular Weight of PBAT/PLA Blends

Molecular weight is an important factor in reactive blending because the mechanical properties of the resulting blends depend largely on the molecular weight of the polymer components. To understand the effect of blending and catalyst concentration on the PBAT/PLA blends, the molecular weights of the neat polymers along with the PBAT/PLA blend compositions with and without catalyst were determined by GPC. The chromatograms are presented in Figure 7.13. Each of the 30:70 PBAT/PLA (Figure 7.13a) blends displayed in multiple peaks, where the 70:30 PBAT/PLA (Figure 7.13b) and the 50:50 PBAT/PLA (Figure 7.13c) blends each exhibited one peak indicating the compatibilization effect of the catalyst at higher PBAT concentrations.

In the 30:70 PBAT/PLA blends, both peaks broadened and decreased in intensity with increasing catalyst concentration, showing predominant

degradation of the PLA phase. The other blend compositions also experienced a shift to higher retention times with increased catalyst concentration indicating lower molecular weights.

The GPC data of the 70:30 PBAT/PLA samples are summarized in Table 7.4. As shown, the molecular weights decreased with SnOct₂ concentration. From the mechanical property data it is assumed that the SnOct₂ promoted transesterification between PBAT and PLA. However, it has been reported that in excess transesterification reactions in PLA are associated with reverse depolymerization, leading to lower molecular weights, broadening of molecular weight distribution, and deterioration of polymer properties.⁴⁸

These data, along with investigation mechanical properties, suggest that transesterification promoted degradation and copolymer formation, both of which contributed to the properties of the blends. When the SnOct₂ content was low (0.05%), copolymer formation dominated the properties, evidenced by increased tensile properties. However, with higher SnOct₂ content the properties were governed by the degradation, explaining the lower molecular weight and decreased strength.



Figure 7.13: GPC traces of PBAT/PLA blends for the following compositions: (a) 30:70; (b) 70:30; (c) 50:50

Blend Composition	M _n (g/mol)	M _w (g/	'mol)	N	l _w ∕M _n
PBAT	80026	± 504	114796	± 693	1.43	± 0.02
PLA PBAT/PLA	105488	± 524	166156	± 497	1.58	± 0.01
70/30 PBAT/PLA/SnOct ₂	85570	± 1324	126477	± 1839	1.48	± 0.05
(70/30/0.05) PBAT/PLA/SnOct ₂	72505	± 1577	113450	± 2737	1.56	± 0.07
(70/30/0.1) PBAT/PLA/SnOct ₂	64164	± 1797	105845	± 2577	1.65	± 0.08
(70/30/0.5)	55772	± 1185	95970	± 1689	1.72	± 0.07

Table 7.4: Molecular Weights and Molecular Weight Distributions of PBAT/PLA Blends

Thermal Properties

Differential Scanning Calorimetry

Within one polymer the presence of another polymer can, in effect, alter the cooperative segmental movement of the polymer chain, changing its thermal transition behavior. Therefore, the determination of the thermal transitions of blends proves to be useful in revealing interactions between respective polymers. Table 7.5 shows the transition temperatures of the physical blends and of the 70:30 PBAT/PLA compositions with varying catalyst concentrations. PBAT and PLA each showed one glass transition (T_g) identified at 59.7°C and -32.5°C, respectively. The blends were characterized by two distinct T_gs , representative of their parent polymers. The T_gs of the PBAT component in the blends shifted to higher temperatures, but were essentially independent of the nominal composition, whereas the PLA component showed minimal change. This represents the lack of significant molecular interactions between the polymers, confirming the presence of separate phases after the initial melting.⁴⁹

In the catalyzed blends, the addition of catalyst appeared to have little effect on the thermal behavior at all blend compositions. Like the neat blends, the catalyzed blends also showed two distinct T_gs , corresponding to the separate polymers, confirming the immiscibility of the polymers, even with added catalyst. At high catalyst concentration, the T_g of the PBAT component shifted from -9.9°C in the physical blend to -6.1°C in the blend containing 0.5% catalyst, while that of the PLA phase shifted from 57.6°C to 48.8°C. Since the T_g is a measure of molecular mobility of the chains, these shifts, although minimal, were attributed to active interaction between PLA and PBAT chains at 0.5% catalyst. The fact that the PLA component shifted by a larger degree shows that the transesterification reaction has more of an effect on the PLA phase than on the PBAT phase.

The temperatures of cold crystallization (T_c) shifted to lower temperatures and exhibited narrower peak widths, indicating an enhanced crystallizability of PLA in the blends containing catalyst. This shift in T_c parallels the convergence in glass transition temperatures and points to the possibility of enhanced compatibility in this temperature regime as a result of high catalyst addition.

The melting behavior of the physical blends was characterized by an endotherm and a small shoulder. In the reactive blends, the addition of catalyst appeared to separate the melting endotherm and shoulder into two distinct endotherms. While multiple endotherms are guite common in PLA-based

polymers ^{50, 51}, their presence quite possibly could indicate the formation of a new crystalline structure induced by the coupling of PLA and PBAT. The lower temperature endotherm shifted to lower temperatures while the higher one remained unchanged with increasing catalyst. The decreased melting temperature is a result of defects in the crystallites resulting from the presence of PLA/PBAT copolymers or other by-products of the interchange reactions.

The degrees of crystallization of the blends, χ_c are also shown in Table 7.5. Of the physical blends, that which contains 70% PBAT possessed the highest crystallinity (52.7%). This value decreased as PLA content increased. In the reactive blends, the crystallinity initially decreased with catalyst concentration to 11.2%, then increased to 23% at 0.5% catalyst. The increased crystallinity at the high catalyst concentration can be related to the lower molecular weight of this system. Within a lower molecular weight polymer, polymer chains can easily rearrange and align themselves to result in a more crystalline structure.

Sample	Т _{g, РВАТ} (°C)	T _{g,PLA} (°C)	T _{m,PBAT} (°C)	T _{m,1} (°C)	Τ _{m.2} (°C)	Τ _c (°C)	х (%)
Compositions withou	<u>it catalyst</u>					6.	
PBAT	-32.5± 0.5	ł	120.1 ± 1.1	1	ł	78.9±1.1 [°]	0.15± 0.0 [−]
PLA	:	59.7 ± 0.8 ^a	ł	150.9 ± 2.0 ^a	ł	$115.8 \pm 2.7^{\rm b}$	1.40 ± 0.2^{0}
PBAT/PLA 70:30	-9.9 ± 0.8 ^b	57.6 ± 0.2 ^a	ł	ł	148.2 ± 0.9 ^a	$114.3 \pm 0.4^{\rm D}$	52.7 ± 0.9 ^c
PBAT/PLA 50:50	-9.3 ± 0.1 ^b	58.3 ± 0.7 ^a	ł	ł	148.3 ± 0.6 ^a	115.1 ± 2.6 ^b	24.3 ± 0.3 ^d
PBAT/PLA 30:70	-7.6 ± 0.4 ^c	58.6 ± 0.9 ^a	ł	ł	148.3 ± 0.4 ^a	113.9 ± 0.4 ^b	20.7 ± 0.4 ^d
Compositions with c	<u>atalyst</u>						
PBAT/PLA/SnOct ₂ 70:30:0.05	-8.1 ± 0.7 ^{bc}	56.5 ± 1.1 ^a	ł	146.9 ± 0.4 ^b	149.12 ±1.2 ^a	105.6 ± 1.3 ^c	17.4 ± 0.3 ^e
PBAT/PLA/SnOct ₂ 70:30:0.1	-4.4 ± 1.2 ^d	55.4 ± 1.5 ^a	ł	147.4 ± 0.1 ^b	153.5 ± 2.5 ^b	111.9 ± 0.8 ^b	11.2 ± 0.6 ^f
PBAT/PLA/SnOct ₂ 70:30:0.5	-6.1 ± 0.2 ^d	48.8 ± 0.3 ^b	ł	139.2 ± 0.6 ^c	148.5 ± 1.0 ^a	93.9 ± 0.4 ^d	23.0 ± 0.2 ^d
Different letters v	within the same c	olumn represent	significant differe	ences at the 95%	confidence level.		

Table 7.5: DSC Data of PBAT/PLA Blends

Thermomechanical Analysis

The dynamic mechanical response of a material is sensitive to the quality of bonding between polymers. Therefore, as a complementary tool to DSC, DMA was used to investigate relaxation phenomena in the blends. The dynamic mechanical properties of the physical PBAT/PLA blends, along with those of the pure polymers, are shown in Figures 7.14 through 7.16. The representative curves of the dynamic storage moduli as a function of temperature are depicted in Figure 7.14. It is apparent that PBAT and PLA each exhibit sharp, one-step glass-to-rubbery transitions whereas the blends show intermediate broad twostep transitions.

The blends showed a progressive increase in storage moduli as the PLA content increased. Increasing the PLA content suitably decreased the flexibility of the blend and correspondingly increased the dynamic storage moduli over that of pure PBAT.



Figure 7.14: Storage modulus curves of PBAT/PLA physical blends

Figure 7.15 shows the loss modulus curves of the blends and of the pure polymers. The maximum peak intensity of the loss modulus curves is directly proportional to the volume fraction of the individual phases present in the blend. Increasing the PLA concentration in the blend resulted in a corresponding increase in peak intensity. In addition, the temperatures corresponding to the peaks represent the T_g s of the polymers. PBAT and PLA have respective peaks at -22°C and 71°C. Their blends had two peaks, each corresponding to the PBAT and PLA components.



Figure 7.15: Loss modulus curves of PBAT/PLA physical blends

Another parameter related to the glass transition is the loss factor (tan δ), which is shown as a function of temperature for the PBAT/PLA blends in Figure 7.16. It represents the changes taking place in the polymer molecules during dynamic mechanical testing. Similar behavior to the loss moduli was seen in which no major shifts in the lower temperature transition was discernible, while the peak corresponding to PLA gradually shifted to lower temperatures with decreasing PLA contents.



Figure 7.16: Tan δ curves of PBAT/PLA physical blends

The storage modulus curves of the 70:30 PBAT/PLA catalyzed blends are shown in Figure 7.17. Similar to the physical blends, two relaxation processes can be distinctively identified and are associated with the transition of each phase. The shapes of the curves were identical; however, the magnitudes of the curves changed with catalyst concentration. The magnitude and nature of the change in the storage modulus are dependent on the overall composition of the polymer blends and are determined both by the intermolecular and intramolecular interactions; the latter having greater influence in the different physical states of the polymer.⁵² The low temperature inflections that correspond to the relaxation of PBAT are apparent between -30°C and -10°C, while the

relaxations around 50°C are attributed to the glass-to-rubber transition of PLA. The blend prepared with 0.05% catalyst displayed the highest storage modulus, followed by the sample prepared with 0.5% catalyst, the physical blend, and finally the blend with 0.1% catalyst. The concentrations of PLA and PBAT in the blends were essentially constant throughout all of the samples, indicating that any differences in moduli are a result of differing morphologies caused varying catalyst concentrations. Going from completely incompatible phases in the physical blend to a more compatible blend, the modulus increased due to an increase in interfacial interaction resulting from the transesterfication reaction. An exception is the sample prepared with 0.1% catalyst, which displayed the lowest storage modulus values across the entire temperature range. This can be explained by the morphological differences in this sample and will be discussed in the following section.



Figure 7.17: Storage modulus curves of PBAT/PLA curves with varying catalyst concentrations

The loss modului of the catalyzed blends are shown in Figure 7.18, in which the peak positions represent the temperatures associated with the glass transitions. The $T_{g}s$ representative of the PLA component were found to slightly shift to lower temperatures, which indicate some interaction between PBAT and PLA with catalyst addition. These temperatures, as well as those of the physical blends, differ significantly from the T_{g} results found by DSC. DSC and DMA have different sensitivities as a result of testing in either static or dynamic modes. DMA is usually more sensitive for identifying transitions in polymeric materials, such as the additional transition that appears at 100°C in the 0.5% catalyst system that is not apparent in its DSC thermogram.

The additional peak, interestingly, was not apparent in any of the other blend compositions. Extra peaks in loss moduli curves of various systems have been reported and result from a variety of different pheonomena.^{53,54} Similarly, the tan δ plots (Figure 7.19) yielded two additional peaks located at around 80°C and 100°C. These additional peaks are attributable to either: (1) the glass transition temperature of the new copolymer formed at the interface as a result of the transesterification reaction; (2) the recrystallization of PLA; or (3) the formation of thermal lag in different portions of the specimen. ^{53, 54, 55}



Figure 7.18: Loss modulus curves of PBAT/PLA curves with varying catalyst concentrations



Figure 7.19: Tan δ curves of PBAT/PLA curves with varying catalyst concentrations

Thermogravimetry

TGA was performed on the samples and the weight loss, due to the volatilization of the degradation products, was monitored as a function of temperature. Figure 7.20 reveals the degradation behavior of the neat polymers and the physical blends. PLA and PBAT each exhibit one-step degradation profiles and the blends show multiple-step degradation processes with varying rates of degradation. In the initial stages of degradation the thermal stabilities of the blends increased as PBAT concentration increased and were intermediate to the two polymers. The reverse was true in the later stages of degradation, where the thermal stabilities of the blends exceeded those of PBAT.



Figure 7.20: TGA thermograms of PBAT/PLA physical blends

TGA profiles of the 70:30 PBAT/PLA catalyzed blends are displayed in Figure 7.21. Each curve shows decreased thermal stability with catalyst addition. To quantify the effect of added catalyst on the thermal degradation of the blends differential thermogravimetry (DTG) profiles were studied. From these first derivative curves (Figure 7.22) the decomposition temperatures (T_{max}) were determined, which represent the maximum rate of weight loss. Each blend exhibits a two-step decomposition profile, except for the blend prepared with 0.5% catalyst. This blend underwent a three-step decomposition confirmed by the presence of a third peak. The additional T_{max} peak was ascribed to the T_{max} of the copolymer that was formed or to that of the degraded polymer, which was possibly facilitated by the thermal degradation products of PLA.



Figure 7.21: TGA thermograms of PBAT/PLA blends showing the effect of catalyst concentration on the decomposition behavior



Figure 7.22: Differential thermogravimetric curves of 70:30 PBAT/PLA films showing effect of catalyst concentration on the decomposition temperatures

Table 7.6 lists the onset temperature ($T_{1\%}$) and the T_{max} values of the catalyzed blends. The $T_{1\%}$ decreased upon catalyst addition with no significant changes thereafter ($p \ge 0.05$). The T_{max} values corresponding to PLA decreased with catalyst concentration, while those corresponding to PBAT remained unchanged until a catalyst concentration of 0.5% was reached, at which time the T_{max} decreased by nearly 30°C. These results indicate that SnOct₂ promoted thermal degradation in PLA more so than in PBAT. The structural changes that resulted from the compatibilization reaction interfered with the thermal stability of the parent polymers, particularly PLA. Such changes apparently resulted in a structure that was more susceptible to thermal degradation.

Sample	T _{1%} (°C)	T _{max} (°C)	T _{max} (°C)	T _{max} (°C)
PBAT	324.7±6.3 ^a	368.8±3.5 ^a		
PLA	316.4±2.1 ^a	330.4±3.1 ^b		
PBAT/PLA 70:30	314.9±3.9 ^a	339.6±3.7 ^b	368.9±2.6 ^a	
PBAT/PLA/SnOct ₂ 70:30:0.05	292.8±3.3 ^b	305.7±5.1 ^c	369.9±4.9 ^a	
PBAT/PLA/SnOct ₂ 70:30:0.1	291.8±4.1 ^b	301.3±2.8 ^c	369.9±1.6 ^ª	
PBAT/PLA/SnOct ₂ 70:30:0.5	277.3±7.1 ^b	285.3±1.2 ^d	340.3±6.1 ^b	373.8±2.7

 Table 7.6: Thermogravimetric Parameters of PBAT/PLA Blends

Different letters within the same column represent significant differences at the 95% confidence level.

Blend Morphology

The majority of polymer blend properties are influenced by the final morphology. Therefore, in studying the compatibilization of polymer blends, it is necessary to understand the relationship between polymer morphology and the properties it dictates. The morphology of the PBAT/PLA blends was analyzed by examination of the cryo-sectioned surfaces of the blend pellets. Contrast was apparent without staining and evolved from the structural differences between the polymers. PLA is considered "electron transparent" because inelastically scattered electrons are transmitted through the objective lens aperture, rather than being intercepted by it.⁵⁶ Because of this, PLA appears as the lighter phase. The PBAT phase, being more electron-dense, was able to scatter and absorb more electrons, therefore appears as the darker phase.

Each blend micrograph depicts a binary structure with one or more of the following phase morphologies:

- Dispersions of one phase containing a portion of the continuous phase to form composite inclusions
- (2) An interpenetrating co-continuous structure in which both phases of equal composition co-exist in an interconnected network structure
- (3) A morphology in which droplets of one phase are dispersed throughout a continuous phase of the other polymer

Examples of each of these phase morphologies are shown in Figure 7.23 through Figure 31. In the PBAT/PLA 70:30 physical blend (Figure 7.23), PBAT is the continuous phase containing PLA island-like domains. Within the PLA phase are PBAT sub-inclusions. This morphology, whereby the dispersed phase contains small domains of the matrix phase, represents a phenomenon known as phase inversion and has been studied by numerous researchers.⁵⁷⁻⁵⁹ This occurrence is believed to be associated with a thermodynamic change where the dispersed phase inverts, becoming the major continuous phase in order to minimize the free energy.⁶⁰ Phase inversion is related to the viscosity ratio and proper control of mixing. It is postulated that the lower viscosity PLA initially formed the matrix containing droplets of PBAT. As the PBAT concentration increased and began to disperse in the PLA component matrix, a percolation threshold was reached, causing the blend to invert in phase continuity. Similar morphology has been reported in studies by Favis and Chalifoux⁶¹ on PE/PS and

PP/PC blends and Astruc and Navard⁶² on PDMS/HPC (hydroxypropylcellulose) blends.

As the PLA content increased, the size of its domains also increased and began to form a semi-continuous phase in which PBAT was dispersed, while PBAT also existed as the continuous phase (Figure 7.24). In this PBAT/PLA 50:50 blend the morphology is considered to be co-continuous. With more PLA, as shown in Figure 7.25, PLA became the continuous phase as a result of the higher concentration and lower viscosity of PLA, both of which promote droplet agglomeration during extrusion processing.²²



Figure 7.23: TEM micrograph of the 70:30 PBAT/PLA physical blend



Figure 7.24: TEM micrograph of 50:50 PBAT/PLA physical blend



Figure 7.25: TEM micrograph of 30:70 PBAT/PLA physical blend

Effect of Catalyst on the Morphology

TEM micrographs representative of the blends prepared with 0.05% SnOct₂ are shown in Figures 7.26 through 7.28. A dramatic morphology change was observed from that of the physical blends. Comparison of the catalyzed and uncatalyzed blends shows that the morphologies transformed from having larger phases to being composed of much smaller, discrete phases. This change is particularly apparent in the 70:30 PBAT/PLA and 50:50 PBAT/PLA blends. Specifically, in the catalyzed 70:30 PBAT/PLA blend (Figure 7.26) the domain size of PLA was significantly reduced as compared to the uncatalyzed blend in Figure 7.23. In the catalyzed blend well defined particles were dispersed throughout the PBAT matrix and elongated parallel to the extrusion direction. In the intermediate composition (50:50 PBAT/PLA), shown in Figure 7.27, the micrograph displayed non-uniformly shaped and dispersed droplets, much different from the co-continuous morphology of the uncatalyzed sample. It is evident that both of these blends were stabilized by the catalyst addition.

Figure 7.28 shows the 30:70 PBAT/PLA blend in which PLA makes up the continuous phase wherein PBAT droplets are dispersed. This composition appeared to be the least affected by catalyst addition as evidenced by the both morphology and the mechanical properities.

The observed differences in morphology between the reactive and the non-reactive blend compositions can be attributed to the differences in melt viscosities of the polymer phases and to the extent of reaction between PLA and PBAT at different blend compositions.⁵⁷ The transesterifcation that is expected to have occurred during melt blending contributed to the formation of copolymers at the interface, which, in effect, aided in suppressing coalescence, promoted finely dispersed phases, and substantially narrowed the size distribution of the dispersed phase.



Figure 7.26: TEM micrograph of 70:30 PBAT/PLA blend prepared with 0.05% $$SnOct_2$$



Figure 7.27: TEM micrograph of 50:50 PBAT/PLA blend prepared with 0.05% SnOct₂



Figure 7.28: TEM micrograph of 30:70 PBAT/PLA blend prepared with 0.05% SnOct₂

The blends that showed changes in morphology with catalyst addition are those that showed improved tensile properties from the physical blends. The enhanced interaction of PLA and PBAT promoted better adhesion between the phases, thus, improved stress transfer across the interface. To further examine the relationship between the properties and their governing morphologies, a closer look was taken at the 70:30 PBAT/PLA blend composition. The effect of the catalyst concentration on the blend morphology development was observed. Figures 7.29 through 7.32 depict the morphology of the blends with varying concentrations of catalyst. Figure 7.29 shows another view of the physical blend displaying the aforementioned subinclusions. From Figure 7.30 it can be seen that the addition of a small amount of catalyst (0.05%) was sufficient to break up the droplets of PLA and hamper particle-particle coalescence while dispersing them throughout the PBAT matrix.

An increase of catalyst (to 0.1%) resulted in a morphology with even smaller, more uniform particles that are better dispersed throughout the matrix (Figure 7.31). Evidence of the relationship between the size of the dispersed phase and the dynamic mechanical properties can be seen here. As shown by the DMA curves (Figures 7.17 and 7.18) in the previous section, it was this composition (containing 0.1% catalyst) that had the lowest loss and storage moduli. The mechanical loss peaks decreased in amplitude with decreasing phase size because of the increasing mechanical isolation of the smaller phases.⁶³ The smaller phase size can also be correlated to the drastic decrease that was seen in the storage modulus. The considerably small phase size of the dispersed PLA in this blend (with 0.1% catalyst) allowed it to only minimally contribute to the stiffening effect of the polymer as shown in Figure 7.18.



Figure 7.29: TEM micrograph of 70:30 PBAT/PLA physical blend.



Figure 7.30: TEM micrograph of 70:30 PBAT/PLA blend prepared with 0.05% SnOct₂



Figure 7.31: TEM micrograph of 70:30 PBAT/PLA blend prepared with 0.1% $$SnOct_2$$

Surprisingly, additional catalyst did not further reduce the particle size. In fact, upon the addition of 0.5% catalyst there was a stronger tendency for phase coarsening. Not only did the PLA phases become larger, they also became much less discrete, making the interface between domains less defined. This system is shown in Figure 7.32. Higher magnifications of this sample permitted the phases to be observed more clearly, as shown in Figure 7.33. This micrograph shows a partially co-continuous morphology along with some phase inversion. This composition also had the lowest tensile properties of any of the blends.

One reason for the phase coarsening and mechanical property decrease could be the decrease in molecular weight with high catalyst concentration. Fortelny et al.⁶⁴ proposed a model that takes into account the classical theory of phase break-up and the coalescence effect. According to his hypothesis a drop in viscosity or a molecular weight decrease lowers the dispersive forces, making phase coalescence more favorable.⁶⁵ In other words the molecular weight of the polymers controls the surface area of the interfacial region where compatibilization takes place, thus, affecting the ultimate phase morphology of the system. Another possible explanation is the possibility of reaching the critical micelle concentration, the concentration at which micelles are formed. If this occurs the copolymer formed at the interface may migrate from this region leading to an increase in domain size.⁶⁶ Nevertheless, the morphology at this composition suggests that a critical concentration of copolymer or compatibilizer is required to saturate the interface of a binary blend.

Another noteworthy observation in the sample prepared with 0.5% catalyst was the appearance of small black particles which are thought to be residual tin particles from the added stannous octoate. These particles, which are in the range of the size necessary to nucleate a polymer, can provide a qualitative explanation for the increased crystallization of this blend, as observed by the DSC data.

It is apparent that the high activity of the catalyst, in excess amounts, could yield adverse results. The best morphology was seen in the sample with 0.1% SnOct₂, however, the highest strength was seen in the sample with 0.05%

SnOct₂. While it is possible that more interaction could have occurred with higher catalyst, degradation also took place, which deteriorated the mechanical properties. Overall these observations lend further support to the fact that these blends were compatibilized during reactive melt blending as a result of SnOct₂ addition.



Figure 7.32: TEM micrograph of 70:30 PBAT/PLA blend prepared with 0.5% SnOct₂



Figure 7.33: TEM micrograph of 70:30 PBAT/PLA blend prepared with 0.5% SnOct₂ taken at 40,000X magnification

CONCLUSIONS

The *in situ* transesterification of PBAT/PLA blends was achieved via reactive compatibilization and the compatibilized products were successfully blown into film. Thermal, mechanical, and morphological properties of blends were investigated and confirmed the use of SnOct₂ to be effective for PBAT/PLA compatibilization. In the PBAT-rich compositions a low but optimum concentration of SnOct₂ gave the highest mechanical properties with an elongation to break of up to 350% and tensile strength improvements of nearly 190% over the physical blend. Thermal data revealed distinct transitions,

indicating immiscibility across the entire composition range. However, shifts in thermal transitions suggested some interaction at the molecular level for the catalyzed samples and enhanced nucleation at high catalyst concentrations.

Molecular weight data showed degradation of the blends with the catalyst addition suggesting the competition between ester-exchange reactions and degradation. Morphological observation confirmed interaction between polymer phases by improved dispersion, distribution, and reduction in domain size.
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Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

In this contribution it has been shown that PLA-based systems are compounds of rather great potential for applications requiring biobased content, biodegradation, and sufficient properties. The goal of this work, as illustrated in Chapter 1, was to develop new PLA-based materials by reactive modification in an effort to overcome some of the inherent drawbacks of PLA. Chapters 4 through 7 describe in detail the work done towards meeting this goal. Detailed conclusions for each project are summarized in its respective chapter, however a general summary is provided below.

The study reported in Chapter 4 of this dissertation showed that maleic anhydride-grafted PLA can be initiated by the use of two structurally different peroxides—L101 and T301. It was reported that T301 yielded products with

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higher molecular weight when compared to L101. It was also discussed that there exists an optimum monomer-to-initiator ratio that should be employed in order to obtain the correct balance between grafting and molecular weight. Nevertheless, the maleated copolymer was shown to be effective when used as an interfacial modifier in PLA-talc composites as presented in Chapter 5. In that chapter, the influence of MAPLA on the mechanical and thermal behavior of the composites was investigated. It was found that MAPLA, when added in an optimum concentration, improved the tensile strength and crystallization of the Furthermore, the thermomechanical analysis together with composite. microscopic observation confirmed the compatibilization effect of MAPLA in PLAtalc composites. In Chapter 6 of this dissertation, it was demonstrated that PLA can be functionalized with vinyltrimethoxysilane and subsequently crosslinked in the presence of moisture. Thermal and mechanical characterization revealed that the crosslinking increased the thermal stability while maintaining the mechanical strength of PLA. In the final project discussed in Chapter 7 blown films comprising of reactively compatibilized PLA-PBAT blends were produced. The films exhibited enhanced interfacial interaction when compared to the physical blends, shown by mechanical property improvements as well as enhanced dispersion and reduced domain size of the dispersed phase. Moreover, the results confirmed the compatibilization effect of the reaction.

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RECOMMENDATIONS FOR FUTURE WORK

Maleated Polylactic Acid (MAPLA) as an Interfacial Modifier in Polylactic Acid-Talc Composites

- Mechanical property determination of PLA/MAPLA/Talc composites containing varying amounts of talc
- Compounding PLA/talc composites using a MAPLA masterbatch formulation to minimize thermal degradation of MAPLA

Reactive Modification of Polylactic Acid by Silane Grafting and Crosslinking Reactions

- Viscoelastic study of the crosslinked PLA to determine the effects of crosslinking on the rheological properties
- Determination of grafting yield by FTIR peak deconvolution and supplemented by elemental analysis techniques
- NMR study of silane-grafted polymer
- Incorporation of biofibers into silane-crosslinked PLA to impart more biobased content and the investigation of the thermal and mechanical properties of the composite for applications requiring thermal stability
- Use of crosslinked PLA as a self-reinforcing agent into linear PLA

Reactive Compatibilization of Polylactic Acid and Polybutylene Adipate co-Terephthlate Blends

- Attainment a suitable solvent to selectively extract one component of the polymer blend to determine relative degree of reaction and further characterization of copolymer
- Deconvolution of GPC peaks to accurately determine the molecular weight of each component
- Water vapor and oxygen permeability study of compatibilized PLA/PBAT blown films
- Use of organic peroxides to compatibilize PBAT and PLA by crosslinking reactions

