Novel bio-based and biodegradable polymer blends

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Novel bio-based and biodegradable polymer blends

by

Shengzhe Yang

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
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ABSTRACT

Most plastic materials, including high performance thermoplastics and thermosets are produced entirely from petroleum-based products. The volatility of the natural oil markets and the increasing cost of petroleum have led to a push to reduce the dependence on petroleum products. Together with an increase in environmental awareness, this has promoted the use of alternative, biorenewable, environmentally-friendly products, such as biomass. The growing interest in replacing petroleum-based products by inexpensive, renewable, natural materials is important for sustainable development into the future and will have a significant impact on the polymer industry and the environment. This thesis involved characterization and development of two series of novel bio-based polymer blends, namely polyhydroxyalkanoate (PHA)/polyamide (PA) and poly(lactic acid) (PLA)/soy protein. Blends with different concentrations and compatible microstructures were prepared using twin-screw extruder. For PHA/PA blends, the poor mechanical properties of PHA improved significantly with an excellent combination of strength, stiffness and toughness by adding PA. Furthermore, the effect of blending on the viscoelastic properties has been investigated using small-amplitude oscillatory shear flow experiments as a function of blend composition and angular frequency. The elastic shear modulus ($G'$) and complex viscosity of the blends increased significantly with increasing the concentration of PHA. Blending PLA with soy protein aims at reducing production cost, as well as accelerating the biodegradation rate in soil medium. In this work, the mechanical, thermal and morphological properties of the blends were investigated using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC),
thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and tensile tests.
CHAPTER 1: GENERAL INTRODUCTION

1.1 Organization

This thesis is composed of a general introduction, a conclusion section, and two main chapters which are each manuscripts to be submitted for publication. The first chapter outlines the motivation of this work and background information of relevant bio-based materials, including the abatement of petroleum plastics usage and the development of bio-based polymers. The second chapter involves the characterization and development of a series of novel bio-based polyhydroxyalkanoate (PHA)/polyamide (PA) blends. A significant improvement of the mechanical properties of PHA was achieved by adding PA, including an excellent combination of strength, stiffness and toughness. The third chapter includes the characterization and biodegradation behavior of poly(lactic acid) (PLA)/soy protein blends. After being buried in soil environments, the morphological and thermal properties of biodegraded samples were characterized at different biodegradation stages, with targets of reducing production cost and increasing degradation rate. The last chapter provides general conclusions and suggestions for future work.

1.2 Motivation and objectives

The motivation behind why we are interested in this field is to reduce our carbon footprint and our dependence on fossil fuels as feedstock for organic materials. Usually,
most of the traditional plastics are derived from fossil carbon, which pollute the natural ecosystems with the accumulation of these discarded and stubborn plastic wastes. Therefore, although petroleum-based plastics possess durability and low-cost, they will be ultimately replaced by renewable and bio-based polymers from the viewpoint of producing green environmentally products. The applications of bio-based polymers appeared since 1980s and have attracted more attention worldwide recently, since they can be produced from renewable resources, thus reducing our carbon footprint [1]. Bio-based and biodegradable polymers are a growing field, which will play nonnegligible roles in the following years. We estimate that the capacity for the production of bio-based plastics will be expected to reach more than three million tons in 2020. The research goal for this thesis is to develop novel bio-based alternatives. This effort is divided into two parts, PHA/PA blends and PLA/soy protein blends, respectively. The section on PHA/PA concentrates on improving mechanical properties of PHA by adding PA while blending PLA with soy protein aims at reducing production cost, as well as accelerating the biodegradation rate in soil medium.

1.3 Background and literature review

1.3.1 Polyhydroxyalkanoate (PHA)

Polyhydroxyalkanoates (PHAs) are bacterial polyesters produced in nature by different microorganisms as a storage material [2, 3]. PHAs contain over 90 types of monomers ranging from rigid plastics to tough elastomers, which predominantly depend
on the molecular structure. Specifically, some of them are constituted by monomers of short chain length consisting of 3-5 carbon atoms (PHA\textsubscript{SCL}). For instance, PHB (poly-3-hydroxybutyrate), is a kind of brittle and rigid homopolymer with high crystallinity [4], which lacks the superior mechanical properties required for packaging applications. Other types of PHAs contain medium chain length monomer consisting of 6-14 carbons (PHA\textsubscript{MCL}), such as carboxymethylchitosan-g-medium chain length polyhydroxyalkanoates. Usually, PHA\textsubscript{MCL} is elastomeric, has high flexibility, but with low crystallinity and mechanical strength compared to PHA\textsubscript{SCL}. The most common PHAs are PHB, PHV (polyhydroxyvalerate), and PHH (polyhydroxyhexanoate). The PHAs chemical structure can be defined as a polymeric chain below and the properties can vary based on the composition of attached R-group.

![Fig. 1.1 General structure of PHA](image)

Fig. 1.1 General structure of PHA
Table 1.1 Representative PHAs defined by their respective R group

<table>
<thead>
<tr>
<th>R-Group</th>
<th>Full Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-H</td>
<td>Polyhydroxypropionate</td>
<td>PHP</td>
</tr>
<tr>
<td>-CH₃</td>
<td>Polyhydroxybutyrate</td>
<td>PHB</td>
</tr>
<tr>
<td>-CH₂CH₃</td>
<td>Polyhydroxyvalerate</td>
<td>PHV</td>
</tr>
<tr>
<td>-CH₂CH₃CH₃</td>
<td>Polyhydroxyhexanoate</td>
<td>PHH</td>
</tr>
</tbody>
</table>

Among the all the family members of PHAs, PHB is simple but has the potential to be a high volume commercial product due to its abundance, which is the first member of PHAs to be discovered in microorganisms. There are multiple diverse products can be obtained from PHB, such as plastics, chemicals and feed supplements. Thanks to its relative simplicity of biosynthesis, it has received the most attention as a target molecular. As biodegradable bioplastics, PHB has a low permeability for water vapor, which makes it possible to play a major role in packaging markets of food industry [5]. In addition, PHB is able to be produced in large amounts from a readily convertible polymeric chemical precursor in biological systems because of the ability as an inert granular material in a cell [3]. Another application of PHB involves food supplements, which has been shown to have nutritional value in studies with sheep, pigs and fish [3, 6, 7].

As for PHAs production, the first report on this area was published in 1992 by Poirier [8]. From then on, hundreds of articles have been reported and researchers have also succeeded in producing PHA_{SCL} as well as PHA_{MCL} by diverting carbon atoms away. For instance, Tilbrook and Gebbie have described the production of PHAs for bioplastics production in high biomass crops [9]. To develop this promising and renewable material, numerous scientists made efforts to make it functionally equivalent to many of the
petroleum-based plastics in the current market. Physical blending and chemical copolymerization of PHAs with suitable polymers are effective methods to improve physical and mechanical properties [10-17]. In this work, physical blending was chosen to produce novel materials with desirable properties.

1.3.2 Polyamide (PA)

Polyamide (PA) is a kind of common engineering plastics containing monomers of amides jointed by peptide bonds. Generally, it has low tensile strength and melting point, but extreme durability and high ductility [18-20]. Such properties make it extensively and commonly used in a wide variety of industrial applications [21-23]. In academic areas, PA also plays a major role that serves as the additive to toughen other well-known polymers such as polypropylene, polyethylene, and poly(vinyl acetate) [24-26]. Different types of PA compose a big polyamide family, including aliphatic and aromatic polyamides. In this project, we used tall-oil based polyamide as an additive to enhance the toughness of PHA.

The manufacture of tall-oil based polyamide starts with tall oil. Tall oil is a viscous yellow-black odorous liquid, which can be obtained from pine tree and as a byproduct of the pulp and paper industry. When getting tall oil, we can use it to make unsaturated fatty acids and after that procedure producing dimer fatty acids through dimerization is available. The last process is polycondensation, and finally this special PA can be obtained, which possesses high flexibility, good processability, as well as excellent water resistance.
1.3.3 Poly(lactic acid) (PLA)

Poly(lactic acid) or polylactide (PLA) is a translucent aliphatic polyester made entirely from various natural sources found in great abundance like tapioca, corn, sugar beets, wheat and etc. It is composed of repeating units of lactide, which is biorenewable and biodegradable. As can be seen from its chemical structure, each repeating unit has a methyl side group, connecting with each other through ester linkages. As with some common polymers, PLA is a semi-crystalline polymer. The degree of crystallinity is about 35-40% [27]. It is a recyclable thermoplastic as the structure doesn’t form crosslinks. Mechanically, it is strong and rigid but brittle.

\[
\begin{align*}
\text{CH}_3 & \\
\text{O} & \\
\text{O} & \\
\text{CH} & \\
\text{C} & \\
\end{align*}
\]

\[n\]

Fig. 1.2 Chemical structure of polylactide

The polymerization pathway of PLA can be performed in two ways. One is the condensation of the lactic acid monomers to form lactides, via using ring opening polymerization (ROMP) with various metal catalysts. The other way is the direct condensation of lactic acid monomers. The process is done at a temperature less than 200 °C. Beyond 200 °C, the lactide monomer will be formed. The problem with direct condensation is that, it will produce a lot of water and that will weaken the polymerization. The polymer chains will be shorter. There is a better stepwise way to do the direct condensation to avoid producing that much water.
PLA has good properties in comparison to other common commercial materials such as high density polyethylene and polystyrene. In some aspects, like tensile strength and tensile modulus, PLA is as good as polyethylene and polystyrene; however, PLA is not good enough in terms of maximum elongation. The good point is that this drawback can be fixed by blending it with other polymers to improve the property and achieve better performance. For instance, Feng et.al (2010) reported that blending PLA with PA for improving the toughness was an efficient method [28]. Hsu et.al (2000) studied PLA/polyurethane blends for the purpose of improving the cellular affinity and tissue repair on polyurethanes [29]. Rodriguez et.al (2006) blended PLA with poly(e-caprolactone) to study their crystallization, morphology and mechanical behavior [30]. In this work, we blended PLA with soy protein aiming at reducing production cost, as well as accelerating the biodegradation rate in soil medium.

1.3.4 Soy protein

Soy protein is a protein that is derived from soybeans. It is renewable, biodegradable, and has been extensively used in a variety of food products including beverage powders, cheeses, frozen desserts, breads, pastas, and salad dressings. After extracting from crushed soybean oil, three kinds of high protein commercial products can be obtained from the residue: soy protein isolate (SPI), soy protein concentrate (SPC), and soy flour. SPI is a high-quality plant protein source with a minimum protein content of 90% on the moisture-free basis [31]. SPC contains 65-72% protein, which is made by removing part of the carbohydrates from defatted soybeans [32, 33]. Soy flour, with about 50% protein content inside, can be produced by grinding soybeans into fine powders.
Soy protein based plastics is a promising and significant product for commercial plastic application [34]. The major drawback of this plastic is the high water sensitivity, which has been reported to increase the weight of soy protein sheets by more than 180% water when submerged in water [34]. Another common issue is that the protein films are often quite stiff and brittle because of extensive intermolecular interactions between molecular chains. This work concentrates on resolving aforementioned issues by plasticizers, in order to induce flexibility and water resistance of soy protein based plastics.

Many of the cyclic anhydrides have been used as the plasticizers to protein based plastics, for example, maleic anhydride (MA) and phthalic anhydride (PA) were compounded in conjunction with glycerol or water to produce relatively water stable products [35-39]. In this work, adipic anhydride (AA) was used to enhance the compatibilization and miscibility of SPA/PLA blends. Adipic anhydride is a derivate of adipic acid prepared by its reaction with an acid chloride, such as acetyl chloride. The chemical structure of adipic anhydride can be defined below.

![Chemical structure of adipic anhydride](image)

**Fig. 1.3 Chemical structure of adipic anhydride**
1.4 Reference


A paper to be submitted to *Journal of Applied Polymer Science*

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2.1 Abstract

A series of bio-based Polyhydroxyalkanoate (PHA) /Polyamide (PA) blends with different concentrations were mechanically melt processed using a twin-screw extruder and evaluated for physical characteristics. The effects of blending on viscoelastic properties were investigated using small-amplitude oscillatory shear flow experiments to model the physical character as a function of blend composition and angular frequency. The mechanical, thermal and morphological properties of the blends were investigated using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and tensile
The elastic shear modulus ($G'$) and complex viscosity of the blends increased significantly with increasing concentration of PHA. In addition, the tensile strength of the blends increased markedly as the content of PHA increased. For blends containing PA at greater than 50 wt%, samples failed only after a very large elongation (up to 465%) without significant decrease in tensile strength. The particle size significantly increased and the blends became more brittle with increasing concentration of PHA. In addition, the concentration of the PA had a substantial effect on the glass relaxation temperature of the resulting blends.

### 2.2 Introduction

The use of petroleum-based plastics for products and packaging has become ubiquitous in industry, a trend that is contributing heavily to ecological problems such as increased CO$_2$ levels, pollution of land and waterways, and overloading of the solid-waste stream. Although petroleum plastics are extremely versatile and fulfil the performance requirements for a multitude of applications, increasing public awareness of their environmental impacts has spurred efforts to replace, petroleum feedstocks with sustainable and eco-friendly alternatives [1-15]. Driven by the desire to reduce our carbon footprint and dependence on fossil carbon sources, bio-based polymers and composites are becoming widely utilized in polymer manufacturing and medical applications [16-18].

Some types of bio-based polymers can be produced by naturally occurring biological systems. For example, polyhydroxyalkanoates (PHAs) are aliphatic thermoplastic
polyesters synthesized via metabolic pathways of microorganisms by fermentation of sugars or lipids [19]. PHAs containing over 90 types of monomers have been synthesized in different microorganisms. The characteristics of PHAs range from rigid plastics to tough elastomers and depend on their molecular structure; specifically, the properties of PHAs are highly dependent on the copolymer composition. Generally, PHAs are rigid but brittle, with poor impact resistance and flexibility, issues that restrict the applications for which PHAs can be used as alternatives to traditional petroleum-based plastics. Most of the efforts aimed at improving the toughness of PHA have focused on blending PHA with other polymers such as polylactide or thermoplastic starch [19-22]. The majority of reports regarding PHA blend focus on only a few aspects of their character, such as viscoelastic or rheological properties, instead of providing a comprehensive characterization of the material, and there have been very few investigations comparing PHA blends with other common commercial polymer blends such as polylactide and polypropylene.

Polyamide (PA) is a resin containing monomers of amides jointed by peptide bonds, and can be made artificially through step-growth polymerization or solid-phase synthesis. PA has been widely used in blends with various polymers such as polylactide to facilitate a good combination of toughness and stiffness [23]. Hydrogen bonding between the molecules results in good mechanical performances both in the crystalline and amorphous states. Most PAs have high viscosity and flexibility, which has led to their wide use as a bio-based polymer binder in the ink industry. Despite its popularity for ink applications, few studies have examined the processing and characterization of PHA/PA blends prepared by melt mixing. In this report we present the results of our evaluation and characterization
of the mechanical, rheological, morphological, and thermomechanical properties of PHA and PA blends prepared by compression molding. The PA we used is tall-oil based, which is manufactured from tall oil and processed through dimerization and polycondensation. Tall oil is a viscous yellow-black liquid that can be obtained from pine tree and as a by-product of the pulp and paper industry. All polymers used in our study were commercially available and bio-based.

2.3 Experimental section

2.3.1 Materials

Polyhydroxyalkanoate Mirel P1003 (Compression molding grade resins) was supplied by Metabolix Inc., Cambridge, MA 02139, and the Polyamide UNI-REZ™ 2651 was obtained from Arizona Chemical Inc., Jacksonville, FL.

PHA (Mirel P1003) is made by fermentation of renewable bio-based feedstock, making it fully bio-based in neat form. Mirel P1003 is a blend of PHB and poly(3-hydroxybutyrate-co-4-hydroxybutyrate). UNI-REZ™ 2651 is a thermoplastic polyamide which was developed for high viscosity, high flexibility, low softening point, low temperature flexibility, and water resistance. 2.3.2 Micro-compounding and Compression Molding

Complete drying of PHA and PA was accomplished by heating the material in a vacuum oven for 8 hours at 60 °C. The desired amounts of PHA and PA granules were fed into a twin-screw microcompounder (DACA Instrument, Santa Barbara, CA) set to 185 °C
and a rotation speed of 100 rpm. The mixing time was controlled for 10 minutes to facilitate homogenous melt compounding. The extruded materials were then compression molded at 185 ºC to prepare the samples for dynamic mechanical analysis (DMA).

2.3.3 Measurements

Scanning electron microscopy

The fracture surface morphology of PHA/PA blends (weight percent ratios of 20/80, 50/50, and 80/20, respectively) was examined using SEM. The tensile-fractured samples were fixed on the SEM holders after sputter coating with a thin gold layer. The prepared samples were characterized using a field-emission scanning electron microscope (FE-SEM, FEI Quanta 250) operating at 10 kV under high vacuum.

Rheological measurements

The rheological properties of blends were investigated under an AR2000ex rheometer (TA Instruments, New Castle, DE) with parallel plates of 25 mm diameter. All measurements were performed under temperature accuracy of ± 0.1 ºC. A platinum resistance thermometer (PRT) sensor positioned at the center of the plate ensured optimum temperature stability and control. The rheological experiments were studied on angular frequency sweeps at 180 ºC to evaluate the complex viscosity and shear storage modulus. All measurements of PHA/PA blends (weight percent ratios of 20/80, 50/50, and 80/20) were examined and compared in frequency sweep testing mode.
DMA measurements

The Dynamic mechanical analysis (DMA) was performed with a DMA Q800 dynamic mechanical analyzer from TA Instruments. All samples were measured with a film-tension mode of 1 Hz. Rectangular specimens of 0.9 mm × 5 mm (thickness × width) were used for the analysis. The samples were cooled and held isothermally for 3 min at -100 °C before the temperature was increased to 100 °C at a rate of 3°C/min.

DSC measurements

Differential scanning calorimetry (DSC) measurements were performed using a thermal analyzer (TA Instrument Q2000) to study the melting and crystallization behavior of PHA/PA blends. All DSC measurements were carried out in nitrogen atmosphere. The samples were heated from room temperature to 200 °C at a heating rate of 20 °C/min to erase their anterior thermal history, equilibrated at 200 °C and then cooled to room temperature at a cooling rate of 20 °C/min. The crystallization temperature ($T_c$) was evaluated using the exothermic crystallization peak. After that, the samples were reheated to 200 °C at the same constant rate, measuring the second heating curves as well as the cooling curves. The melting temperature ($T_m$) of all samples was determined from the maximum of the endothermic melting peak. Samples of 5 mg were cut from the films and used for analysis.

TGA measurements

A Q50 (New Castle, DE) thermogravimetric analyzer (TGA) from TA Instruments
was employed to investigate the thermal stability of PHA/PA blends. The samples were heated from room temperature to 600°C at a heating rate of 20°C/min under nitrogen atmosphere. Generally, 20 mg samples were used for the TGA.

**Mechanical properties**

The tensile performance of the samples was determined using an Instron universal testing machine at extension rate of 50.0 mm/min using a static load cell (±2 kN). Rectangular specimens of 50 mm × 10 mm (length × width) were used. Average values were calculated from at least three replicates of each sample. The toughness of the polymer was determined from the area under the corresponding tensile stress-strain curves.

**2.4 Results and discussion**

Scanning electron microscopy (SEM) is a kind of well-established techniques widely employed to investigate the internal structure or morphology of biodegradable polymers [24-27]. For the PHA/PA blends, the fracture surface morphology was investigated with different weight ratios. Fig. 2.1 shows the facture morphology of specimens after the tensile testing. Two-phase structure can be easily observed for different blend compositions. A relatively smooth surface topography was observed for the PHA/PA (20/80) blend. With increasing PHA content, the particle size significantly increased and the surface eroded that etched with well-defined pits. When the PHA concentration increased to 50 weight percent, the spherical particles of PHA were pulled out from the
surface, which shows strong interfacial adhesions of the two phases. With the PHA content up to 80 weight percent, the blend agglomerated into ca. 60-80 μm large, individual irregular pieces during melt compounding. It is apparent that the blends become more brittle with increasing concentration of PHA.

SEM micro graphics for the PHA/PA (80/20) blend are shown at different magnifications in Fig. 2.2. The landform on the fracture surface was disorderly and resembled unsystematic crushed aggregates. The two components appeared completely separated, which allowed the hybrid to be easily broken into small pieces. Because the final mechanical properties of composites are highly dependent on their morphology [28,29], the fragile character of the PHA/PA (80/20) blend led to difficulty in testing the tensile strength of this specific specimen.
Fig. 2.1. SEM images of fracture surface morphologies of PHA/PA blends (a) PHA/PA (20/80); (b) PHA/PA (50/50); (c) PHA/PA (80/20).
We hypothesized that the weight percent ratio of the PHA/PA blends would have a significant influence on the viscoelastic properties. For this reason, the rheological behavior of this blend was studied as a function of classical angular frequency by using small-amplitude oscillatory shear flow experiments. Fig. 2.3 compares the effect of dynamic frequency on the viscoelastic behavior in PHA/PA blends, showing the dependence of complex viscosity, $\eta^*$, at the same temperature, 180 °C. It is apparent that $\eta^*$ decreased gradually and systematically with increasing PA content over angular frequencies ranging from 0.1 to 10 rad/s. This phenomenon indicated that the incorporated PA particles led to less viscous PHA granules because the molten PHA was more sticky than PA at elevated temperature. A possible explanation is that PHA has greater intermolecular chains interaction than PA [30]. The elastic shear modulus ($G'$) of the blends also exhibited an increase with increasing PHA load in the PA matrix, which was attributed to the stiffness imparted to the overall matrix by the PHA particles.
The effect of blend ratio of PHA and PA on the dynamic mechanical properties of the material was investigated in the temperature range from -100 °C to 100 °C. The variation of the storage modulus (E') and loss tangent (tan δ) of the pure PHA, PA and their blends are shown in Fig. 2.4. The sample of PHA/PA (80/20) is not included because it is too brittle to prepare reliable dimensions for the DMA measurements. As can be seen from Fig. 2.4(a), the storage modulus at the glassy region decreased dramatically as the amount of PA increased. With increasing PA loadings up to 50 weight percent, the storage modulus of the PHA blends showed a noticeable decrease to almost one third of the neat PHA. At the rubbery plateau this trend became more prominent. When the temperature elevated above
50 °C, it was observed that the storage modulus of the blends decreased much more remarkably than that of the pure PHA. At higher temperatures (T \geq 75 °C), E’ decreased very sharply due to the melting of the crystalline region in the blend and the possible explanation for this phenomenon is the slippage of large-scale molecular chains [31].

The tan δ curve of the PHA/PA blends as a function of blend composition is presented in Fig. 2.4(b). Clearly, the concentration of the PA has a considerable effect on the glass relaxation temperature of the resulting blends. The tan δ peak magnitudes of blends decreased after the loading of PA, related to the modulus drop. Meanwhile, the position of the relaxation peak shifted towards lower temperature with increasing PA content. It is known that relaxation peak can be directly associated with the glass transition temperature \( T_g \) of the hybrid as well as to the drop of storage tensile modulus [32]. Consequently, determined from the position of relaxation peak, \( T_g \) became lower as the amount of PA increases. Since the tan δ curve of neat PHA seems irregular compared with the rest, this warrants further investigation.
Fig. 2.4. Comparison of (a) dynamic storage moduli, $E'$, and (b) tan $\delta$ curves of the PHA/PA blends as a function of blend composition.
Differential scanning calorimetry was used to measure the temperatures and heat flow during thermal transitions of PHA/PA blends. The crystallization behavior of semi-crystalline polymers has a substantial effect on their mechanical properties and the second phase additives affect the crystallinity of the binary polymer blends [33, 34]. The DSC traces for PHA/PA blends during the second heating scan as a function of blend composition are shown in Fig. 2.5. The first heating process, from room temperature to 200 °C at a heating rate of 20 °C/min, was used to destroy all memory of past thermal history and stress. For the pure PHA, PHA/PA (80/20) and PHA/PA (50/50), the curves displayed two endothermic peaks due to primary and secondary crystallization processes. These double melting peaks were found after the complete crystallization cooling from the melting also confirmed and ascribed to the existence of melt-recrystallization mechanisms [35-38]. The less perfect crystals melted at lower temperature firstly, and after that, at higher temperature, the sample reorganized into more perfect crystals and melt during the heating process. Table 2.1 compares the melting enthalpy ($\Delta H_m$) and melting temperature ($T_m$) of PHA, PHA/PA (80/20) and PHA/PA (50/50), exhibiting that the melting points of the blends decreased as the concentration of the polyamide increased. The $\Delta H_m$ calculated by integrating for the area of two bimodal melting peaks. As a function of blend composition, $\Delta H_m$ decreased dramatically with increasing polyamide content as seen from the data in the table. For pure PA and PHA/PA (20/80), no melt endothermic peak in the obtained DSC curves can be observed, showing no apparent phase transitions in the temperature range of room temperature to 200 °C. Compared with the values of the $\Delta H_m$
and $T_m$, they show the same declining trend, indicating that amorphous substance PA did a negative impact on the appearance of the melting peak.

![DSC heating scan for PHA/PA blends](image)

**Fig. 2.5.** DSC heating scan for PHA/PA blends: The DSC measurements were carried out at 20 °C/min heating rate (second heating run).

The DSC was also carried out to determine the release of heat in the exothermic cold crystallization process of PHA/PA blends. The latent heat is released during the phase change. This macroscopic process is closely related to the rate of the crystallization process [39, 40]. The DSC thermograms for PHA/PA blends during the first cooling scan as a function of blend composition are shown in Fig. 2.6. Noticeable are the samples containing higher PHA loadings that exhibit even sharper and more intense peaks than the rest. The pure PHA underwent a remarkable cold crystallization process with the peak of cold
crystallization temperature ($T_c$) at approx. 108 °C. Likewise, for PHA/PA (80/20) and PHA/PA (50/50), they experienced similar tendencies of crystallization process. As can be seen from Table 1, the value of cold crystallization enthalpy ($\Delta H_c$) and cold crystallization temperature ($T_c$) for PHA, PHA/PA (80/20) and PHA/PA (50/50) decreased systematically as the concentration of the polyamide increased.

Fig. 2.6. DSC cooling scan for PHA/PA blends: The DSC measurements were carried out at 20 °C /min cooling rate (first cooling run).

The degree of crystallinity ($X_c$) was estimated from the melting enthalpies determined by calorimetry, and the higher the crystallinity, the more the melting heat needed for
destroying the crystal structure. $X_c$ was ascertained by Eq.(1) [41], considering a melting enthalpy of 142 J/g for 100% crystalline PHB as cited in literature [42,43].

$$X_c = \frac{\Delta H_m}{W_p \times \Delta H_{m100\%}} \times 100\%$$ (1)

Where $X_c$ is the crystallinity (%), $\Delta H_m$ is the melting enthalpy of the polymer (J/g), $W_p$ is the proportion of the polymer in the blend, and $\Delta H_{m100\%}$ is the melting enthalpy of the 100% crystalline polymer.

Table 2.1. Summary of melting enthalpy, melting temperature, cold crystallization enthalpy, cold crystallization temperature and degree of crystallinity of PHA and PHA/PA blends under nitrogen atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>Neat PHA</th>
<th>PHA/PA (80/20)</th>
<th>PHA/PA (50/50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_m$ (J/g)</td>
<td>32.30</td>
<td>25.45</td>
<td>10.78</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>166.48</td>
<td>162.76</td>
<td>161.59</td>
</tr>
<tr>
<td>$\Delta H_c$ (J/g)</td>
<td>30.52</td>
<td>23.61</td>
<td>10.72</td>
</tr>
<tr>
<td>$T_c$ (°C)</td>
<td>108.76</td>
<td>107.13</td>
<td>103.65</td>
</tr>
<tr>
<td>$X_c$ (%)</td>
<td>22.75</td>
<td>22.40</td>
<td>15.18</td>
</tr>
</tbody>
</table>

On the basis of results in Table 1, the degree of crystallinity depends substantially on the blend composition. Specifically, the degree of crystallinity decreased with increasing PA concentration. Overall, the quantity of amorphous substance resulted in an overall decrease in the crystallization behavior.
The thermal degradation behavior of PHA/PA blends was studied by TGA, which uses heat to induce chemical and physical changes in materials and performs a corresponding measurement of mass change as a function of temperature. The TGA profile, as seen from Fig. 2.7, suggests that decomposition started during melting and terminated with a weight loss corresponding to the content of blend composition. It was found that the pure PHA and PA degraded in only a one-stage process; while the PHA/PA blends showed a very distinct two-stage degradation pattern. The bio-based blends experienced significant weight loss between 200 and 450 °C, with the weight loss peak at approximately 250 °C and 400 °C. Above 600 °C no obvious further weight loss was observed during pyrolysis in inert nitrogen atmosphere.
Fig. 2.7. Comparison of (a) thermal degradation and (b) derivative weight changes of the PHA/PA blends at a heating rate of 20 °C/min under nitrogen atmosphere.

Table 2.2. Summary of thermogravimetric analysis of PHA/PA blends under nitrogen atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>Neat PHA</th>
<th>PHA/PA (80/20)</th>
<th>PHA/PA (50/50)</th>
<th>PHA/PA (20/80)</th>
<th>Neat PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{10} (°C)</td>
<td>252.75</td>
<td>233.30</td>
<td>245.07</td>
<td>241.78</td>
<td>364.09</td>
</tr>
<tr>
<td>T_{50} (°C)</td>
<td>265.28</td>
<td>246.38</td>
<td>352.46</td>
<td>396.96</td>
<td>402.29</td>
</tr>
<tr>
<td>T_{\text{max}} (°C)</td>
<td>267.09</td>
<td>244.69</td>
<td>253.85</td>
<td>404.13</td>
<td>403.34</td>
</tr>
</tbody>
</table>

Table 2.2 compares the degradation temperatures of PHA/PA blends at different percentage weight loss. T_{10} denotes the temperature at which the samples lost 10% of their original mass. On the basis of data, PA exhibited higher thermal resistance arising
from amide linkages which results in stiff macromolecular chains that interact with each other via strong hydrogen bonds [44,45]. Another degradation temperature investigated was the temperature at half weight loss, designated as $T_{50}$. Regardless of the sample PHA/PA (50/50), the $T_{50}$ values for all of the samples are roughly the same as the $T_{\text{max}}$, the maximum degradation temperature. It is evident that from this thermogram, $T_{\text{max}}$ was enhanced with increasing incorporated PA, which indicated that the thermally stable PA noticeably contributed to the thermal stability improvement of the PHA blends.

Fig. 2.8. Comparison of tensile stress-strain curves of PHA/PA blends. The inset-plot gives details of the mechanical testing data from 0% to 15% tensile strain.
In general, the mechanical properties of binary polymer blend systems are useful, and many are important [46]. Tensile strength is an important mechanical parameter for materials that are designed to be stretched or under tension. Material toughness can be considered as tensile toughness and impact strength [47]. Fracture behavior of the specimen in the tensile test varied significantly from brittle fracture of pure PHA to ductile fracture of pure PA, which is demonstrated in stress-strain curves as shown in Fig. 2.8. The sample of PHA/PA (80/20) is not included because it is too brittle to prepare reliable dimensions for the tensile test. Neat PHA showed a distinct yield point with

Fig. 2.9. Effects on the mechanical properties of PHA/PA blend with different PA concentration. The error bars represent standard deviations based on three samples.
subsequent stage before failure, resulting from the two components inside it, as referred in materials section. Its strain at break was only around 4.6%, as can be seen from Fig. 2.9. When the concentration of PA in the blend was more than 50 weight percent, the PHA/PA blends showed noticeable ductile characteristics with the appearance of distinct yielding and neck formation.

The effects of PA content on the mechanical properties of PHA/PA blends are depicted in Fig. 2.9, which exhibits the tensile strength of specimen decreased systematically as the content of PA increased. When the content of PA was less than 50 weight percent, the elongation of the blend increased slightly, while tensile strength declined significantly. Above 50 weight percent of PA, the samples failed at very large elongation which was changed tremendously from 22% to 465% without obvious decrease of the tensile strength.

### 2.5 Conclusions

This study highlights the PHA/PA blends that melt blended using a twin screw extruder, in order to improve the toughness of PHA and investigate a variety of fundamental properties on the blends. For all of the samples studied by SEM, biphasic separation was observed, indicating that PHA was not miscible with PA in the melt. DMA results confirmed that the blend is an immiscible two-phase system. Rheological results revealed that the melt viscosity of the blends increased with the content of PHA. On the basis of DSC results, both of the melting and crystallization temperatures of the blends
systematically decreased as the concentration of the PA increased. TGA curves depicted that the thermal stability of the blends increased significantly at high temperatures as PA loadings increased. In addition the tensile toughness of the PHA blend was greatly enhanced by the addition of PA.

2.6 Acknowledgements

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2.7 References


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CHAPTER 3: CHARACTERIZATION AND BIODEGRADATION

BEHAVIOR OF BIO-BASED POLY(LACTIC ACID) [PLA] AND SOY

PROTEIN BLENDS

A paper to be submitted to polymer

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3.1 Abstract

Adipic anhydride-plasticized soy protein was blended with poly(lactic acid) (PLA) at two concentrations, 50/50 and 33/67. After being buried in soil for designated time intervals, the residual degraded samples were analyzed to determine morphological and thermal properties at sequential stages of biodegradation. Samples were characterized by scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The results indicated that there was a miscible system between SPA and PLA in the melt. Incorporation of SPA accelerated the biodegradation rate of this binary blend significantly compared with pure PLA. Before degradation, both the glass transition
temperatures and melting temperatures of the blends containing SP.A decreased as the concentration of the soy protein increased. With increasing degradation time of the blended samples in soil, the glass transition temperatures increased in the early stages of biodegradation then decreased, a trend associated with the decrease in the molecular weight of the blends as a result of biodegradation. In addition, the thermal stability of blends increased gradually with increasing degradation time, suggesting faster biodegradation loss of the soy component of the SP.A/PLA blends.

3.2 Introduction

The continuously rising cost of petroleum and the growing awareness of the environmental costs related to the use of fossil carbon have prompted the development and use of sustainable, bio-based alternatives to petroleum-based polymers. Bio-based polymers and composites have been widely considered for use in agricultural, industrial, and medical applications due to their excellent biocompatibility and biodegradability [1-14]. The amount of single-use plastic consumed in agricultural systems is extensive, an issue that has generated a strong desire to develop biorenewable products that can satisfy the needed function, then biodegrade in soil under natural field conditions [15].

Among the environmentally friendly bio-based polymers, Poly(lactic acid) (PLA) is one of the most promising commercially available biopolymers on the market. The common method for production of commercial PLA is the ring-opening polymerization with metal catalysts of lactides that are typically derived from starch fermentation. PLA is
a highly versatile thermoplastic material that possesses high biocompatibility and bio-absorbability [16], making it attractive for bio-disposable plastic products. PLA is considered biodegradable by many definitions and can degrade into water, carbon dioxide and other small molecules under compost conditions [17]; however, the biodegradation rate of PLA is relatively low and its commercial cost is presently greater than that of traditional petroleum-based plastics. Modifying PLA by creating composite materials may help resolve these issues [18].

Blending PLA with other natural polymers can be an effective method for toughening the material or improving its properties. For example, studies have examined the processing and properties of PLA composites with polyethylene oxide, poly(ε-caprolactone), and aliphatic polyesters [19-21]. Others have found that PLA can be blended with biodegradable polymers and fillers, such as starch, corn stover, or soy protein to substantially reduce the cost of material [22, 23]. Soy protein is a natural protein material isolated from soybean, which is one of the major agricultural crops in the U.S. There are three main types of high-protein commercial products processed from soybean: soy flour (approximately 50% protein), soy protein concentrate (SPC) (approximately 70% protein), and soy protein isolate (SPI) (at least 90% protein). From an industry perspective, SPI serves an important role as an initial ingredient for many food products, and it has been widely studied due to its low cost, ample availability, and biodegradability. However, SPI cannot be blended directly with PLA because of the weak interfacial bonding between two components and the wide difference in their melting temperatures. Plasticizers such as glycerol must be included to lower the melting
temperature of PLA, and water is needed as a solvent for SPI. Many of the cyclic anhydrides, such as maleic anhydride (MA), phthalic anhydride (PA), tetrahydrophthalic anhydride (THPA), have been used as the plasticizer for soy protein based plastics [24]. In this study, adipic anhydride (AA) was included in the raw soy polymer to enhance the compatibilization and miscibility of soy/PLA blends, and the soy material used was a 50/50 mixture of SPI and soy flour to form the soy protein adipic anhydride (SP.A).

The objective of this study was to evaluate, compare, and characterize blends of SP.A and PLA that were designed for use in eco-friendly plant containers that can degrade in landscape and garden soils, thereby eliminating the need for disposal. Neat PLA and two blends of SP.A/PLA (50/50 and 33/67 by weight) were characterized for morphological and thermal properties, and were evaluated to determine the effects of blend composition and biodegradation time on their material properties. We hypothesized that mixing SP.A with PLA would be an effective way to decrease the production cost of PLA-based polymer, to increase the rate of biodegradation compared with neat PLA, and to achieve a composite material with properties that could fulfil the functions required for container-crop agriculture, then could degrade to indiscernible organic matter in soil. Very little has been reported on soy-protein polymers plasticized by adipic anhydride or the biodegradation behaviour of SP.A/PLA blends degraded in agricultural soil in situ. In this work, we used scanning electron microscopy (SEM) to investigate the morphologies of neat PLA and SP.A/PLA blends at different stages of biodegradation, and used dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analyzer (TGA) to characterize the thermal properties of neat PLA and
SP.A/PLA blends at different stages of biodegradation and SP.A/PLA blended at two weight-percentage ratios.

3.3 Experimental section

3.3.1 Materials

PLA was supplied by NatureWorks LLC. and SP.A was made from SPI and soy flour provided by The Solae Company, St. Louis, MO. The detailed formulation for the SP.A polymer was soy protein isolate (26%), soy flour (26%), water (31%), glycerin (8%), phthalic anhydride (4%), adipic anhydride (4%), sodium sulfite (1%), and potassium sorbate (<1%). For the blended materials, SP.A and PLA were first dried in a vacuum oven for 6 hours at 80 °C, then were compounded on a Leistritz twin-screw extruder (Leistritz Micro18, L/D ratio 30, American Leistritz Corp., Somerville, NJ) to produce plastic extrudate that was pelletized with a pellet mill (Scheer Bay Inc. WI). To perform biodegradation experiments, an 85-ton JSW injection-molding machine was used to mold prototype 4.5-inch plant containers (11.4 cm OD at top) of the PLA and SP.A/PLA materials.

3.3.2 Biodegradation experiments

Biodegradation experiments were conducted in soil medium at the Horticulture Research Station near Gilbert, IA. The soil type was Clarion loam, a fine-loamy, mixed, superactive, mesic Typic Hapludolls. The biodegradability of the samples was investigated using one-fourth injection molded plant container pieces, cut from prototype containers with a top diameter of 11.4 cm, height of 9.7 cm, and volume of 680 cm$^3$. The
weighed samples were prepared by placing each in a non-degradable mesh bag and burying them 10 cm below the soil surface and 0.5 m apart in a randomized complete block design. The mean soil temperature was 21.1 °C, and the soil plot was irrigated evenly with approximately 2.5 cm of water once a week. A subset of degraded samples was removed from the soil every 4 weeks for up to 24 weeks, and samples were washed with water under gentle agitation, wiped clean with a soft, dry paper tissue, and then dried at 33 ± 5 °C and 26% Relative Humidity for 9 days. After drying, the specimens were held for 24 hours in the same laboratory environment where the initial weights were measured in order to reach equilibrium with ambient humidity, and were then re-weighed. The percentage weight loss ($W_{\text{loss}}\%$) of each sample was calculated by Eq. (1) [25],

$$W_{\text{loss}}\% = \frac{W_0 - W_1}{W_0} \times 100\%$$

where $W_0$ and $W_1$ represent the weights of the dried sample before biodegradation step and the biodegraded sample after being buried in soil and cleaned, respectively.

3.3.3 Scanning electron microscopy

The surface morphology of neat PLA and SP.A/PLA blends with weight percent ratios of 33/67 and 50/50 were examined using SEM after six sequential durations of biodegradation in soil (0, 8, 12, 16, 20, and 24 weeks). The measured samples were fixed on the SEM holders after sputter coating with a thin gold layer. The prepared samples were characterized using an FEI Quanta 250 field emission scanning electron microscope (FE-SEM) at 10.00 kV under high vacuum.
3.3.4 DMA measurements

The Dynamic mechanical analysis (DMA) was performed with a DMA Q800 dynamic mechanical analyzer from TA Instruments. All samples after different biodegradation times were measured with a film-tension mode of 1 Hz. Rectangular shape specimens of 1.2 mm thick and 8.3 mm wide were used for the analysis. The samples were cooled under nitrogen atmosphere and held isothermally for 2 min at -50 °C before the temperature was increased to 140 °C at a rate of 3°C/min.

3.3.5 DSC measurements

Differential scanning calorimetry (DSC) measurements were performed using a thermal analyzer (TA Instrument Q20) to assess the effect of biodegradation on the thermal transition behavior of SP.A/PLA blends, as well as the thermal properties of the blends. All DSC measurements were carried out in nitrogen atmosphere. The samples were firstly quenched from room temperature to -50 °C, then heated from -50 °C to 200 °C at a heating rate of 20 °C/min to erase their anterior thermal history, equilibrated at 200 °C and then cooled. Liquid nitrogen from a dewar was used to quench the molten specimen until the temperature was reach to -50°C again. After that, the samples were reheated to 200 °C at the same constant rate, measuring the second heating curves. The melting temperature (Tm) of all samples at different biodegradation stages was determined from the maximum of the endothermic melting peak. Samples of 5 mg were cut from the films and used for analysis.
3.3.6 TGA measurements

The thermal stability of SP.A/PLA blends at different biodegradation stages was investigated by a Q50 (New Castle, DE) thermogravimetric analyzer (TGA) from TA Instruments. The samples were heated from room temperature to 850°C at a heating rate of 20°C/min. The experiment was run with nitrogen as the purge gas. About 10 mg samples each were used for this test.

3.4 Results and discussion

The effect of different biodegradation time on the weight loss of the neat PLA, SP.A/PLA (33/67) and SP.A/PLA (50/50) blends in soil medium is presented in Fig. 3.1, while relevant photographs of blend samples before and after 24 weeks of burial degradation time under soil conditions are exhibited in Fig. 3.2. Obviously, significant damage and weight loss were observed for PLA compounded with SP.A after 24 weeks biodegradation time. The blend surfaces became gray with shallow crevices and unevenly distributed black spots throughout the degradation process. Both blends of SP.A/PLA showed a high initial weight loss as a result of the fast rate of decomposition of soy protein from the blends, results consistent with observations that nutrients such as proteins and amino acids generally biodegrade easily in soil [26-28]. The sharp decrease in weight of samples likely resulted from microbial activity (enzymatic degradation) and hydrolysis, which are the dominant processes for rapid biodegradation and continued weight loss [29-32]. Blends of SP.A/PLA showed a much higher degradation rate than unaltered PLA, indicating that the biodegradation of PLA-based material can be
significantly accelerated by increasing the amount of SP.A. Weight loss after 8 weeks of biodegradation in soil for the SP.A/PLA (50/50) blend was about twice that of SP.A/PLA (33/67) under identical biodegradation conditions, demonstrating that the loading of SP.A enhanced the biodegradation process of PLA-based material. It is likely that interfacial adhesion contributed to the coalescence of the two components and was another key factor accelerating the biodegradation rate of SP.A/PLA blends compared with that of pure PLA.

Fig. 3.1. Degradation weight-loss percentages (%) for the neat PLA, SP.A/PLA (33/67) and SP.A/PLA (50/50) blends in soil medium, with mean-separation statistics included.
Fig. 3.2. Photographs of SP.A/PLA (33/67) and SP.A/PLA (50/50) blends specimens before and after 24 weeks of degradation time in soil medium.

Scanning electron microscopy (SEM) is a tool that is widely employed to investigate the internal structure and surface morphology of biodegradable polymers [33-37]. The surface changes of neat PLA with burying time throughout the degradation process were investigated, as can be seen from Fig. 3.4. A clean and smooth surface morphology was observed for unaltered PLA, indicating that degradative damage was inconspicuous and minimal, especially in duration from 0 week to 16 weeks. The micrographs of 8 and 12 weeks (not shown) exhibited very similar morphological characteristics compared to the undegraded PLA surfaces. After 24 weeks many gray spots appeared on the surface, demonstrating that PLA had degraded in spite of the relatively low biodegradation rate.
For SPA/PLA (33/67) blend and SPA/PLA (50/50) blend samples, their typical surface morphologies were also examined by SEM at different stages of biodegradation, as presented in Fig. 3.4 and Fig. 3.5. Relatively smooth surface topographies were observed for non-degraded samples of SPA/PLA, demonstrating strong interfacial adhesions of the two components. With increasing biodegradation time, numerous cracks and tiny corrosive holes appeared in the early stages of biodegradation process. The cracks became larger and holes became deeper as the degradation time increased, and the interior portions of the samples became exposed due to erosion of the surface regions. After 24 weeks of biodegradation, noticeably rough surfaces developed that were aggregated by small eroded regions and irregular pits. The phase structure of the SPA/PLA blends changed from fine to coarse, resulting in prominent weight loss compared to neat PLA. As illustrated in Fig. 3.4 and Fig. 3.5, the SEM images of SPA/PLA (33/67) and SPA/PLA (50/50) differed, demonstrating that blend composition played a role in the degradation mechanisms of the two blends. Compared to the
SPA/PLA (33/67) blend, the surface of SPA/PLA (50/50) exhibited more corrosive holes and disorderly erosive aggregates. SPA positively affected the degradation patterns of SPA/PLA blends, accelerating their biodegradation rate in soil. Degradation of pure soy protein in the soil is very fast, with most of the weight loss occurred in the first week and nearly 95% of the original weight degrading within 5 weeks [38].
Fig. 3.4. SEM micrographs of surface morphology for SP.A/PLA (33/67) blends before and after biodegradation under soil condition
Fig. 3.5. SEM micrographs of surface morphology for SP.A/PLA (50/50) blends before and after biodegradation under soil condition

DMA measurements in the range of temperatures from -50 °C to 140 °C were used to characterize the dynamic mechanical properties of SP.A/PLA blends and to compare them.
with the properties of pure PLA. The variations in the storage modulus (E') and loss tangent (tan δ) of the pure PLA and SP.A/PLA blends are shown in Fig. 3.6. The storage modulus of the blends at glassy region decreased as the amount of SP.A increased, resulting from the influence of plasticizers like adipic anhydride. Specifically, the heat treatment was not expected to result in completely crystallinity but that the amorphous regions might accelerate the chain mobility with respect to the crystallization of PLA in the presence of plasticizers [39, 40]. The unaltered PLA exhibited a sharper and higher loss tangent peak compared to SP.A/PLA blends. Meanwhile, the storage modulus declined sharply at approximately 65°C related to the glass relaxation processes (α-relaxation) of the amorphous regions in PLA. The glass transition temperature of the blends shifted systematically to lower temperature with increasing SP.A loadings, demonstrating that the plasticizer accelerated sort of the polymer chain mobility. After heating above 100 °C, the storage moduli increased again, corresponding to the appearance of the second relaxation process. Typically, for PLA, this phenomenon appeared because of the cold crystallization [41, 42]. At higher temperature, the crystalline region in the samples began to melt, therefore the storage moduli decreased again due to slippage of large scale molecular chains.
Fig. 3.6. Representative tan δ and storage modulus (E’) curves as a function of temperature at a frequency of 1 Hz and 3 °C/min heating rate for unaltered PLA, SP.A/PLA (33/67) and SP.A/PLA (50/50) before biodegradation under soil conditions.

The effect of different biodegradation durations on the thermomechanical properties of the SP.A/PLA blends is presented in Fig. 3.7. Representative tan δ and storage modulus (E’) curves as a function of temperature for every biodegradation stage up to 24 weeks were obtained. Similarly, two relaxation processes appeared for SP.A/PLA blends in this temperature range as they did in pure PLA curves. As can be seen from the curves, the biodegradation process apparently decreased the storage modulus of the samples. With increasing burying time of the sample in soil, the change in positions of tan δ peaks can be classified into two stages. In the early stage of the biodegradation process, most of amorphous soy protein degraded, resulting in an increasing percentage of crystalline
portions (PLA) in the blends. Therefore, a noticeable shift of $\alpha$-relaxation peak to higher temperature occurred. After approximately 8 weeks, the second stage began, with gradual bioabsorption and removal of soy protein by microbial, chemical, and physical activities in the soil medium [43]. The glass transition temperature of the samples shifted slightly toward lower temperatures, an occurrence likely associated with the decrease of the molecular weight of the blends as a result of biodegradation. From this point, both of SP.A/PLA (33/67) and SP.A/PLA (50/50) blends showed a similar trend, indicating that different biodegradation time intervals had a measurable impact on the thermomechanical properties of SP.A/PLA blends.
Fig. 3.7. Representative tan δ and storage modulus (E’) curves as a function of temperature at a frequency of 1 Hz and 3 °C/min heating rate for (a) SPA/PLA (33/67) (b) SPA/PLA (50/50) after different durations of biodegradation under soil conditions.

Differential scanning calorimetry was carried out to determine the temperatures and heat flow during thermal transitions of SPA/PLA blends. Research has shown that second phase additives can substantially affect the crystallinity of binary polymer blends [44]. The miscibility of blended polymers can be determined effectively by measuring the glass
transition temperature ($T_g$) of the blends [45, 46]. Polymer blends are miscible when their components exhibit one single composition-dependent $T_g$. The DSC traces for SP.A/PLA blends, as seen from Fig. 3.8, indicate only one $T_g$ for each of the materials. These results are consistent with those obtained from DMA, and verify the miscible system between SP.A and PLA. Table 3.1 compares the glass transition temperatures and melting temperatures of pure PLA and SP.A/PLA blends, showing that both the $T_g$ and melting points of the blends containing SP.A decreased as the concentration of soy protein increased. These results also demonstrate that the percentage of crystalline region decreased due to the effects of amorphous plasticizers, which effectively accelerated the segmental motion of the polymer chains in the blends. As expected, the DSC traces reflected the loss of molecular order, gelatinization, and enthalpic changes associated with the structure relaxations [47].

<table>
<thead>
<tr>
<th></th>
<th>Neat PLA</th>
<th>SP.A/PLA (33/67)</th>
<th>SP.A/PLA (50/50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C)</td>
<td>60.17</td>
<td>40.03</td>
<td>39.72</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>169.31</td>
<td>157.52</td>
<td>156.79</td>
</tr>
</tbody>
</table>
Fig. 3.8. DSC heating scan for unaltered PLA and SP.A/PLA blends before degradation. The DSC measurements were carried out at 20 °C /min heating rate (second heating run) under nitrogen atmosphere.

To analyze the morphology revolution of the SP.A/PLA (33/67) and SP.A/PLA (50/50) blends, and to better determine the $T_g$ values during the degradation, calorimetric scans were performed for samples degraded for different periods of time in soil. Results of the scans are displayed Fig. 3.9. Non-degraded samples (0 week) exhibited relatively broad endothermic peaks. With increasing degradation time in soil, the endothermic peak intensity increased in the early stages of degradation and then decreased progressively, suggesting a complex series of changes over time. The changes caused by degradation were difficult to interpret because the separate contributions from PLA and SP.A degradation appeared to overlap, but some of these changes can be described by results of more than
one of the analyses. Under soil conditions, the PLA underwent a complex but slow rate of degradation [48, 49], which was evident from subtle indicators on the thermographs. The DSC results for glass transition and melting temperatures of the blends determined by using the program of heat-cool-heat are presented in Table 3.2. The results for $T_g$ and $T_m$ revealed similar trends related to the effects of degradation in soil, showing increases in both values related to the degradation of amorphous SP.A, a conclusion also confirmed by DMA results. After the first stage of biodegradation, $T_g$ and $T_m$ of the blends decreased slightly due to the reduction of molecular weight, confirming the loss of the soy protein component by degradation in soil.
Fig. 3.9. DSC heating scan for (a) SP.A/PLA (33/67) (b) SP.A/PLA (50/50) blends after different durations of biodegradation in soil. The DSC measurements were carried out at 20 °C/min heating rate (second heating run) under nitrogen atmosphere.

Table 3.2. Comparison of the glass transition temperatures ($T_g$) and melting temperatures ($T_m$) of SP.A/PLA (33/67) and SP.A/PLA (50/50) blends after different degradation time intervals in soil medium.

<table>
<thead>
<tr>
<th></th>
<th>SP.A/PLA (33/67)</th>
<th></th>
<th>SP.A/PLA (50/50)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$ (°C)</td>
<td>$T_m$ (°C)</td>
<td>$T_g$ (°C)</td>
</tr>
<tr>
<td>0 week</td>
<td>40.03</td>
<td>157.52</td>
<td>0 week</td>
</tr>
<tr>
<td>8 weeks</td>
<td>48.84</td>
<td>160.98</td>
<td>8 weeks</td>
</tr>
<tr>
<td>16 weeks</td>
<td>48.23</td>
<td>168.43</td>
<td>16 weeks</td>
</tr>
<tr>
<td>24 weeks</td>
<td>43.32</td>
<td>167.33</td>
<td>24 weeks</td>
</tr>
</tbody>
</table>

To investigate the effect of blend composition on thermal degradation behavior of SP.A/PLA blends before biodegradation in soil medium, thermogravimetric analyses were
performed to evaluate mass change as a function of temperature (Fig. 3.10). Results of these analyses show that pure PLA and SP.A/PLA blends exhibited different thermal degradation behavior. The temperature at initial weight loss was quite different for the three samples before biodegradation, demonstrating that the incorporated soy protein significantly decreased the thermal stability of the SP.A/PLA blends (Fig. 3.10). This is consistent with other research showing that thermal decomposition of soy protein begins around 125 °C and terminates at approximately 350 °C [26, 29, 50], thermal behavior very distinct from that of unaltered PLA.
Fig. 3.10. Comparison of thermal degradation and derivative weight change of unaltered PLA, SP.A/PLA (33/67) and SP.A/PLA (50/50) before biodegradation in soil under nitrogen atmosphere.
The duration of biodegradation may have a strong influence on the thermal degradation properties of SP.A/PLA blends. TGA was performed to investigate how biodegradation time affected thermal stability of samples (Fig. 3.11). The non-biodegraded samples underwent two major changes in molecular weight during TGA, but the samples
that biodegraded in soil for 24 weeks showed only one change. SP.A/PLA samples held 24 weeks in soil showed a large reduction in mass that occurred with only one thermal-degradation stage. These results are similar to the thermal-degradation behavior of pure PLA, confirming the bioabsorption and loss of soy protein during biodegradation of SP.A/PLA blends in soil. Table 3.3 and Table 3.4 compare the degradation temperatures of SP.A/PLA blends at different percentage weight loss. T₅ and T₁₀ denote the temperature at which the samples lost the initial 5% and 10% of their original mass, respectively. Regardless of the blend ratio of SP.A/PLA, T₅ and T₁₀ gradually and systematically increased with increasing biodegradation time in soil, and the temperature at half weight loss, T₅₀, was roughly the same as the T₉₅, the maximum degradation temperature. For both blends of SP.A/PLA, T₉₅ increased with increasing biodegradation time in soil, and T₉₅ for both blends after 24 weeks of biodegradation was nearly the same as that of pure PLA, reconfirming the loss of most or all of the soy-protein component through biodegradation in soil.
Table 3.3. The TGA results in nitrogen atmosphere for SP.A/PLA (33/67) samples before and after biodegradation in soil.

<table>
<thead>
<tr>
<th></th>
<th>$T_5$ (°C)</th>
<th>$T_{10}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>338.12</td>
<td>347.25</td>
<td>372.90</td>
<td>376.94</td>
</tr>
<tr>
<td>SP.A/PLA (33/67)</td>
<td>248.45</td>
<td>278.46</td>
<td>318.90</td>
<td>318.84</td>
</tr>
<tr>
<td>0 week</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP.A/PLA (33/67)</td>
<td>286.05</td>
<td>306.67</td>
<td>345.07</td>
<td>347.89</td>
</tr>
<tr>
<td>8 weeks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP.A/PLA (33/67)</td>
<td>294.66</td>
<td>310.35</td>
<td>345.53</td>
<td>351.12</td>
</tr>
<tr>
<td>12 weeks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP.A/PLA (33/67)</td>
<td>296.93</td>
<td>316.84</td>
<td>352.80</td>
<td>356.77</td>
</tr>
<tr>
<td>16 weeks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SP.A/PLA (33/67)</td>
<td>298.16</td>
<td>317.74</td>
<td>352.96</td>
<td>358.38</td>
</tr>
<tr>
<td>20 weeks</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SP.A/PLA (33/67)</td>
<td>309.21</td>
<td>322.95</td>
<td>359.76</td>
<td>369.68</td>
</tr>
<tr>
<td>24 weeks</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.4. The TGA results in nitrogen atmosphere for SP.A/PLA (50/50) samples before and after biodegradation in soil.

<table>
<thead>
<tr>
<th></th>
<th>T₅ (°C)</th>
<th>T₁₀ (°C)</th>
<th>T₅₀ (°C)</th>
<th>Tₘₐₓ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>338.12</td>
<td>347.25</td>
<td>372.90</td>
<td>376.94</td>
</tr>
<tr>
<td>SP.A/PLA (50/50) 0 week</td>
<td>231.82</td>
<td>265.48</td>
<td>314.80</td>
<td>309.96</td>
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<tr>
<td>SP.A/PLA (50/50) 8weeks</td>
<td>285.57</td>
<td>304.29</td>
<td>343.59</td>
<td>350.31</td>
</tr>
<tr>
<td>SP.A/PLA (50/50) 12weeks</td>
<td>313.63</td>
<td>329.52</td>
<td>359.91</td>
<td>365.26</td>
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<tr>
<td>SP.A/PLA (50/50) 16weeks</td>
<td>306.38</td>
<td>319.81</td>
<td>349.95</td>
<td>355.15</td>
</tr>
<tr>
<td>SP.A/PLA (50/50) 20weeks</td>
<td>316.09</td>
<td>327.89</td>
<td>359.46</td>
<td>364.83</td>
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<tr>
<td>SP.A/PLA (50/50) 24weeks</td>
<td>316.39</td>
<td>330.95</td>
<td>365.70</td>
<td>373.71</td>
</tr>
</tbody>
</table>

3.5 Conclusions

This study characterizes the morphological and thermal properties of blended polymers of soy protein and PLA (SP.A/PLA blends) during different stages of biodegradation in soil. We confirm that adipic anhydride can be used successfully as a plasticizer for soy-protein polymer to help facilitate melt blending with PLA. For all the samples comparatively investigated by DSC, only one Tₖ was observed, suggesting a miscible system between adipic anhydride-plasticized soy protein (SP.A) and PLA in the melt, results also confirmed by DMA. SEM patterns revealed that SP.A accelerated the biodegradation rate of binary blends of SP.A/PLA compared to that of pure PLA under soil.
conditions. DMA investigations revealed changes in $T_g$ of SP.A/PLA blends in response to biodegradation in soil, and thermomechanical properties of the blends were affected differently depending on the duration of biodegradation. We conclude that these changes in thermomechanical properties were related to a loss of the soy-protein component from the binary polymer and bioabsorption of the soy component by the soil medium. TGA curves showed that the thermal stability of the blends increased gradually with increasing biodegradation time in soil. Addition of SP.A to PLA may be a useful method for decreasing material costs and improving the biodegradability of PLA-based materials in soil.

### 3.6 Acknowledgements

This research was supported in part by the USDA Specialty Crops Research Initiative (USDA-SCRI project # IOW05306). We thank NatureWorks LLC. for providing PLA, and we thank Solae Company, St. Louis, MO for providing SPI and soy flour. We also thank Kyle Haubrich and Samuel Schrader for their technical assistance during prototype development, trial establishment, and data collection.

### 3.7 References


CHAPTER 4: GENERAL CONCLUSIONS

The mechanical, thermal and morphological properties of the novel bio-based PHA/PA blends and SPA/PLA blends were successfully investigated. In the case of PHA/PA blends, the addition of PA significantly enhanced the mechanical properties of PHA with an excellent combination of strength, stiffness and toughness. The SEM micrographs revealed that this blend is an immiscible but compatible two-phase system. The thermal stability of the blends increased noticeably at high temperature with adding PA content. In addition, the elastic shear modulus (G’ ) and complex viscosity of the blends increased significantly with increasing the concentration of PHA.

Another major chapter involved the morphological and thermal properties of the SPA/PLA blends during different biodegradation stages under soil condition. Adipic anhydride was successfully used to plasticize soy protein before melt blended with PLA. The SEM micrographs revealed that SPA apparently accelerated the biodegradation rate of this binary blend under soil conditions. The thermal stability of the blends increased systematically with increasing burying time in soil, confirming the biodegradation and removal of the soy protein by soil medium. Furthermore, due to the relative low cost of soy protein, substituting a percentage of PLA with soy protein to form a blend can offer some savings. A conclusion can be reached in this work is that addition of SPA to PLA was not only able to decrease material costs, but accelerate the biodegradation rate in soil.