Processing and characterization of bio-based composites

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Processing and characterization of bio-based composites

by

Hong Lu

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:
Samy Madbouly, Co-Major Professor
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Iowa State University
Ames, Iowa
2014

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ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my co-advisor Dr. Samy Madbouly, for his great kindness, thoughtful guidance and encouragement throughout the duration of my graduate program. I would also like to thank Dr. Lawrence Genalo, Dr. Xiaoli Tan and Dr. David Grewell for serving on my advisory committee and providing valuable guidance. A special thank you is to be given to my former co-advisor Dr. Michael Kessler for his kind help, encouragement and suggestions during the first year of my research process.

I would like to thank Dr. James Schrader for providing the degradation containers. In addition, I would like to thank Dr. Jerry Amenson from the Materials Analysis Research Laboratory and Dr. Arkady Ellern from the Chemistry Department for the training and advice on the SEM and XRD. I would also like to thank current and former members of the polymer composites research group for their technical support and friendship. It is a memorable, valuable experience to be a member of the group. Especially, Kunwei Liu assisted me during the early stages of my research process; Dr. Samy Mabouly trained me for Rheometer; Chaoqun Zhang, Yuzhan Li and Hongyu Cui, who trained me for the TA Instruments; Rui Ding, Hongchao Wu, Chaoqun Zhang, Ruqi Chen, Danny Vernerberg, and Shengzhe Yang deserve many thanks for their exchange of thoughts and help.

I am grateful to Jacqueline Kester for the help on program issues during the past two years. I also want to thank my friends for their encouragement and company. Finally, I would like to thank my parents for their love and support throughout my life, without whom I will never have enjoyed such a wonderful life.
ABSTRACT

Much research has focused on bio-based composites as a potential material to replace petroleum-based plastics. Considering the high price of Polyhydroxyalkanoates (PHAs), PHA/ Distiller’s Dried Grains with Solubles (DDGS) composite is a promising economical and high-performance biodegradable material. In this paper, we discuss the effect of DDGS on PHA composites in balancing cost with material performance.

Poly (lactic acid) PLA/DDGS composite is another excellent biodegradable composite, although as a bio-based polymer its degradation time is relatively long. The goal of this research is therefore to accelerate the degradation process for this material.

Both bio-based composites were extruded through a twin-screw microcompounder, and the two materials were uniformly mixed. The morphology of the samples was examined using a Scanning Electron Microscope (SEM); thermal stability was determined with a Thermal Gravimetric Analyzer (TGA); other thermal properties were studied using Differential Scanning Calorimetry (DSC) and a Dynamic Mechanical Analyzer (DMA). Viscoelastic properties were also evaluated using a Rheometer.
CHAPTER 1: GENERAL INTRODUCTION

1.1 Organization

This thesis is divided into four chapters. Chapter 1 introduces background information about bio-based polymers and composites, including polyhydroxyalkanoate (PHA), poly (lactic acid) (PLA), Distiller’s Dried Grains with Solubles (DDGS), and soybean protein. Biodegradation mechanisms and factors are also discussed. Chapter 2 discusses the processing and characterization of PHA with varying DDGS content. Chapter 3 describes the biodegradation behavior of PHA with DDGS and soybean-protein composites buried in soil under landscape conditions. Chapter 4 gives conclusions resulting from this research work.

1.2 Background introduction

Plastics are widely used in virtually all aspects of modern life, including applications in packaging, textile, automobiles, medicine, etc. The global consumption of plastics derived from crude oil is presently over 400 million tons and growing at about 5% per year.\(^1\) Because of this strong dependence on crude oil and natural gas, and with prices of those commodities increasing year-by-year, there is naturally a great desire to develop and utilize alternative materials. Petroleum-based plastics such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), and polypropylene (PP) have been widely used because of their desirable mechanical properties and relatively low cost. These materials have been applied in various industrial areas in various compositions, but their non-biodegradability and resulting environmental problems have
restricted their use. Since petroleum-based resources are not infinite, prices are likely to increase with that of crude oil. Moreover, the carbon dioxide released by plastic processing contributes to the serious problem of global warming. According to the Association of Plastics Manufactures’ database published in 2009\(^2\), each ton of petroleum-based plastic results in the emission of approximately 1.9 tons of CO\(_2\). It is clearly necessary to find new resources and materials to replace petroleum-based materials, so in the last several decades there have been expanding research efforts focusing on new bio-based materials with high performance\(^3\). The motivation of this thesis is to contribute to such efforts.

Bioplastics are plastics derived from renewable resources. Biocomposites reinforced with natural fibers and biopolymers have gained more and more attention over the past few decades. With respect to utilization, plant-produced natural fibers could be divided into two primary and secondary categories. A primary plant is one grown mainly for its fiber, and a secondary plant is one producing fiber as a by-product.\(^6\) Usually the basic types of natural fibers are divided into six groups: bast fibers, leaf fibers, seed fibers, core fibers, grass fibers, and other types. The properties of natural fibers vary a great deal depending on the chemical composition, dimension, structure, defects, microfibrillar angle, and physical and mechanical properties. All fibers have the shortcoming that their characteristics vary over a much greater range than that of synthetic fiber. This lack of consistency in fiber qualities is due to variations in environmental growth conditions like temperature, moisture, and location.
Typically, the concentration of natural fibers in biocomposites ranges from 10% to 50% by weight. A specific value of fiber concentration can reduce the cost of production, and could enhance biodegradability and other physical properties such as thermal stability, color, and flame retardance.

1.2.1 Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are a group of linear polyesters produced by many types of microorganisms as carbon and energy storage materials in bacteria. (Fig.1.1) PHAs have attracted a great deal of interest because of their inherent biodegradability, sustainability, and environmentally-friendly properties. Furthermore, PHAs can become 100% degradable in a culture medium through bacteria fermentation. More than 150 different types of monomers have been reported. For the different constituents of monomers, PHAs exhibit a crystallinity ranging from 30% to 70% and melting points ranging from 50°C to 180°C. Their various areas of application include packaging, electronics, sensors, energy-related applications, and the biomedical industry.
The historical development of PHAs can be divided into three stages. The first stage was the identification of Poly (3-hydroxybutyrate) (PHB), first reported by Lemoigne M. in 1926. It is the most common and simplest monomer of the PHA family. Although PHB has properties very similar to those of traditional petroleum-based plastics like polypropylene, its stiffness and brittleness resulting from high crystallinity has limited its industrial application. Through incorporation of another HA units monomer, Wallen L. and Rohwedder K. in 1974 reported additional HA monomers to PHB, marking the beginning of the second phase of PHA development. HB and HV copolymers with enhanced properties were the first ones introduced into industrial production. During this period, it became well known that HA polymers could be synthesized in both
gram-negative and gram-positive bacteria, and about 125 different HA versions were discovered\textsuperscript{17}. The third stage of development mainly dealt with cloning and genetics involved in the biosynthesis of reserve polyesters\textsuperscript{18}.

1.2.2 Poly(lactic acid) (PLA)

The development of PLA was initiated using lactide production formulas published by Bischoff and Walden\textsuperscript{19} in 1983. There are two different isomers for lactic acid, as shown in Fig.1.2. L-lactic acid rotates the plane of polarization clockwise, and D-lactic acid rotates it the opposite way. Usually a 50-50 percentage (by weight) of L-lactic acid and D-lactic acid is produced using petrochemical procedures.

![Chemical structure of L and D lactic acid](image_url)

**L-Lactic acid**  
**D-Lactic acid**

Fig. 1.2 Chemical structure of L-and D- lactic acid\textsuperscript{20}

Later, in 1932, Carothers (DuPont) successfully produced low molecular weight PLA by heating lactic acid under vacuum through use of a lactide ring opening and polymerization\textsuperscript{21}. To achieve a high molecular weight, water must be removed at high vacuum and high temperature\textsuperscript{22}.
PLA has several advantages that have lead to its wide present-day use. First, it is derived from renewable agricultural resources such as corn, rice, and wheat, resulting in biodegradable, compostable, and recyclable properties\(^\text{23}\). Secondly, it is biocompatible with biomedical materials. Moreover, PLA has excellent thermal processability and can be produced through injection molding, film extrusion, blow molding, thermo-forming, fiber-spinning, and film-forming. In addition, about 25-55% less energy is required for PLA production than for petroleum-based polymers.

PLA does, however, have drawbacks that limit its application. Although PLA has both a high tensile strength and elastic modulus, its toughness is very poor, and its elongation at break is less than 10%\(^\text{24}\). Furthermore, as a biodegradable polymer, the degradation rate of PLA is slow and may require up to many years in some situations\(^\text{25}\). This slow degradation rate will limit its application for in vivo implant. In addition, PLA does not contain reactive side-chain groups, which makes modifications in both its surface and in bulk difficult. Finally, the price of PLA is still high (~$1.6 per kilogram of lactic acid\(^\text{26}\)) compared that of traditional synthesis polymers. Many studies have therefore been attempted to reduce or eliminate these unsatisfactory PLA properties.

Blending is a widely-used approach for improving PLA’s mechanical properties and reducing its cost. PLA can be blended with various plasticizers, polymers, and fibers to overcome its limitations. Mascia L.\(^\text{27}\) has suggested that plasticizers can increase PLA ductility and improve its processability. These targeted properties have already been achieved by controlling the molecular weight, polarity, and chemical functional group of
the plasticizer material. Blending with non-degradable polymer or filler is also a promising method for compensating for DNA’s poor mechanical properties. However, there have been fewer studies about adding non-degradable components than for incorporation of biodegradable polymers or fiber with PLA.

PLA has been proposed as an alternative to petroleum-based plastics. With increased concerns about environmental and sustainability issues in recent years, the applications for PLA seem very likely to continue to increase.

1.2.3 DDGS

Distiller’s Dried Grains with Solubles (DDGS) is a low-cost non-fermentable cereal co-product of the corn-ethanol fuel industry; DDGS have a complex component that includes protein, fiber, lipid, and solubles, and are mainly used for feeding livestock. With increasing growth of ethanol fuel production, the by-product DDGS has begun to saturate the livestock market, with production of more than 42 million tons of DDGS each year in the United States. It is thus important to develop other attractive and higher-value applications for DDGS, and one such use is as a biofiller material in plastic.

1.3 Biodegradation mechanisms

Biodegradable plastics refer to plastics capable of being decomposed by microorganisms. Decomposition events occur in two stages. During the first stage, bacteria, algae, or fungi excrete specific enzymes to reduce the molar mass and size of the polymer. Only when the molecular weight has been reduced to the point that is water-soluble can the microorganisms transport these polymer materials into their cells.
and feed on them to produce a metabolic pathway\textsuperscript{31}, the second stage of biodegradation. Although chain-length reduction caused by an enzyme is the primary process in many situations, polymers could also degrade when they are exposed to abiotic conditions. Such abiotic conditions include mechanical, light, thermal and chemical conditions leading to a weaker polymer structure, either in the first stage only or in the whole process in parallel.\textsuperscript{32}

1.3.1 Mechanical degradation

Compression, tension, and shear forces can produce mechanical degradation. Often degradation results from such damage might not be immediately noticed since it may have just begun at a molecular level.\textsuperscript{33} Although these mechanical factors do not play an important role during biodegradation, they could accelerate the rate of degradation to some degree.\textsuperscript{34}

1.3.2 Thermal degradation

Thermal degradation happens when thermoplastic polymers transform from a solid to a liquid state above the melting temperature. Usually the polymer’s melting temperature is much higher than the environmental temperature, so thermal degradation seldom occurs. However, there are some polymers or composites that exhibit melting temperatures nearer to the environmental temperature, e.g., PCL with a 60°C\textsuperscript{35} melting point.

1.3.3 Light degradation
Light degradation mainly focuses on photosensitive materials whose polymer-chain scission occurs by irradiation. Norrish reactions can transform the polymer to small molar masses through photoionization and chain scission.

1.3.4 Chemical degradation

The most common degradation is through hydrolysis, the cleavage of chemical bonds by addition of water. This type of degradation requires a polymer containing hydrolysable covalent bonds, such as in ester, ether, anhydride, amide, and ester amide chemical groups. For polyesters, the hydrolysis mechanism is a two-stage process first reported by Chu in the early 1980s. The first stage occurs when water diffuses into the amorphous regions of the polymer, producing hydrolytic scission in the ester and followed by hydrolysis of crystalline regions. The linkage and degree of polymer crystallinity will increase during the first state.

Oxidation is another chemical degradation effect. Different forms of oxygen (O₂ or O₃) could attack the polymer chain covalent bonding and produce free radicals that could lead to a crosslinking reaction or chain scissions and reduce the molecular weight.

1.4 Biodegradation process factors

Biodegradation of plastics depends on their environment, the polymer’s chemical structure, and other factors. Environmental factors include temperature, moisture, oxygen, pH, and microorganisms. The chemical structures are those chemical functional groups having esters, amide, or carbonate hydrolysable bonds. Other factors include crystallinity, molecular weight, and polymer composite composition.
Moisture could affect biodegradation rate in two ways. First, moisture is essential for the growth of microorganisms. The more plentiful the water, the more microbial activity, and the faster that polymers will degrade. Second, hydrolysis plays an important role in the biodegradation process for both polyesters and other specific polymers. For these polymers, if the environment is moisture-rich, there will more chain scission reactions and the chain mobility will be increased, so the degradation rate will also be increased. Kai-Lai et al.\textsuperscript{39} suggested that PLA degradation rate was also enhanced by an increase in relative humidity of the environment.

There are two oxygen conditions for microorganisms: aerobic and anaerobic. For aerobic microorganisms, if the oxygen concentration is very low (less than 6\textsuperscript{\%})\textsuperscript{40}, their metabolism rate will change and thereby reduce the biodegradation rate of the polymer. On the other hand, for anaerobic microorganisms, if the oxygen concentration is sufficiently high the degradation rate will decrease.

For hydrolysable polymers, the rate of degradation could also be affected by pH and temperature, because the hydrolysis reactions may be either acid or base catalyzed. In addition, both the rate of hydrolysis and the microorganisms’ growth may be affected.

Microorganisms for bacteria and fungi can secrete enzymes to decompose a polymer. The type of enzyme will vary with each specific case. For example, the enzyme produced by Aspergillus nigers will more readily degrade aliphatic polyesters than other enzymes. Thus, the type of microorganisms affecting polymer degradation depends on the specific enzymes derived from them.
The term flexibility refers to the energy needed to move atoms closer to or further from each other. Usually the more flexible the polymer chain is, the more accessible it is for the hydrolysis process, and the faster its degradation rate. Conformational flexibility depends on both the backbone and side groups of the polymer. For backbone structure, bond stability decreases in the following order: amides, esters, and anhydrides. Double bonds and oxygen or nitrogen could also increase the flexibility. Side chemical groups will increase the energy for rotation and decrease flexibility. The higher the rotational barrier is, the less the polymer flexibility. For example, poly(glycolic acid) is more flexible than poly(lactide acid) because poly(lactide acid) has a methyl side group that inhibits chain movement.

Hydrolytic reactions are determined by the rate of water diffusion into the polymer, and they are less likely for water diffused through crystalline regions. Therefore, amorphous regions are more flexible with respect to hydrolysis than are crystalline regions. Auras R. suggested that hydrolytic scission of PLLA chains occurs mainly in amorphous regions rather than crystalline regions, and that the overall degradation rate of PLLA films decreased with increasing crystallinity of PLLA. Amass W. also has suggested that changing the degree of crystallinity could control the rate of degradation.

Molecular weight affects the biodegradation rate in microorganisms’ decomposition and hydrolysis processes. First, if the molecular weight is high, it is difficult for microorganisms to penetrate into the polymer so they tend to only degrade low molecular weight regions, and hydrolysis is an important mechanism for reaching the highest molecular weight point at which microorganisms could enter. Hydrolysis is also affected
by molecular weight. Usually high molecular weight is related to a high glass-transition temperature, meaning that the polymer becomes more glass-like and less flexible. A high molecular weight polymer usually has a long chemical chain containing more chemical bonding. Both these effects will lead to a longer time for the hydrolysis process, so a given polymer will degrade faster than one with a higher molecular weight.

Adding filler or an additional polymer into a polymer will decrease regularity of its polymer chains and usually reduce its crystallinity, thereby increasing the degradation rate. However, this incorporation may also enhance biodegradability, because if the filler or copolymer contains hydrolysable groups, biodegradability will be increased. Chiellini et al.\textsuperscript{43} found that the degradation rate was increased by the addition of lignin fiber. Madbouly et al.\textsuperscript{44} reported that DDGS filler could improve the biodegradability for a PHA matrix.
CHAPTER 2: NOVEL BIO-BASED COMPOSITES OF PHA/ DDGS

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2.1 Abstract

PHA/DDGS composite is a promising low-cost, bio-based material for use in the plastic cropping container industry. This research effort has quantified the effects on mechanical and thermal properties of adding different DDGS content to a PHA matrix. PHA and DDGS were mixed using a twin-screw microcompounder. Fracture surface morphology and, thermal and rheological properties were evaluated using scanning electron microscope (SEM), thermogravimetric analysis, (TGA) dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and rheometer measurement. With the increase in DDGS content from 10\% to 30\% the adhesion between PHA and DDGS became poorer. Melting temperature and crystalline temperature decreased with the increasing content of DDGS filler, indicating that PHA and DDGS favorably interacted. Since the storage modulus and glass transition temperature seldom change with different ratios of DDGS, the filler decreased neither the dynamic mechanical properties nor the glass transition temperature. In addition, the complex viscosity and elastic shear modulus were increased by the increasing DDGS content.
2.2 Introduction

Bio-based plastics have received much attention in recent years because of limited fossil-based resources and environment pollution caused by petroleum-based plastics. Bio-based plastics are materials produced from renewable agricultural and forestry feedstock. With advantages of environmental friendliness and decomposability, the bio-based plastic market is currently growing at an annual rate of 30%. Many researchers are working to derive new materials from biological resources.

Polyhydroxyalkanoates (PHAs) are a group of linear polyesters produced by many types of microorganisms as carbon and energy storage entities in bacteria. They possess similar properties to traditional synthetic thermoplastics and could replace more than 50% of the polymers derived from crude oils. Moreover, PHAs can be 100% degraded to water and carbon dioxide constituents by microorganisms in soil, sea, and sewage. Members of the PHA family could exist as both homo-polymers and copolymers. At present approximately 150 different types of PHA hydroxyalkanoic acid monomers have been reported. Depending on the monomer composition, PHAs can exhibit a wide variety of properties ranging from crystalline to elastic. Because of the diversity of PHA’s properties, their areas of application vary and range widely over packaging, electronics, sensor, energy applications, and the biomedical industry.

Poly (3-hydroxybutyrate) (PHB) is the most commonly used member of PHAs. It has mechanical properties very similar to those of petroleum-based plastics like polypropylene. The processing method for PHB could be extruded, molded, or spun into fibers. Although PHB offers many potential benefits, its applications are limited due to its
high cost and rather poor physical properties\(^{55}\). PHB cost depends on microorganisms, carbon and nitrogen sources, fermentation conditions, recovery, and purification processes.\(^ {56}\) The price for PHB is about 7.45$ per kilogram if accounting 5.12$ per kilogram for cultivations procedure.\(^ {57}\) And its high melting temperature (about 175°C) makes processing procedure difficult. In addition, PHB still has the drawbacks such as stiff, highly crystalline, and brittle. With respect to these shortcomings, blending PHB with economical fibers appears promising as an approach for reducing its production price and enhancing properties.

PHB can be blended with various biodegradable polymers and fibers, and PHB and Polyhydroxyvalerate (PHV) copolymers were those most extensively investigated. PHV is another PHA produced by chromobacterium violaceum.\(^ {58}\) The incorporation of PHV could increase the break elongation and impact strength of PHB, and the melting temperature would also decrease with increasing 3HV content. For the choice of reinforced fibers, Distiller’s Dried Grains with Solubles (DDGS) is a good candidate. DDGS is a low-cost non-fermentable cereal co-product of the corn-ethanol fuel industry. It has a complex component including protein, fiber, lipid and solubles.\(^ {59}\) The explosive growth of the ethanol fuel industry in North America will produce about 35-70 million metric tons of DDGS per year by 2020.\(^ {60}\) To avoid saturating the livestock feed market, the main use for DDGS, various potential research studies on applications of DDGS have been proposed, including uses as bio-filler, bio-plastic, and human food additives.\(^ {61}\) Bio-filler and bio-plastic applications have attracted particular interest during recent years due to their potential for low cost and biodegradability.
This paper first discusses the application of prepared PHA/DDGS in low-cost and bio-based plastic cropping containers. From this starting point, it further discusses the effects of DDGS on the rheology, mechanical properties, and thermal stability of PHA/DDGS composites. PHA/DDGS composites were mixed in a twin-screw microcompounder. Fracture-surface morphology was examined using scanning electron microscope (SEM) and thermal stability was studied using a thermal gravimetric analyzer (TGA). Thermal mechanical behavior and other thermal properties (such as glass transition and crystallization) were examined using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). In addition, the viscoelastic properties of the composite were investigated using a rheometer.

2.3 Experimental section

2.3.1 Materials

Polyhydroxyalkanoate (PHA) Mirel P1003 (Compression molding grade resins) was obtained from Metalbolix Inc., Cambridge, MA 02319. Mirel is a blend of Polyhydroxybutyrate(PHB) copolymers. DDGS were supplied by Lincoln Way Energy LLC, Nevada, Iowa.

2.3.2 Preparation of PHA/DDGS composites

PHA pellets and DDGS were dried in a vacuum oven at 60°C for 24 hours. Mixtures of PHA with 0, 10, 20, or 30% DDGS (by weight) were mixed in a Twin Screw Microcompounder (DACA Instruments) for 5 min at 180°C at a 100 rpm rotational speed. The PHA/DDGS composites were quenched to room temperature to obtain stable
morphology. When cooled, the composites were cut into small pieces suitable for compression molding. The rectangular samples (30 ×10×2 mm³) were compression-molded at 180°C for 5 min with a Carver hot press (Carver, Wabash, IN), cooled to room temperature, then removed from the mold to await analysis.

2.3.3 Scanning Electron Microscope

Scanning Electron Microscope (SEM) was used to examine the fracture surface morphology of PHA/DDGS composites. The samples were first placed into liquid nitrogen environments and then broken to reveal the fracture surface for SEM examination. The fracture surface was coated with 5mm Iridium. The prepared samples were examined using a field-emission scanning electron microscope (FEI Quanta FEG 250) with x500 magnification.

2.3.4 TGA measurements

Thermal stability was determined with a Q50 Thermal Gravimetric Analyzer (TA Instruments). About 5 mg of each sample was placed in the platinum pan and heated from 25°C to 800°C at a heating rate of 20°C/min.

2.3.5 DSC measurements

A DSC Q2000 from TA Instruments was used to evaluate the thermal effects of adding DDGS to PHA polymers. The prepared 5 mg samples were placed in a standard aluminum pan and covered with an aluminum lid. All samples were first heated from -50°C to 200 °C at 20 °C/min heating rate, then held at 200°C for 1 min, and then cooled.
to 25°C at a cooling rate of 10°C/min. Finally, the samples were heated once again from -50°C to 200°C at a 20°C/min scan rate. Nitrogen gas was used with a flow rate of 50 mL/min during all the DSC measurements. The second heat scan examined the thermal behavior of PHA/DDGS composites without previous thermal history. Crystallinity ($X_c$%) was estimated according to the following equation:

$$X_c\% = \frac{\Delta H_m}{X_p \times \Delta H_{m100\%}} \times 100$$

Where $\Delta H_m$ is the calculated enthalpy of composite, $\Delta H_{m100\%}$ is the theoretical enthalpy of melting for 100% crystalline PHA with a value of 114.6 J/g$^{62}$, and $X_p$ is the PHA fraction in the composite.

2.3.6 DMA measurements

DMA tests were performed on a Q800 dynamic mechanical analyzer (TA Instruments) in film tension mode at 1 Hz frequency. The rectangular samples (20×3×2 mm$^3$) were heated from -50°C to 200°C at a heating rate of 3°C/min and a frequency of 1 Hz under a helium atmosphere. The oscillating amplitude was 15 µm. The storage modulus and tan delta were recorded as a function of temperature.

2.3.7 Rheological measurements

Rheological properties were measured using an AR2000ex rheometer (TA Instruments) with 25 mm diameter parallel plates. In the frequency-sweep experiment, the angular frequency was typically increased from 0.1 to 100 rad/s at a constant temperature 180°C, and a strain value of 5% was consequently chosen.
2.4 Results and discussion

2.4.1 Fracture surface morphology analysis

The morphology of PHA/DDGS composites and pure PHA matrix were investigated by SEM. Fig. 2.1 shows the fracture-surface morphology of plastic blends with DDGS contents of 0%, 10%, 20%, and 30%. In Fig. 2.1a, it is possible to see a compatible microphase in the pure PHA polymers, even though Mirel P1003 PHA is a blend of P3HB and P4HV. The rough surface is attributed to its brittle mechanical characteristic. A similar morphology was observed for PHA/DDGS 90/10 composite in fig. 2.1b, indicating that the two materials are compatible to each other. While there are some small holes in the film, they may have been caused by the exit of filler and air during the processing procedure.
Compared with Fig. 2.1b, there are more exit holes in the PHA/DDGS 80/20 composites in the fracture surface. In Fig. 2.1d a different morphology is observed. At the bottom of this figure, there are some small particles could be found. This change in behavior means that the adhesion between two components has become poorer as the DDGS content increases.

2.4.2 Thermal Properties

Thermal degradation of the pure PHA and PHA/DDGS composites were studied by TGA in Fig. 2.2 It was found that all the samples decomposed through a three-state weight-loss process, with the first weight-loss peak occurring at about 300 °C, a second weight-loss peak at 410°C, and a third at 680°C. The first step could be attributed to the
decomposition of PHA since it is similar to the curve of neat PHA. PHA degrades fast at this temperature due to the chain scission reaction that leads to drastic molecular weight decrease\textsuperscript{63}. The second step exhibits a broader decomposition range than that of PHA because DDGS has complex components such as protein, lipids, and carbohydrates. This different degradation temperature range suggests that PHA and DDGS could be separated through a thermal degradation process. The characteristics of the TGA curves for all samples are listed in Table 1. The charring residues were about 0.27%, 0.7%, 1.55%, and 2.74% for 0%, 10%, 20% and 30% DDGS contents. The residue weight above 800°C increased with increasing content of DDGS. This increasing residue percentage occurs because DDGS has a higher carbohydrate content with higher ash content than PHA polymer.

Figure 2.2b shows enlarged curves of the selected temperature (250-285°C) region of Figure 2.2a. The onset of the decomposition temperature slightly decreased with increasing DDGS and PHA ratios. All the TGA traces shifted to a lower temperature for decomposition onset. As can be seen from Table 2, the onset degradation temperature at the 5% weight loss also decreased from 276.34°C to 263.56 °C with 0% and 30% DDGS filler. Moreover, Figure 2.2.c illustrates the derivative rate of all the samples. It can be seen that $T_{\text{max}}$ (the inflection point of the thermal degradation curve, corresponding to the maximum reaction rate) also decreased with increasing DDGS content. The specific values of $T_{\text{onset}}$ and %Char are also listed in Table 2.1. This behavior indicates that the increasing content of DDGS decreased the thermal degradation temperature of the composites. Other studies of polyester composites have shown similar results. For
example, Ohkita T.\textsuperscript{64} reported that the thermal stability of PLA was decreased by the addition of cornstarch, although thermal stability was reduced slightly because of the addition of DDGS, and could be compensated for by the composite’s low cost.

![Figure 2.2a. TGA traces of pure PHA and PHA/DDGS composites under a 60ml/min](image-url)
Fig 2.2b. Enlarged TGA trace of selected temperature region in (Fig. 2.2a)

Fig 2.2c. DTG thermogram pure PHA and PHA/DDGS composites under a 60 ml/min
Table 2.1 Thermogravimetric analysis of pure PHA and PHA/DDGS composites

<table>
<thead>
<tr>
<th>DDGS 0%</th>
<th>DDGS 10%</th>
<th>DDGS 20%</th>
<th>DDGS 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;onset&lt;/sub&gt;</td>
<td>276.34</td>
<td>273.02</td>
<td>269.05</td>
</tr>
<tr>
<td>%Char</td>
<td>0.27</td>
<td>0.7</td>
<td>1.55</td>
</tr>
</tbody>
</table>

To illustrate the effect of DDGS on the thermal behavior of composites, DSC traces of pure PHA and PHA/DDGS composites are shown in Fig. 2.3 and Fig. 2.4. The second heating scan removed most of the thermal history and reveals a more accurate thermal transition of the samples. The glass transition and melting transition of all the materials can be seen in Fig.7. All blends exhibited a single T<sub>g</sub> value, indicating that the two components were compatible in the amorphous phase. In addition, the presence of DDGS had little influence on the glass-transition temperature (T<sub>g</sub>) that varied by just 2°C for different filler ratios. Other studies have shown similar T<sub>g</sub> results. For a higher DDGS content, the T<sub>g</sub> is not so clear as in the curve; this may be caused by composite crystalline structure changes. The two endothermic peaks shown in Fig.7 are related to the existence of two crystalline phases in PHA samples. The presence of DDGS decreased the two melting temperatures a small amount compared with those of pure PHA polymers, indicating that PHA and DDGS interact with each other well. The melting temperature of the composites depended on various factors like morphology, crystallization, and composite composition. Detailed values of melting temperature and melting enthalpy are shown in Table 2.2. It was found the melting enthalpy was also decreased by the addition of DDGS. This thermal behavior may either be due to DDGS...
decreasing the crystalline structure of PHA contents or by DDGS decreasing the melt viscosity. Reis C. K. has found similar behavior for PHA/starch blends.\textsuperscript{69} In Reis’ research, $H_m$ and the two values of $T_m$ decreased with an increase in fiber contents. The cold-crystallization temperature ($T_{cc}$) can be seen in Figure 8. It can be seen that, with the incorporation of DDGS into the composites, the cold crystallization peaks shift to a lower temperature. $T_{cc}$ decreased with the addition of DDGS, another indication that the PHA and DDGS interacted favorably. The characteristic parameters of $T_c$ and $\Delta H_c$ are also reported in Table 2.2. Similar to the melting enthalpy behavior, the crystallization enthalpy also showed a decreased trend with increasing DDGS contents in composites.

![DSC thermogram of PHA and PHA/DDGS composites from the second heat scan](image-url)

Fig 2.3 DSC thermogram of PHA and PHA/DDGS composites from the second heat scan
Fig 2.4 DSC thermogram of PHA and PHA/DDGS composites from the cooling scan

Table 2.2 DSC parameters of PHA/DDGS blends from second heating scan.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>DDGS 0%</th>
<th>DDGS 10%</th>
<th>DDGS 20%</th>
<th>DDGS 30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g/°C$</td>
<td>-4.81</td>
<td>-8.01</td>
<td>-6.83</td>
<td>-5.71</td>
</tr>
<tr>
<td>$T_{m1}(°C)$</td>
<td>145.97</td>
<td>142.92</td>
<td>141.86</td>
<td>139.10</td>
</tr>
<tr>
<td>$T_{m2}(°C)$</td>
<td>162.61</td>
<td>160.06</td>
<td>159.44</td>
<td>159.71</td>
</tr>
<tr>
<td>$T_{cc}(°C)$</td>
<td>94.62</td>
<td>93.25</td>
<td>90.08</td>
<td>82.49</td>
</tr>
<tr>
<td>$\Delta H_m$(J/g)</td>
<td>26.916</td>
<td>25.613</td>
<td>21.101</td>
<td>18.288</td>
</tr>
<tr>
<td>$\Delta H_c$(J/g)</td>
<td>32.30</td>
<td>30.48</td>
<td>25.53</td>
<td>24.93</td>
</tr>
<tr>
<td>$X_c$(%)</td>
<td>23.49</td>
<td>22.35</td>
<td>18.41</td>
<td>15.96</td>
</tr>
</tbody>
</table>

\textsuperscript{a}: $T_g$ is the glass transition temperature, determined as the inflexion point in the DSC scan; $T_{cc}$ is the cold crystallization and it was taken as the onset of crystallization; $\Delta H_c$ is the crystallization enthalpy; $T_{m1}$ and $T_{m2}$ are the first and second melting
temperatures taken as the melting peaks; $\Delta H_m$ is the total melting enthalpy and $X_c$ is the degree of crystallinity of films.

The effects of DDGS on the dynamic mechanical properties of bio-based plastics were measured by DMA. The sample PHA/DDGS 70/30 was not included because it was too brittle to undergo the stress and strain of the DMA measurements. Tan $\delta$ of pure PHA and PHA/DDGS composites is shown in Fig. 2.5. The $\alpha$-relaxation of the polymers could be demonstrated from this curve, and $T_g$ could be identified as the peak of tan $\delta$. According to Fig. 2.5, $T_g$ remained nearly constant as the content of DDGS increased from 0% to 20%.

![Fig 2.5 Tan delta versus temperature for pure PHA and PHA/DDGS composites](image)

Fig 2.5 Tan delta versus temperature for pure PHA and PHA/DDGS composites

As shown in Fig. 2.6, the storage value of pure PHA as well as all the composites decreases with increasing temperature over the temperature range studied. This may be
due to the polymer chain mobility increase at high temperature; the retrain for polymer motion also decreased. Meanwhile, the storage modulus was almost unaffected by adding 10% DDGS compared to the pure PHA matrix. This result demonstrates that the addition of DDGS did not modify the mechanical properties of the composite materials even above $T_g$. For 20% DDGS contents, the storage modulus increased only slightly. The increase was more obvious at the temperature above $T_g$, especially for the range 60-80°C.

Fig 2.6 Storage modulus versus temperature for pure PHA and PHA/DDGS composites

Since the weight percentage ratio of DDGS may influence its viscoelastic properties of blends, the rheological behavior was examined by rheometer. Fig. 2.7 shows the frequency sweeps for PHA/DDGS composites. It was found that the complex viscosity
was affected by the addition of DDGS fillers to PHA matrix. At low angular frequency, the viscosity increased with an increasing ratio of DDGS to PHA. For example, the viscosity was 160.1 Pa.s, 243.8 Pa.s and 1219.0 Pa.s for DDGS contents of 10%, 20% and 30% at angular frequency 0.5 rad/s. For PHA with 30% DDGS composites, the viscosity was more than 7 times higher than that for 10% DDGS composites. Dimitry has suggested that cellulose particles could disturb normal polymer flow and hinder the mobility of the polymer chain, and the increase in viscosity seen here may result from the same mechanism, because DDGS is rich in cellulose particles. Therefore, the greater DDGS contents, the higher the viscosity of the blends.

Fig 2.7 Angular frequency dependence of complex viscosity at 180 °C for PHA/DDGS composites with different filler contents
Fig. 8 is a typical melting rheogram for PHA/DDGS composites. As can be seen, the elastic shear modulus ($G'$) of all the samples increased with increasing angular frequency. This increase may be due to solid-like behavior due to the high molecular weight of PHA. In addition, Fig. 8 also illustrates that $G'$ clearly increased with increasing weight percentage of DDGS, indicating that the DDGS enhanced the solid-like PHA properties. Moreover, this rheological behavior might also be explained using the same reasoning as for the increase in viscosity mentioned above.

![Diagram](image.png)

**Fig 2.8** Angular frequency dependence of storage modulus at 180 °C for PHA/DDGS composites with different filler contents
2.5 Conclusions

This study demonstrated the potential of using PHA/DDGS composites in low-cost and bio-based plastic cropping containers, and discussed the effect of filler content on thermal and mechanical properties. The PHA/DDGS composites were mixed uniformly with a twin-screws extruder. A morphological study using SEM revealed that the adhesion between two components has become poorer with the addition of DDGS. Increasing the DDGS content in composites caused more small holes compared to the pure PHA matrix. The TGA test demonstrated a three-stage degradation process, and DDGS slightly decreased the thermal stability of the composites, but this reduction probably is compensated for by the low material cost. Both the melting temperature and crystalline temperature decreased with increased DDGS filler content, indicating that PHA and DDGS interacted favorably. Neither the storage modulus nor the glass transition temperature changed significantly with the addition of DDGS, indicating that the filler reduced neither the dynamic mechanical properties nor the glass transition temperature. In addition, the dynamic viscosity and elastic modulus of the composites were increased with increasing DDGS content. Both the PHA matrix and DDGS filler composites could be good candidates for bioplastic container systems.

2.6 Acknowledgements

This research was supported in part by the USDA Specialty Crops Research Initiative (USDA-SCRI project # IOW05306). The authors thank Metabolix, Inc. for providing Mirel PHA, and polycomp group for their technical assistance.
CHAPTER 3: BIODEGRADATION BEHAVIOR OF POLY (LACTIC ACID)/
DISTILLER’S DRIED GRAINS WITH SOLUBLE COMPOSITES

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3.1 Abstract

Poly (lactic acid) (PLA) and Distiller’s Dried Grains with Solubles (DDGS) are potential bio-based materials for industrial applications. This article will discuss the biodegradation behavior of PLA/DDGS (80/20 by weight) composites as economical and biodegradable crop containers. Biodegradation experiments were performed in soil under landscape conditions. Surface morphology and thermal properties were evaluated by scanning electron microscope (SEM), dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). Adding 20% DDGS can accelerate the degradation rate of pure PLA and enhance the storage modulus of pure PLA. The weight loss of PLA/DDGS composite after 24 weeks of degradation time is 10.5\%, while the weight loss for pure PLA is only 0.5\% after such an interval. Cracks and voids on the surface were clearly observed with increasing degradation time due to the loss in chain length and erosion. With the increasing degradation time, thermal stability was enhanced.
Glass transition temperature and melting temperature increased first and then decreased slightly. As a biodegradable filler, DDGS reduced cost, enhanced mechanical properties, and only slightly affected the thermal properties of the materials.

3.2 Introduction

Approximately 140 million tons of petroleum-based polymers are produced each year. Environmental pollution from such short service-life products has been recognized as a large problem, so a great deal of research in recent years has focused on bio-based polymers and composites in an attempt to replace petroleum-based polymers. Biopolymers can fulfill nearly all the functions of petroleum-based materials in applications ranging from packaging to durable products.

Bio-based polymers and composites are materials produced from renewable agricultural and forestry feedstock. A sustainable bio-based product should have both recycling capability and biodegradability. Bio-based composites typically consist of a combination of biofiber and bioplastic. For bioplastic derived from renewable resources, thermoplastics play a more important role than thermosets due to their recyclability. Polyesters comprise a family of bioplastic groups that are important because of their hydrolysable ester bonds. They have been used commercially in industrial products in the form of polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), poly (lactic acid) (PLA), polycaprolactone (PCL), and polyhydrohexanoate (PHH), etc.
PLA is a linear aliphatic thermoplastic polyester derived from renewable resources such as cornstarch, and it can be totally decomposed by microorganisms like bacteria. In natural under-soil conditions, it will also be degraded, but less so than other biodegradable polymers. Considering that it is a renewable, sustainable, and biodegradable plastic, with mechanical properties similar to traditional polymers such as polyethylene terephthalate (PET), PLA can be used in a wide range of industrial products ranging from packaging to fibers and foams. Although the plastic market demand for commercialized PLA is growing at 5-8% yearly, and the annual world market for PLA production is expected to reach 367,300 metric tons by 2017, its application is still limited because of its relatively high cost (~$1.6 per kilogram of lactic acid).

Fillers, in concentrations usually ranging from 10% to 50% (by weight), are often used to improve PLA’s overall properties and lower its cost in industrial applications. Fillers can be organic, inorganic, natural, or synthetic. Commonly-used fillers include glass, limestone, wood flour, metals, bamboo, coconut shells, clay, etc. Since PLA has a low rate of degradation in soil, because of the concerns for conserving petroleum resources, enhancing biodegradability, and reducing costs, it is often blended with various low-cost natural fillers such as starch, lignin, sugar cane, soy protein, wood flour, and distillers dried grains with solubles (DDGS).

DDGS is a non-fermentable cereal co-product of the corn-ethanol fuel industry. It has a complex constituency that includes protein, cellulosic fiber, oils, and ash. In fact, DDGS has been used in large scale as a livestock feed. Supplies of DDGS in the North America market have increased greatly during the last 10 years, with expected
volume of more than 42 million tons per year\textsuperscript{83}. It is crucial to develop alternate approaches to using this co-product to avoid market saturation. Because of its low cost, low density, biodegradability, and renewability it has recently found use as bio-based filler in polymer composite materials. Therefore, combining DDGS with higher-protein filler is a good way to both form a better composite and accelerate its degradation rate.

Some recent studies have been directed toward developing a processing method for associating DDGS with PLA composites, and to quantify mechanical and thermal properties for different filler content\textsuperscript{84,85,86,87}. However, there are few reports about the degradation behavior of these composites. The biodegradation process is governed by a variety of factors including organisms, additives, molecular weight, type of functional group, crystallinity, chemical structure, and mobility\textsuperscript{89}. Degradation processes lead to changes in materials’ properties through bond scission and chemical transformations\textsuperscript{90}. These changes generally involve cracking, color change, and general changes in physical and thermal properties\textsuperscript{91}.

In this study, the feasibility of using PLA/DDGS (80/20) composites as economical and biodegradable crop containers was evaluated. Biodegradation rates in soil under landscape conditions were evaluated. The surface morphology of composite containers with different degradation times was studied by Scanning Electron Microscope (SEM). Thermal properties were determined by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The crystalline performance of containers in their early state were tested by X-ray diffraction (XRD). These results will provide useful
information about the biodegradation behavior of these two systems of bio-based plastic composites.

3.3 Experimental section

3.3.1 Materials

Polylactic Acid (PLA) was provided by NatureWorks LLC, Minnetonka, MN. Distillers Dried Grains with Solubles (DDGS) was supplied by Lincoln Way Energy LLC, Nevada, IA. The PLA pellets and ground DDGS were dried in a vacuum oven for 6 hours at 80 °C.

3.3.2 Preparation of PLA/DDGS and PLA/DDGS with soybean protein composites

The PLA/DDGS 80/20 (w/w) was extruded in a Leistritz compounding twin-screw extruder (Leistritz Micro18, L/D ratio 30, American Leistrits Crop., Somerville, NJ). The temperature profile during extrusion was 180 °C from the hooper-mixing-die for all formulations.

3.3.3 Biodegradation experiments

Biodegradation experiments were carried out in soil under landscape conditions at the Iowa State University Horticulture Research Station. PLA, PLA/DDGS samples were comprised of one-fourth injected containers. First each sample was weighed and placed in a non-degradable mesh bag. Then the one-fourth containers were buried 10 cm below the soil surface in a greenhouse. The soil was fine-loamy, mixed, and super active from Typic Hapludolls. The soil temperature was kept at 21.1 °C and irrigated by about 2.5 cm of
water per week. At the end of each targeted biodegradation time, samples were extracted from the soil and washed and dried at 33±5°C for 9 days until their weights stabilized to constant values. Finally, they were once again weighed at the same location where initial weights were measured.

Weight loss can be calculated using the following equation:

\[ W_{\text{loss}} \% = \left( \frac{W_0 - W_1}{W_0} \right) \times 100 \]

Where \( W_{\text{loss}} \% \) is the relative weight loss, \( W_0 \) is the initial specimen weight (g), and \( W_1 \) is the final specimen weight (g).

3.3.4 Scanning Electron Microscope

After degradation tests, Scanning Electron Microscope (SEM) was used to examine the surface morphology of differently degraded (0, 8, 16, 24 weeks) PLA/DDGS composites. The samples were placed on SEM holders and sputtered with a 5mm layer of Iridium. The samples prepared in this way were examined using a field-emission scanning electron microscope (FEI Quanta FEG 250) operating at 8 kV under high vacuum at a magnification of x200.

3.3.5 TGA measurements

Thermal stability was determined with a Q50 Thermal Gravimetric Analyzer (TA Instruments). About 7 mg of each sample was placed in a platinum pan and heated from 25°C to 800°C at a heating rate of 20°C/min under a 60 ml/min rate of air flow and a 40 ml/min rate of nitrogen flow.
3.3.6 DMA measurements

DMA tests were performed on a Q800 dynamic mechanical analyzer using a film-tension system. The rectangular samples were heated from -50 °C to 150 °C at a 3 °C/min heating rate. A tension clamp was used at a frequency of 1 Hz and an oscillation amplitude of 5 μm.

3.3.7 DSC measurements

A DSC Q20 from TA Instruments was used to evaluate the effects of biodegradation on thermal behavior of PLA/DDGS composites. The prepared samples were fit into standard aluminum pans and covered with aluminum lids. All the samples were heated from -50°C to 200 °C at a 20 °C/min heating rate. Nitrogen gas was used with a flow rate of 50 mL/min during all the DSC measurements.

Crystallinity \( (X_c \%) \) was estimated using the following equation:

\[
X_c \% = \frac{\Delta H_m}{X_p \times \Delta H_{m100\%}} \times 100
\]

Where \( \Delta H_m \) is the calculated enthalpy of composite, \( \Delta H_{m100\%} \) is the theoretical enthalpy of melting for 100% crystalline PLA polymer (a value of 93.7 J/g \(^2\)), and \( X_p \) is the PLA fraction in the composite.

3.3.8 X-ray diffraction

X-ray diffraction (XRD) measurements were performed with a Rigaku Ultima IV at 40kV and 44mA and monitored by Standard Measurements software. The operational
mode was BB with a monochromator. All measurements were made in the scattering-angle range $1^\circ \leq 2\theta \leq 35^\circ$ with a scan speed of $1^\circ$/min.

$$X_c\% = \frac{I_{\text{crystalline}}}{I_{\text{crystalline}} + I_{\text{amorphous}}} \times 100$$

Where $X_c$ is the degree of crystallinity, $I_{\text{crystalline}}$ is the diffracted intensity of the crystalline phase, and $I_{\text{amorphous}}$ is the diffracted intensity of the amorphous phase. This equation can be transformed into another form for easier calculation of $X_c$.

$$X_c\% = \frac{A_{\text{crystalline}}}{A_{\text{crystalline}} + A_{\text{amorphous}}} \times 100$$

Where $A_{\text{crystalline}}$ is the area under the crystalline peaks and $A_{\text{amorphous}}$ is the area under the amorphous peaks. The true area of the crystalline peaks and amorphous peaks can be determined using Origin Pro. Software.

3.3.9 Rheological measurements

Rheological properties were measured using an AR2000ex rheometer with 25mm diameter parallel plates. In the frequency sweep experiment, the angular frequency was increased logarithmically from 0.1 to 100 rad/s at a constant temperature of 180°C and with a 1.25% strain.

3.4 Results and discussion

3.4.1 Degradation Behavior

PLA is one of the most promising alternatives to petroleum-based materials currently available on the market. DDGS is a low-cost organic filler with protein and cellulose. The protein derived from DDGS and SP.A may provide favorable interaction
and improved adhesion with the PLA matrix in bio-based composites to positively affect the degradation and thermal behavior of PLA.

According to K. Chung et al. (2000)\(^{94}\), the higher the surface-to-volume ratio of the samples, the faster the rate of weight loss. In this study, all specimen were one-fourth injection-molded container fragments with identical dimensions to keep the relevant parameters constant. Fig. 3.1 shows the biodegradation time dependence of weight loss for neat PLA, PLA/DDGS 80/20 composites in soil medium. It is obvious that the biodegradation rate of neat PLA was quite slow. During the first 12 weeks of degradation testing, the weight loss was 0%; after 16 weeks of degradation in soil, the weight loss finally reached 0.1%. Although PLA is a biodegradable polymer, its degradation rate in soil is slow and full degradation may require many years in some situations\(^{95}\). Usually adding a biofiller will speed biodegradability and, as expected, the biodegradation rate of PLA was accelerated by adding 20% (by weight) of DDGS filler.

Table 1 shows that the weight loss increased rapidly during the first 8 weeks of biodegradation time, then leveled off and finally approached 10.5% after a 24-week degradation test. The slope of the curve represents the degradation rate. Fig.1 confirms that DDGS successfully enhanced the degradation process. This result is similar to that from an earlier study by Madbouly et al\(^{96}\). DDGS, rich protein, and amino acid provide a high C: N ratio in composite materials. A higher C: N ratio is more likely to accelerate the biodegradation process. Because of the high protein content from the DDGS, the degradation process was greatly improved. Additionally, when used as a low-cost bio-based filler, DDGS is non-toxic, so safety is a feature of this bio-based container.
Fig. 3.1 Biodegradation time dependence of weight loss of Pure PLA and PLA/DDGS 80/20 composites in soil medium

Table 3.1 Degradation weight-loss percentages (%) for PLA blends and composites in soil from the bioplastic container trials

<table>
<thead>
<tr>
<th></th>
<th>0w</th>
<th>4w</th>
<th>8w</th>
<th>12w</th>
<th>16w</th>
<th>20w</th>
<th>24w</th>
</tr>
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<tbody>
<tr>
<td>Neat PLA/ %</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>PLA/DDGS/ %</td>
<td>0</td>
<td>5</td>
<td>6.5</td>
<td>7.3</td>
<td>9.0</td>
<td>10.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

3.4.2 Surface morphology analysis

Polymer degradation is associated with a change in characteristics like shape, surface morphology, and mechanical properties. SEM is widely used to evaluate the morphology of different degradation periods. After degradation tests, a surface morphological analysis of neat PLA, PLA/DDGS 80/20 composites were performed by SEM. Micrographs of both non-degraded and 24-week degraded PLA are shown in
Fig. 3.2. As can be seen in Fig. 3.2, neat PLA without degradation has a very smooth surface. After 24 weeks of degradation in soil, the surface morphology changed very little, with the appearance of only a few small surface cracks, and these cracks may have been the result of some chain-length loss and PLA erosion.

Fig. 3.2 SEM micrographs of surface morphologies of neat PLA with (a) 0 week and (b) 24 weeks degradation times

The surface morphologies of PLA/DDGS were also examined by SEM. From Fig. 3.3a it can be seen that PLA/DDGS 80/20 has a very smooth surface like that of the PLA shown in Fig. 3.2a before degradation testing. Fig. 3.3b shows that the surface became very tough after 8 weeks of degradation. The cracks and voids shown in Fig. 3.3c show that remarkable plastic degradation occurred after 16 weeks. These cracks and voids can also result from the chain loss and surface erosion by microorganisms. Such erosion could also corroborate the weight loss data presented in Fig. 3.1. Moreover, with increasing degradation time, interfacial bonding between PLA and DDGS became weaker with the absorption of more water; the cracks also became deeper, as can be observed in Fig. 3.3d.
Comparing this result to that for the PLA after 24 weeks of degradation (Fig. 3.2b) confirms that DDGS provides some special bonding with PLA to enhance material degradability. In addition, it could be seen by the naked eye that the color became lighter, and the shape was transformed through surface erosion as shown in Fig. 3.4.

Fig 3.3 SEM micrographs of surface morphologies of PLA/DDGS 80/20 composites after different degradation times: (a) 0 week; (b) 8 weeks; (c) 16 weeks; (d) 24 weeks
3.4.3 Thermal properties

DMA measurements for neat PLA, PLA/DDGS, and PLA/DDGS composites with different degradation times were performed to determine the effects of degradation on thermal properties. Fig. 3.5 presents the storage modulus-temperature curve for all the samples. PLA is a high-modulus and brittle biomaterial, and blending it with natural fibers could enhance its mechanical properties and reduce cost. DDGS contains fiber and has a lower density of about 1300 kg m$^{-3}$ compared to inorganic fillers.$^{98}$ As expected, Fig. 3.5 shows that the addition of 20% DDGS filler slightly increases the storage modulus of the material. Fig. 3.5 also illustrates that, for PLA/DDGS composites, the storage modulus decreases with increasing biodegradation time over a wide range of temperatures ranging from -45°C to 60 °C. This result is associated with chain loss and decrease in molecular weight through the bulk hydrolysis. A reduction in storage modulus with increasing degradation time can be observed.
Fig. 3.5 Storage modulus versus temperature for pure PLA without degradation test and PLA/DDGS 80/20 composites with different degradation time (0 week, 8 weeks, 16 weeks, 24 weeks)

Fig. 3.6 shows the evolution of glass-transition temperature (Tg) for different degradation times. It can be seen that Tg decreased with the addition of DDGS when compared to neat PLA without degradation. This is mainly because the molecular weight decreased after blending with fillers, and the filler affects the crystalline structure of the composite. Tg was found to increase after 8 weeks of degradation time, but during the interval between 8 weeks and 24 weeks it varied only slightly compared to PLA/DDGS composites before degradation testing. Usually, once a composite begins to degrade, the decrease in molecular weight will reduce the glass transition temperature. This unexpected phenomenon may occur because the crystalline structure has been changed.
after degradation. PLA/DDGS composites are semi-crystalline materials, and degradation processes occur in both crystalline and amorphous regions. According to the two-state process reported by Chu\textsuperscript{99}, hydrolysis will first occur in the amorphous region and subsequently in the crystalline region. Minna Hakkarainen\textsuperscript{100} has also suggested that degradation kinetics may have been influenced by crystallinity, and the amorphous regions hydrolyzed first for PLA/PGA composites. DDGS constitutes part of the amorphous region, so most of the DDGS degraded during this earlier state. During this period, the decomposition of amorphous regions will lead to a relatively higher-percentage crystalline region and a higher degree of crystallinity. The loss in weight shown in Fig. 3.1 supports this idea. As shown in Fig. 3.1, the weight-loss rate is highest in the first 8 weeks of degradation time, after which it changes less rapidly. After 16 weeks of degradation time, the rate of the degradation process in crystalline and amorphous regions achieved balance and the Tg values didn’t change much.
Figure 3.6. Tan delta versus temperature for pure PLA before degradation test and PLA/DDGS 80/20 composites with different degradation time

DSC curves of PLA/DDGS 80/20 composites with different degradation time are shown in Fig. 3.7. Tg was shifted to higher values as degradation time increased. This is consistent with the results obtained by the DMA instrument. The crystalline temperature ($T_c$) and melting temperature ($T_m$) exhibit the same trends as Tg. They increase slightly, indicating that the DDGS filler did not lead to significant changes in thermal properties. In addition, the Xc firstly increased and then after 16 weeks degradation decreased. The detail values could be seen in Table 3.2.
Fig. 3.7 DSC thermograms of pure PLA without degradation and PLA/DDGS composites with different degradation time (0 week, 8 weeks, 16 weeks, 24 weeks)

Table 3.2 DSC parameters of PLA/DDGS blends

<table>
<thead>
<tr>
<th></th>
<th>0w PLA</th>
<th>0 weeks</th>
<th>8 weeks</th>
<th>16 weeks</th>
<th>24 weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g/°C$</td>
<td>60.10</td>
<td>51.65</td>
<td>52.25</td>
<td>52.16</td>
<td>57.57</td>
</tr>
<tr>
<td>$T_m/°C$</td>
<td>169.71</td>
<td>162.68</td>
<td>165.94</td>
<td>165.39</td>
<td>170.43</td>
</tr>
<tr>
<td>$T_c/°C$</td>
<td></td>
<td>102.72</td>
<td>102.64</td>
<td>107.43</td>
<td>110.66</td>
</tr>
<tr>
<td>$\Delta H_m$(J/g)</td>
<td>16.59</td>
<td>37.12</td>
<td>40.63</td>
<td>39.82</td>
<td>39.00</td>
</tr>
<tr>
<td>$X_c$(%)</td>
<td>17.71</td>
<td>39.62</td>
<td>43.36</td>
<td>42.50</td>
<td>41.62</td>
</tr>
</tbody>
</table>

X-ray diffraction also provides a good way of monitoring changes in crystallization caused by degradation. XRD was studied to further verify the result of DSC measurements especially the period from 8 weeks to 16 weeks. As shown in Fig. 3.8, the
ratio of the area under the crystalline peak to areas under all peaks for the first 12 weeks is higher than for the 8 weeks composites, indicating that the degree of crystallinity for 12 weeks of degradation time does still increase compared to that of PLA/DDGS composites before degradation testing. The value of crystallinity could be seen in Table 3.3. After 16 weeks of degradation time, the degree of crystallinity decreased slightly, both the amorphous region and crystalline region begun to degrade. Although the values are not the same, this trend is still in good agreement with our suspicion about the mechanism of degradation.

Fig. 3.8 XRD diffraction patterns of PLA/DDGS composites after different degradation time (8 weeks, 12 weeks, 16 weeks)
Table 3.3 XRD parameter of PLA/DDGS composite

<table>
<thead>
<tr>
<th>Time</th>
<th>8w</th>
<th>12w</th>
<th>16w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xc/ %</td>
<td>28.9</td>
<td>33.9</td>
<td>29.2</td>
</tr>
</tbody>
</table>

Thermal stability of all the container samples was studied by TGA. Fig. 3.9 shows the influence of the degradation process on the thermal decomposition curve. For neat PLA, the sample decomposed in one step at about 400°C. With the addition of DDGS filler, the composites decomposed through a two-stage process. The first step that occurred at about 375°C was attributed to the PLA matrix. The second step exhibited a wider temperature range because DDGS contains complex components such as protein, fiber, and oil. It should be noticed that, with increasing degradation time, both the $T_{onset}$ (5% weight loss) and $T_{max}$ (the inflection point of the thermal degradation curve) shifted to lower temperatures, indicating that thermal stability was diminished with the addition of DDGS. However, the achievement of lower cost could compensate for this slight reduction in thermal stability. Meanwhile, as illustrated in Figure 3.9 the enlarged curve for weight losses ranging from 0% to 10%, it can be seen that thermal stability was enhanced with increasing degradation time. All the values of $T_{onset}$ and $T_{max}$ are listed in Table 3.4. This behavior has two possible explanations. First, as already discussed, DDGS filler degrades faster than PLA matrix, so the content of DDGS in the composites will diminish with increasing degradation time. Second, compared with neat PLA, it is known that increasing DDGS content would decrease the thermal-decomposition
temperature. There are similar studies describing biodegradation behavior of thermoplastic composites. Morancho J.\textsuperscript{101} et al., studied the thermogravimetric behavior of PP/EVOH blends, and they found that $T_{\text{onset}}$ and $T_{\text{max}}$ increased with increasing degradation time. Schilemmer D.\textsuperscript{102} et al. also reported the decomposition temperature of PP/ starch composite was shifted to a higher value after 6-month soil burial tests.

Fig. 3.9a TGA traces of non-degraded neat PLA and PLA/DDGS composites for different degradation time
Fig. 3.9b Enlarged TGA trace of selected temperature region in (Fig. 3.9a)

Table 3.4. Thermogravimetric analysis of non-degrade neat PLA and PLA/DDGS composites with different degradation time

<table>
<thead>
<tr>
<th></th>
<th>0w PLA</th>
<th>0w</th>
<th>8w</th>
<th>16w</th>
<th>24w</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{onset}}$</td>
<td>339.27</td>
<td>287.84</td>
<td>291.81</td>
<td>310.23</td>
<td>321.15</td>
</tr>
<tr>
<td>$T_{\text{max}}$</td>
<td>380.18</td>
<td>335.86</td>
<td>362.99</td>
<td>367.05</td>
<td>372.37</td>
</tr>
</tbody>
</table>

The biodegradation process may significantly influence the viscoelastic properties of PLA/DDGS composites. The rheological behavior was measured using a Rheometer. Fig. 3.10 shows the dependence of complex viscosity ($\eta^*$) at 180°C for angular frequencies ranging from 0.1 to 100 rad/s. It was found that the complex viscosity of
PLA/DDGS composites decreased with increasing degradation time. This decrease is attributed to soil degradation, since viscosity is proportional to molecular weight.

Fig. 3.10. Angular frequency dependence of complex viscosity at 180 °C for PLA/DDGS 80/20 composites after different durations of biodegradation

Fig. 3.11 showed the elastic shear modulus (G’) of PLA/DDGS composites for different degradation times. It can be seen that G’ increase with increasing angular frequency, indicating a solid-like response of PLA. Combined with the study of Lin et al\textsuperscript{103}, Alhmed J. et al\textsuperscript{104}, this suggests that this behavior can be attributed to the higher molecular weight of PLA. This could also explain the reduction in G’ for the composites after degradation testing. From Fig. 8 it is obvious that G’ decrease with increasing degradation time
because PLA/DDGS composites decomposed to a lower molecular weight after soil degradation testing.

Fig. 3. 11. Angular frequency dependence of $G'$ at 180 °C for PLA/DDGS 80/20 composites after different durations of biodegradation

3.5 Conclusions

In this paper, we have presented biodegradation behavior of PLA/DDGS 80/20 composites. Adding DDGS can accelerate the degradation rate by 10.5%, compared to the same conditions in pure PLA, after 24 weeks of degradation time. Using an SEM instrument, an increased number of surface cracks and voids could be clearly observed as degradation time increased. Analysis of the bio-container samples by DMA showed that adding 20% DDGS enhanced the mechanical properties of pure PLA. For PLA/DDGS composites, the storage modulus decreased with increasing degradation time. Combined
with the results of DSC and X-ray analysis, thermal properties remained virtually unchanged. Thermal stability was reduced with the addition of DDGS filler and, with increasing degradation time, both $T_{\text{onset}}$ and $T_{\text{max}}$ shifted to higher values. As a bio-based filler, DDGS reduced the cost of materials, increased the storage modulus, and had little effect on the thermal properties of the materials. PLA/DDGS composites can be utilized in sustainable plastic containers that are both economically feasible and satisfactorily fulfill the functions of PLA plastic products.

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 Lincoln Way Energy LLC. for providing DDGS. We also thank Kyle Haubrich and Samuel Schrader for their technical assistance during prototype development, trial establishment, and data collection.
CHAPTER 4: GENERAL CONCLUSIONS

In this thesis, two systems of bio-based composites were developed and evaluated. For PHA/DDGS composites, the main goal was to reduce the cost while maintaining their useful properties. PHA/DDGS composites with 10%, 20% and 30% DDGS (by weight) were uniformly mixed using a twin-screw extruder. Compared with neat PHA polymers, the fracture surface morphology of the composites became rough, indicating that the composites became more brittle with increasing DDGS content. Moreover, for PHA with 30% DDGS composite, a greater number of holes and small particles were observed, indicating that adhesion between the two components became poorer when using a higher-percentage filler. TGA results also indicated that the thermal degradation temperature of the composites was shifted to a lower value, with \( T_{\text{onset}} \) decreasing from 276.34 °C to 263.53 °C for a DDGS change from 0% to 30%. However, this change was relatively small and the resulting cost reduction could offset this thermal-stability reduction. Other thermal properties were little affected by the addition of the DDGS. DSC studies suggest that composite melting and crystalline temperatures decreased with the DDGS content, indicating that PHA and DDGS favorably interacted with one other. DMA tests also show that the glass transition temperature, storage modulus, and loss modulus ranged over a very small temperature interval. Also, the melting theogram of the samples clearly showed that complex viscosities \( G' \) and \( G'' \) were enhanced with an increasing DDGS ratio, indicating that the DDGS enhanced the solid-like properties of PHA, especially at low angular frequency rate.
The degradation behavior of different stages was studied for PLA/DDGS composites-based biodegradation systems. During a 24-week degradation test in soil under landscape conditions, it was found that adding DDGS could significantly accelerate the degradation rate. SEM morphology results showed that cracks and voids became more clearly evident during this degradation process. DMA results also indicated that the dynamic mechanical properties of this material were enhanced through incorporation of DDGS. In addition, when combined with DSC tests, glass transition temperature changed very slightly. Due to the chain loss and hydrolysis of the composites, DDGS degraded faster than PLA, suggesting that the degree of crystallinity increased during the early state of the degradation process. Furthermore, the thermal stability and melt viscosity also decreased with increasing burial time in soil. In general, PLA with DDGS composites could achieve the goal of cost saving through exhibiting faster degradation.
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