



Study of Synthesis and characterization of Bio-composites from Poly(lactic acid) and DDGS

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ABSTRACT

Distillers dried grains with solubles (DDGS), an ethanol industry coproduct, is used mainly as a low-value feedstuff. Poly(lactic acid) (PLA) is a leading biodegradable polymer, but its applications are limited by its relatively high cost. Mechanical, morphological, and thermal properties of the composites were studied. The coupling mechanism of MDI in the PLA/DDGS system was confirmed via Fourier-transform infrared spectra. Crystallinity of PLA in the composites was higher than that in pure PLA. Composites with MDI had higher storage moduli at room temperature than pure PLA. This novel application of DDGS for biocomposites has significantly higher economic value than its traditional use as a feedstuff.

Keywords: Crystallinity, Biocomposites

1 INTRODUCTION

In 2006, about 13.2 million metric tons of DDGS were produced in the United States, and this number may increase to 25 million metric tons by 2011. DDGS contains about 26.8-33.7% protein (dry weight basis), 39.2-61.9% carbohydrates (including fibers), 3.5-12.8% oils, and 2.0-9.8% ash. Currently, the ethanol industry's only outlet for DDGS is animal feed ingredients. Most research publications about DDGS focus on its feed applications.

In recent years, DDGS production has far exceeded its consumption rate as feed. It is predicted that DDGS may have to be disposed of via landfilling, creating an environmental burden. Consequently, development of new outlets for DDGS has become an urgent need and is crucial to maintaining economic viability of the ethanol industry. Several potential alternatives have been proposed including extracting higher value protein and cellulose from DDGS and using DDGS for phenolic/DDGS composites, biocomposites, and bioadhesives. In this study, we explore the feasibility of using DDGS for biodegradable composites with poly(lactic acid) (PLA).

PLA is derived from sugar-based materials. It is the leading biodegradable polymer and considered a sustainable alternative to petroleum-based plastics. PLA exhibits mechanical properties similar to those of some traditional polymers. However, its applications are limited by several unsatisfactory characteristics, such as modest strength and modulus, brittleness, low heat distortion temperature, and relatively high cost. Therefore, PLA has been compounded with various low-cost natural biopolymers including wood flour, sugar cane, lignin, flax, soy flour, soy protein, and starch to reduce its cost and enhance its modulus and biodegradability. It has made achievements in preparing PLA/starch composites. When a mixture of 55% PLA and 45% starch (w/w) was thermally compounded with 0.5% methylene diphenyl diisocyanate (MDI) as coupling agent, the composite showed enhanced mechanical properties and storage modulus above glass transition temperature.

DDGS is a multiple-component biopolymer that has not been studied for use in PLA composites but exhibits several advantages over other

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fillers. First, the cost of DDGS is only 2-3 cents per kg, which is lower than the cost of starch (5-10 cents per kg), wood fibers (~5 cents per kg), and soy flour (~5 cents per kg). Second, MDI used as a coupling agent for the PLA/DDGS system could further improve compatibility and interfacial adhesion. MDI has two isocyanate groups, which react with nucleophiles such as hydroxyl groups, carboxyl groups, and amino groups to form urethane or urea linkages. Consequently, MDI can act as a chain extender for pure PLA. However, no significant effect of MDI on the thermal and mechanical properties of pure PLA were observed. The proposed coupling mechanism between PLA and DDGS with MDI is shown in Figure 6.1. Potential applications for these novel composites include vehicle interiors, appliance components, service utensils, and packaging materials. The objectives of this study were to develop value-added biocomposites from DDGS with PLA matrix and investigate the composites' mechanical, morphological, and thermal properties.

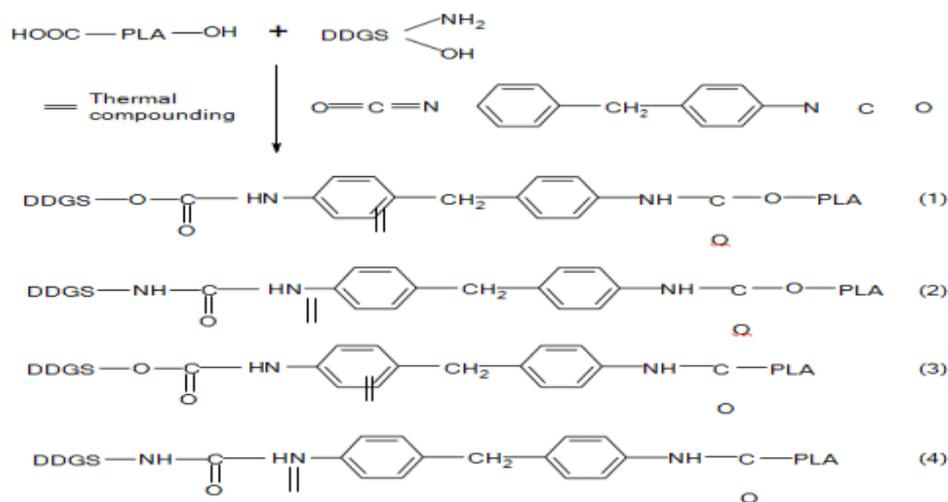


Figure 7.1 Proposed coupling mechanism between PLA and DDGS with MDI.

2 EXPERIMENTAL SECTION

Preparation of PLA/DDGS Composites

PLA pellets were ground through a 2 mm screen. DDGS was also ground with the same mill through a 1 mm screen. Ground PLA and DDGS were dried in a vacuum oven at 80 °C for 24 h. Mixtures of ground PLA with 20, 30, 40, or 50% DDGS (based on total weight) were mixed in a stand mixer for 10 min. The mixtures were thermal blended for 3 min at 180 °C and 130 rpm. When cool, mixtures were ground into 2 mm powder. Pure PLA was treated with the same procedures as the control. Composites of PLA/20%DDGS with varying ratios of MDI (0.25, 0.5, 1, and 2% based on 100 parts of PLA/DDGS mixture) were prepared similarly to further investigate the effectivity of MDI as coupling agent. Tensile bars were compression molded at 180 °C and 8000 lb for 5 min, according to ASTM Method D 638-91 (1992), cooled to room temperature in air, and then removed from the mold. Five tensile bars were prepared for each type of composite, and bars were conditioned at 25 °C with a relative humidity of 50% for at least 48 h prior to characterization.

3 RESULTS AND DISCUSSION

FTIR

Figure 6.2 shows the representative FTIR spectra of MDI, DDGS, PLA, and the PLA/20%DDGS/1%MDI composite. The strong absorption peak at 2292 cm⁻¹ for MDI was attributed to the free -N=C=O groups. For DDGS, the broad band centered at 3364 cm⁻¹ was assigned to the stretching vibration of -OH and -NH from carbohydrates and protein, the peak at 2930 cm⁻¹ to the stretching of -CH from lipids, the peak at 1654 cm⁻¹ to the amide absorption of corn protein, and the peaks at the region of 1250-1000 cm⁻¹ to carbohydrates. These results confirm that DDGS is composed of carbohydrates, protein, and lipids. PLA exhibited -OH vibration bands at 3500 cm⁻¹; -CH stretching and bending vibration bands at 2994, 2944, and 1454 cm⁻¹; and -C=O vibration bands at 1772 cm⁻¹. After thermal compounding of PLA and DDGS with MDI, the peak of -N=C=O in the composites totally disappeared, indicating that all free isocyanate groups from MDI were consumed during thermal compounding. Moreover, the strong absorption peak of -OH and -NH observed in DDGS became very weak, indicating that most -OH and -NH groups were reacted with MDI in forming urethane and urea linkages. The urea-urethane and alcohol-urethane groups were expected to be found at 1647 cm⁻¹ and 1704-1727 cm⁻¹, respectively, which were overlapped with amide and -C=O absorption.

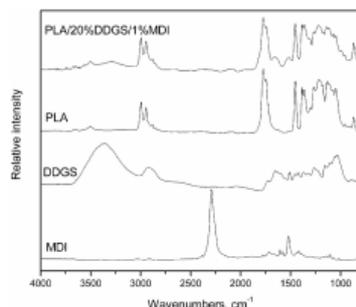


Figure 6.2 FTIR spectra of MDI, DDGS, PLA, and PLA/20%DDGS/1%MDI composite

Mechanical Properties

Pure PLA exhibited tensile strength (σ) of 77 MPa, elongation (ϵ) of 6.2%, and Young's modulus (E) of 2.0 GPa (Table 6.1). With 20% DDGS, σ and E decreased to 27 MPa and 1.8 GPa, respectively, whereas ϵ increased significantly to 16%, as shown in the stress-strain curve (Figure 6.3).

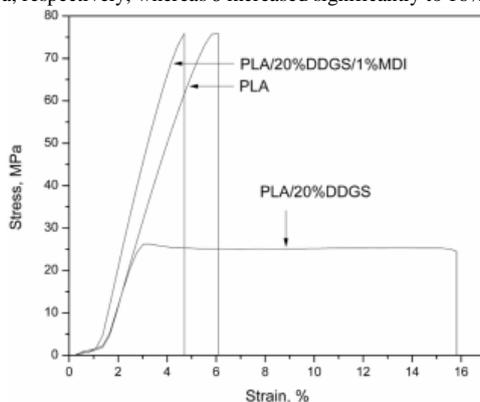


Figure 6.3 Tensile stress-strain curves of PLA and typical PLA/DDGS composites.

As the DDGS loading further increased, σ and E kept decreasing, whereas ϵ remained higher than that of pure PLA. When DDGS content reached 50% in the composite, σ and E decreased to about 10 MPa and 0.8 GPa, respectively, and ϵ was 7.8% (Table 6.1). These results indicated that interfacial adhesion between the PLA matrix and DDGS particles was poor because of their immiscible characteristics.

Table 6.1 Mechanical properties of PLA/DDGS composites without coupling agent

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Pure PLA	77.10 ± 0.76	6.18 ± 0.37	2.04 ± 0.02
20% DDGS	27.44 ± 0.68	15.65 ± 2.36	1.81 ± 0.04
30% DDGS	20.24 ± 1.11	11.62 ± 2.08	1.51 ± 0.05
40% DDGS	13.55 ± 0.94	10.95 ± 3.57	1.20 ± 0.14
50% DDGS	9.72 ± 0.51	7.77 ± 1.90	0.80 ± 0.05

The loading ratio of DDGS was then fixed at 20% to investigate the effect of coupling agent (MDI) on mechanical properties of composites (Table 6.2). The σ and E of PLA/20% DDGS composites increased dramatically by incorporating MDI, compared with composites without MDI, whereas ϵ decreased slightly compared with that of pure PLA. With 0.25% MDI, σ and E increased to 54 MPa and 2.4 GPa, respectively. For composites with 0.5% MDI, σ further increased to 68 MPa, whereas E remained almost unchanged. Optimum mechanical properties were obtained at 1% MDI, at which σ (77 MPa) was the same as that of pure PLA, E (2.5 GPa) was 25% higher, and (ϵ 5.0%) was slightly decreased. As MDI ratio further increased to 2%, mechanical properties decreased.

As expected, DDGS particles in the PLA matrix without a coupling agent acted as stress concentrators under tensile stress, often inducing fractures and resulting in low tensile strength. Moreover, because of the poor packing properties of DDGS, some pores were observed in the tensile bars without MDI, which also resulted in low strength. However, in contrast to the immediate fracture after reaching maximum load for PLA, the PLA/20% DDGS composite showed distinct yielding and stable neck growth (Figure 6.3). Because of the formation of covalent linkages between hydroxyl or carboxyl groups from PLA into PLA-MDI and hydroxyl or amine groups from DDGS into DDGS-MDI (Figure 6.1), interfacial adhesion between the PLA matrix and DDGS particles was greatly improved, resulting in increased strength and modulus. Meanwhile, with formation of DDGS-MDI, packing properties of DDGS were improved, and porosity of the composites significantly decreased as indicated in the SEM images (Figure 6.4), which also enhanced mechanical properties. However, excess PLA-MDI and DDGS-MDI segments were formed with extra MDI (2%), and these segments might interfere with effective entanglements or segmental crystallization between DDGS particles and the PLA matrix, resulting in decreased strength and

modulus. Similar results were reported for PLA/sugar beet pulp composites with MDI ranging from 0 to 3% .

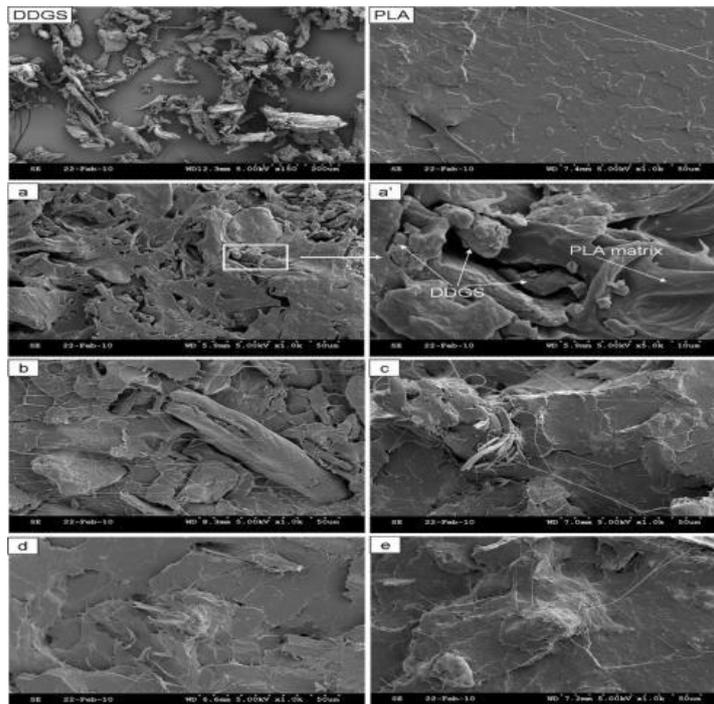


Figure 6.4 SEM images of PLA and PLA/20%DDGS composites with (a and a') 0%MDI, (b) 0.25%MDI, (c) 0.5%MDI, (d) 1%MDI, (e) 2%MDI.

Morphology

As shown in Figure 6.4, DDGS exists in irregular shapes and various sizes (20-200 μm) and has coarse surfaces. Pure PLA has a smooth and continuous fracture surface, indicating a brittle fracture behavior that corresponds to its low elongation value shown in Table 6.1. Surface roughness of the PLA matrix obviously increased with inclusion of 20% DDGS as observed from SEM images (Figure 6.4, a and a'), indicating that remarkable plastic deformation occurred. As discussed previously, because there was not sufficient interfacial adhesion, DDGS particles debonded from the PLA matrix at the interface during fracturing. Void formation due to cavitation localized at the particle/matrix interfaces was visible together with PLA matrix strands surrounding voids (Figure 6.4, a and a'), and the stress state in the PLA matrix was altered. During the debonding process, these PLA matrix strands were plastically stretched, fibrillized, and finally broken down. The toughening mechanism of particle-filled semicrystalline polymers has been explained in detail. With the naked eye and SEM, we also observed some pores attributed to the poor packing properties of DDGS. As DDGS loading ratio further increased, more pores were observed (SEM images not shown), which corresponds to the decreased strength and elongation of composites.

With 0.25% MDI added, fracturing extending through DDGS particles was observed in addition to debonding, and the porosity decreased obviously (Figure 6.4, b), indicating the greatly improved wettability of DDGS particles by the PLA matrix and penetration of PLA into the porous DDGS. With increasing amounts of MDI, almost no evidence of debonding could be observed at the fracture surfaces (Figure 6.4, c-e). Instead, DDGS particles ruptured together with the PLA matrix at the plane of the fracturing surfaces. For composites with 1% and 2% MDI, few individual DDGS particles could be observed, and those that were distinguishable appeared to be completely coated and penetrated by the PLA matrix (Figure 6.4, d-e). Moreover, no pores could be observed in the tensile bars. The SEM images provide clear evidence that MDI addition established strong interfacial bonding between the PLA matrix and DDGS particles that led to greatly improved stress transfer between the matrix and fillers, corresponding to measurements of the mechanical properties.

Thermal Properties

Figure 6.5 shows DSC thermograms of compression-molded PLA and PLA/20%DDGS composites. The thermograms were obtained from the first heating scan to reveal the glass transition and crystalline status of the PLA component in the composites. Table 6.3 . The T_g of the composite without MDI was 3 $^{\circ}\text{C}$ lower than that of pure PLA (62.1 $^{\circ}\text{C}$). With addition of MDI, T_g increased slightly, indicating that some coupling effects from MDI occurred. An endothermic peak around the glass transition region was observed for PLA and composites because of physical aging during storage at ambient temperature. The peak area of PLA, PLA composites without MDI and with 0.25% MDI was larger than that of composites with a higher MDI loading ratio. Samples with a higher degree of aging have smaller free volume as well as smaller enthalpy and potential energy than samples with a lower degree of aging.

Therefore, when the aged samples are heated, more energy is required for the glass transition, thus increasing the area of the endothermic peak. Crystallinity of PLA in the composites was higher than that of pure PLA. However, crystallinity of the composite with 2%MDI was slightly lower than that of other composites.

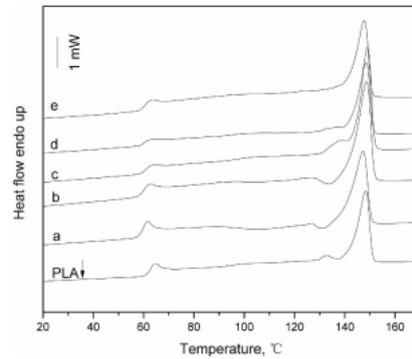


Figure 6.5 DSC thermograms of PLA and PLA/20%DDGS composites with (a) 0%MDI, (b) 0.25%MDI, (c) 0.5%MDI, (d) 1%MDI, (e) 2%MDI (first scan).

This might be caused by the excess PLA-MDI and DDGSMDI segments that occurred with extra MDI loading, which would interfere with segmental crystallization, as discussed previously in the mechanical properties section. TGA and derivative TGA thermograms of DDGS, PLA, and PLA/20%DDGS composites are shown in Figure 6.6 (A) and (B), and the TGA data are summarized in Table 6.4. Because of its multiple components (carbohydrates, protein, lipids, etc.), DDGS exhibited a much broader decomposition range than PLA; onset, end, and peak decomposition temperatures (T_{onset} , T_{end} , and T_{max}) of DDGS were 298.8, 418.6, and 383.1 °C, respectively, and T_{onset} , T_{end} , and T_{max} of PLA were 344.5, 388.9, and 381.7 °C, respectively. The composite without MDI showed slightly higher decomposition temperatures than PLA with T_{end} and T_{max} of 401.2 and 385.5 °C, respectively. All composites with MDI showed similar decomposition temperatures with T_{max} values slightly lower than that of PLA. Because DDGS has higher tar and ash content than PLA, the residue weight of PLA/DDGS composites above 425 °C is higher than that of PLA but lower than that of DDGS.

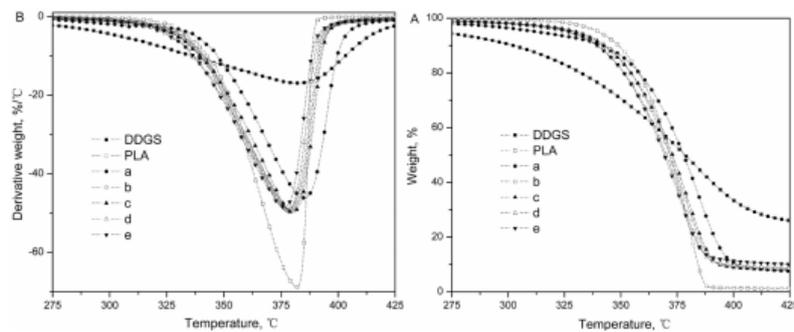


Figure 6.6 TGA (A) and derivative TGA (B) thermograms of DDGS, PLA, and PLA/20%DDGS composites with (a) 0%MDI, (b) 0.25%MDI, (c) 0.5%MDI, (d) 1%MDI, (e) 2%MDI.

For PLA and PLA/20%DDGS composites with and without MDI, storage modulus (E') increased gradually with heating between 20 and 61 °C, reached a peak value, dropped sharply at the glass transition region, and then reached a rubbery plateau (Figure 6.7, A). The increase of E' between 20 and 61 °C was a kinetic unfreezing of a none equilibrium disordered structure at the low heating rate (3 °C /min) and sinusoidal frequency (1 Hz) and a consequence of molecular structure densification and aging. For all samples, the competing effects of aging and relaxation led to the fluctuation of E' before its sharp drop. An increase in E' around 100 °C was attributed to cold crystallization of PLA components. When the E' values of PLA and composites at room temperature (25 °C) were compared, composites without MDI showed a smaller E' (1.02 GPa) than PLA (1.12 GPa), corresponding to its lower mechanical strength. With MDI, an obvious increase in E' was observed for all composites, indicating effective coupling between PLA and DDGS.

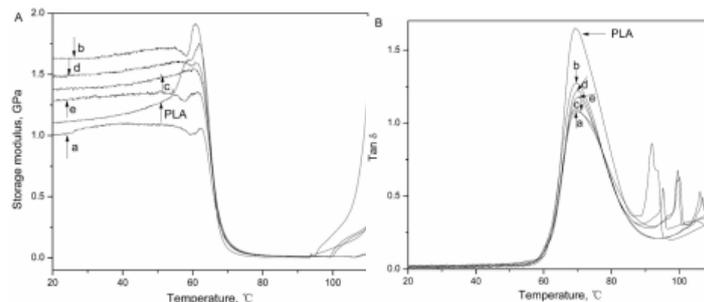


Figure 6.7 Flexural storage modulus (A) , (B) of PLA and PLA/20%DDGS composites with (a) 0%MDI, (b) 0.25%MDI, (c) 0.5%MDI, (d) 1%MDI, (e) 2%MDI

The loss factor of PLA and PLA/20%DDGS composites during heating is presented in Figure 6.7 (B). The peak that appeared at about 69 °C is known as T_g from DMA measurement. Pure PLA had the largest (1.65) at T_g , indicating that it contains a greater amorphous phase portion than the composites, which corresponds to the lowest crystallinity value of pure PLA determined from DSC. In a composite system with filler, the filler would limit mobility of the matrix molecular chain, thereby affecting relaxation of the matrix chains and causing a lower damping in the transition zone compared with a pristine polymer.

4 CONCLUSION

PLA/DDGS composites with mechanical properties similar to those of pure PLA were successfully prepared via thermal compounding. FTIR spectroscopy verified that MDI was an effective coupling agent for the PLA/DDGS system. Without a coupling agent, tensile strength and Young's modulus of composites decreased dramatically as DDGS content increased. For PLA/20%DDGS composites, as MDI loading ratio gradually increased from 0.25 to 1%, tensile strength and Young's modulus increased and approached values similar to those of pure PLA. Morphology of the fracture surfaces showed that addition of MDI established strong interfacial bonding between the PLA matrix and DDGS particles and decreased the porosity of composites. Crystallinity of PLA in the composites was higher than that of pure PLA. Composites with MDI had higher storage moduli at room temperature than pure PLA. These results indicate that using low-cost DDGS as filler can result in biodegradable composites that have properties similar to those of pure PLA but cost significantly less. This novel application of DDGS for biocomposites has significantly higher economic value than its traditional use as a feedstuff.

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