Biodegradation Behavior of Poly(lactic acid) (PLA)/Distiller's Dried Grains with Solubles (DDGS) Composites

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ABSTRACT: Poly(lactic acid) (PLA) and distiller's dried grains with solubles (DDGS) are biobased materials with strong potential for industrial applications. This paper reports the biodegradation behavior of PLA/DDGS (80/20 by weight), a composite material developed for use in high-quality, economical, biodegradable, crop containers for the horticulture industry. Biodegradation experiments were performed in soil under landscape conditions. Surface morphology and thermal properties were evaluated by scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). We found that adding 20% DDGS to form the PLA/DDGS composite can accelerate the biodegradation rate and enhance the storage modulus compared to pure PLA. The weight loss of the PLA/DDGS composite during 24 weeks of degradation time was 10.5%, while the weight loss of pure PLA was only 0.1% during the same time interval. Cracks and voids caused by erosion and loss of polymer chain length were clearly observed on the surface of the composite material in response to increasing degradation time. The thermal stability of the composite increased with increasing degradation time. The glass transition temperature and melting temperature increased during early stages of biodegradation (up to 16 weeks) and then decreased slightly. We confirm that DDGS can function as a cost-effective biodegradable filler for PLA composites that can provide enhanced mechanical properties with only slight changes in thermal properties when compared to pure PLA.

KEYWORDS: *Poly(lactic acid), DDGS, Composites, Biodegradation, Horticulture industry*
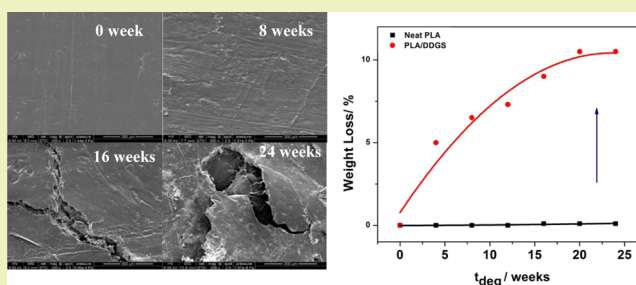
■ INTRODUCTION

Approximately 140 million tons of petroleum-based polymers are produced each year.[1] A large proportion of this polymer is used in products that have short service lives, and disposal of these nondurable products is seen as an important environmental problem. A great deal of research has been performed in recent years to develop and evaluate biobased polymers and composites in an effort to replace petroleum-based polymers with more sustainable materials.[2−4] Biopolymers have been developed that can fulfill nearly all of the functions of petroleum-based materials in applications ranging from packaging to durable goods.[5]

Biobased polymers and composites are materials produced from renewable agricultural and forestry feedstocks. A sustainable biobased product should have both recycling capability and biodegradability. Biobased composites typically consist of a combination of biofiber and bioplastic polymer. Of the bioplastics derived from renewable resources, thermoplastics are more often utilized than thermosets due to their

recyclability.[6] Polyesters comprise a family of bioplastics that are important because of their hydrolyzable ester bonds. Biobased polyesters that have been used commercially in industrial products include polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), poly-(lactic acid) (PLA), polycaprolactone (PCL), and polyhydrohexanoate (PHH).

PLA is a linear aliphatic thermoplastic polyester derived from renewable resources such as cornstarch, and it can be completely decomposed by microorganisms under suitable conditions.[7] PLA can degrade in soil under natural conditions, but it does so more slowly than other biodegradable polymers. Because PLA has 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,[8] yet it is renewable, recyclable, and biodegradable. Although the market demand for commercialized PLA is growing at 5% to 8% per year,[9] and the annual worldwide production of PLA is expected to reach 367,300 t by 2017, its use is still limited somewhat by its relatively high cost (~$1.6 per kilogram of lactic acid).[10]

Fillers in concentrations ranging from 10% to 50% (by weight) have been used to improve the overall properties of PLA and to lower its cost for industrial applications. Fillers can be organic, inorganic, natural, or synthetic. Commonly used fillers include glass, limestone, wood flour, metals, bamboo, coconut shells, and clay. Various low-cost biobased fillers such as starch, lignin, sugar cane, soy protein, wood flour, and distiller's dried grains with solubles (DDGS) have been considered for use as composite materials for PLA in order to reduce costs, improve biodegradability in soil, or to improve the performance of PLA-based materials for specific applications.

DDGS is a nonfermentable cereal coproduct of the corn–ethanol fuel industry. It has a complex composition that includes protein, cellulosic fiber, oils, and ash,[11] and it has been utilized on a large scale as a livestock feed.[12] Supplies of DDGS in the North American market have increased greatly during the last 10 years, with quantities expected to reach more than 42 million tons per year.[13] It is crucial to develop alternate uses for DDGS to avoid market saturation of this coproduct of ethanol biofuel. Because of its low cost, low density, biodegradability, and renewable source, DDGS has recently found use as biobased filler in polymer composite materials. Therefore, combining DDGS with PLA may be an effective and inexpensive way to both form a better composite and accelerate its degradation rate.

Some recent studies have evaluated processing methods for associating DDGS with thermoplastic polymers to form composite materials, and others have quantified mechanical and thermal properties for various filler contents.[14−18] However, there are few reports defining the biodegradation behavior of these composites. The biodegradation process is governed by a variety of factors including molecular weight, type of functional group, crystallinity, the type of additives, and chemical structure of the material, as well as the type of organisms in the degradation environment and their mobility.[19] Degradation processes lead to changes in a materials' properties through bond scission and chemical transformations.[20] These changes generally include cracking, color change, and general changes in mechanical and thermal properties.[21]

The goals of this study were to characterize the thermal and mechanical properties of PLA/DDGS (80/20) composite before and during early stages of biodegradation, to compare the material properties of the composite to those of neat PLA, and to quantify the effects of biodegradation in soil in order to confirm the suitability of the PLA/DDGS (80/20) composite as an economical high-performing material for use in biodegradable crop containers for the horticulture industry. Biodegradation rates in soil under landscape conditions were evaluated. The surface morphology of composite materials and neat PLA were studied by scanning electron microscopy (SEM) over a series of degradation times up to 24 weeks. Thermal properties were determined by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The crystalline performance of PLA/DDGS (80/20) and neat PLA in their early stages of biodegradation were tested by X-ray diffraction (XRD). Results of this study will provide data for

design and engineering decisions related to bioplastic crop containers and other applications where biorenewable biodegradable composites will be evaluated as alternatives to petroleum plastics.

■ EXPERIMENTAL SECTION

Materials. PLA (3001D) was supplied by NatureWorks LLC with specific gravity of 1.24 g/cm^3, melt flow index of 22g/10 min (210 °C), and average molecular weight (M_w) of 136,000g/mol. 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 h at 80 °C. 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 hopper mixing die for all formulations.

Biodegradation Experiments. Biodegradation experiments were performed in soil under landscape conditions at the Iowa State University Horticulture Research Station near Gilbert, Iowa. PLA and PLA/DDGS samples were one-fourth container pieces (injection molded plant containers with a top diameter of 11.4 cm, height of 9.7 cm, and volume of 680 cm^3, cut into four identical pieces). Each sample was weighed and placed in a nondegradable mesh bag. Then, the one-fourth container samples were buried 10 cm below the soil surface in a garden plot. The soil was a fine, loamy, mixed, superactive, mesic Typic Hapludolls. The mean 10 cm soil temperature was 20.3 °C, and the plot was irrigated with 2.5 cm of water per week. At the end of each targeted biodegradation time interval, samples were extracted from the soil, washed gently with water to remove soil debris, and dried at 33 ± 5 °C for 9 days until their weights stabilized to constant values. After drying, samples were weighed a second time to determine final weight after the degradation period in soil.

Weight loss was calculated using the following equation

$$W_{loss}\% = \frac{W_0 - W_1}{W_0} \times 100 \qquad (1)$$

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

Scanning Electron Microscope. A scanning electron microscope (SEM) was used to examine the surface morphology of the PLA/DDGS (80/20) composite and neat PLA samples after degradation treatment intervals of 0, 8, 16, and 24 weeks. The samples were placed on SEM holders and sputter coated with 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.

TGA, DMA, and DSC 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 to 800 °C at a heating rate of 20 °C/min.

DMA tests were performed on a Q800 dynamic mechanical analyzer using a film-tension system. The rectangular samples were heated from −50 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.

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 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

$$X_c\% = \frac{\Delta H_m}{X_P \times \Delta H_m 100\%} \times 100 \qquad (2)$$

where ΔH_m is the calculated enthalpy of the composite, $\Delta H_m 100\%$ is the theoretical enthalpy of melting for a 100% crystalline PLA polymer (value of 93.7 J/g),[22] and X_P is the PLA fraction in the composite.

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

$$X_c\% = \frac{I_C}{I_C + I_A} \times 100 \tag{3}$$

where X_c is the degree of crystallinity, I_C is the diffracted intensity of the crystalline phase, and I_A is the diffracted intensity of the amorphous phase. This equation can be transformed into another form for easier calculation of X_c.

$$X_c\% = \frac{A_C}{A_C + A_A} \times 100 \tag{4}$$

where A_C is the area under the crystalline peaks, and A_A is the area under the amorphous peaks.

Rheological Measurements. Rheological properties were measured using an AR2000ex rheometer with 25 mm 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 (linear viscoelastic regime).

RESULTS AND DISCUSSION

Pure DDGS has a very large particle size in the range of 0.5–1.0 mm. Processing of PLA with DDGS at high temperature and shear rate led to breakup the DDGS particles into very small particles with an average of 0.5 μm as clearly seen in the SEM morphology of PLA/DDGS 80/20 composite (Figure 1a). This morphology confirms a partial miscibility of PLA and DDGS. It is also evident that the DDGS particles are not simply coated with PLA.

Biodegradation Behavior. PLA is among the most promising alternatives to petroleum-based plastic materials currently available on the market. DDGS is a low-cost organic filler with a composition that includes protein and cellulose.[23] The protein component of DDGS may provide a favorable interaction and improved adhesion with the PLA matrix in biobased composites to positively affect the degradation and thermal behavior of PLA.

According to Chung et al.,[24] the higher the surface-to-volume ratio of the samples is, the faster the rate of weight loss from biodegradation is. In this study, all specimens were one-fourth injection-molded container fragments with identical dimensions to keep the relevant parameters constant. Figure 1b shows the biodegradation time dependence of weight loss for neat PLA and PLA/DDGS (80/20) composite in soil medium. Our results with neat PLA were consistent with those of other researchers and show that the biodegradation rate was very slow under natural soil conditions. During the first 12 weeks of degradation testing, the weight loss of neat PLA was 0%, and after 16 weeks in soil, the weight loss finally reached 0.1%. Although PLA is a biodegradable polymer, its degradation rate in soil is slow compared to other biodegradable plastics, and full degradation may require many years under some conditions.[25]

Adding DDGS filler to form the PLA/DDGS (80/20) composite improved the rate of biodegradation significantly over that of neat PLA (Figure 1b, Table 1). The weight loss of PLA/DDGS (80/20) increased rapidly during the first 8 weeks of biodegradation time and then leveled off at 10.5% after 20 weeks in the 24 week degradation test. The decrease in weight loss of PLA/DDGS (80/20) composite after 20 weeks was
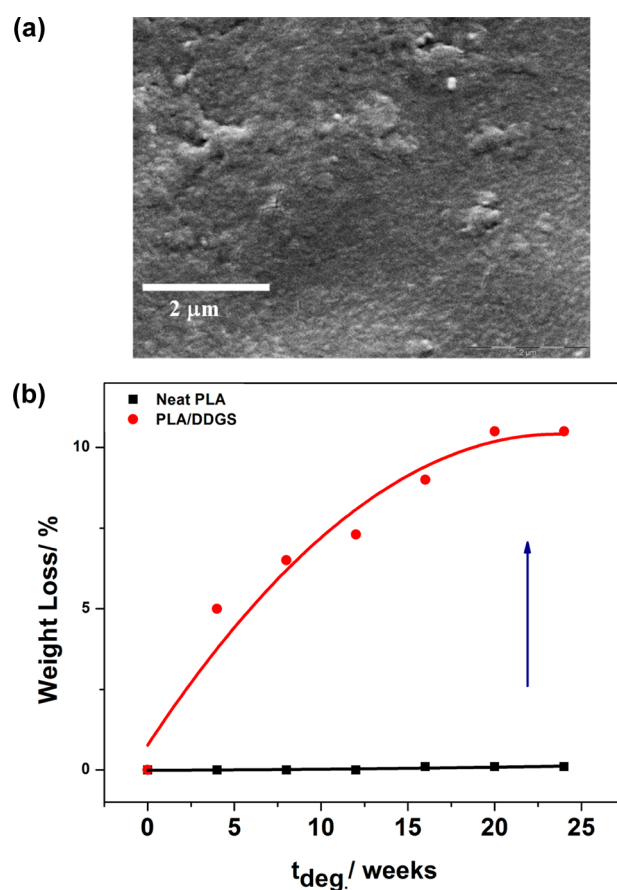
Figure 1. (a) SEM micrographs of PLA/DDGS 80/20 composite after processing. (b) Biodegradation time dependence of weight loss of pure PLA and PLA/DDGS (80/20) composites in soil medium.

likely due to two main factors: the decreasing availability of the DDGS component of the composite and the decrease in microbe activity in the soil medium as the mean temperature of soil in the test plot decreased at the end of the normal growing season (Table 1). With this decrease in natural temperatures in the soil after 20 weeks, the microbial activity and rate of biodegradation in the soil would be expected to decrease.

The slopes of the curves in Figure 1b illustrate the degradation rates of neat PLA and the PLA/DDGS (80/20) composite and confirm that DDGS successfully enhanced the degradation process. This result is in agreement with our recent study for PHA/DDGS composites. We have found that DDGS increased biodegradation in soil compared to that of the pure PHA base polymer. As shown with PHA/DDGS,[26] the addition of DDGS to PLA improves the nutrient composition of the material for microbial metabolism. The proteins and amino acids from the DDGS improve the carbon-to-nitrogen (C:N) ratio of the material. In compost, a C:N ratio of 30:1 is considered optimum for microbial nutrition. Because the nitrogen content of neat PLA is negligible, it is very difficult for microbes to begin degradation. The N content of DDGS is approximately 4.1%, which is a C:N ratio of 12:1. Addition of DDGS at 20 wt % brings the C:N ratio of the PLA/DDGS composite to approximately 61:1, a ratio that is much more favorable for biodegradation. DDGS is also nontoxic, which is another characteristic that makes it appealing as a biobased filler for ecofriendly horticultural crop containers.

Table 1. Degradation Weight Loss Percentages for Neat PLA and PLA/DDGS (80/20) Composite in Field Soil[a]

samples	0 week	4 weeks	8 weeks	12 weeks	16 weeks	20 weeks	24 weeks
neat PLA (%)	0	0	0	0	0.1	0.1	0.1
PLA/DDGS (%)	0	5	6.5	7.3	9.0	10.5	10.5
mean 10 cm soil temp. (°C)		19.1	26.1	24.6	26.3	18.0	8.1

[a]Also included are the mean daily soil temperatures at 10 cm below the surface for each 4 week interval.

Surface Morphology Analysis. Polymer degradation is associated with changes in characteristics such as shape, color, surface morphology, and mechanical properties.[27] SEM is widely used to evaluate the morphology of different degradation periods. After degradation tests, a surface morphological analysis of neat PLA and the PLA/DDGS (80/20) composite were performed by SEM. Micrographs of nondegraded PLA and PLA degraded for 24 weeks are shown in Figure 2. Nondegraded PLA has a very smooth surface
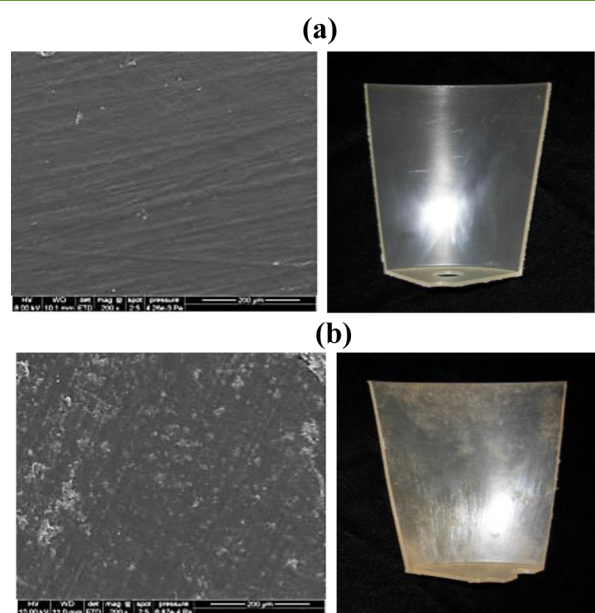
Figure 2. SEM micrographs of surface morphologies and photographs of neat PLA after (a) 0 and (b) 24 weeks degradation times.

(Figure 2a) and is nearly transparent. After 24 weeks of degradation conditions in soil, the surface morphology changed very little, with the appearance of only a few small surface cracks (Figure 2b), which were likely the result of onset of biodegradation process. The color also changed slightly to a faint yellow after 24 weeks of degradation time in soil.
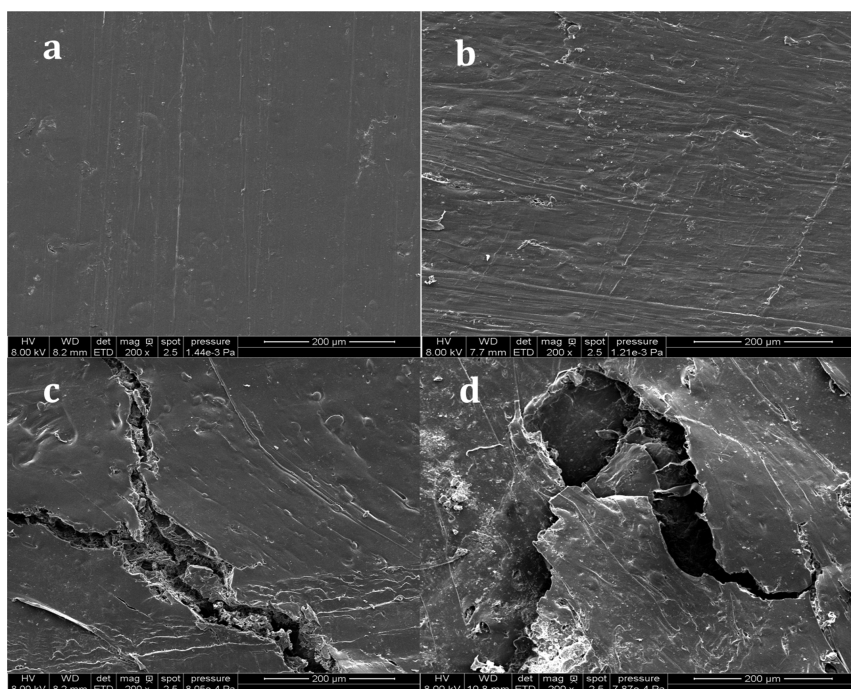
The surface morphologies of PLA/DDGS were also examined by SEM. Before the degradation treatment, PLA/DDGS (80/20) has a very smooth surface (Figure 3a) like that of neat PLA shown in Figure 2a. Figure 3b shows that the surface became rough after 8 weeks of degradation. The cracks and voids shown in Figure 3c show that considerable plastic degradation occurred during 16 weeks in soil. These cracks and voids are also likely the result of chain loss and surface erosion facilitated by soil microorganisms. The degree of surface erosion is consistent with the weight loss data shown in Figure 1b.

With increasing degradation time, interfacial bonding between PLA and DDGS became weaker with the absorption of more water, and the cracks became deeper as shown in Figure 3d. Comparing the surface morphologies of PLA (Figure

2b) and the PLA/DDGS composite (Figure 3d) after 24 weeks of degradation confirms that DDGS bonds with PLA in a way that enhances material biodegradability. In addition, it is apparent without magnification that the color of samples became lighter and their shapes had deteriorated through surface erosion as illustrated in Figure 4.

Thermal Properties. DMA measurements for neat PLA and the PLA/DDGS composite after different degradation times were performed to determine the effects of degradation on thermal properties. Figure 5 presents the storage modulus—temperature curve for all the samples. PLA has a high modulus and larger T_g compared to the PLA/DDGS 80/20 composite and is a relatively brittle biomaterial. Blending it with natural fibers has the potential to enhance its mechanical properties and reduce cost. DDGS contains fiber and has a lower density (≈ 1300 kg m^{-3}) compared to inorganic fillers.[28] As expected, Figure 5 shows that the addition of 20 wt % DDGS filler slightly decreases the storage modulus of the material. Figure 5 also illustrates that the storage modulus for the PLA/DDGS composite decreases with increasing biodegradation time across a wide range of DMA temperatures ranging from −45 to 60 °C, a result associated with chain loss and a decrease in molecular weight through bulk hydrolysis. A sharp decrease in storage modulus takes place at the glass transition temperature of the samples. A considerable increase in the storage modulus for all samples has been also observed in the temperature range of 75−95 °C. This increase in the storage modulus is attributed to the fact that the PLA component crystallized with increasing temperature. This experimental fact will be supported by DSC measurement in the next section.

Figure 6 shows temperature dependence of tan δ for nondegraded neat PLA and PLA/DDGS composites over different degradation times up to 24 weeks. For nondegraded samples, the glass transition temperature (T_g) determined from the temperature at a peak maximum of tan δ decreased with the addition of DDGS when compared to neat PLA. The shift in tan δ of PLA to lower temperature by adding DDGS indicates that PLA and DGGS are partially miscible composite (see the SEM morphology in Figure 1). Across degradation times, T_g of the PLA/DDGS composite increased with increasing degradation time, with its highest T_g (57.57 °C) after 24 weeks of degradation, a T_g that approached that of nondegraded neat PLA (Table 2). Normally when a composite begins to degrade, the decrease in molecular weight reduces the glass transition temperature. The unexpected increase in T_g of PLA/DDGS composite may be the result of changes in the crystalline structure during early stages of biodegradation. PLA/DDGS composites are semicrystalline materials, and degradation processes can occur at different rates in crystalline and amorphous regions. According to the two-state process reported by Chu,[29] hydrolysis occurs first in the amorphous regions and subsequently in the crystalline regions. Similarly, Hakkaranien et al.[30] suggested that degradation kinetics can be influenced by crystallinity and concluded that amorphous regions hydrolyze before crystalline regions in PLA/poly-

Figure 3. SEM micrographs of surface morphologies of PLA/DDGS (80/20) composite after degradation times in soil of (a) 0, (b) 8, (c) 16, and (d) 24 weeks.
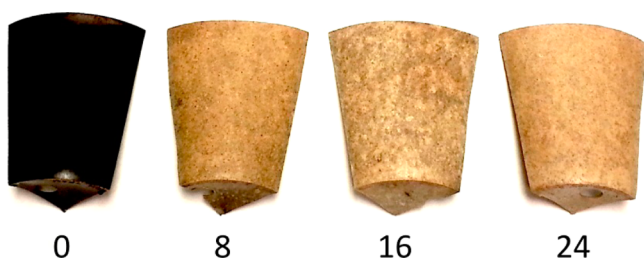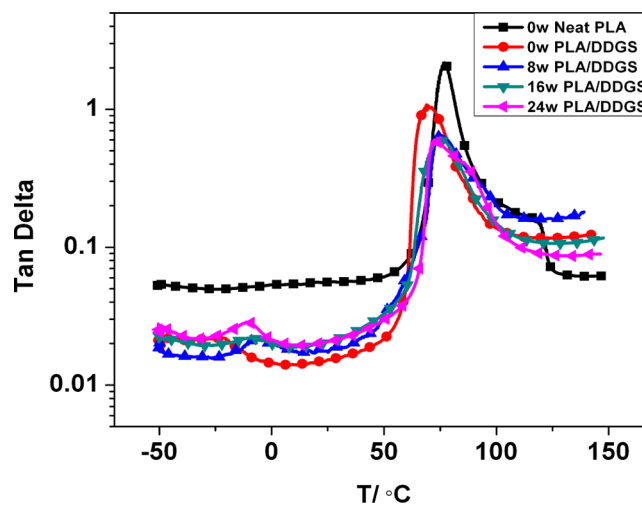

Figure 4. Photograph of one-fourth injection-molded PLA/DDGS container samples after 0, 8 16, and 24 weeks degradation time in field soil.
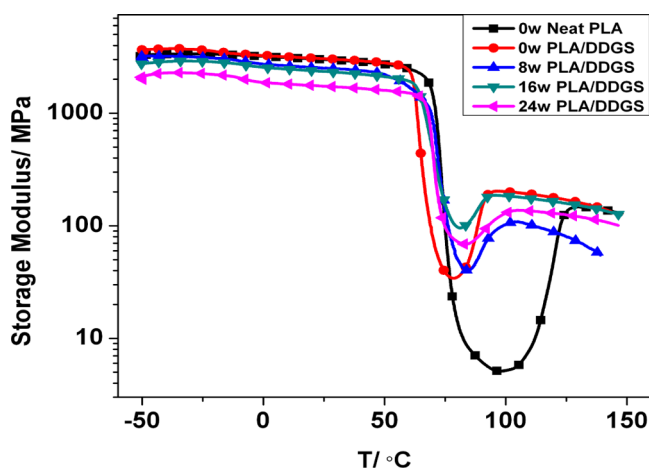
Figure 5. Storage modulus versus temperature for pure PLA without degradation and PLA/DDGS (80/20) composite that had degraded in soil for 0, 8, 16, and 24 weeks.

Figure 6. Tan delta versus temperature for nondegraded pure PLA and PLA/DDGS (80/20) composite with different degradation times.

Table 2. Thermal Properties of Nondegraded PLA and PLA/DDGS (80/20) Composite with Different Degradation Times

	0 week PLA	0 week	8 weeks	16 weeks	24 weeks
T_g (°C)	60.10	51.65	52.25	52.16	57.57
T_m (°C)	169.71	162.68	165.94	165.39	170.43
T_c (°C)		102.72	102.64	107.43	110.66
ΔH_m (J/g)	16.59	37.12	40.63	39.82	39.00
X_c (%)	17.71	39.62	43.36	42.50	41.62

glycolic acid (PGA) composites. DDGS constitutes a large part of the amorphous region of the PLA/DDGS composite. It degrades more quickly than the PLA component of the material

and likely accounts for most of the weight loss during early stages of biodegradation. During these early stages, the decomposition of amorphous regions will lead to a higher percentage of crystalline content and a higher degree of crystallinity. The loss in weight of the PLA/DDGS composite

shown in Figure 1b supports this conclusion. The rate of weight loss is highest in the first 4 weeks of degradation, after which it slows and remains relatively steady until after 20 weeks of degradation, when it slows significantly. After 20 weeks of degradation, a large amount of the amorphous content has decomposed, leaving mostly the crystalline component, which degrades more slowly. The higher T_g for the composite after 24 weeks of degradation reflects the thermal behavior of material that has a greater percentage of crystalline content than the original nondegraded PLA/DDGS composite.

DSC curves for nondegraded neat PLA and the PLA/DDGS (80/20) composite with different degradation times are shown in Figure 7. The T_g was shifted to higher values as degradation
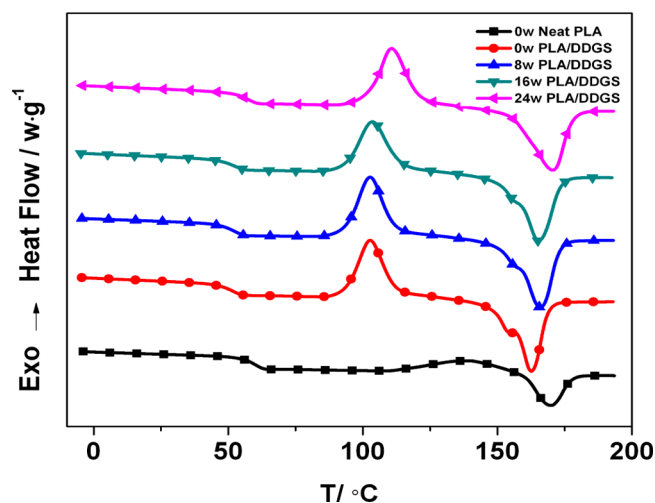

Figure 7. DSC thermograms of nondegraded pure PLA and PLA/DDGS composites with different degradation times (0, 8, 16, and 24 weeks).

time increased. This is consistent with the results obtained by the DMA instrument. The crystalline temperature (T_c) and melting temperature (T_m) exhibited similar trends as that shown for T_g. Both measurements increased only slightly for the composite, indicating that the DDGS filler did not lead to significant changes in thermal properties. In addtion, the X_c increased during early biodegradation, up to 16 weeks, and then decreased slightly after 20 and 24 weeks of degradation. The crystallization increases until 16 weeks because the amorphous part started to degrade first and then the crystalline part. The specific values for these parameters are presented in Table 2.

It is well established that DDGS is a rich source of protein (26.8−33.7% dry weight basis), carbohydrates (39.2−61.9% including fibers), oils (3.5−12.8%), and ash (2.0−9.8%). Chemically, DDGS has a wide range of amino acids (e.g., alanine, arginine, cysteine, etc.), minerals (calcium, phosphorus, potassium, and magnesium), and fatty acids. Therefore, it is expected that a small amount of DDGS will be miscible with PLA during processing, and this led to a decrease in T_m. However, on the other hand, some other components dispersed in the PLA matrix in a microscale size (see morphology in Figure 1a). This microsize dispersed phase can act as nucleating agent for the crystallization process of PLA. This is why the X_c of the composite is higher than that of pure PLA.

X-ray Diffraction (XRD). The XRD provides a good way to monitor changes in crystallization that result from degradation. XRD was studied to further verify the result of DSC

measurements and was especially useful for investigating the effects of degradation on the PLA/DDGS composite during the period from 8 to 16 weeks. As shown in Figure 8, the area
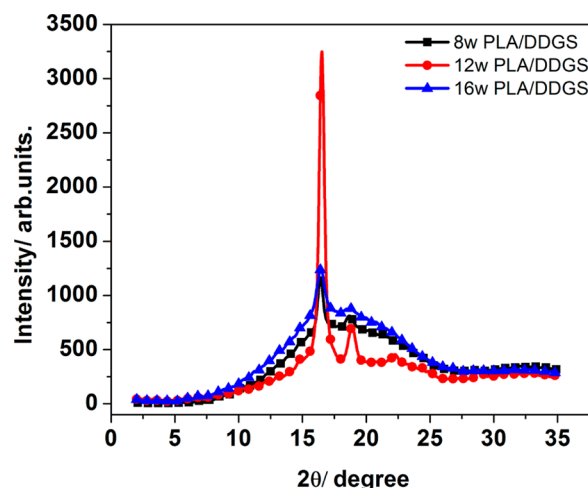
Figure 8. XRD patterns of PLA/DDGS composites after different degradation times (8, 12, and 16 weeks).

under the crystalline peak was greater for samples in the 12 week degradation treatment than for samples in the 8 or 16 week treatments, indicating that the degree of crystallinity of the PLA/DDGS composite is greatest at 12 weeks of degradation in soil. The values of cystallinity after 8, 12, and 16 weeks of degradation were approximately 29%, 34%, and 29%, respectively. After 16 weeks of degradation, the degree of crystallinity decreased, suggesting that both the amorphous region and crystalline region had begun to degrade. These results provide further evidence that biodegradation of PLA/DDGS composite proceeds more quickly in the amorphous regions of the composite during the early stages of degradation in soil (approximately 12 weeks), after which time the amorphous content becomes scarce and degradation in the crystalline regions becomes evident.

Thermal Stability. Thermal stability of nondegraded neat PLA and PLA/DDGS (80/20) composite exposed to 0, 8, 16, and 24 weeks of degradation were studied by TGA. Figure 9 shows the influence of the degradation process on the thermal decomposition curve. Neat PLA decomposed in one step at approximately 400 °C. With the addition of the 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 proteins, fibers, and oils. Comparing the results for non-degraded samples of neat PLA to those of the nondegraded composite shows that both the T_{onset} (5% weight loss) and T_{max} (inflection point of the thermal degradation curve) were lower for the PLA/DDGS composite (Figure 9, Table 3), 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, and the increase in thermal stability of the composite with increasing degradation time suggests that the material will remain thermally stable even when used in applications in which some biodegradation will take place. These results provide additional support for the conclusion that the DDGS filler degrades faster than the PLA component, and the content
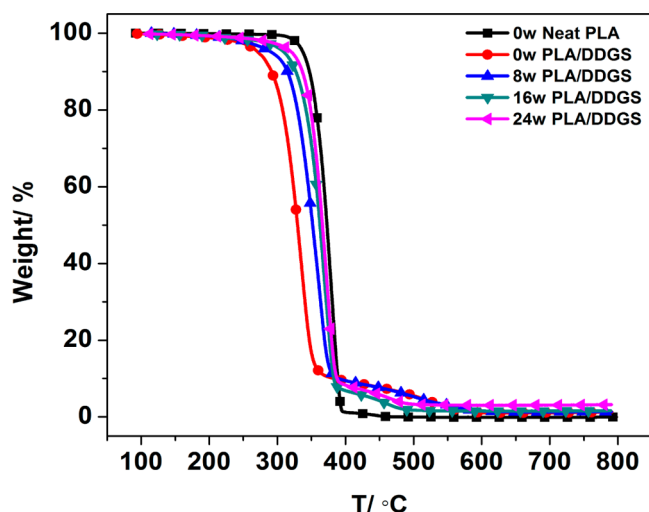
Figure 9. TGA traces of nondegraded neat PLA and PLA/DDGS composite at different degradation times under 20 °C/min heating rate.

Table 3. Thermogravimetric Analysis of Nondegraded Neat PLA and PLA/DDGS Composite with Different Degradation Times

	0 week PLA	0 week	8 weeks	16 weeks	24 weeks
T_{onset}	339.27	287.84	291.81	310.23	321.15
T_{max}	380.18	335.86	362.99	367.05	372.37

Figure 10. Angular frequency dependence of complex viscosity at 180 °C for PLA/DDGS (80/20) composite after different durations of biodegradation in soil.

Figure 11. Angular frequency dependence of G' at 180 °C for PLA/DDGS composite after different degradation times.

of DDGS in the composite diminishes with increasing degradation time. Our results are consistent with other research that describes the effects of soil degradation treatments on the thermal behavior of certain polypropylene (PP) composites. Morancho et al.[31] studied the thermogravimetric behavior of PP/EVOH blends and found that T_{onset} and T_{max} increased with increasing degradation time. Schilemmer et al.[32] also reported that the decomposition temperature of PP/starch composite shifted to a higher values after being burried in soil for 6 months.

Rheological Behavior. The biodegradation process may significantly influence the viscoelastic properties of PLA/DDGS composites. The rheological behavior was measured using a rheometer, and Figure 10 shows the dependence of complex viscosity (η^*) at 180 °C for angular frequencies ranging from 0.1 to 100 rad/s. It was found that the complex viscosity of the PLA/DDGS (80/20) composite decreased with increasing degradation time. This decrease is consistent with the current theory that viscosity is proportional to molecular weight. The molecular weight of the composite material decreased as the material biodegraded, and the complex viscosity decreased proportionally to the decrease in molecular weight.

Figure 11 illustrates the elastic shear modulus (G') of the PLA/DDGS composite for different degradation times. Regardless of degradation treatment, G' was shown to increase with increasing angular frequency.[33,34] Our results show a reduction in G' for the PLA/DDGS composites after degradation in soil. We conclude that G' decreased with increasing degradation time because the composite material decomposed to lower molecular weight during biodegradation, a conclusion consistent with results of other analyses in our study.
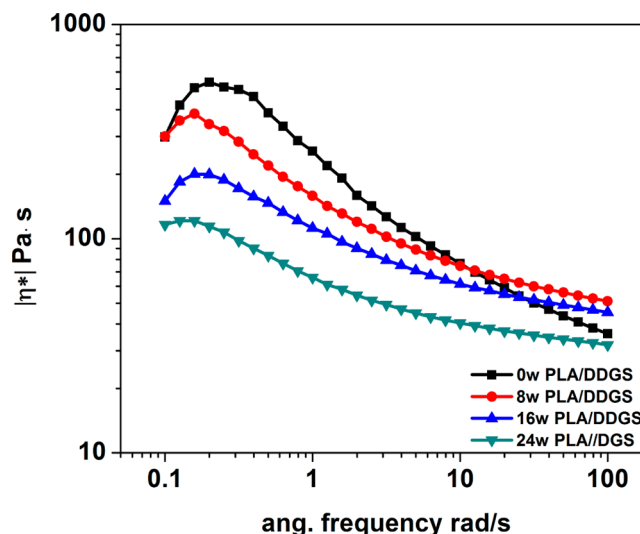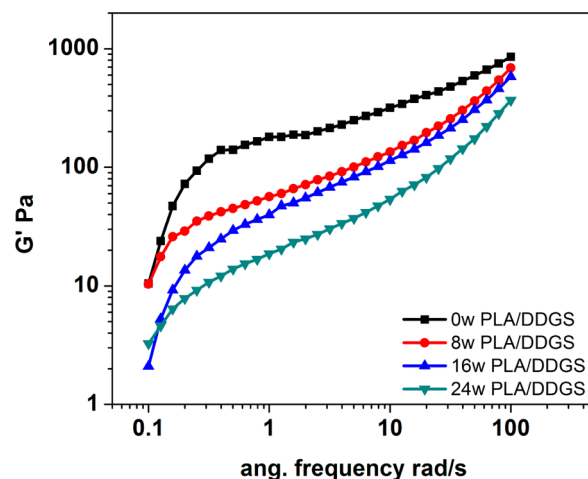
It must be stated here that the DMA, DSC, TGA, X-ray, and rheology data are almost identical for pure PLA before and after 24 weeks of degradation time. For this reason, it is not necessary to show the data of pure PLA determined by the above techniques after 24 weeks of degradation time in all of the presented figures.

■ CONCLUSIONS

In this paper, we describe the biodegradation behavior of PLA/DDGS (80/20) composites. Adding DDGS to PLA can increase biodegradation from 0.1% to 10.5% during the first 24 weeks in soil. Using a SEM instrument, an increased number of surface cracks and voids were clearly observed as degradation time increased. Analysis of the biocontainer samples by DMA showed that adding 20 wt % DDGS enhanced the mechanical properties compared to pure PLA. For the PLA/DDGS (80/20) composite, the storage modulus decreased with increasing degradation time. These results together with those of DSC and X-ray analysis show that the thermal properties of the PLA-based material were nearly unchanged after adding DDGS at 20 wt %. Thermal stability was reduced slightly with the addition

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of DDGS filler, but both T_{onset} and T_{max} increased with increasing degradation time. After 24 weeks of biodegradation, these values were nearly the same as those of pure PLA. As a biobased filler, DDGS reduced the cost of materials, increased the storage modulus, and had little effect on thermal properties compared to neat PLA. On the basis of these results, we conclude that PLA/DDGS composites possess suitable thermal and mechanical properties for use as bioplastic crop containers for the horticulture industry. The improved rate of biodegradation provided by DDGS filler indicates the potential for development of PLA-based containers that can end their life cycle as organic matter in soil.

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Notes

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