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Disciplines

Bioresource and Agricultural Engineering | Horticulture | Polymer and Organic Materials

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Novel bio-based composites of polyhydroxyalkanoate (PHA)/distillers dried grains with solubles (DDGS)

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Abstract: The PHA/DDGS composite is a promising low-cost, bio-based material for use in crop containers for the horticulture industry. This research effort has quantified the effects on mechanical and thermal properties of adding different amounts of DDGS 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 microscopy (SEM), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and rheometer measurements. The adhesion between PHA and DDGS decreased with an increase in DDGS content from 10% to 30%. Melting temperature and crystalline temperature decreased with the increasing content of DDGS filler, indicating that PHA and DDGS interacted favorably. The complex viscosity and elastic shear modulus of the blends were increased by the increasing DDGS content. The storage modulus and glass transition temperature showed little change across the different ratios of DDGS, indicating that DDGS should be a useful filler that can decrease the cost of PHA-based materials significantly while preserving the dynamic mechanical properties and glass transition temperature.

Introduction

Bio-based plastics have received much attention in recent years because of limited fossil-based resources and environmental pollution caused by petroleum-based plastics.¹⁻⁴ Bio-based plastics are materials produced from renewable agricultural and forestry feedstocks. With advantages of sustainability, environmental friendliness, and decomposability, the bio-based plastics market is currently growing at an annual rate of 30%.⁵ Many researchers are working to derive new materials from biological sources.

Polyhydroxyalkanoates (PHAs) are a group of linear bio-based polyesters produced in nature by the fermentation of sugars or lipids by bacteria that utilize the polymer for carbon and energy storage in their cells. The PHAs accumulate in the bacteria as highly refractive granules that can be recovered by disrupting the cells. Various kinds of homopolymers or copolymers of PHAs with different hydroxyalkanoic acids can be easily obtained based on the type of microorganism and the culture conditions. PHAs possess similar properties to traditional synthetic thermoplastics and could replace more than 50% of the polymers derived from crude oil.⁶ Moreover, PHAs can be 100% degraded to water and carbon dioxide constituents by microorganisms in soil, sea, and sewage.⁷ Members of the PHA family can exist as both homopolymers and copolymers. At present approximately 150 different types of PHA hydroxyalkanoic acid monomers have been reported.⁸ Depending on the monomer composition, PHAs can exhibit a wide variety of properties ranging from crystalline to elastic. Because of the diversity of properties of PHAs, their areas of application vary widely and range across the areas of packaging, electronics, sensors, energy applications, and the biomedical industry.⁹

Poly(3-hydroxybutyrate) (PHB) was the first PHA identified and is the most commonly used.⁹ It has mechanical properties very similar to those of petroleum-based plastics like polypropylene, and PHB can be processed by extruding, molding, or spinning into fibers. Although PHB offers many potential benefits, its applications are limited due to its higher cost and less robust physical properties that result from their high crystallization, stiffness, and brittleness compared to those of petroleum plastic.¹⁰ The production and cost of PHB depends on the microorganisms, carbon and nitrogen sources, fermentation conditions, recovery, and purification processes.¹¹ The current price for PHB is about \$7.45 per kilogram, with approximately \$5.12 per kilogram of this cost related to the culture of organisms to accumulate the material.¹² For some applications, the high melting temperature of PHB (about 175 °C) can make processing procedures difficult. In addition, PHB is considered to be relatively stiff, highly crystalline, and somewhat brittle, properties that are considered to be drawbacks for many applications. With respect to these shortcomings, blending PHB with low-cost fibers appears to be a promising approach for reducing production costs and enhancing material properties.

PHB can be blended with various biodegradable polymers and fibers, and polyhydroxyvalerate (PHV) is a copolymer that has been most extensively investigated for blending with PHB. PHV is another type of PHA and is produced by *Chromobacterium violaceum*.¹³ The incorporation of PHV with PHB could increase break elongation and impact strength, and the melting temperature would decrease with increasing PHV content. Natural plant fiber, glass fiber, carbon fiber and Distillers Dried Grains with Solubles (DDGS) are among the good candidates for use as reinforcing fibers for PHB-based composites. DDGS is a low-cost non-fermentable cereal co-product of the corn-ethanol fuel industry. It is a complex material that contains protein, fiber, lipids, and solubles.¹⁴ With the wide-scale growth of the ethanol fuel industry in North America, it is predicted that production of DDGS will reach approximately 35–70 million metric tons per

year by 2020.¹⁵ To avoid saturating the livestock feed market, which is currently the main use for DDGS, various research studies have been proposed to investigate potential for using DDGS in other applications, including uses as bio-filler, bio-plastic, and human food additives.¹⁶ Use of DDGS in bio-filler and bio-plastic applications has attracted particular interest during recent years because of its low cost and biodegradability.

The objectives of our research were: (1) to quantify the effects of blending DDGS with PHA; (2) to characterize the thermal, morphological, rheological, and mechanical properties of PHA/DDGS composites at three different load ratios (90/10, 80/20, and 70/30); and (3) to compare the material properties of these PHA/DDGS composites with those of neat PHA. Results were examined to assess the suitability of using PHA/DDGS composites in the model application of bio-based horticulture crop containers that could provide equal function to that of petroleum-plastic containers, then biodegrade harmlessly in soil after use. PHA/DDGS composites were blended in a twin-screw microcompounder. Fracture-surface morphology was examined using scanning electron microscopy (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.

Experimental section

Materials

The PHA, Mirel™ P1003 (Compression molding grade resin) was obtained from Metabolix Inc., Cambridge, MA. Mirel™ is a blend of PHB copolymers, which is commonly referred to the general designator “PHA”. DDGS was supplied by Lincoln Way Energy LLC, Nevada, IA. The DDGS is wet distillers grains (70% moisture) that have been dried to a moisture content of 10–12%. 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.

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 and 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.

Scanning electron microscopy

Scanning Electron Microscopy (SEM) was used to examine the fracture surface morphology of PHA/DDGS composites. The samples were first placed into liquid nitrogen and then broken to reveal the fracture surface for SEM examination. The fracture surface was coated with 5 nm Iridium. The prepared samples were examined using a field-emission scanning electron microscope (FEI Quanta FEG 250) with ×500 magnification.

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⁻¹ under a 60 mL min⁻¹ air flow.

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⁻¹ heating rate, then held at 200 °C for 1 min, and then cooled to 25 °C at a cooling rate of 20 °C min⁻¹. Finally the samples were heated once again from -50 °C to 200 °C at a scan rate of 20 °C min. Nitrogen gas was used with a flow rate of 50 mL min⁻¹ during all DSC measurements. The second heat scan examined the thermal behavior of PHA/DDGS composites without previous thermal history. Crystallinity percentage (X_c (%)) was estimated according to the following equation:

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

where ΔH_m is the calculated enthalpy of melting for the composite, $\Delta H_{m100\%}$ is the theoretical enthalpy of melting for 100% crystalline PHA with a value of 114.6 J g⁻¹ and X_p is the PHA fraction in the composite.¹⁷

DMA measurements

DMA tests were performed on a Q800 dynamic mechanical analyzer (TA Instruments) in film tension mode. The rectangular samples (20 × 3 × 2 mm³) were heated from -50 °C to 200 °C at a heating rate of 3 °C min and a frequency of 1 Hz under a nitrogen atmosphere. The oscillating amplitude was 15 μm. The storage modulus and tan δ were recorded as a function of temperature.

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⁻¹ at a constant temperature of 180 °C, and a strain value of 5% was consequently chosen in the linear viscoelastic regime.

Effectiveness in the model application

PHA/DDGS composites were evaluated for their effectiveness as bio-based materials for use in crop containers for the horticulture industry. The goal for the application was to create a bioplastic horticulture container that would function as well as, or better than, petroleum-based containers during plant production and sale, but then could be broken to smaller pieces, installed with the plant, and biodegrade in the soil within one or two growing seasons. The composite-container prototypes were evaluated and compared to containers made of petroleum plastic (polypropylene), containers made of the base resin (PHA Mirel™ P1003), and a commercially available bio-based container (paper fiber, ITML) in three experimental trials to assess performance under greenhouse-application conditions (4 plant species, 6 week production cycle), long-range durability when used for a medium-cycle greenhouse crop

(Cyclamen, for 16 weeks), and biodegradation in soil over 6 months. A randomized complete block design was used for all three application trials.

Results and discussion

Fracture surface morphology analysis

The morphology of PHA/DDGS composites and pure PHA matrix were investigated by SEM. [Fig. 1](#) shows the fracture-surface morphology of plastic blends with DDGS contents of 0%, 10%, 20%, and 30%. In [Fig. 1a](#), a miscible microphase is evident in the pure PHA sample, 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 the PHA/DDGS 90/10 composite in [Fig. 1b](#), indicating that the two materials are miscible 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. 1b](#), there are more exit holes in the fracture surface of the PHA/DDGS 80/20 composite ([Fig. 1c](#)). In [Fig. 1d](#), a different morphology is observed. At the bottom of this figure, small particles are visible. This change in behavior is evidence that the adhesion between the two components decreased as the DDGS content increased.

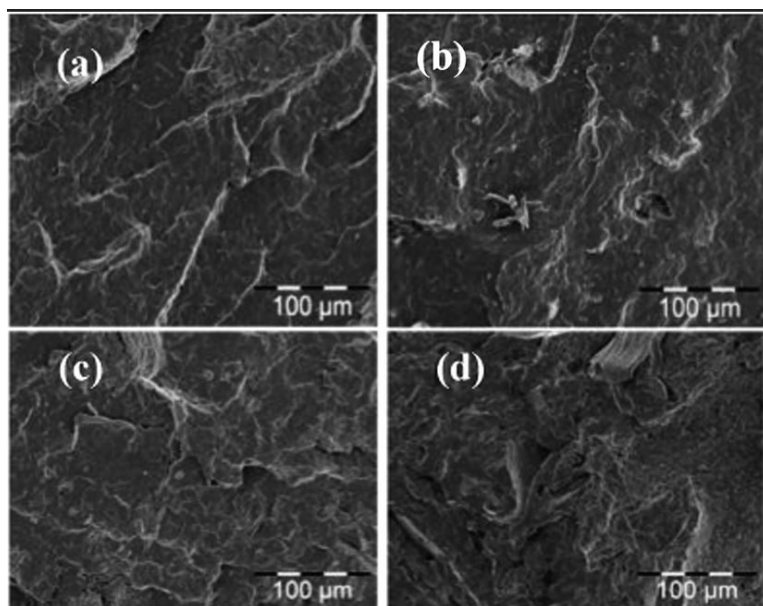


Fig. 1 SEM images of PHA/DDGS composites at $\times 500$ magnification. (a) Neat PHA; (b) PHA/DDGS 90/10; (c) PHA/DDGS 80/20; (d) PHA/DDGS 70/30.

Thermal properties

Thermal degradation of the pure PHA and PHA/DDGS composites was studied by TGA, and results are illustrated in [Fig. 2a](#). It was found that all of the composite samples decomposed through a three-stage 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 because it is similar to the curve of neat PHA. PHA degrades quickly at this temperature due to the chain scission reaction that leads to a large decrease in molecular weight.¹⁸ The second step exhibits a broader decomposition range than that of pure PHA because DDGS is made up of complex components such as

protein, lipids, and carbohydrates. The different degradation temperature range of the two components suggests the possibility 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 approximately 0.27%, 0.7%, 1.55%, 2.74%, and 10% for 0%, 10%, 20%, 30%, and 100% DDGS contents, respectively. The residue weight at 700 °C increased with increasing content of DDGS. This increasing residue percentage occurs because DDGS has greater carbohydrate content with greater ash content than that of PHA polymer.

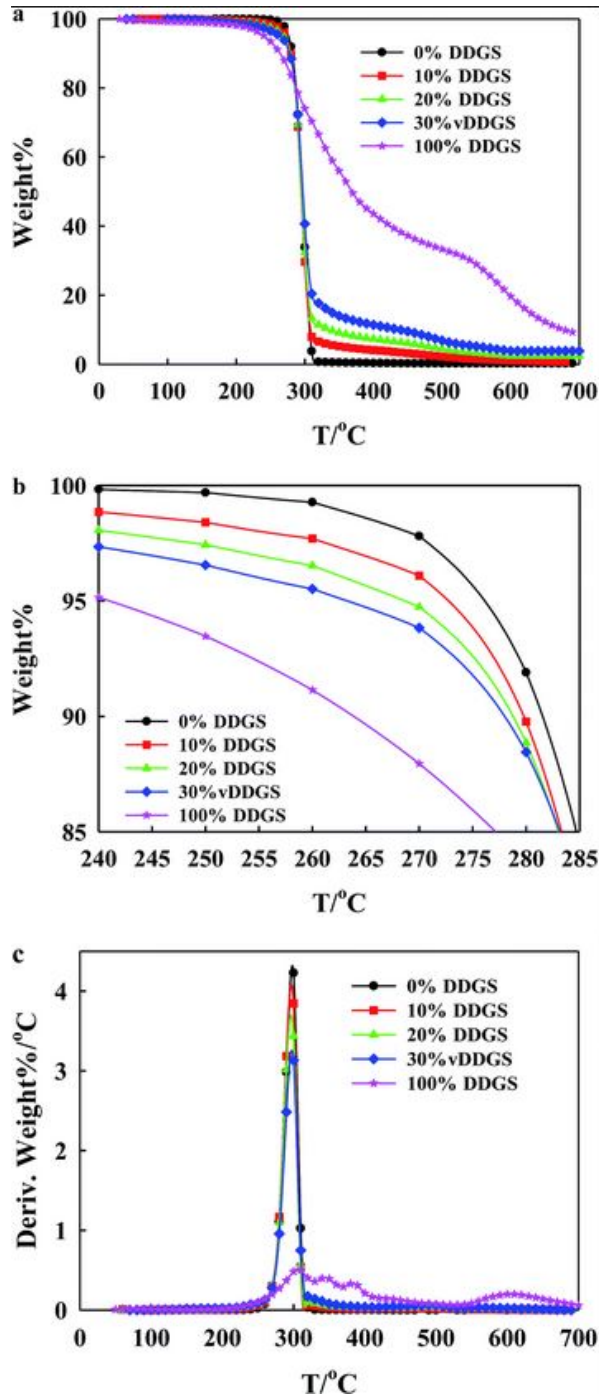


Fig. 2 (a) TGA traces of pure PHA and PHA/DDGS composites under a 60 mL min⁻¹ air flow; (b) enlarged TGA trace of selected temperature region of (a); (c) DTG thermogram of pure PHA and PHA/DDGS composites.

Table 1 Thermogravimetric analysis of pure PHA and PHA/DDGS composites

	DDGS 0%	DDGS 10%	DDGS 20%	DDGS 30%	100%DDGS
$T_{5\%}/^{\circ}\text{C}$	267.34	273.02	269.05	263.56	240
%Char	0.27	0.7	1.55	2.74	10

Fig. 2b shows an enlarged view of the 240–285 °C temperature region from Fig. 2a. The temperature at the onset of decomposition decreased slightly with increasing DDGS to PHA ratio of the materials, and the TGA traces were shifted proportionally with the percentage content of DDGS (Fig. 2b).

As seen in Table 1, the onset degradation temperature at the 5% weight loss also decreased from 276 °C to 240 °C with increasing DDGS content from 0% to 100%. Moreover, Fig. 2c illustrates the derivative rate of all the samples. It can be seen that T_{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_{onset} and % char are also listed in Table 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 et al.¹⁹ reported that the thermal stability of PLA was decreased by the addition of corn starch. Although thermal stability was reduced slightly by the addition of DDGS, use of the DDGS filler could be justified for many applications because it will effectively lower the cost of material without substantially altering the thermal properties.

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. 3a and b. 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 are evident in Fig. 3a. All blends exhibited a single T_g value, indicating that the two components were miscible or highly compatible in the amorphous phase. In addition, the presence of DDGS had little influence on the T_g , which varied by less than 3 °C for different filler ratios. Other studies have shown similar T_g results.^{20,21} The two endothermic peaks shown in Fig. 3a are related to the existence of two crystalline phases in PHA samples.²² The presence of DDGS decreased the two melting temperatures compared with those of pure PHA polymers, indicating that PHA and DDGS interact with each other well.

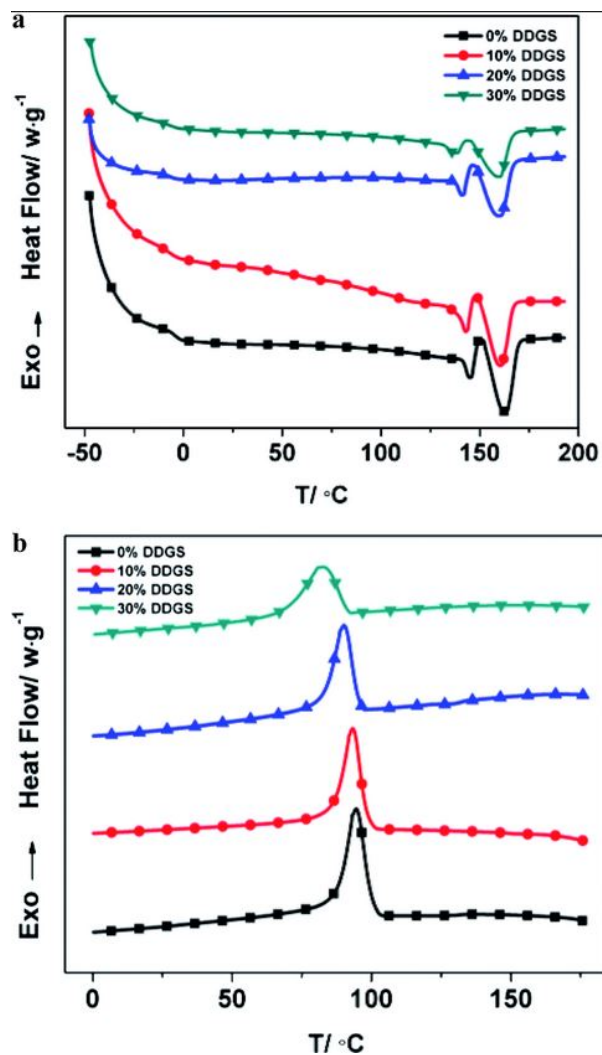


Fig. 3 (a) DSC thermograms of pure PHA and PHA/DDGS composites from the second heat scan; (b) DSC thermograms of pure PHA and PHA/DDGS composites from the cooling scan.

The melting temperature of the composites was influenced by various factors such as morphology, crystallization, and composite composition.²³ Detailed values of melting temperature and melting enthalpy are shown in [Table 2](#). Results showed that the melting enthalpy was also decreased by the addition of DDGS. This thermal behavior may be due to either the DDGS decreasing the crystalline structure of the PHA contents or DDGS decreasing the melt viscosity. Reis et al. has found similar behavior for PHA/starch blends, showing that ΔH_m and the two values of T_m decreased with an increase in starch content.²⁴

Table 2 DSC parameters of PHA/DDGS composites from [Fig. 3^a](#)

Samples	DDGS			
	0%	10%	20%	30%
T_g (°C)	-4.81	-8.01	-6.83	-5.71
T_{m1} (°C)	145.97	142.92	141.86	139.10
T_{m2} (°C)	162.61	160.06	159.44	159.71
T_{cc} (°C)	94.62	93.25	90.08	82.49
ΔH_m (J g ⁻¹)	26.916	25.613	21.101	18.288
ΔH_c (J g ⁻¹)	32.30	30.48	25.53	24.93
X_c (%)	23.49	22.35	18.41	15.96

a Where 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; ΔH_c is the crystallization enthalpy; T_{m1} and T_{m2} are the first and second melting temperatures taken as the melting peaks; ΔH_m is the total melting enthalpy; and X_c is the degree of crystallinity of films.

The cold-crystallization temperature (T_{cc}) can be seen in [Fig. 3b](#). 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_{cc} and ΔH_c are also reported in [Table 2](#). Similar to the melting enthalpy behavior, the crystallization enthalpy also showed a decrease with increasing DDGS content in composites.

The effects of DDGS on the dynamic mechanical properties of PHA/DDGS composites were measured by DMA. The PHA/DDGS 70/30 sample 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. 4a](#). The α -relaxation process of the polymers was demonstrated from this curve, and T_g was identified as the peak of $\tan \delta$. Based on results in [Fig. 4a](#), T_g remained nearly constant as the content of DDGS increased from 0% to 20%.

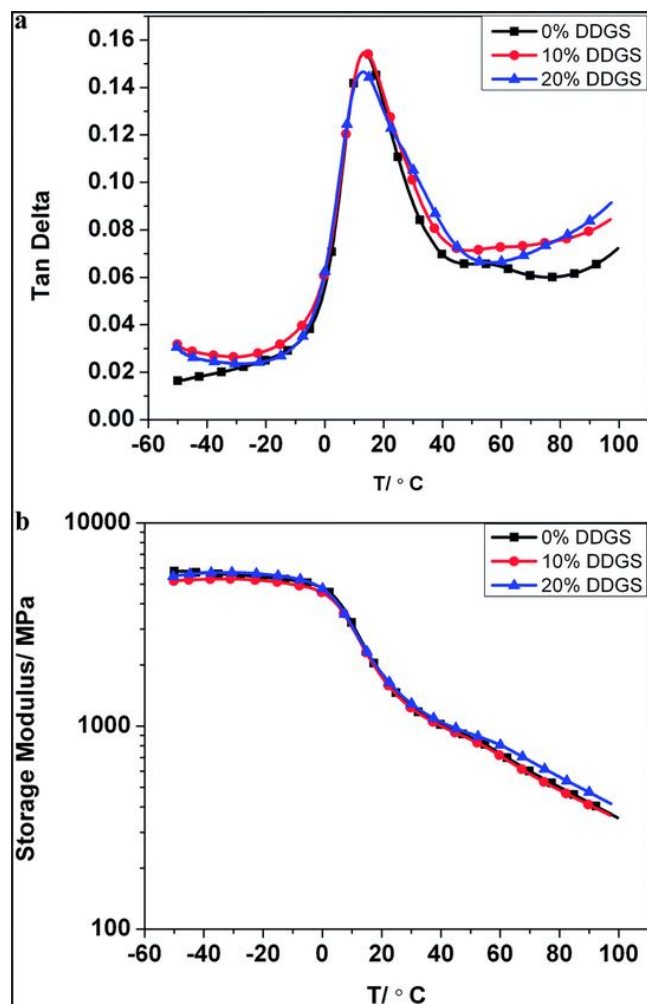


Fig. 4 (a) Temperature dependence of $\tan \delta$ for pure PHA and PHA/DDGS composites; (b) storage modulus versus temperature for pure PHA and PHA/DDGS composites.

As shown in [Fig. 4b](#), the storage modulus of pure PHA and the composites decreased with increasing temperature over the temperature range studied. This behavior is attributed to the increase in polymer chain mobility at high temperature. The storage modulus was nearly 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 at temperatures greater than T_g . For the composite containing 20% DDGS, the storage modulus increased only slightly. This increase was more obvious at the temperatures above T_g , especially for the range of 60–80 °C.

Because the weight percentage ratio of DDGS could influence the viscoelastic properties of blends, the rheological behavior of composites was examined by rheometer. [Fig. 5a](#) shows the angular frequency sweeps for PHA/DDGS composites. It was found that the complex viscosity was affected by the addition of DDGS filler to PHA matrix. At low angular frequency, the viscosity increased with an increasing ratio of DDGS to PHA. For example, the viscosity was 160 Pa s, 243 Pa s and 1220 Pa s for DDGS contents of 10%, 20% and 30%, respectively, at the

angular frequency of 0.5 rad s^{-1} . For PHA composites with 30% DDGS, the viscosity was more than 7 times greater than that for 10% DDGS composites. Dmitri et al.²⁵ has suggested that cellulose particles can disturb normal polymer flow and hinder the mobility of the polymer chain. The increase in viscosity shown by our research may result from the same mechanism because DDGS is rich in cellulose particles. Therefore, the greater the filler content of the DDGS, the higher the viscosity of the composites.

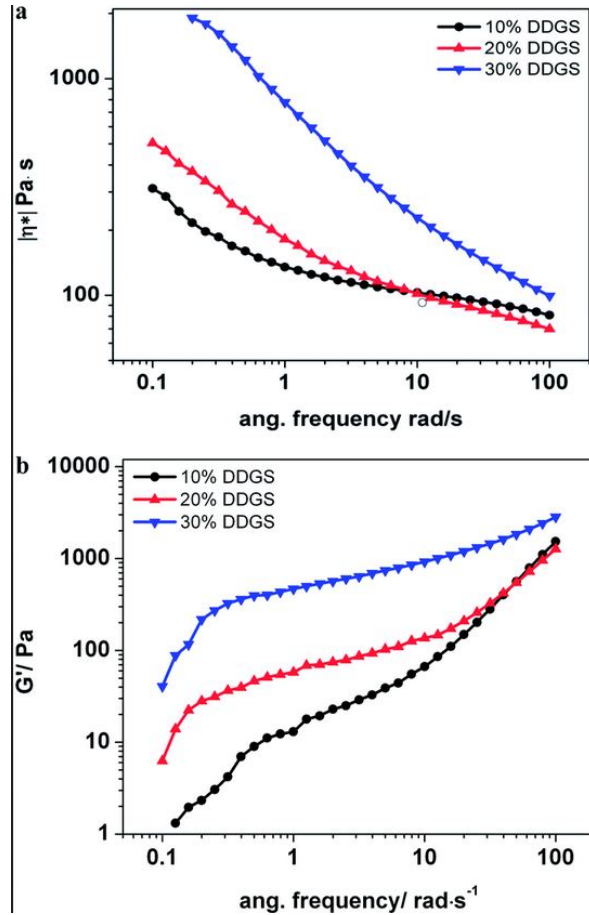


Fig. 5 (a) Angular frequency dependence of complex viscosity at $180 \text{ }^{\circ}\text{C}$ for PHA/DDGS composites with different filler contents; (b) angular frequency dependence of storage modulus at $180 \text{ }^{\circ}\text{C}$ for PHA/DDGS composites with different filler contents.

Fig. 5b is a typical melt elastic shear modulus (G') rheogram for PHA/DDGS composites. As can be seen, the elastic shear modulus of all samples increased with increasing angular frequency. This increase may be due to solid-like behavior resulting from the high molecular weight of PHA. In addition, Fig. 5b 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.

Effectiveness in the model application

PHA/DDGS composites performed exceptionally well for the target application (Fig. 6). Based on ratings of plant growth and health and container appearance, strength, and durability, prototype containers made of PHA/DDGS composite performed just as well as the standard petroleum-plastic container, slightly better than containers made of the PHA base polymer, and significantly better than a top-performing commercially available fiber container (Table 3). Blending DDGS with PHA to form a composite, strongly improved biodegradation in soil, a feature that is considered very important for the target application. Since very few greenhouse crops have a production cycle greater than 16 weeks, our results show that the prototype horticulture container made of PHA/DDGS composite fulfilled all of the function required for the culture of nearly all greenhouse crops, yet had a faster rate of biodegradation in soil than the paper-fiber container. Although PHA materials currently cost more than the standard petroleum-based material used for the application, the future increase in manufacturing capacity for PHA is projected to bring the price much lower,²⁶ and we found that incorporation of DDGS at 20% by weight reduced the cost of material for our prototype by 19.1%. Therefore, blending DDGS with PHA to form a composite for use in horticulture crop containers, both reduced the cost of material and improved the function to achieve the target capabilities for the application.



Fig. 6 Marigold plants grown under standard application conditions in horticulture containers made of PHA/DDGS composite (left), PHA base resin (middle), and standard petroleum-based polypropylene (right).

Table 3 Performance under application conditions for horticulture containers made of PHA/DDGS composite, PHA base resin, petroleum-based polypropylene, or a commercially available paper fiber^a

Container material	6 week greenhouse	16 week durability	Biodegradation in soil (%)
PHA/DDGS	79	100	47
PHA only	74	100	15
Petroleum control (PP)	79	100	0
Commercial biobased (paper fiber)	69	89	14

^a Results for the 6 week greenhouse trial are ratings from 0 to 100 based on mean plant growth and health, and container appearance, strength, and durability. Results for the 16 week trial represent ratings from 0 to 100 based on container appearance, strength, and durability only. Results for biodegradation are the percentage weight loss of the material samples during 6 months buried in a garden plot near Gilbert, IA.

Conclusions

This study quantifies the effects of blending DDGS with PHA and characterizes the thermal, morphological, rheological, and mechanical properties of PHA/DDGS composites at three different load ratios (90/10, 80/20, and 70/30). The PHA/DDGS composites were mixed uniformly with a twin-screw extruder. A morphological study using SEM revealed that the adhesion between the two components decreased with increasing amounts of DDGS filler, but that the properties of blend ratios evaluated in this study would likely be appropriate for many applications. The TGA test demonstrated a three-stage degradation process. DDGS slightly decreased the thermal stability of the composites, but use of the DDGS filler should be justified for many applications because it will effectively lower the cost of material without substantially altering the thermal properties. 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 significantly with increasing DDGS content. These results demonstrate that both the PHA matrix and PHA/DDGS composites possess thermal and physical properties that are suitable for our model application, and that PHA composites with DDGS fillers are good candidates for use in low-cost, bio-based plastic horticulture crop containers.

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References

1. A. Mohanty, M. Misra and L. Drzal, Sustainable Bio-Composites from Renewable Resources: Opportunities and Challenges in the Green Materials World, *J. Polym. Environ.*, 2002, 10(1), 19–26
2. A. Shah, F. Hasan, A. Hameed and S. Ahmed, Biological degradation of plastics: A comprehensive review, *Biotechnol. Adv.*, 2008, 26(3), 246–265
3. C.-S. Wu, Preparation, characterization and biodegradability of crosslinked tea plant-fibre-reinforced polyhydroxyalkanoate composites, *Polym. Degrad. Stab.*, 2013, 98, 1473–1480
4. G. Tan, L. Zhong, X. Lan and X. Sun, A Study on PHA/PLA/Talc Ternary Composite, *Appl. Mech. Mater.*, 2014, 467, 166–171

5. M. Reddy, S. Vivekanandhan, M. Misra, S. Bhatia and A. Mohanty, Biobased plastics and bionanocomposites: Current status and future opportunities, *Prog. Polym. Sci.*, 2013, 38(10–11), 1653–1689
6. Biodegradable polymers for industrial applications, ed. R. Smith, CRC Press, Woodhead, Cambridge, 2005
7. S. Khanna and A. Srivastava, Recent advances in microbial polyhydroxyalkanoates, *Process Biochem.*, 2005, 40(2), 607–619
8. A. Steinbuchel, Perspectives for Biotechnological Production and Utilization of Biopolymers: Metabolic Engineering of Polyhydroxyalkanoate Biosynthesis Pathways as a Successful Example, *Macromol. Biosci.*, 2001, 1(1), 1–24
9. N. M. Norrahim, H. Ariffin, A. M. Hassan, A. N. Ibrahim and H. Nishida, Performance evaluation and chemical recyclability of a polyethylene/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blend for sustainable packaging, *RSC Adv.*, 2013, 3, 24378–24388
10. Z. Liu, Y. Wang, N. He, J. Huang, K. Zhu, W. Shao, H. Wang, W. Yuan and Q. Li, Optimization of polyhydroxybutyrate (PHB) production by excess activated sludge and microbial community analysis, *J. Hazard. Mater.*, 2011, 185(1), 8–16
11. A. Javadi, Y. Srithep, S. Pilla, J. Lee, S. Gong and L. Turng, Processing and characterization of solid and microcellular PHBV/coir fiber composites, *Mater. Sci. Eng., C*, 2010, 30(5), 749–757
12. J. Naranjo, J. Posada, J. Higuera and C. Cardona, Valorization of glycerol through the production of biopolymers: The PHB case using *Bacillus megaterium*, *Bioresour. Technol.*, 2013, 133, 38–44
13. N. Berezina, Novel approach for productivity enhancement of polyhydroxyalkanoates (PHA) production by *Cupriavidus necator* DSM 545, *New Biotechnol.*, 2013, 30(2), 192–195
14. V. Cheesbrough, K. Rosentrater and J. Visser, Properties of distillers grains composites: a preliminary investigation, *J. Polym. Environ.*, 2008, 16(1), 40–50
15. C. Vanessa, R. Kurt and V. Jerry, Properties of Distillers Grains Composites: A Preliminary Investigation, *J. Polym. Environ.*, 2008, 16, 40–50
16. P. Fallahi, K. Rosentrater, K. Muthukumarappan and M. Tulbek, Effects of Conditioner Steam, Extruder Water and Screw Speed on Physical Properties of DDGS-Based Extrudates in Twin-Screw Extrusion, An ASABE Meeting Presentation Paper Number, 1110887.
17. S. Naznin and K. Tareef, In Vitro Degradation of PHBV Scaffolds and nHA/PHBV Composite Scaffolds Containing Hydroxyapatite Nanoparticles for Bone Tissue Engineering, *J. Nanomater.*, 2012, 190950
18. B. Ferreira, C. Zavaglia and E. Duek, Films of poly(L-lactic acid)/poly(hydroxybutyrate-co-hydroxyvalerate) blends: in vitro degradation, *Mater. Res.*, 2001, 4, 34–42
19. T. Ohkita and S. Lee, Thermal Degradation and biodegradability of Poly(lactic acid)/Corn Starch Biocomposites, *J. Appl. Polym. Sci.*, 2006, 100, 3009–3017
20. T. Elena, T. Joel, B. David, J. Long and W. Michael, Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate/cellulose nanowhiskers composites), *Polymer*, 2010, 51, 2652–2660
21. S. Madbouly, J. A. Schrader, G. Srinivasan, K. Liu, K. G. McCabe, D. Grewell, W. R. Graves and M. R. Kessler, Biodegradation Behavior of Bacterial-based Polyhydroxyalkanoate (PHA) and DDGS composites, *Green Chem.*, 2014, 16, 1911–1920
22. M. Silvia, S. Julia, F. Farayde, D. Alicaja, M. Bernhard and S. Wim, Obtention and characterization of poly(3-hydroxybutyric acid-co-hydroxyvaleric acid)/mcl-PHA based blends, *LWT–Food Sci. Technol.*, 2012, 47, 386–392
23. P. Matzinos, V. Tsuki, A. Kontoyiannis and C. Panayiotou, Processing and characterization of starch/polycaprolactone products, *Polym. Degrad. Stab.*, 2002, 77, 17–24
24. C. K. Reis, J. Pereira, A. Simth, C. Carvalho, N. Wellner and I. Yakimets, Characterization of polyhydroxybutyrate-hydroxyvalerate (PHB-HV)/maize starch blend films, *J. Food Eng.*, 2008, 89, 361–369

25. S. Dmitri, T. Elvia, K. Andre and M. Piller, Rheological and Mechanical Properties of Poly (lactic) Acid/Cellulose and LDPE/Cellulose Composites, *Mater. Sci.*, 2011, 17(1), 32–37
26. ReportsnReports, PHA (Polyhydroxyalkanoate) Market, By Application (Packaging, Food Services, Bio-medical, Agriculture) & Raw Material-Global Tends & Forecasts to 2018, April 2013, http://www.academia.edu/3443379/PHA_Polyhydroxyalkanoate_Market.