A R T I C L E   I N F O

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A B S T R A C T

The biodegradability of three types of bioplastic pots was evaluated by measuring carbon dioxide produced from lab-scale compost reactors containing mixtures of pot fragments and compost inoculum held at 58 °C for 60 days. Biodegradability of pot type A (composed of 100% polylactic acid (PLA)) was very low (13 ± 3%) compared to literature values for other PLA materials. Near infrared spectroscopy (NIRS) results suggest that the PLA undergoes chemical structural changes during polymer extrusion and injection molding. These changes may be the basis of the low biodegradability value. Biodegradability of pot types B (containing 5% poultry feather, 80% PLA, 15% starch), and C (containing 50% poultry feather, 25% urea, 25% glycerol), were 53 ± 2% and 39 ± 3%, respectively. More than 85% of the total biodegradation of these bioplastics occurred within 38 days. NIRS results revealed that poultry feather was not degraded during composting.

1. Introduction

Over four billion pounds of chicken feather waste is generated by the US poultry industry each year. Although feathers are typically treated as a waste, they possess characteristics of potential interest for biopolymer production. Feathers are composed of over 90% keratin, a fibrous and insoluble structural protein extensively cross linked by disulfide bonds that is resistant to digestion by animals, insects, and microbial proteases (Fraser and MacRae, 1980). Unfortunately, it is likely that the recalcitrance of feather fiber will retard the biodegradation of feather-based bioplastic materials.

The objective of this work was to characterize the biodegradability of poultry feather fiber (PFF)- and polylactic acid (PLA)-based bioplastics that were produced by extrusion and injection molding. We evaluated the biodegradability of these bioplastics by measuring carbon dioxide (CO2) produced during extrusion and injection molding. We further determined which components of the bioplastics were resistant to biodegradation using near infrared (NIR) spectroscopy. This combined approach allows for assessment of the overall biodegradability of these biomaterials and reveals the differential degradation of their individual components during composting.

2. Methods

2.1. Bioplastic pots

Three types of bioplastic flower pots were tested. Type A pots (composed of 100% PLA) were commercially produced by Summit Plastic Company (Akron, OH). Type B pots (composed of 5 wt.% PFF, 80 wt.% PLA, 15 wt.% starch) and type C pots (composed of 50 wt.% PFF, 25 wt.% urea, 25 wt.% glycerol) were prepared and molded in our laboratory as described below. Pots were cut into 0.5 cm square pieces prior to biodegradation tests. Characteristics of the components used for bioplastic pots types B and C are shown in Table 1. In order to minimize absorbed and adsorbed moisture and to minimize void formation, PFF, starch, and the PLA resin were dried at 80 °C under vacuum for 18 h before use, and then stored over desiccant in sealed containers.

For type B bioplastic, 100 g batches of the PLA, PFF, and starch mixture were homogenized using an internal mixer attached to an extruder (Plasticorder, Brabender GmbH & Co., Duisburg, Germany) prior to extrusion. For type C bioplastic, 50 g batches of the urea and glycerol mixture were manually mixed for 5 min prior to mixing for 3 min using a Hobart mixer (Hobart Corporation, Troy, OH). PFF (50 g) was manually incorporated into the mixture using a plastic spatula. The mixture was then mixed (four 10 min intervals) using the Hobart mixer to completely incorporate the liquid into the poultry feather. After each 10 min interval, the mixer was allowed to cool so as to keep the mixture below 40 °C.
A 3/4 inch single-screw extruder (Brabender GmbH & Co.) was used for bioplastic extrusion (Barone and Arikan, 2007). Temperature zones were maintained at 183°C and 176°C for extrusion of type B and C bioplastic, respectively. Extruded bioplastic strands were chopped using a pelletizer (Bay Plastics Machinery, Bay City, MI). Pelletized material was dried at 70°C, then molded using a Niigata injection molding machine (model NE55-UA4, Wood Dale, IL). For type B bioplastic pots the nozzle temperature was 185°C and the set point temperature was 183°C. For type C bioplastic pots the nozzle temperature was 157°C and the set point temperature was 155°C. For both types of pots, the cooling time was 50 s and the injection pressure was 1800 psi.

2.2. Biodegradability test

Biodegradability of the pots was evaluated by measuring carbon dioxide (CO₂) produced during incubation at 58°C for 60 days. The mass of CO₂ produced from composting was determined using a pressure sensor method (Ahn et al., 2008). Three replicate inoculum-only bottles (1 L volume) were loaded with 30 g (wet basis) of screened four month old dairy manure compost inoculum (Barone and Arikan, 2007). Triplicate bottles for each of the three types of bioplastic contained 30 g (w.b.) of inoculum and 5 g (w.b.) of bioplastic pieces. Carbon dioxide resulting from degradation was absorbed by sodium hydroxide (NaOH) pellets within each bottle. In order to maintain aerobic conditions, bottles were flushed daily for the first 7 days with humidified air for 2 min, and the NaOH was replenished. Bottles were flushed every 2 days from days 7 to 21, and flushed every 3 days from days 22 to 60. Pressure drops caused by the oxygen consumption during composting were logged using a pressure sensor datalogger head (Oxi-Top-C WTW, Weihem, Germany) and CO₂ production was calculated as previously described (Ahn et al., 2008).

2.3. Compost sample analysis

To determine the characteristics of the bioplastics and inoculum and their degradability, initial and final samples were collected from each bottle and analyzed for moisture content, volatile solids (VS), total carbon (TC), total nitrogen (TN), and by NIR spectroscopy. Moisture and VS content of samples were analyzed according to Standard Methods (APHA, 1998). Total carbon and TN were analyzed using an elemental analyzer (Elementar Vario Max CNS). For NIR analysis, all samples were ground to pass a 0.5 mm screen using a Udy Cyclone Sample Mill (Udy Corp., Fort Collins, CO). Samples were scanned in the NIR as described (Reeves, 2001).

Table 1

<table>
<thead>
<tr>
<th>Source</th>
<th>Density (g cm(^{-3}))</th>
<th>Molecular formula (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>1.25</td>
<td>(C(_3)H(_4)O(_2))(_n) (50 %)</td>
</tr>
<tr>
<td>Poultry feather fiber</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>Starch</td>
<td>1.5</td>
<td>(C(_3)H(_6)O(_2)(_2))(_n) (44 %)</td>
</tr>
<tr>
<td>Urea</td>
<td>1.32</td>
<td>CH(_4)N(_2)O (20%)</td>
</tr>
<tr>
<td>Glycerol</td>
<td>1.26</td>
<td>C(_3)H(_5)(OH)(_3) (39 %)</td>
</tr>
</tbody>
</table>

a Carbon content.

Cumulative CO₂−C production from bottles containing the compost inoculum alone and combined with each of three different bioplastics is shown in Fig. 1. Cumulative CO₂−C production from mixture A (compost inoculum plus bioplastic A) was very similar to CO₂−C production from the inoculum-only treatment. Mixtures containing bioplastics B and C showed similar amounts of CO₂−C production during the first 25 days but the bioplastic B material produced more CO₂−C than bioplastic C after this point. More than 85% of the CO₂−C production from bioplastics B and C occurred within the first 38 days.

3. Results and discussion

3.1. Bioplastic biodegradation patterns

Visual inspection of compost mixtures revealed that pieces of type A bioplastic (100% PLA) showed no change during the 60 days of incubation. Pieces of type B bioplastic (composed of 5 wt.% PFF, 80 wt.% PLA, 15 wt.% starch) became thinner and smaller over the incubation period. In contrast, pieces of type C bioplastic (50 wt.% PFF, 25 wt.% urea, and 25 wt.% glycerol) disappeared completely in less than two weeks at 58°C. Although the mass loss results do not reveal the basis of the structural changes in type C bioplastic, these changes were not due to extensive mineralization because only about 10% of initial carbon was released as CO₂.

Fig. 1. Cumulative CO₂−C production from compost inoculum and bioplastic pots (bioplastic A: 100% PLA, bioplastic B: 5% PFF, 80% PLA, 15% starch, bioplastic C: 50% PFF, 25% urea, 25% glycerol). Values are means ± SE of three replicates.
We speculate that urea mineralization likely contributed to bioplastic C particle disappearance. The carbon loss during the first two weeks roughly corresponds to the amount of urea carbon in the type C bioplastic (about 13% of bioplastic carbon).

### 3.2. Mass balance of bioplastic materials

Characteristics of the compost inoculum and bioplastics are shown in Table 2. Table 3 shows the average initial mass of C of inoculum and bioplastic pots and the cumulative loss of C as CO₂. After 60 days of composting, cumulative loss of C from type A bioplastic (100% PLA) was only 13 ± 3%. This result is very different from those of previous composting studies demonstrating high biodegradation values (>60% PLA mineralization within 60 days) (Kijchavengkul et al., 2006; Kale et al., 2007). It is possible that our low value was caused by chemical changes to PLA during pot production (by the extrusion process and/or high molding temperatures and pressure) or by unlisted components added during the manufacturing process.

Biodegradability of bioplastic B (53 ± 2% carbon loss) was 4-fold higher than that of bioplastic A (Table 3) and is comparable to previously reported values for PLA-based bioplastics. Since the composition of bioplastic B (5 wt.% PFF, 80 wt.% PLA, 15 wt.% starch) differed only slightly from the listed composition of bioplastic A (100% PLA), we expected that the biodegradability values of the two polymers would be quite similar. These results support the possibility that the commercially produced bioplastic A may contain unlisted components that inhibited biodegradation.

Carbon loss from bioplastic C was approximately 40% after 60 days of composting. This value corresponds to the combined carbon content contained in the urea and glycerol portions of this bioplastic (38% of bioplastic carbon).

### 3.3. Near infrared spectroscopy

NIR spectra of bioplastics A and B and PLA resin revealed a prominent peak at 7200 cm⁻¹ that is present in the spectra of both bioplastics A and B and in a laboratory produced injection molded PLA bioplastic (not shown). The spectrum of raw PLA resin (which is identical to the spectra of PLA-based bottles and cups) does not contain this peak but does contain a peak at 5500 cm⁻¹ that is not present in bioplastics A and B (not shown). It is likely that the spectral difference between the resin and injection molded materials are indicative of chemical changes caused by the molding process. However, given the very different biodegradabilities of bioplastics A and B, there is currently no definitive link between these spectral differences and specific molding parameters or with the extent of biodegradability.

Since pieces of bioplastic C disintegrated within the first 14 days of incubation, we could not obtain direct spectra of this composted bioplastic after 60 days. However, the spectral contribution of the composted bioplastic C (Fig. 2) could be determined by spectral subtraction using the respective spectra of the bioplastic C inoculum mixture and the inoculum without added bioplastic. NIR spectroscopy results revealed that, in contrast to other bioplastic components, PFF was not degraded during composting. Prior to composting the spectra of type C bioplastic contained peaks similar...
to those seen in the spectra of glycerol and urea. However, the spectra of composted type C bioplastic closely matched that of pure poultry feather fiber. Due to its resistance to proteolytic enzymes, feather keratin is not easily biodegradable. Our results agree with those from previous studies illustrating the recalcitrance of feather keratin during composting (Barone and Arikan, 2007; Ichida et al., 2001; Bohacz and Kornillowicz-Kowalska, 2009; Kornillowicz-Kowalska and Bohacz, 2010). It is likely that PFF- bioplastics need to be composted using keratin degrading bacteria such as *Bacillus licheniformis* and *Streptomyces* sp. (Ichida et al., 2001; Bohacz and Kornillowicz-Kowalska, 2009).

4. Conclusions

PLA-based polymers are considered readily biodegradable materials through composting. However, our results showed that samples from commercially produced injection molded PLA pots evolved only 13% of initial carbon as CO₂ during 60 days at 58 °C. NIR spectral results suggest that PLA in this biopolymer undergoes chemical changes during polymer extrusion and molding. These chemical changes may inhibit biodegradation. Feather fiber differed from other bioplastic components because it was not easily degraded under the conditions utilized in this study. Inoculation with keratinase producing microbes may improve feather fiber polymer biodegradability.

References


