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Anaerobic Biodegradation of Bioplastic Packaging Materials

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Abstract: With multiple initiatives to keep food-waste away from landfills, packaging systems that are compatible with the alternative end of life scenario (e.g., composting, biodigestion) are required. Anaerobic digestion converts biodegradable materials into energy-rich biogas. However, currently, the plastic packaging for handling food scraps have to be separated before digestion even if the plastic is regarded as biodegradable because they do not degrade in the required timeframe. If the biodegradation rate of bioplastics can match that of organic waste, the food-waste and packaging can be comingled in a single stream. Polymers such as polylactic acid (PLA), polycaprolactone (PCL) and polybutylene succinate (PBS) have a diverse range of applications. However they take a prolonged period to degrade completely. On the contrary, thermoplastic starch and polyhydroxyalcanoate (PHA) stand out as fast degrading polymers that can be compounded into polylactic acid to improve biodegradation. This study investigated the anaerobic biodegradation of commercially available bioplastics and potential ways to increase biodegradation rates. Commercial polymers were melt blended and converted into films including PLA and PLA blends with PCL and PBS. The effect of calcium carbonate as an additive was also evaluated. A laboratory scale automated methane potential testing system was used to study the degradation behavior. Calcium carbonate at low concentrations showed potential to improve biodegradation rates by providing a pathway for microbial activity. Co-digestion of PLA with food-waste resulted in a 10% increase in biomethane potential, indicating a synergistic effect. The results showed the potential for developing packaging solutions for handling food-waste that can readily degrade in industrial anaerobic digestion facilities.

Keywords: Anaerobic biodegradation, polylactic acid, calcium carbonate, bioplastics

1. Introduction:

Diverting food waste has been identified as a way to alleviate landfill burden, reduce methane emissions and create value-added alternatives. To protect the environment and improve the economics of food waste management, California, Massachusetts, Vermont, Connecticut and Rhode Island have already implemented the organics ban policy. With multiple initiatives to keep food-waste away from landfills, packaging systems that are compatible with the alternative end of life scenario (e.g., composting, biodigestion) are required. At many large institutional waste generators, food waste and plastics are often co-mingled and difficult to separate. The availability of readily degradable bioplastics can enable the combined conversion of multiple waste feedstocks in a single process, thus eliminating a significant fraction of materials being disposed of in landfills. However, currently, the plastic packaging for handling food scraps have

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to be separated before waste management even if the plastic is regarded as biodegradable because they do not degrade in the designated timeframe.

In 2013, the United States generated 253 million tons of municipal solid waste, of which nearly 13% accounted for plastics [1]. Less than 10% of the plastics generated is being recycled [1]–[3]; therefore, the unrecovered plastic materials are either landfilled or incinerated. Increasing quantity of plastic waste is causing land and water pollution and biodiversity threat by continuing accumulation in land and oceans [4]. It is inevitable to avoid continuous accumulation of petroleum plastics as they lead to environmental deterioration. On the other hand, biodegradable plastics, due to their short half-life offer suitable solutions to the problems created by disposal of conventional plastic packaging materials. Biodegradable plastics are synthesized either from renewable resources or using chemical methods to incorporate biodegradable entities. Bioplastics are the most attractive option in sustainable food packaging owing to their biodegradability. Bioplastics can mineralize into carbon dioxide, water and methane under appropriate conditions, therefore are acceptable feedstock for composting or anaerobic digestion during the end of life phase.

The goal of this project is to develop strategies to increase the biodegradation rate of commercially available bioplastics using anaerobic digestion process. Anaerobic digestion is a microbial process, where the complex biological polymers like polysaccharides, protein, and lipids are broken down into simpler molecules to produce a biogas that is rich in methane and carbon dioxide. Methane is an energy-rich gas used to generate electricity or can be used as a vehicle fuel. Anaerobic digestion is a versatile technology in the types of feedstocks it can process. Bioplastics degrade in anaerobic digester mainly by enzymatic hydrolysis as microbes secrete external enzymes into the digestion medium where long-chain polymers are converted into oligomers and monomers. The oligomers and monomers which are small molecules then diffuse through the cell wall and further break down by the action of internal enzymes [5].

Biomass-based polymers like polylacticacid (PLA), polyhydroxyalkanoates (PHA) and starch are readily biodegradable, while petroleum-based plastics like polycaprolactone (PCL) and polybutylene succinate (PBS) have relatively slow degradation rates [1], [2]. In this study, anaerobic degradation behavior of various bioplastics materials were investigated for degradation rate and methane production under thermophilic conditions (52 ± 2^0C). The materials studied were polylactic acid (PLA), polyhydroxyalkanoates (PHA), a blend of PLA and Polybutylene succinate (PLA: PBS), a blend of PLA and polycaprolactone (PLA: PCL), blends of PLA and PHA and Calcium carbonate filled PLA: PBS. The results from co-digestion of PLA, PHA, PLA: PBS and PLA: PCL with food waste is also reported in this paper to evaluate any possibility of synergistic relationships offered by nutrients available from food waste.

2. Methods:

2.2. Inoculum and substrates:

The inoculum (i.e., microbial suspension) used in the experiments was effluent from a running digester that co-digests industrial food waste with manure at mesophilic temperature. The effluent was incubated in a BOD (Biological Oxygen Demand) incubator at 52°C to acclimate

the microorganisms to process condition for a duration of 7-10 days. The inoculum total solids (TS) and volatile solids (VS) were measured after the pre-incubation using EPA Method 1684 [3].

2.1.Experimental procedure

The bioplastics samples used in this study are listed in Table 1. The positive contrl used in the experiment was analytical grade cellulose, and the inoculum without any added substrate was the control. The food waste used in the co-digestion experiment was obtained from the university cafeteria at RIT. Food waste was a mix of pre and post-consumer waste, which contains vegetables, cooked meat, bread, rice and pasta, and fruits. Food waste was finely ground to a particle size of less than 2mm before use. Bioplastic samples were prepared to obtain an inoculum to substrate ratio (ISR) of 2 (g VS inoculum: g VS substrate added). The volatile solids content of the inoculum and bioplastic material were measured using EPA Method 1684. Samples were purged with nitrogen to create an anaerobic environment and incubated at 52±2°C with mixing at 160 rpm, with an 'ON' cycle of 10 seconds and 'OFF' cycle of 50 seconds. The BMP tests were done using 500mL reactors with 300mL working volume using an Automated Methane Potential Testing System (AMPTSII). The AMPTS II system (Bioprocess control Inc. Lund, Sweden) records the biomethane production continuously at regular time intervals (Figure 1).

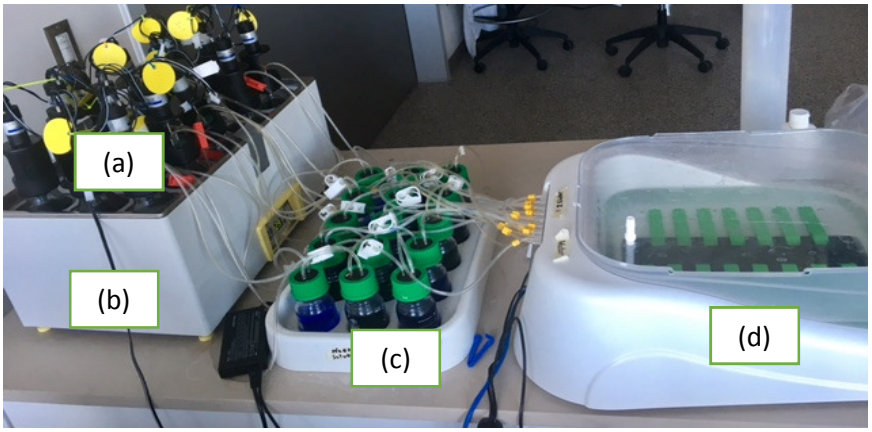

Figure 1. AMPTSII system used in studying degradation of bioplastic materials under anaerobic conditions. A water bath incubator (b) set to the desired temperature helps to maintain the optimum temperature of reactors (a). Biogas mainly contains methane and CO_2. A Carbon dioxide fixing unit (c) connects to the biogas outlet tubing of the reactors. The fixing unit absorbs CO_2 from the biogas and methane passes through a flow cell detector (d). The flow cell detector records methane production continuously (data acquisition at intervals of 15 min, 1h or 1day).

Table 1: Description of samples used in the study (samples were melt mixed and converted into sheets)

Sample		Ratio by mass	Resin/filler Name	Supplier's name
1	PLA	100:00	Polylactic acid	Natureworks 4043D
2	PLA/PHA	95:5	Polyhydroxyalkanoate	Metabolix Mirel P5001
3	PLA/PHA	90:10	Polyhudroxyalkanoate	Metabolix Mirel P5001
4	PLA/PCL	70:30	Polycaprolactone	Perstrop CAPA 6800
5	PLA/PBS	80:20	Polybutylene succinate	Showa Bionelle 1001MD
6	PLA/PBS/CC1	76:19:5	Calcium Carbonate	Omya TP39914
7	PLA/PBS/CC2	76:19:5	Calcium Carbonate	Omya TP39968

2.2.Calculation of percent biodegradation

Biodegradability (or percent biodegradation) was calculated as the ratio of observed biomethane potential (BMP) to the calculated theoretical maximum BMP as shown in Equation 1.

$$\%\ \text{biodegradation} = \frac{\text{Observed BMP}, {}^{\text{mL CH}_4}/_{\text{g VS}}}{\text{Theoretical maximum BMP}, {}^{\text{mL CH}_4}/_{\text{g VS}}} \qquad \text{Eq. 1}$$

The theoretical maximum BMP for different materials have been estimated using reaction stoichiometry for anaerobic digestion suggested by the literature [4].

3. Results and discussions:

3.1. Degradation of PLA and PLA blends with and without food waste

The anaerobic degradation of PLA powder under thermophilic and mesophilic conditions was compared in a study where the authors observed 80% degradation in 40 days under the thermophilic condition [5]. However, the mesophilic condition showed much lower degradation rate. A biogas potential of 677 $mLCH_4gTS^{-1}$ has been reported for PLA under thermophilic conditions, which is equivalent to approximately 410 $mLCH_4gVS^{-1}$ of methane potential [6]. A BMP of 409 mL/gVS was observed for PLA in this study which is in complete agreement with the study mentioned above. Figure 2 (a) shows biomethane potential of PLA, PLA: PBS and PLA: PCL. The daily BMP values normalized to the maximum BMP (i.e., percent degradation) show 4.7%, 35.4% and 82% degradability of PLA on day 10, 20 and 30 respectively. The overall percent degradation of PLA reached 90% on day 36 and plateaued after this time point. The initial 7 days indicated a lag phase, 8-28 days exponential phase and after 36 days the degradation attained a steady state with no further methane production. A very low degradability of PBS under anaerobic conditions has been reported. A BMP as low as 11 $mLCH_4gVS^{-1}$ was observed after 100 days of thermophilic digestion of PBS polymer [4]. Cho et al., reported a BMP of 554 $mLCH_4gVS^{-1}$ for PCL: starch blend after 139 days of incubation corresponding to 83% degradation [4]. In one study, there was no observed biogas production after 43 days of anaerobic digestion of PCL powder under thermophilic conditions. The biodegradability of PCL after 43 days in the above-mentioned study was 92% [5]. The polymers-PLA and PBS are tough to degrade unless blended with another degradable polymer. Very low BMPs have been reported for PBS and PCL polymers alone in the literature, however, PLA blends of PBS and PCL showed significantly higher BMP than the reported studies for their respective control samples. The results indicate that when PCL and PBS are blended with other readily degradable materials, the overall biodegradation will improve. The readily degradable polymers would degrade first, exposing more surface area for the microbes to act, which further improves degradation of PCL and PBS. The observed daily biomethane potential for PLA: PBS and PLA: PCL is shown in Figure 2. Even though, the blends did not produce higher methane yield than the PLA control, PLA: PBS resulted in a slightly improved BMP than PLA: PCL. However, since very poor degradation has been reported for PBS and PCL in the literature, blending of these materials with

highly degrading PLA is a reasonable option to consider. Among the blended components, PLA helps improve the biodegradation and PBS, and PCL help improve the mechanical properties. The PLA: PBS blend showed an improved BMP after 30 days of the experiment compared to PLA: PCL. The ultimate BMPs of 354 and 297 $mLCH_4gVS^{-1}$ were observed for PLA: PBS and PLA: PCL respectively.

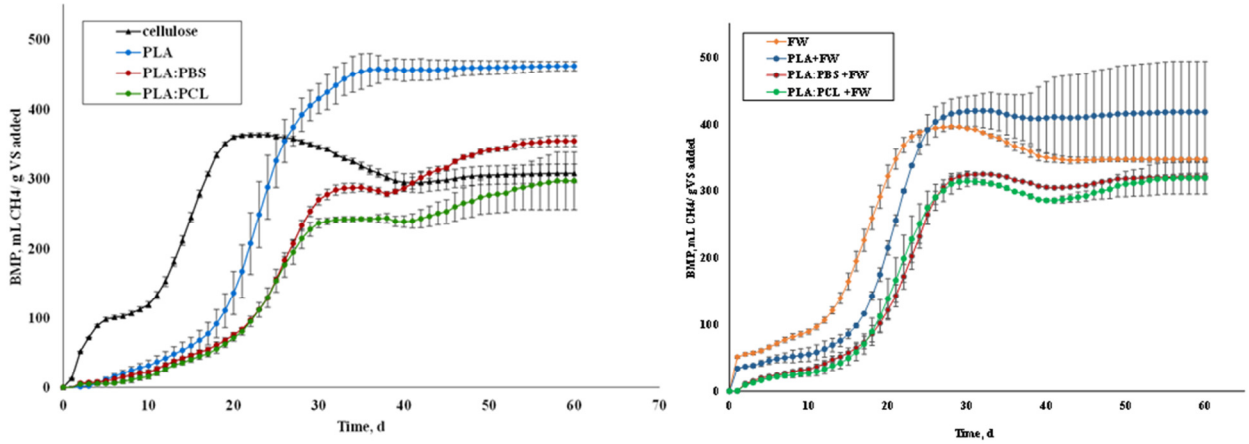

Figure 2 (a, left) and 2(b, right): Biomethane potential of PLA based polymers without and with food waste.

Further, the biodegradability of these polymers was estimated for digestion experiments with and without food waste. Figure 2 (b) shows percent biodegradation of different experiments. As bioplastics have a long lag time before they start to degrade, co-digestion of these polymers with food waste was investigated. Food waste contains necessary nutrients required for anaerobic digestion and helps to balance the carbon to nitrogen ratio. The cumulative daily BMP from food waste co-digestion experiments is shown in Figure 3. No significant difference was observed in BMP when PLA was co-digested with food waste. The biomethane production rate was slightly higher in the co-digestion mix compared to PLA resulting in a 10% improvement in the ultimate BMP. However, 8% reduction in BMP was observed in PLA: PBS blend and a 7.5% improvement were observed in PLA: PCL blend. These changes in BMP are nevertheless statistically significant. Even though food waste co-digestion had no significant impact on the overall BMP, the co-digestion mixes showed a shorter lag time and reached the final BMP faster than their controls. The ultimate BMP was reached on day 24 and 35 for PLA with and without food waste and day 49 and 61 for PLA: PCL with and without food waste. Co-digestion of PLA: PBS with food waste was found to be slightly antagonistic showing inhibitory effects and hence needs more experiment to draw further conclusions. Percent degradation of all the materials with and without food waste is shown in Figure 3.

3.2. Effect of CaCO3 (filler) addition on anaerobic degradation of PLA: PBS blend:

The effect of adding a small amount of calcium carbonate (CC) on anaerobic degradation of PLA: PBS was studied for 70 days. Calcium carbonate with two particle sizes and surface treatment was used at 5 wt.% loading. The control and CC blends had a lag time of 8 days, and CC blends resulted in a slightly higher BMP than the control after day 14. Both the CC blends (CC1 and CC2) showed no significant difference in BMP until day 35, however, after this CC2 resulted in significantly higher BMP than CC1 as shown in Figure 1. Overall average

degradation was 37% in control, 45% in CC1 blend and 49% in CC2 blend. These results indicate that calcium carbonate has a positive influence on improving the degradation rate of bioplastics.

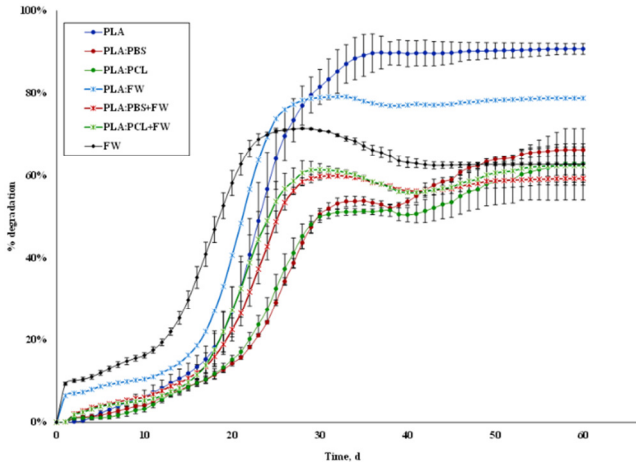

Figure 3. Percent degradation of PLA and PLA blends with and without food waste.

3.2. Effect of CaCO3 (filler) addition on anaerobic degradation of PLA: PBS blend:

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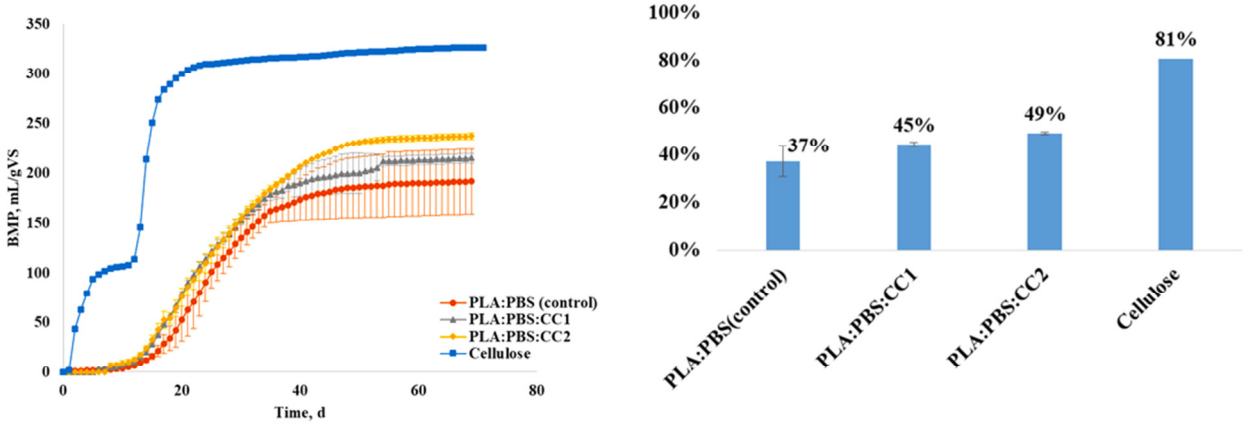

Figure 4. (a, left) and (b, right): Cumulative biomethane potential of PLA: PBS blend with and without CaCO3 and percent degradation on day 60 of the experiment compared with cellulose control.

Addition of fillers like calcium carbonate into plastics not only reduces the cost but also improves mechanical performance such as fluid barrier properties, thermal stability, and

biodegradation [7]. The gap between bioplastic matrix and the filler offers a channel for microbial attachment hence providing a larger surface area of the bioplastic available for microbial action [8]. In CC blends, the variation among of the degradation of triplicate samples was reduced compared to PLA: PBS control, which possibly could be a result of an improved surface area of contact between the microbial cells and the bioplastic. Moreover, a different matrix could result in a stronger effect. Additionally, CaCO3, when released to the aqueous medium, offers a buffering action and helps to prevent acidic pH that could result from degradation of a polymer matrix into lactic acid and succinic acid.

3.3. Effect of blending PHA with PLA on thermophilic degradation

Figure 5a shows the BMP for PLA with 5 and 10 wt.% of PHA. A higher degradation rate was observed for the sample with 10% PHA compared to 5%. This suggests that PHA can help initiate the degradation process reducing the lag time and increasing the rate of degradation of PLA. Though the blend with 10% PHA had a higher methane production rate in the beginning, because of the high variability among replicates it is not statistically significant after day 50. This high variability was observed in samples of 100% PHA at thermophilic conditions (see Figure 5b), which contrast a high biodegradation rate and low variability at mesophilic conditions (i.e., 37°C). However, PLA control samples resulted in a percent degradation of 88-91% in 60 days compared to 52-56% for the blends.

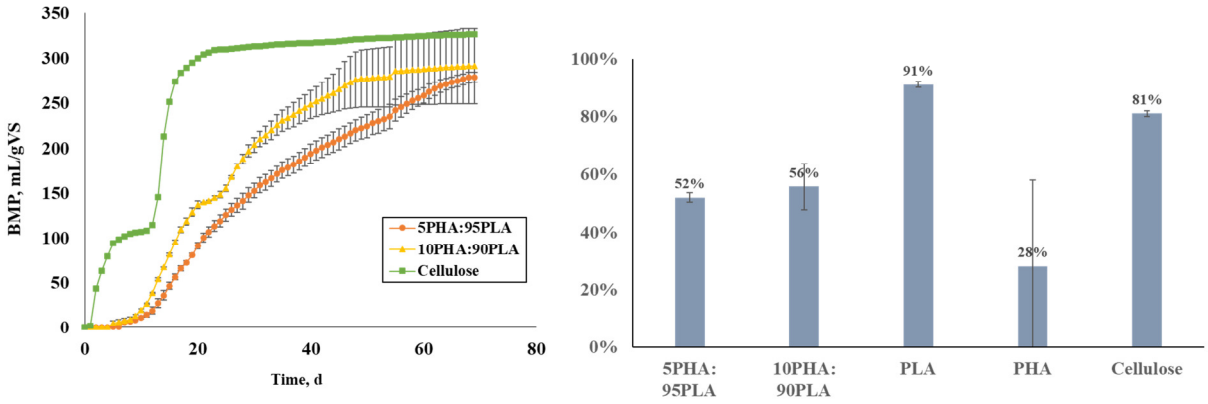

Figure 5. Cumulative biomethane potential of PLA: PHA blends and percent degradation on day 60.

The PLA and PHBV (Polyhydroxy butyrate/valerate) were reported to be immiscible at any composition from 10-90% PLA [9] which could be a reason for reduced degradation patterns. A co-digestion approach of mixing PLA and PHA in the digestion mix could also be another option where there is a possibility of synergistic effects. This results point at the importance of the degradation conditions especially the temperature (mesophilic vs thermophilic). Material formulation could be tuned depending on these conditions. PLA degrades better under thermophilic conditions whereas PHA degrades better under mesophilic conditions.

3. Conclusions

This study explored different strategies for enhancing the biodegradation rate of PLA based bioplastics under anaerobic conditions. PLA blends with PBS showed higher biodegradation than

blends with PCL, however this trend was reversed when comingle plastic and food waste. Even though food waste co-digestion had no significant impact on the overall BMP, the mixture showed a shorter lag time and reached the final BMP faster than their controls. Calcium carbonate proved to improve the degradation rate and biomethane potential of PLA: PBS. Adding a small amount of PHA (up to 10%) in a PLA matrix showed a potential to reduce the lag time and increase the rate of biodegradation, however the overall biodegradation was reduced compared to neat PLA.

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