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Assessment of anaerobic degradation of Ingeo™ polylactides under accelerated landfill conditions

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ABSTRACT

Ingeo™ polylactide (PLA)[1] biopolymers are used world-wide in a diverse range of applications and, after the useful life of the particular application, they can be recycled (either mechanically or chemically) or disposed of via various end-of-life options, such as composting, incineration and landfilling. The use of compostable materials for food packaging could be an enabling technology to allow the diversion of food waste from landfills into composting facilities. However, despite many new initiatives and existing programs it is still true that a significant part of industrial and household waste still ends up in landfills. Because polylactide polymers are known to be compostable the question is often raised about the behaviour of these materials in landfills.

In order to study the behaviour of Ingeo polylactides (PLA) in landfills two studies were performed aimed at generating reliable information on the anaerobic biodegradation of PLA under conditions of extended time and modest temperatures. The first test (under accelerated landfill conditions) was done at 21 °C, and three moisture levels, extending to 390 days and the second test (a high solids anaerobic digestion test under optimal and significantly accelerated conditions) was conducted at 35 °C for 170 days. Each test is meant to represent an accelerated test of what could happen under anaerobic landfill conditions. These two tests each had accelerated the biological degradation sufficiently that they were in some sense equivalent to approximately a century of a "typical" biologically active landfill.

The semicrystalline polylactide samples did not produce a statistically significant quantity of biogas during either test. The amorphous PLA did generate a small amount of biogas in the test at 35 °C, but none in the test at ambient temperature. Here it should be noted that the tests were conducted under accelerated, optimal landfill conditions, the biodegradation was observed in a 100 year timeframe and the market volume of amorphous PLA is low. We conclude that semicrystalline PLA (typical of >96 wt% of resin used to manufacture products), under anaerobic biological conditions typical of a landfill at moderate temperatures (where PLA hydrolysis is slow), will not lead to significant generation of methane, and that no significant population of organisms is available under anaerobic conditions to directly degrade high molecular weight PLA. Because there was no direct biological degradation of PLA under the anaerobic conditions, it is likely that any degradation of PLA in a landfill would require a chemical hydrolysis step prior to any biodegradation, which is analogous to the situation in aerobic composting. At 20 °C this process is estimated to take 100+ years, and under those conditions the degradation of the PLA would be extremely low. Additional data on the time/temperature history experienced in landfills will be needed to understand the net effect for disposal of PLA globally.

1. Introduction

Polylactide (PLA) is an aliphatic polyester produced from lactic acid or the cyclic diester, lactide. It is among the most widely available biobased thermoplastics, with a production capacity of over 140,000 metric ton/year [1]. There are many reasons for the increasingly widespread adoption of biobased materials in general,

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and PLA specifically. A desire both to reduce the depletion of fossil resources and to reduce greenhouse gas emissions, are typically driving adoption of these new materials. The life cycle inventory (or eco-profile) for Ingeo PLA, from NatureWorks LLC, has been published previously [1] and recently updated [2]. These papers contain the information on various environmental indicators for all the stages used in manufacturing the polymer, from corn planting, growing, and harvesting, through corn milling, lactic acid fermentation, and lactide production and polymerization. The eco-profile for Ingeo is attractive relative to all commercially available polymers. The greenhouse gas emission (GHG) for Ingeo is currently 1.3 kg CO_2 eq./kg polymer, compared to approximately 2.0 kg CO_2 eq./kg polymer for petroleum based polyolefins, 3.2 kg CO_2 eq./kg polymer for poly(ethylene terephthalate) (PET), and 3.4 kg CO_2 eq./kg polymer for general purpose polystyrene (GPPS). The eco-profile, however, only tells a part of the story of the overall life cycle assessment (LCA). A full LCA requires that the entire chain be considered, that is, not just cradle to factory gate, but cradle to factory gate to production of an article, use, disposal, and final end-of-life. Thus, a LCA requires inputs of the polymer eco-profile and additional data for the moulding of articles, their transport, and the final disposition.

Depending on the material and its properties, many end-of-life options are available, dependant on local infrastructure. For polymers, typical options include recycling (reprocessing as a polymer, typically with some degradation of properties), monomer recovery (recovery of lactic acid from PLA) and subsequent use of the recovered monomer, incineration with energy recovery, composting, anaerobic digestion [3] and landfill. Evaluation of the societal benefits or burdens of each approach require data on the inputs and outputs of each process [4,5].

It is widely known that organic wastes such as grass, leaves, and food scraps are among the fastest degrading materials [6], and contribute to the methane emissions from landfills. In many areas the disposal of yard waste in landfills has already been banned or discouraged through active recycling programs. The problem of food waste in landfills remains unsolved.

One approach to mitigating the problem of methane generation in landfills is to capture and utilize the methane for power. In a well managed system this can provide positive benefits, although the food waste is still a net GHG generator [7]. The challenge with food waste is the speed of degradation, which can lead to methane emissions before the collection and utilization facilities are in place. This problem can be addressed through diversion of food waste (along with other organic materials) to composting facilities [8].

A close look at EPA waste estimates [9] shows that while recycling rates for “clean” materials, such as lead batteries (99%), aluminium beverage cans (49%), and newspaper (78%) are relatively high, the recycling of food contaminated packaging is very low (aluminium foil and food cans 9%, paper cartons 22%). A typical recycling facility is not equipped to deal with food contaminated packaging and so currently most of this material is disposed of in landfills.

The promise of compostable packaging is not, as once proposed, a reduction in landfill volume, but is actually as a technology to enhance the collection of food waste and food contaminated packaging to enable diversion of these materials from landfill to composting or to anaerobic digestion facilities. The ability to divert food wastes from landfill would enable a tremendous reduction of the methane generation. The large scale use of compostable packaging for this specific function will take some time, because of the availability of these materials, the acceptance in the market place (from technology and economic perspective) and the availability and access to composting and anaerobic digestion facilities. In the interim we need to understand the behaviour of these packaging materials under current, mainly anaerobic landfill conditions. During the anaerobic biodegradation of organic materials (including biodegradable plastics), a mixture of gases, principally methane and carbon dioxide, are the final decomposition products while some of the organic material will be assimilated for cell growth. This paper reports on the extent and rate of biodegradation of Ingeo polylactides (PLA) under anaerobic conditions at moderate temperatures.

2. Background

There appears to be relatively few microorganisms which biodegrade PLA while it is a high molecular weight polymer [10,11]. In studies performed with synthetic polyesters, such as PLA, compared to bacterial polyesters such as poly 3-hydroxybutyrate (PHB), copolymers of 3-hydroxybutyrate with 3-hydroxyvalerate or 3-hydroxyoctanoate, or starch blends, PLA is always far less reactive in aerobic or anaerobic degradation tests [12–15]. Typically both the poly(3-hydroxyalkanoates) and starch materials are considered to be directly attacked by the microorganism cultures, whereas relatively few organisms have been found to colonize PLA [10,11,13,14,16]. Data on molecular weight loss and mass loss over time support the idea that polyhydroxybutyrate-valerate (PHBV) is attacked at the chain ends, leading to generation of gas with little molecular weight loss, whereas the PLA undergoes random chain scission to fragments and oligomers, with a requirement that there be extensive hydrolysis prior to any biotic attack [14].

The degradation of PLA under aerobic conditions present in compost is now well established. The process is understood to proceed via a sequential mechanism wherein the first step involves a simple chemical hydrolysis to reduce the molecular weight of the PLA, followed by assimilation by microorganisms which utilize the lactic acid oligomers as an energy source [17,18]. This is consistent with the relative paucity of organisms which have been reported to directly biodegrade the high molecular weight PLA. The end result of the process is compost and near quantitative release of CO_2 back into the atmosphere.

The aerobic degradation is known to be highly temperature dependant [12], with essentially complete biodegradation in 3–4 months at 55–60 °C, and little degradation at mesophilic temperatures. This is consistent with the proposed two step mechanism, wherein chemical hydrolysis is a prerequisite to assimilation and biodegradation. Chemical hydrolysis of PLA is a complex phenomenon. Tsuji [19] provides a good overview of some of the many factors which are involved, such as water content, temperature, crystallinity, pH, and other factors. Further, factors such as blended component polymers, residual lactide content, hydrolysis stabilizer packages, end group composition, and physical form of the specimen must be taken into account. Lyu et al. [20] provide a detailed assessment of the hydrolysis kinetics for amorphous polylactide, including a model of the temperature response for degradation via hydrolysis. At temperatures well below the glass transition temperature the polymer matrix is essentially locked into position, with little cooperative movement in the structure. This lack of cooperative motion can then result in dramatically reduced rates of reaction. This is not uncommon behaviour for polymer systems. Data on hydrolysis of semicrystalline PLA fibres [21] shows a drop in the hydrolysis rate of more than two orders of magnitude as the temperature is reduced from 55 to 23 °C. Time series for individual samples fit well to a simple rate form $\ln(M_n/M_{n0}) = -kt$, although the pseudo-first order rate constant, k, is dependent [21] on all of the sample specific factors mentioned above. The median value of the rate constant k for the fibre samples at 50% relative humidity is $9 * 10^{-2}$ day^{-1} at 70 °C, $8 * 10^{-3}$ day^{-1} at 55 °C, and $4 * 10^{-5}$ day^{-1} at 23 °C. Amorphous pellets have a higher rate of hydrolysis. From

these data, one can estimate that even after 100 years at 20 °C and 50% relative humidity a polymer with initial molecular weight of 100,000 g/mol will still be at 36,000 g/mol molecular weight, which is above the point where biodegradation by aerobic microorganisms has been observed. Extrapolation of the Lyu model suggests a rate drop of more than three orders of magnitude between 55 °C and 23 °C, and predicts even longer lifetimes at low temperatures. This "thermal trigger" effect is why a material can be stable for very long periods at moderate temperatures or cooler, and yet degrade rapidly in a hot, humid environment.

Standard tests are available for evaluating the compostability of polymers, such as ASTM D6400, EN 13432, and ISO 17088. Depending on fabrication techniques, and part design, articles made of PLA and other materials have been independently verified to pass these standard tests [22]. Reflecting conditions of actively managed compost systems, these tests require that the temperature be greater than 60 °C for 1 week, and at least 40 °C for at least 4 consecutive weeks. In some cases, there is also a requirement to meet higher temperature standards, for the purposes of pathogen reduction.

The UK government for example has published Publicly Available Specifications (PAS) for composted materials. These documents describe a number of requirements which the products of composting or digestion need to meet, amongst others sterilisation requirements.

PAS100:2005 describes the requirements for composted materials [23]. In terms of sterilisation it is required that during the composting period, a temperature of 65 °C or more is maintained for at least 7 days. The compost at that point needs to contain at least 50% moisture. It is also required that during this period, the compost is mixed or turned at least twice. High temperature, high humidity conditions such as those specified in PAS100:2005 lead to the rapid breakdown in molecular weight and ultimate biodegradation of PLA.

In contrast to the well characterized degradation behaviour of PLA under *aerobic* composting conditions, the degradation behaviour of PLA under a variety of anaerobic conditions has been less studied, and with mixed results. Studies have shown that at thermophilic temperatures (50 °C or higher) there is a measurable degradation of PLA [12], whereas at mesophilic conditions little or no degradation is observed [13–15]. Soil burial for a year (0–22 °C) was reported to have no effect at all on physical properties of PLA test bars [16].

Anaerobic conditions are important for a number of end-of-life scenarios, including deep sea marine disposal, high throughput anaerobic digestion systems designed for power recovery, and landfill. Each of these will have distinctly different characteristics in terms of solids loading, microbial populations, temperature, and exposure time. The engineered high throughput anaerobic digestion systems are typically operated in the mesophilic (approx. 35 °C) or thermophilic (approximately 52–55 °C) regime. Marine disposal would be characterized by low temperatures, depending on the water depth. Landfills have been reported to have temperatures dependant on local conditions, with lower temperatures in the older waste [24]. Moisture content also varies considerably [25]. Diversion of food waste, a rapidly degradable component of the MSW stream, from landfill to more actively managed processes, such as composting, will also reduce both the rate of degradation and the ultimate amount of degradation, which directionally will lower the landfill temperature. On the opposite end, a few landfills are now being actively managed to act as "bioreactors", to intentionally cause microbial degradation of the waste with collection and utilization of the by-product gas.

Conditions in landfills vary considerably by geography, by management practices, by age of waste, etc [24,25]. The decomposition of waste, and the potential production of methane, are active topics and being actively modelled in the context of greenhouse gas warming potential and the ability to collect and utilize landfill gas as a source of power [26–28]. Even so, although the major biodegradable components of municipal solid waste (cellulose and hemicellulose), have been widely studied in the laboratory, field studies of individual components are still needed [29]. Recent work has aimed at developing methodology for scaling results from laboratory systems to model behaviour in the field [7].

In order to study the behaviour of Ingeo polylactides (PLA) in landfills two studies were performed [30,31] to generate reliable information on the anaerobic biodegradation of PLA under conditions of extended time, high microbial activity, and modest temperatures. The first test (under accelerated landfill conditions) was done at 21 °C, and three moisture levels, extending to 390 days and the second test (a high solids anaerobic digestion test under optimal and significantly accelerated conditions) was conducted at 35 °C for 170 days. Each test is meant to represent an accelerated test of what could happen under anaerobic landfill conditions.

3. Test methods and materials

3.1. Test 1 (ALC test – accelerated landfill conditions)

This test follows the guidelines of ASTM D.5526-94 (2002): "Determining Anaerobic Biodegradation of Plastic Materials under Accelerated Landfill Conditions". This static anaerobic biodegradation test determines the biodegradability of a material in a landfill environment. The digesters are filled with a high amount of pretreated municipal solid waste fraction, as described in 3.3.1, and a low amount of concentrated anaerobic inoculum (sludge) from an anaerobic digester. After addition of the test material, the reactors are incubated at ambient temperature (21 °C) for a period of at least 6 months. In parallel, a blank (without any test material) and a reference (with cellulose as reference material) are operated. Three test series were prepared with moisture concentrations of 49%, 55% and 65% (in the original test design the target was a 40% moisture level, but because it was not possible to reach this level without excessive drying it was set at 49%). Two replicates of each sample were run, at each of the three moisture contents. There were three PLA test samples (two semicrystalline, one amorphous), a blank, a cellulose reference, and an oak leaf reference, for a total of 36 test fermentation vessels (6 samples × 3 moisture levels × 2 replicates).

The municipal solid waste fraction provides a matrix for support of the microbial colonies required for the biodegradation and sufficient macro and micro nutrients for the microbial colonies. The concentrated anaerobic inoculum ensures that a healthy population is available to accelerate the biodegradation process. A concentrated waste water sludge is used to inoculate which is representative for real life situations since in the US waste water sludge is often landfilled to keep the landfill biologically active and so stimulate landfill gas production.

Oxygen, originally present, is quickly consumed after which the biodegradation turns anaerobic. Through anaerobic biodegradation organic carbon is converted into methane (CH_4) and carbon dioxide (CO_2). This biogas production volume is measured through the observed increase in pressure. The methane content of the gas was also determined periodically (each time that gas was released) in order to calculate the overall methane generation.

Pressure build up in the test vessels was monitored using a manometer attached to the lid of the vessel. Each time gas was released (maximum capacity is 1 bar overpressure) a more accurate device was used to measure the pressure. Measurements are overpressure relative to ambient atmospheric pressure (so each

time atmospheric pressure was also measured). Multiplying the pressure in the vessel with the headspace volume results in the volume of gas produced. This volume is then recalculated to Standard conditions of Temperature and Pressure (STP) using the universal gas law (STP = 273.15 K and 1013 mbar).

3.2. Test 2 (HSAD test – high solids anaerobic digestion)

This test followed a modification of ISO 15985: "Plastics – Evaluation of the ultimate anaerobic biodegradability and disintegration under high solids anaerobic digestion conditions – Method by analysis of released biogas" and ASTM method D.5511-02: "Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic Digestion Conditions".

The standard test protocol is in the thermophilic regime (approx. 52 °C) and a test period of 15–30 days. In this procedure we tested at 35 °C for 170 days, to be more representative of landfill conditions (as opposed to the high solids anaerobic processes which operate at thermophilic conditions). As such, this is not an official test of accelerated landfill conditions, which is covered in test 1 (ALC), but a second version of an accelerated test to see if any anaerobic degradation could be observed.

During the anaerobic biodegradation of organic materials, a mixture of gases, principally methane and carbon dioxide, are the final decomposition products while some of the organic material will be assimilated for cell growth. The volume of the biogas produced is measured and the methane content determined each time gas is released. After correcting for the gas produced in the blank reference, the net volume of the biogas produced can be used to calculate the amount of CH_4 and CO_2 produced per unit weight of sample. If the carbon content of the sample is known the percentage of biodegradation can be calculated as the percentage of solid carbon of the sample which has been converted to gaseous, mineral C. The biogas composition can be used to calculate the total methane produced, and this can then also be compared to the theoretical methane potential as a second indicator of the extent of biodegradation as well as to estimate the ultimate methane production potential for use in landfill models.

A small amount of test compound is added to a larger amount of highly active inoculum that has been stabilised prior to the start of the digestion period. Optimal conditions with regard to pH, nutrients, buffering capacity, volatile fatty acids, etc. are provided and the mixture is left to ferment batch-wise.

3.3. Materials

3.3.1. Test and reference materials

The PLA test samples were provided by NatureWorks, and included two semicrystalline grades and one amorphous grade. All are commercial samples, and represent a large portion of the overall production (the semicrystalline grades in particular). Table 1 shows the properties of the PLA test samples. All tests were performed on pellets. The crystallinity of polylactides is strongly influenced by the optical composition of the lactide used to produce the polymer, and generally if the D-lactic acid content is less than about 6 wt% then the polymer can be considered as a semicrystalline grade for practical purposes. If the D-lactic acid content is >6 wt% then the material will, for most purposes, be amorphous. Over 95% of current production volume is for the semicrystalline grades, with only a speciality market for the amorphous grades.

The cellulose reference was native cellulose powder for thin layer chromatography (Avicel) (Merck Art. Nr. 2331 – Batch n° K37734831860). Oak leaves were used as a second reference, representing a real life reference with a "slow" degradation rate. Polyethylene was used as a negative control in the HSAD test.

Before starting the tests, all test and reference items were analyzed for total solids (TS), volatile or organic solids (VS), and carbon content. The total solids (TS) or dry matter was determined by drying the sample at 105 °C until a constant weight was reached, and is expressed as a percentage of the original weight (ISO 13040-1999). The volatile solids (VS) or organic matter is determined by the weight reduction after treating the dry matter for 4 h at 550 °C, and is expressed as the percentage of the total solids (TS), based on ISO 13039-2000. The results are summarized in Table 2. The percent carbon numbers agree well with the theoretical values of 50.0% for the PLA test samples and 44% for dry cellulose.

3.3.2. Test 1 – ALC-matrix and inoculum preparation

Each landfill test is started by adding waste and the inoculum sludge to a reactor.

The waste type chosen for this test was VFG (vegetable, fruit and garden) waste, which is the most biologically active component of typical municipal solid waste streams, and should therefore be expected to support a concentrated microbial consortium and help accelerate testing. The downside of using this type of waste is that it is very humid. Before using it in a landfill test it needs to be pre-composted and dried to reach the desired dry matter content.

VFG waste of 1 week old was used for the two most humid test series. It was dried overnight at 45 °C for the 65% moisture series and for two days at 45 °C for the 55% moisture series. It was not possible to dry this 1 week old waste sufficiently to achieve the 49% moisture matrix (without losing the biological activity), and so older VFG waste (4 weeks) was used for that test series, with three days of drying at 45 °C to achieve the desired moisture content.

The inoculum sludge used in the ALC test came from anaerobic sewage water treatment. The sludge was first dewatered by collecting the "solid" fraction retained on an 80 μm sieve, followed by one day of air drying at 45 °C, with a resulting dry solid content of 9.3 wt%.

3.3.3. Test 2 – HSAD-matrix and inoculum preparation

The inoculum for the HSAD test was taken from a lab digester fed with maize silage as its main substrate, though other substrates such as manures and sludges were regularly digested in this lab digester. This deviates from the ASTM standard, where inoculum from pre-treated MSW is used. Because mesophilic inoculum from pre-treated MSW was not available, the inoculum from maize silage was used. This inoculum was, however, a suitably rich source of microbes, as demonstrated by the cellulose reference (discussed later).

Table 1
Properties of the polylactide test samples.

PLA grade	Crystallinity [%][a]	Morphology	GPC M_w[b]	D-level [%]	RV[c]	T_m [°C]	T_g [°C]	Typical application	Market volume
2002D	35	Semicrystalline	208 K	4.25 ± 0.55	4.00 ± 0.10	145–160	55–60	Sheet thermoforming	High
4032D	50	Semicrystalline	190 K	1.4 ± 0.2	4.00 ± 0.10	155–170	55–62	High heat BIAX films	High
4060D	0	Amorphous	190 K	12 ± 1.0	3.50 ± 0.25	NA	55–60	Heat seal layer	Low

[a] Tests were performed on polymer pellets.
[b] GPC weight average molecular weight relative to polystyrene standards.
[c] Relative viscosity using Viscotek Viscometer.

Table 2
Overview of analyses on the test and reference items.

Test item	Total solids [%]	Volatile solids [% of TS]	Percent carbon [%]	Theoretical percent carbon [%]
Cellulose	100.0	100.0	41.7–43.1	44.4
Oak leaves	92.6	92.8	43.6–47.1	Unknown
4032D	99.8	100.0	52.5	50
4060D	99.9	100.0	50.5	50
2002D	99.9	100.0	52.0	50
Polyethylene	99.9	100.0	84.0	85.7

3.4. Equipment and test set-up

3.4.1. Test 1 – ALC

The analysis of the matrix, inoculum, and loadings are presented in Table 3. The cellulose reference was added at a level of 15 g for all test series, the polylactide samples were added at a level of 40 g for all test series (a high amount used to maximize ability to detect degradation), and the oak leaves were added at 15 g for the 66% and 55% humidity series and 6.8 g for the 49% humidity series (due to limited sample available). The reactors were well mixed, closed and put in an acclimatized room at 21 °C. The total test duration was 13 months (390 days), significantly longer than the ASTM standard of 180 days.

3.4.2. Test 2 – HSAD

A set of 14 equal reactors with a volume of 2 l each was used. Each reactor contained 1000 g of inoculum, with the same source of inoculum used in all tests. A sample of 15 g of the test materials or reference materials were added to each of the reactors, except for the oak leaves which were tested at 20 g (higher amount is used as lower gas production is expected). The incubation temperature was 35 °C and the test lasted 170 days in total. Gas measurement was done volumetrically for the first 15 days to handle the high biogas production rate (of cellulose) during the first few days of testing. Later, biogas production was measured by manometer, as with the lower biogas production rates, it was safe to store the biogas in pressure vessels.

The incubation temperature was chosen at 35 °C which is mesophilic and in an optimal temperature range for anaerobic digestion while still representative for ambient temperature and hence a landfill. A test duration of 170 days is extremely long, as the average test duration is 30 days for the HSAD test.

4. Results and discussion

4.1. ALC test – blank analysis

Fig. 1 presents the data for total biogas evolved during the course of the ALC testing for the blank controls (matrix + inoculum only). Each of the samples in Fig. 1 shows signs of a plateau. In addition, the results for the 4 week old VFG waste (performed at 49% moisture content) display a much lower ultimate level of gas production than the results for the 1 week old VFG waste (55 and 65% moisture contents). This is likely due to a reduced methane generation potential for the older, more pre-composted, less putrescible waste. Only one curve is shown for the 49% moisture content due to a leak in the second blank reactor.

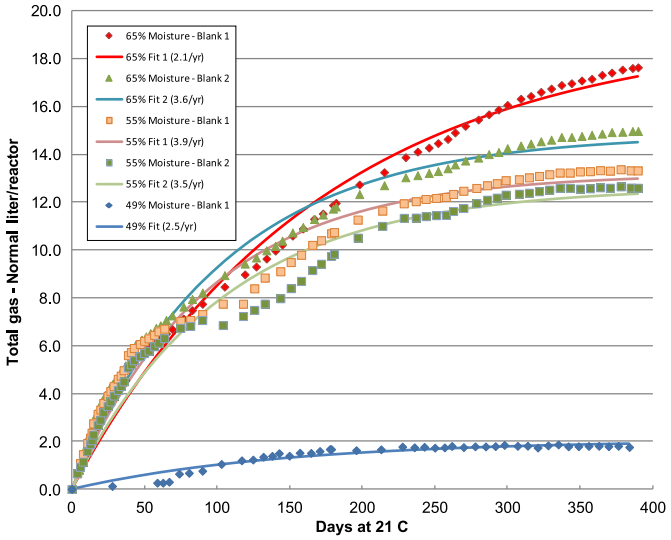


Fig. 1. Cumulative biogas evolution for blank references for ALC test, reference reactors at three humidities.

Fig. 1 also shows the model results obtained by using a non-linear least squares fit of a first order decay model to the experimental data. The best fit time constants were found to range from 2.1 yr^{-1} to 3.9 yr^{-1}, with a median of 3.5 yr^{-1} for the pre-composted matrix. This model form is the same as used in the standard US EPA models. In the terminology of De LA Cruz et al. [6] this rate constant is the laboratory scale rate constant. Recently, Levis and Barlaz [7] have used the ratio of laboratory scale rate constants to a reference material (MSW) and the estimated field decay rate of MSW to estimate a field rate constant for the component of interest. Analogously, the ratio of the laboratory scale rate constant to the field decay rate constant can be used to estimate the acceleration factor of the test.

For mixed MSW the rate constant for use in the standard US EPA model [28] ranges from 0.02 yr^{-1} (arid regions) to 0.057 yr^{-1} (wet regions), with a recommended default value of 0.04 yr^{-1}. Levis and Barlaz reported a lab scale rate constant of 10.5 yr^{-1} for their MSW, which would be an acceleration factor of 260 (10.5/0.04). To the extent that the pre-composted matrix in the present test is analogous to mixed MSW, the acceleration factor in this test is estimated to be 87-fold. The actual test time was 390 days (1.1 years), which combined with the acceleration factor gives an equivalent test period of 90 years.

Fig. 2 presents the instantaneous rate data calculated from the basic data. The instantaneous rate is the rate at a particular moment in time or in the case of Fig. 2, the particular biogas evolution rate per day. The instantaneous rates for all samples are seen to peak early in the test and decrease to nearly zero at the conclusion of the testing. The instantaneous rates drop by roughly an order of magnitude from the initial part of the test to the conclusion. These results for the blank controls shows that by the end of this extended test period the biodegradation process was essentially complete. The replicates for the 55% moisture series and for the 65% moisture series also show the inherent variability involved with these types of tests.

Table 3
Overview of matrix, inoculum, and loadings for ALC test.

Material	Total solids of the matrix [%]	Matrix charged [g]	Inoculum charged [g]	Calculated solid content [%]	Calculated moisture content [%]
Matrix for 65% moisture test	43.3	400	150	34.0	66.0
Matrix for 55% moisture test	60.8	325	150	44.5	55.5
Matrix for 49% moisture test	72.5	240	120	51.4	48.6
Inoculum	9.3				

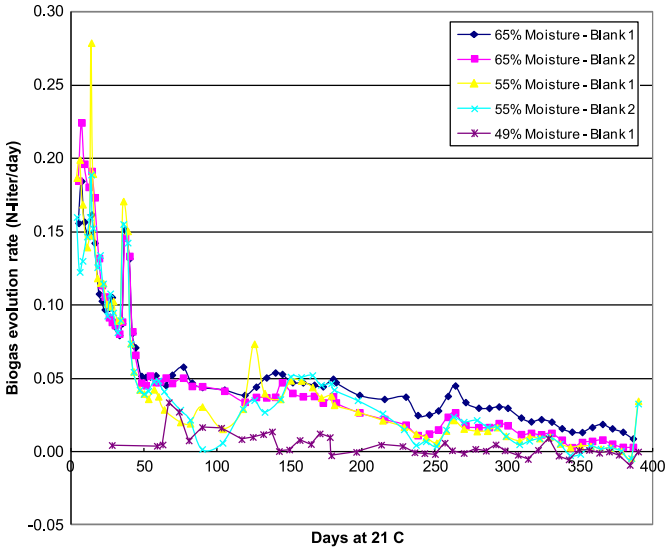


Fig. 2. Instantaneous rate of biogas evolution for ALC test, reference reactors at three humidities.

Fig. 3 shows the results of gas phase compositional analyses during the ALC test. A sample of gas was analyzed each time that gas was released from the fermentation vessel (gas was released to relieve prevent over-pressuring). The oxygen content was already less than 2% at 14 days for the 65% moisture test, and less than 2% at 27 days for the 55% and 49% tests. In all cases the concentration of methane increased steadily over the test, ending the tests at approximately 70 vol% methane for the final gas production. The gas volume and composition data were also used to calculate an integrated gas composition over the life of the test. The results are shown in Table 4, and averaged approximately 55 vol% methane for each of the tests. This is consistent with expectations for municipal solid waste, with an expected composition of 55 vol% methane and 45 vol% carbon dioxide [26].

The change in gas composition over time is consistent with a multistep process, wherein the first steps can involve acetogenesis forming simple acids and alcohols with some CO_2 release, and the subsequent steps involve methanogenesis with the production of methane [26,29]. The combined gas volume and composition data were used to calculate the methane production over time for each sample. The methane potential for these previously composted VFG wastes are less than those reported by Eleazer et al. [32] for fresh food and grass, and are more similar to the well decomposed refuse tested in that study. This seems reasonable, based on the 1 week pre-composting of the 65 and 55% moisture matrix and the 4 week pre-composting of the 49% moisture matrix.

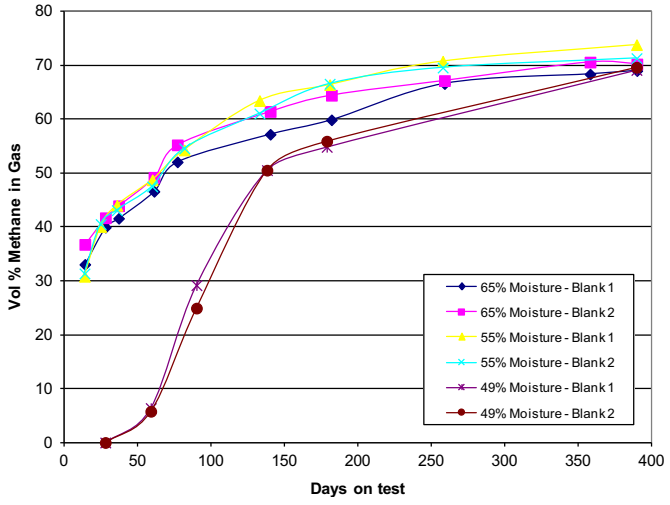


Fig. 3. Gas composition over time for ALC test, reference reactors at three humidity levels.

Table 4
Gas composition over time and integrated methane content for gas released from test vessels during ALC test.

Sample	Final methane vol%	Integrated methane vol %	Total gas volume (N-liter/ dry kg)	Methane production of matrix (N-liter/ dry kg)
65% moisture blank 1	69.0	55.0	101.8	56.0
65% moisture blank 2	70.2	55.0	86.4	47.5
55% moisture blank 1	73.8	54.9	65.2	35.8
55% moisture blank 2	71.3	54.9	61.7	33.9
49% moisture blank 1	69.1	53.8	9.7	5.2
49% moisture blank 2	69.6	NA (leak)	NA	NA

4.2. ALC test – reference material analysis

The test method calls for the addition of a reference material, in order to verify that everything is functioning as it should be and to verify the viability of the biology. To measure the gas evolution which can be attributed to the cellulose (or test sample) it is necessary to subtract the contribution of the matrix, as determined from the blank control. Recall that each vessel in a series contains the same amount of matrix and inoculum, and that the test sample or cellulose control is an added mass of material (15 g for the cellulose, 40 g for the test samples).

This test inherently measures only the gas which is evolved, and does not include any contribution due to biomass production (biomass yield). Thus, to the extent that some material is converted to biomass the reported biodegradation would be too low. This effect is not typically an issue in aerobic systems such as soil or composting, where the responsible bacteria can enter a state where the existing biomass is cannibalized. However, in anaerobic systems the biomass yield is estimated at 10–30% of the mass of the degraded material, as there is little or no cannibalism when food sources are limited. Anaerobic bacteria are more likely to go into a relative dormant stage while also there is no real fungal activity. To bracket the extent of biodegradation we have reported two scenarios, the first is as measured, and the second for a 25% assumed biomass yield.

Table 5 presents the data for the biogas evolution for the references and for the blanks. The net biogas production is calculated by subtracting the blank (which contains the same level of matrix and inoculum). It is then normalized to the dry weight sample basis. The percentage biodegradation is then calculated using the measured sample carbon content and total gas evolution measurements. From data presented in the table, the cellulose reference had an extent of biodegradation of 54% (74%) and 73% (100%) for the 49% moisture and 65% moisture series, respectively.

Table 5
Biodegradation and methane generation in positive control samples during ALC test.

Test item	Total biogas (N-liter/vessel)	Net biogas (N-liter/kg test item)	Biodegradation[a] (%)	Biodegradation[b] (%)	Methane generation (N-liter/dry kg cellulose)
Blank – 65%	16.3 ± 1.9	–	–	–	
Cellulose – 65%	25.1 ± 3.6	586.5	73.2	100.3	331
Blank – 55%	13 ± 0.5	–	–	–	
Cellulose – 55%	14.0[c]	66.3	8.3	11.3	37
Blank – 49%	1.7[c]	–	–	–	
Cellulose – 49%	7.9 ± 1.5	433.4	54.1	74.1	157

[a] Biodegradation calculated based on biogas production (carbon release).
[b] Biodegradation calculated based on biogas production but adjusted to allow 25% of the carbon to be used for bacterial growth.
[c] Only one replicate was used for the calculations as one reactor appeared to be leaking.

The 55% moisture series showed only 8%(11%) biodegradation based on total biogas production.

The gas volume, coupled with the gas composition analysis, also allows a direct measure of the methane production. Again, the methane generated in the blank control sample is subtracted to get the net methane generation due to the test sample, and adjusted to a dry solid basis.

The methane generation potential of pure cellulose ($C_6H_{10}O_5$) can be calculated to be 415 N-liter/dry kg [at 0 °C], based on the reaction below. The expected total methane content of the biogas produced form cellulose is thus 50%.

$$C_6H_{10}O_5 + H_2O \rightarrow 3\,CH_4 + 3\,CO_2$$

The methane generation during the 49% moisture series and the 65% moisture series were 157 and 331 N-liter/dry kg, respectively. The 55% moisture series yielded only 37 N-liter/dry kg. Note that methane production (and overall methane content of the biogas) is lower when the cellulose has not yet fully degraded (49% moisture and 55% moisture series). This is consistent with the multistep process of biodegradation: in the first phases (acidification) more CO_2 is produced, in the final phases more methane is produced (methanogenesis).

We conclude that for the tests at 49% and 65% moisture had satisfactory conversion of the cellulose, as determined both from total biogas production and from specific methane yield. The test at 55% showed much lower biodegradation for cellulose. Unfortunately, the second reference for that series was a failure, due to a gas leak. Poor biodegradation of the reference material means that it will not be possible to draw conclusions for the 55% moisture series with regard to a lack of degradation, however, the test data were still analyzed to determine if any of the test samples showed a positive degradation [in which case the failure of the reference material would be less relevant]. The success of the 65% moisture control, which used the same inoculum and nearly the same matrix as the 55% series, and the overall comparable biodegradation of the blank matrix for the 55 and 65% series, suggests that the problem was with the particular cellulose reference, rather than a systemic problem with the equipment or materials. One possibility is that the relatively young matrix used in the 55% and 65% series was prone to acidification, and that the addition of the cellulose test sample, combined with relatively low moisture in the 55% series, resulted in severe acidification and inhibition (which is confirmed by the low methane content of the biogas). We note, however, that the blank matrix still produced methane at a rate near to that of the 65% series, demonstrating that the matrix alone was not inhibited. It is also of interest that the 49% moisture series, where the base matrix was already relatively degraded and therefore less putrescible and producing little methane (Table 4) still was able to successfully degrade the cellulose control.

4.3. ALC test – statistical analysis of test samples

A means comparison was performed, using Dunnett's method with a control group (the blank), in order to determine which, if any, of the test samples were statistically different from the control group. Fig. 4 presents the data from this analysis, performed at a 90% significance level. Groups which are statistically different than the control are marked in the data table with a positive difference relative to the least significance difference. They are also identified in the figure with a gray circle. The samples labelled in

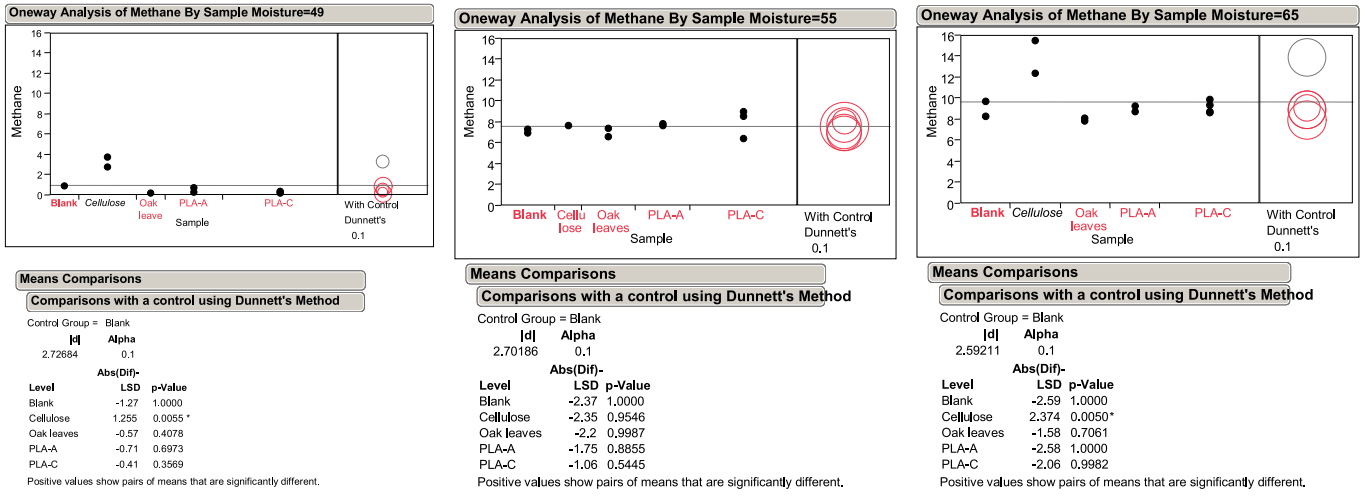


Fig. 4. Dunnett's means comparison for all samples against blank control. ALC test.

red (in web version) did not generate methane to an extent which was significantly different than the control.

It can been seen from the analysis that for the 65% moisture series the only statistically significant difference from the control is for the cellulose, which is different at a 99% confidence level. The polylactides and the oak leaves are not statistically different than the blank. For the 49% moisture series the same result holds, again with the cellulose showing a difference which is significant with greater than a 99% confidence level, and none of the other test materials showing a difference which is statistically different than the blank. For the 55% moisture series neither the cellulose nor any of the test items were significantly different from the blank.

Fig. 5 presents the data for overall gas generation for the 65% humidity series, net of the blanks, converted to an extent of biodegradation based on sample size and carbon content. It can be seen that in this year long ALC test the amorphous and semi-crystalline PLA samples have generated no significant gas volume.

It can also been seen in Fig. 5 that the oak leaves generated an apparent "negative biodegradation". It is important to remember that the test method uses the difference between the blank reactors and the reactors with the same charge of inoculum but with the addition of the test material. In this case, then, a small amount of inhibitory effect of the test material slowing down the biodegradation of the large background reference will lead to an apparent "negative biodegradation". The negative biodegradation should be interpreted as zero biodegradation.

4.4. HSAD test analysis

The methodology used in Section 4.1 was also used to fit the gas generation of the blank reference samples used in this test. Fig. 6 shows the experimentally measured values and the best non-linear least squares fit of the model. The model provides an adequate fit to the data. The best fit rate constants for the two blank references were 10.9 yr^{-1} and 11.3 yr^{-1}, with an average of 11.1 yr^{-1}. Again, compared to the standard rate constant found for landfills, 0.04 yr^{-1}, this indicates a test acceleration factor of 280-fold. The calendar time of this test was 170 days (0.47 year), which with the acceleration factor gives an equivalent test time of 130 years.

Table 6 shows the gas production results for the blank and for the cellulose reference during the 35 C HSAD test. The cellulose reference, was biodegraded to 74% conversion within 6 days, and

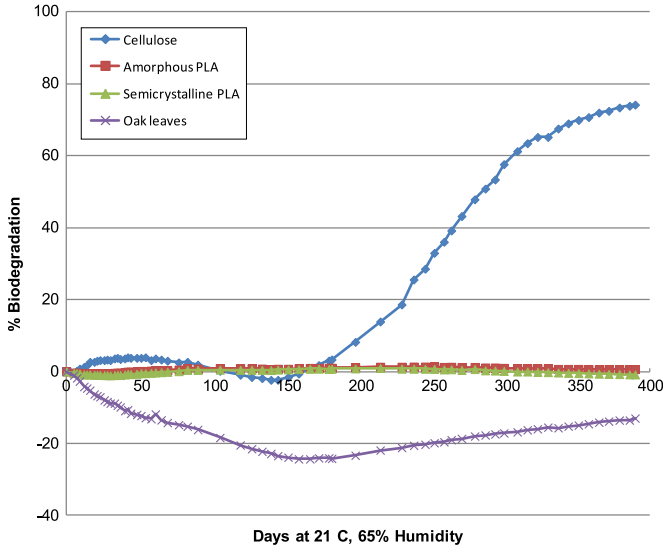


Fig. 5. Calculated biodegradation for ALC test at 65% humidity.

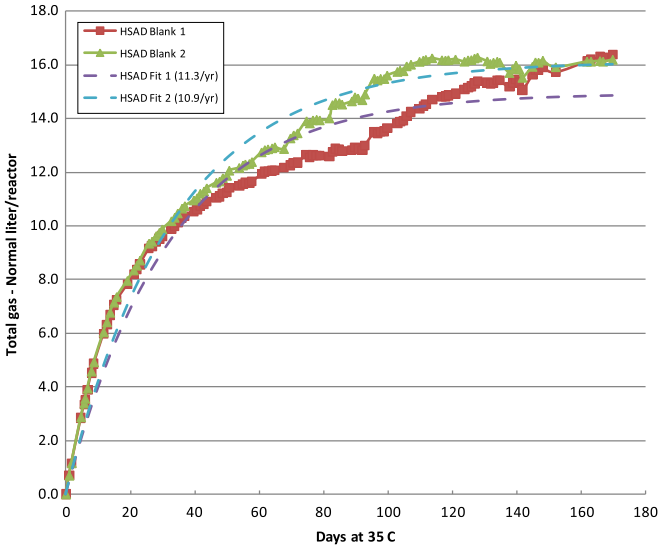


Fig. 6. Overall gas production of blank reactors, HSAD test.

was 94% biodegraded at 15 days. The final extent of biodegradation was 95%, based on total biogas released. The test was continued for a total of 170 days, or more than 40 times the half life of the cellulose control. The methane generation potential of the cellulose in this test was 460 N-liter/dry kg, which is somewhat higher than the theoretical potential for cellulose.

The remaining test samples were analyzed in a manner similar to that described previously, using Dunnett's Method for comparison of multiple means. Fig. 7 shows the results of the means comparison for methane generation. In addition to the cellulose, the oak leaves and the amorphous PLA showed statistically significant degradation, relative to the blank. The test was conducted at a significance level of 90%. The polyethylene and the semi-crystalline PLA did not show statistically significant methane generation in this test.

Oak leaves were included in the test as a "real life" reference of something which is slow to degrade in an anaerobic environment. The total methane generation potential for the oak leaves, based on the total methane produced during this test, was 129 N-liter/dry kg. This is a relatively high value for leaves compared to the values reported by Eleazer [31]. In that study, leaves were found to yield 30.6 N-liter/dry kg after 135 days at approximately 40 °C. The total biogas generation for leaves in our study was found to be 230 N-liter/kg, which translates to 25% biodegradation based on the measured carbon content. This corresponds to essentially complete degradation of the cellulose and hemicellulose content, which was measured as 26% combined in the Eleazer study. This high level of degradation for a recalcitrant material such as oak leaves provides additional support that the test reported here was an aggressive and accelerated test.

The total methane generation potential of the amorphous PLA sample was determined to be 189 N-liter/dry kg. The theoretical methane generation potential for PLA, based on the stoichiometric reaction:

$$C_6H_8O_4 + 2\,H_2O \rightarrow 3\,CO_2 + 3\,CH_4$$

is 467 N-liter/dry kg for 100% anaerobic biodegradation. The measured result, based on methane generation, is then equivalent to 40% biodegradation. This is in good agreement with the estimate of 36% obtained by total biogas production and the carbon content

Table 6
Biodegradation and methane generation in positive control samples during HSAD test.

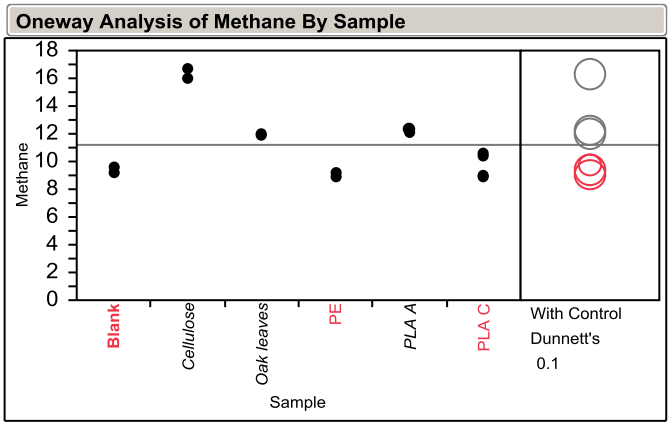
Test item	Total biogas (N-liter/vessel)	Net biogas (N-liter/kg test item)	Average methane content vol %	Biodegradation (%)	Methane generation	
					N-liter/dry kg inoculum	(N-liter/dry kg cellulose)
Blank	16.3 ± 0.1	–	58.2	–	88.4[a]	
Cellulose	27.4 ± 0.6	740	59.8	95%		460

[a] Based on a dry solids level of 10.73%.

for the amorphous PLA. There was no statistically significant methane generation for the semicrystalline PLA samples.

Fig. 8 shows the cumulative biogas production of the averaged test samples, net of the averaged blank controls, and the non-linear least square model fit to the first order decay model. The parameters of the model fit are included in Table 7. The model fitting allows what should be an improved estimate of the ultimate methane potential (L_0), especially for slowly degrading materials. For the amorphous PLA we derived the ultimate biogas potential to be 444 N-liter/kg (48% ultimate biodegradation), which with a methane content of 58.3% yields $L_0 = 260$ N-liter/kg and a field decay rate of 0.011 yr^{-1}. These parameters suggest that an amorphous PLA would yield approximately 174 N-liter/kg (37% of the 467 N-liter/kg theoretical potential) over a 100 year period, very similar to the 189 N-liter/kg determined in the current test. Again, for emphasis, the semicrystalline samples did not generate a statistically significant volume of methane during this test.

It can also be seen in Fig. 8 that the difference between the two blank samples "Blanks – delta control", ranged from 0 to 2 N-liter of gas. The semicrystalline PLA samples averaged less than 1 N-liter of gas, and based on testing of the means, this was not statistically significant.



Means Comparisons

Comparisons with a control using Dunnett's Method

Control Group =Blank

|d|	Alpha
2.63306	0.1

Level	Abs(Dif)-LSD	p-Value
Blank	-1.53	1.0000
Cellulose	5.376	<.0001*
Oak leaves	1.031	0.0085*
PE	-1.16	0.9396
PLA A	1.301	0.0047*
PLA C	-1.01	0.9427

Fig. 7. Dunnett's means comparison for HSAD test.

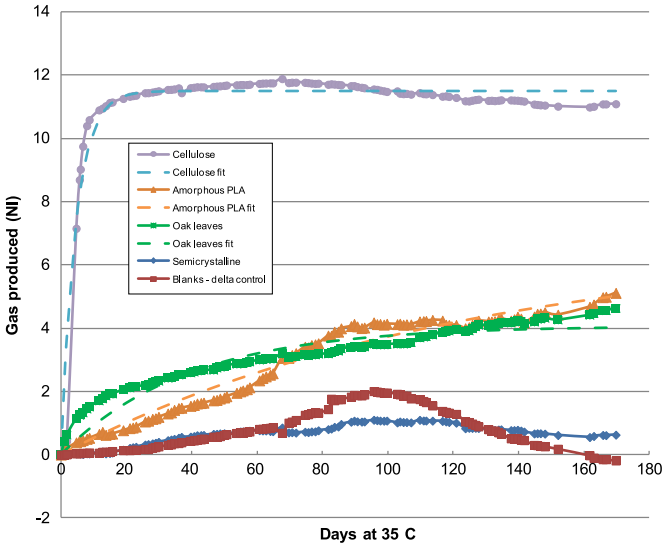


Fig. 8. Cumulative gas production by sample type, HSAD test.

For additional reference, Fig. 9 shows the data from Fig. 8, but adjusted based on sample size and sample carbon content to calculate overall biodegradation of the sample.

The LCA practitioner can best use these results in the context of a broader-based simulation, such as provided by Levis and Barlaz [7]. These simulations take into account the distribution of landfill types and conditions to estimate the net global warming potential (GWP). The data in their Fig. 3 show that either a "recalcitrant biogenic material", which has 0% biodegradation, or biogenic materials which degrade at sufficiently slow rates for a given biodegradation can have a GWP of less than zero, effectively acting as a carbon sink even when disposed of in landfills. Semicrystalline PLA would appear to fit in this category, based on the data of this study. Amorphous PLA, which represents a very small market segment, degraded measurably but slowly with the model results suggesting 37% biodegradation in a 100 year time frame. These results can now be used to simulate in a broader scenario the role of compostable and biogenic polymers as an enabling technology for diversion of food waste from landfills, with the attendant (transitional) disposal of some fraction of the material into landfill, in an attempt to determine the overall balance of the GWP.

Table 7
Model fitting parameters for HSAD test for sample with statistically significant mineralization.

	Ultimate N-liter gas	L_0 (N-liter/kg)	k_{lab} (yr^{-1})	Est. k_{field} (yr^{-1})
Blank	15.5	9.1	11.1	0.04
Cellulose	11.5	450	80.2	0.29
Oak leaves	4.07	119	9.4	0.034
Amorphous PLA	6.69	260	3.0	0.011

L_0 from fit of volumetric gas data, using dry sample weight and 58.7% methane content (average of all samples). This is the methane generation potential.

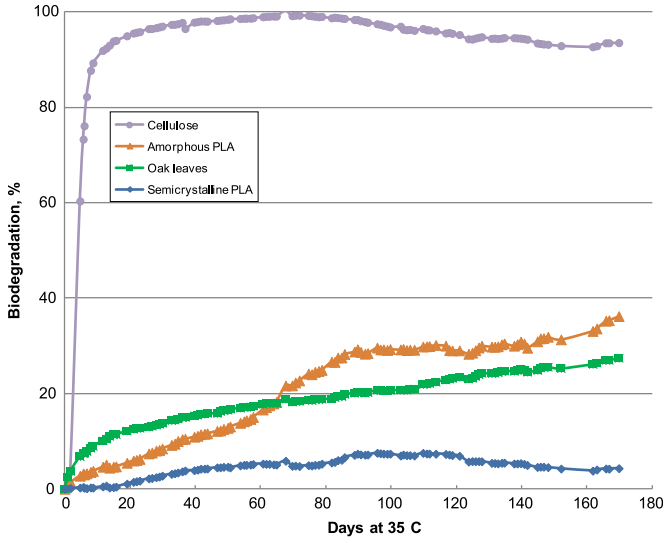


Fig. 9. Calculated biodegradation based on gas evolution, HSAD test.

5. Conclusions

Two methods have been used for the evaluation of the methane generation potential of polylactide polymer under accelerated landfill conditions. In the first, the Accelerated Landfill Condition test, three different humidity levels were examined at ambient conditions, measuring the total biogas evolution and methane composition over a period of 390 days. The reference material, cellulose, was found to degrade at both 49 and 65% humidity under these test conditions. The test at 55% humidity was inconclusive, due to failure of the reference material (one leaked, the other did not degrade to a significantly measureable extent). The stabilized matrix produced on the order of 30–50 N-liter/dry kg (at 55% and 65% humidity) over the course of test, and the instantaneous gas production rate dropped from a value of 0.2 N-liter/day in week 1 to a value of less than 0.02 N-liter/day at the end of the 390 day test. The biomass generation of the matrix is consistent with the stabilized seed (matrix) value reported by Eleazer. The matrix in the 49% humidity test was older and less active, generating only 5 N-liter/dry kg over the entire 1 year + test period. The cellulose was extensively degraded, nevertheless. The biogas composition at all three humidity levels evolved from CO_2 rich at the beginning of the test period to CH_4 rich by the end, resulting in an overall volumetric average of 55 vol% methane, consistent with expectations for this feedstock. None of the polylactide samples exhibited a statistically significant generation of biogas.

The second test, a High Solids Anaerobic Digestion test carried out for 170 days at 35 °C, resulted in a complete degradation of the cellulose control, which was at 94% degraded by day 15. The oak leaves were also essentially fully degraded (for the cellulose and hemicellulose components) as determined by the methane generation. These indicators suggest that this was a very aggressively accelerated test. The amorphous PLA sample also degraded, with a biogas contribution suggesting approximately 36% degradation. The total methane generation during this test for this amorphous sample was 189 N-liter/dry kg. Neither the negative control (polyethylene) nor the semicrystalline polylactide produced a statistically significant volume of biogas during this 170 day accelerated test.

These two tests each had accelerated the biological degradation sufficiently that they were in some sense equivalent to approximately a century of a “typical” landfill. The semicrystalline polylactide samples did not produce a statistically significant quantity of biogas during either test. The amorphous PLA did generate a small amount of methane in the test at 35 °C, but none in the test at ambient temperature. Here it should be noted again that the tests were conducted under accelerated, optimal landfill conditions, the biodegradation was observed in a 100 year timeframe and the market volume of amorphous PLA is low. We conclude that semicrystalline PLA (typical of >96 wt% of resin used to manufacture products), under anaerobic biological conditions typical of a landfill at moderate temperatures (where PLA hydrolysis is slow) will not lead to significant generation of methane, and that no significant population of organisms is available under anaerobic conditions to directly degrade high molecular weight PLA.

Because there was no direct biological degradation of PLA under the anaerobic conditions, it is likely that any degradation of PLA in a landfill would require a chemical hydrolysis step prior to any biodegradation, which is analogous to the situation in aerobic composting. Semicrystalline PLA samples at low temperatures, say 20 °C, require many decades to hydrolyze to the point where microbes begin to consume the oligomers, and under those conditions the generation of methane from PLA would be extremely low. Landfills have extremely variable conditions depending on geography, type of waste, age of waste, management style, and many other factors and so additional data on the time/temperature history experienced in landfills will be needed to understand the net effect on GWP potential for disposal of PLA globally.

Nomenclature

ALC	Accelerated landfill conditions
GHG	Greenhouse gas
HSAD	High solid anaerobic digestion
N-liter	Normal liter: volume normalized to standard conditions for pressure (1013 mbar) and temperature (0 °C–273,15 K)
PLA	polylactide, poly(lactic acid)
TS	Total solids
VFG	Vegetables, Fruit, Garden
VS	Volatile solids
PHB	poly 3-hydroxybutyrate
PHBV	polyhydroxybutyrate-valerate

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