

Test Method

Biodegradability of polylactide bottles in real
and simulated composting conditionsGaurav Kale^a, Rafael Auras^{a,*}, Sher Paul Singh^a, Ramani Narayan^b^a*School of Packaging, Michigan State University, 140, Packaging Building, East Lansing, MI 48824-1223, USA*^b*Chemical Engineering and Material Science, Michigan State University, East Lansing, MI 48824-1223, USA*

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Abstract

As new biodegradable polymers and their packaging applications are emerging, there is a need to address their environmental performance. In particular, there is a need to understand the time required for their complete disintegration, before these materials are deployed in commercial composting processes. Standards developed by ASTM and ISO evaluate the biodegradation of biodegradable plastic materials in simulated controlled composting conditions. However, a more detailed understanding of the biodegradation of complete packages is needed in order to have a successful composting operation. This paper investigates the biodegradation performance of polylactide (PLA) bottles under simulated composting conditions according to ASTM and ISO standards, and these results are compared with a novel method of evaluating package biodegradation in real composting conditions. Two simulated composting methods were used in this study to assess biodegradability of PLA bottles: (a) a cumulative measurement respirometric (CMR) system and (b) a gravimetric measurement respirometric (GMR) system. Both CMR and GMR systems showed similar trends of biodegradation for PLA bottles and at the end of the 58th day the mineralization was $84.2 \pm 0.9\%$ and $77.8 \pm 10.4\%$, respectively. PLA bottle biodegradation in real composting conditions was correlated to their breakdown and variation in molecular weight. Molecular weight of 4100 Da was obtained for PLA bottles in real composting conditions on the 30th day. The biodegradation observed for PLA bottles in both conditions explored in this study matches well with theoretical degradation and biodegradation mechanisms; however, biodegradation variability exists in both conditions and is discussed in this paper.

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1. Introduction

According to ASTM, a biodegradable plastic is “a plastic that degrades because of the action of naturally occurring microorganisms such as bacteria,

fungi, and algae,” and a compostable plastic is “a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues [1].” Standards developed by ASTM and ISO are used to assess the biodegradability of biodegradable plastics in different environments such as

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composting (ASTM D5338 and ISO 14885-1), anaerobic digestion (ASTM D5511 and D5526 and ISO 15985), and wastewater treatment (ASTM D5210 and D5271 and ISO 14853) [2]. In order to fulfill a cradle-to-cradle approach, one of the most attractive alternatives besides reusing and recycling would be to have biodegradable plastics composted at the end of their useful life and later used in sustainable agricultural practices. For this scenario, addressing the efficiency of the plastic's biodegradability process becomes essential [2,3].

ASTM D6400 [1] addresses the compostability of plastic materials, and standard specifications and terminologies for biodegradable plastics as well as guidelines using test method ASTM D5338 [4]. ASTM D5338 is a method used to assess biodegradability of biodegradable plastics under simulated or controlled composting conditions which correlates biodegradability to the total mineralization of organic carbon (CO_2 evolved) in the polymer. A 60% or higher mineralization value for a material containing a single polymer (homopolymer and random copolymer) certifies that the material is biodegradable and further ecotoxicity tests are carried out in accordance with ASTM D6400 to certify that it is compostable. ISO 14855-1 [5] gives similar guidelines to that of ASTM D5338 except that the mineralization of an unknown biodegradable material should be 90% of the value obtained for a reference material to prove its biodegradability. In both methods, the amount of CO_2 evolved due to biodegradation can be measured using acid–base titration, or by using a direct measurement such as infrared or gas chromatography, as suggested in the Refs. [1,5].

ASTM and ISO standard guidelines are limited to the biodegradability evaluation (biodegradation, disintegration, compost quality) of plastic material or a plastic material from a package; however, the European Committee for Standardization (CEN) has developed a standard EN 13432 [6], which provides detailed guidelines for evaluation of biodegradability and compostability of packaging and packaging components based on their characterization, biodegradability, disintegration, and compost quality/ecotoxicity.

ISO has a standard under development, ISO 14855-2, which measures mineralization of a polymer by a gravimetric method. ISO 14855-2 [7] is similar to 14855-1 except for the method of CO_2 measurement and the amount of compost and sample used. In addition, inert materials such as

sea sand or vermiculite can be used with the compost for providing better aeration and retention of moisture content. The mixture of compost and sea sand or vermiculite is periodically taken out from the closed system to turn or agitate to prevent channeling of air in the biodegradation vessel.

Biodegradation of biodegradable packages in real composting conditions has been reported and correlated to visual changes and variation in physical properties of the materials [8,9]. Real composting studies give clear representation of the biodegradability nature of the whole package configuration and the time required for the disintegration in different compost recipes and composting processes. This information can further provide a basis for deciding on compostable packaging materials and the planning of composting processes. Real composting conditions are governed by the outer atmosphere, the type of compost, and the compost parameters such as temperature, moisture, and pH. Hence, they may differ from the controlled composting conditions as proposed by ASTM and ISO standards for materials and whole packages.

As new standards for assessment of biodegradability of materials are becoming available and usage of biodegradable plastic packages increases, there is a need to find a reliable method which would give a clear understanding of the biodegradability of a package with respect to the time required for disintegration and the efficiency of disposal to justify its compostability. To the best of the authors' knowledge, there has not been any study done which compares biodegradability in real and simulated conditions. This paper investigates and compares the biodegradability of polylactide (PLA) bottles under different testing methods of existing standards, standards under development, and a novel method of evaluating biodegradability of biodegradable materials under real composting conditions.

2. Materials and methods

2.1. Samples

PLA bottles (500 mL) used for packaging of spring water, commercialized by Biota brands of America (Telluride, CO), were obtained from NatureWorksTM PLA (Blair, NE). The PLA bottles were composed of 96% L-lactide with bluetone additive and had dimensions of 0.2 m height and 0.065 m in base diameter. The organic carbon



Fig. 1. PLA bottle.

content of the PLA bottle was 49.5%, which was determined by elemental analysis (Organic Elemental Analysis, Perkin-Elmer, Shelton, CT). A picture of the PLA bottle is shown in Fig. 1.

2.2. Real composting conditions

A compost pile made of cow manure, wood shavings, and waste feed (i.e., the feed that the cows left) was prepared at Michigan State University composting facility (East Lansing, MI) and used for assessing the biodegradability of the PLA bottles. The biodegradation study was carried out for 30 days. The dimension of the pile was 6 m in width, 24 m long, and 3 m in height, and it was built on an asphalt pad. The initial temperature, relative humidity, and pH of pile were $65 \pm 5^\circ\text{C}$, $63 \pm 5\%$, and 8.5 ± 0.5 , respectively, and temperature was monitored throughout the duration of the biodegradation study with a thermocouple type J attached to a datalogger from Onset Computer Corporation (Bourne, MA). External atmosphere parameters such as temperature, relative humidity, and solar radiation which may affect the performance of the composting process were recorded

through the Michigan Automated Weather Network (East Lansing, MI) for the entire period of the study [8,9]. A novel method was developed to track and trace the PLA bottles in the compost pile. A wooden box of dimensions $0.6\text{ m} \times 0.3\text{ m} \times 0.1\text{ m}$ was built with a mesh bottom to retain and easily identify the samples and the surrounding compost for further analysis. Initially, compost was added on the bottom mesh, and later the PLA bottle was placed on it and completely covered with compost. The box was placed approximately 1.2 m above the ground and 1 m inside the compost pile where a uniform composting temperature of 65°C was obtained. For a detail description of the system, the readers can refer to Refs. [8,9]. Fig. 2 shows how the packages were located in the compost pile. After the packages were covered with compost, the pile was closed and the temperature of the pile reached normal composting temperature.

The PLA bottles were taken out periodically from the compost pile for analysis of variation in its molecular weight. In addition, the bottles were visually inspected, and pictures were taken for visual evaluation of its biodegradation trend.

2.3. Molecular weight analysis

Molecular weight analysis was conducted using a standard gel permeation chromatography (GPC) technique. A Waters 600 multisolvent delivery system with a Waters 717 autosampler and Waters 2410 refractive index detector was used; all manufactured by Waters Corporation (Milford, MA). Inhibitor free tetrahydrofuran (THF) obtained from Sigma-Aldrich (Milwaukee, WI) was used as a solvent for diluting and preparing the PLA bottle samples [8,9].

2.4. Cumulative measurement respirometric (CMR) system

A CMR system based on ASTM D5338 [4] and ISO 14855-1 [5] was built. This system was designed to yield the percentage of carbon dioxide from the organic carbon content of the sample. Three-month-old mature compost obtained from MSU composting facility was used for biodegradation purpose. The compost was sieved through a 5 mm sieve and inert materials such as glass, stones, and metal were removed. Vermiculite grade number 4 soil conditioner manufactured by Therm-O-Rock (New Eagle, PA) was used for mixing with compost



Fig. 2. Placement of packages in the compost pile.

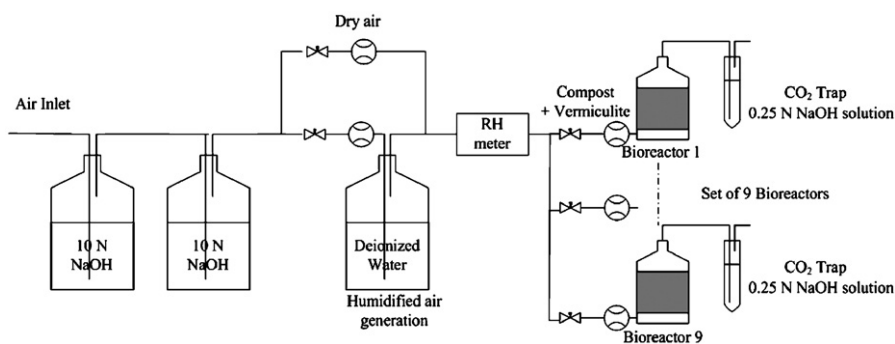


Fig. 3. Schematic of CMR system.

to provide better aeration and to retain moisture, as also demonstrated by Ref. [10]. Dry compost (400 g) was mixed with 100 g of dry weight vermiculite, and the moisture level was adjusted so that the mixture retains 90% of its water holding capacity [11]. PLA bottles were cut into 0.01 m × 0.01 m pieces (excluding part of the neck and cap threads) to be used as samples for biodegradability evaluation. Cellulose powder obtained from Sigma-Aldrich (Milwaukee, WI) was used as the known reference material (i.e., positive control). The organic carbon content of the cellulose was 42.5% determined by elemental analysis. Currently, ASTM D5338 recommends using a negative control, such as polyethylene, in the same form as of the same material. This is planned to be removed in the new version of D5338

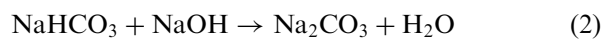
and, since ISO 14855-1 does not recommend using a negative control for this experiment, a negative control was neglected in this study. The current system is comprised of nine bioreactors; three blanks, three positive controls (cellulose), and three samples (PLA bottles) placed in a temperature-controlled system—an environmentally controlled room manufactured by Lab-Line Instruments Inc. (Melrose Park, IL). A schematic of CMR system is shown in Fig. 3.

Initially, pressurized air of 2 psi was passed through 10N sodium hydroxide (NaOH) solution to remove the CO₂ present in the air. Later, the air was passed through deionized water to humidify and maintain uniform moisture level during the experiment of between 50% and 60%. The moisture

was controlled by mixture of dry and humidified air and was monitored by an RH meter produced by HygroDynamics (Jessup, MD). The air was divided and passed through flowmeters for each bioreactor at a flow rate of 60 mL/min. Two 2 mm screens mounted at the bottom of the bioreactor and above the air inlet were introduced to equally distribute the air in the compost and avoid channeling [12]. A solution with 200 mL 0.25N NaOH was used for trapping the CO₂ from the bioreactors, and the amount of CO₂ content in solution was calculated through acid–base titration. NaOH solution was changed every time that CO₂ was calculated. Ten milliliter aliquots were removed from the 200 mL trapping NaOH solution and titrated with 0.186N hydrochloric acid (HCl) solution to obtain the value of CO₂ in solution. The CO₂ content in the 10 mL solution was correlated to the 200 mL solution and actual CO₂ amount was determined. The CO₂ trapping reaction was done in a two step reaction as described in ASTM D5338 and mentioned below:



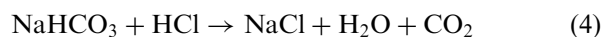
then



Similarly, during titration CO₂ is removed through the following reactions:



then



Initially, a few drops of phenolphthalein indicator were added to the 10 mL NaOH aliquot and further titrated until it turned from pink to colorless. At this point, the Na₂CO₃ is converted into NaHCO₃ and NaCl. Further, few drops of methyl orange indicator were added and titrated till the solution turned from orange to red. The NaHCO₃ reacted with HCl to form NaCl, H₂O, and CO₂. Hence, the amount of HCl consumed in the second reaction could be used to find CO₂ concentration in solution according to the following formula:

$$g\text{CO}_2 = \frac{V \times C \times 44}{1000} \quad (5)$$

where $g\text{CO}_2$ is the amount of evolved carbon dioxide in grams; V is the volume of HCl consumed in the second reaction (4); C is the concentration of HCl solution. The percentage mineralization was further calculated by comparing the amount of

carbon dioxide in the positive control and the sample with the blank by the following equation:

$$\% \text{ Mineralization} = \frac{g\text{CO}_2 - g\text{CO}_2b}{g_{\text{material}} (\% C_{\text{material}}/100) (44/12)} \times 100, \quad (6)$$

where $g\text{CO}_2$ is the amount of evolved carbon dioxide in grams in the sample and the positive control; $g\text{CO}_2b$ is the amount of evolved carbon dioxide in grams in blank; g_{material} is the mass of the bottle or sample; $\% C_{\text{material}}$ is the percentage organic carbon content of the bottle/sample.

2.5. Gravimetric measurement respirometric (GMR) system

The GMR system construction is based on draft ISO 14855-2 [7] which differs from ISO 14855-1 and ASTM D5338 in respect of: (a) the amount of compost/vermiculite mixture and sample used; (b) the number of blanks; (c) the positive control; (d) the sample bioreactors; and (e) the method of CO₂ measurement. ISO 14855-2 recommends using two blanks, two positive reference materials, and two samples to be analyzed for the biodegradation measurement. ASTM D5338 and ISO 14855-1 recommend using compost and sample in a ratio of 6:1 and the commonly used quantity is 600 g of compost to 100 g of sample, whereas in ISO 14855-2 a 1:10 ratio of compost/sample is used. A GMR system according to some of these specifications has been built by Hissan Trading Co. Ltd. (Tokyo, Japan), and is commercialized under the name of microbial oxidative degradation analyzer (MODA). A MODA system was provided by Saida UMS Inc. (Tokyo, Japan) for part of the test presented in this work. The MODA system consists of four bioreactors, one for blank, one for positive control (cellulose), and two for samples. Similar to the CMR, in the MODA system pressurized air is passed through a column containing soda lime from Fluka (Steinheim, Germany) with CO₂ absorption indicator from Sigma-Aldrich to make it CO₂ free. Later, the air is bubbled through a flask containing deionized water to maintain the humidity in the compost mixture and in the reaction column constant. The reaction column consists of a column covered with a heating jacket and a thermosensor to maintain the temperature at 58 °C. Air is passed through each bioreactor and later through an ammonia eliminator, moisture remover, and finally to a CO₂ trap column. A schematic representation

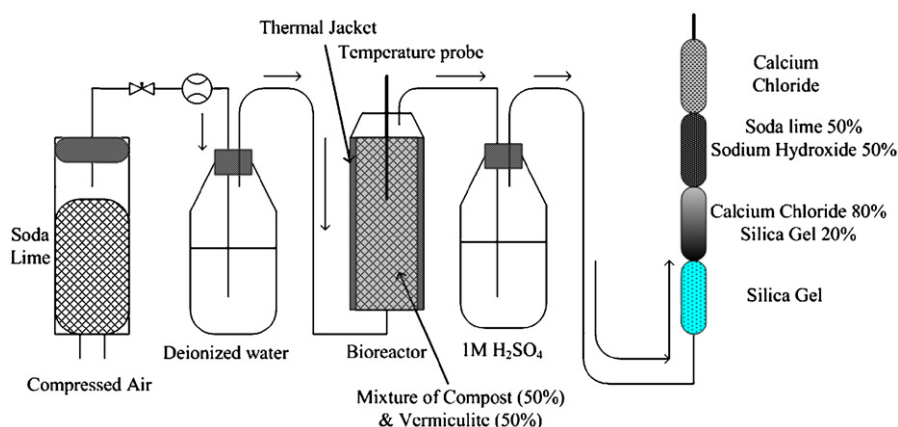


Fig. 4. Schematic of MODA system.

of the MODA system with a single bioreactor and column connections is shown in Fig. 4.

The standard test soil for the MODA system was a mixture of mature compost as previously described for the CMR system (60 g dry weight) and vermiculite (60 g dry weight). Initially the moisture was adjusted up to 90% of its water holding capacity. Vermiculite (18 g dry weight) was also added at the bottom of the reaction column to absorb the water drips from the compost and also provide equal aeration to the compost mixture. The vermiculite and compost mixture were separated by sponge disks and stainless disk net as shown in Fig. 5.

Initially, a sponge disk was placed at the bottom of the reaction column followed by wet vermiculite and again a sponge disk on top of it. A 1 mm ring was introduced above the sponge disk to provide spacing between it and the stainless steel disk (with 1 mm holes) as shown in Fig. 5. The compost mixture was added on top of the stainless steel disk and, finally, the reaction column was closed with a lid having an attached thermosensor which stayed in contact with the compost mixture. The reaction column was covered with a thermal jacket at a temperature of 58 °C, which was continuously controlling the compost mixture. In addition to the carbon dioxide, ammonia and water were also generated from the reaction column which was eliminated by passing the output of the reactors through 2N sulfuric acid (H₂SO₄) in the ammonia absorption flask, and the neutralization of ammonia by H₂SO₄ was monitored by methyl red. Later, the air was passed through moisture removal columns 1 and 2 as shown in Fig. 4. Silica gel (type 3) obtained from Sigma-Aldrich (St. Louis, MO) was used for

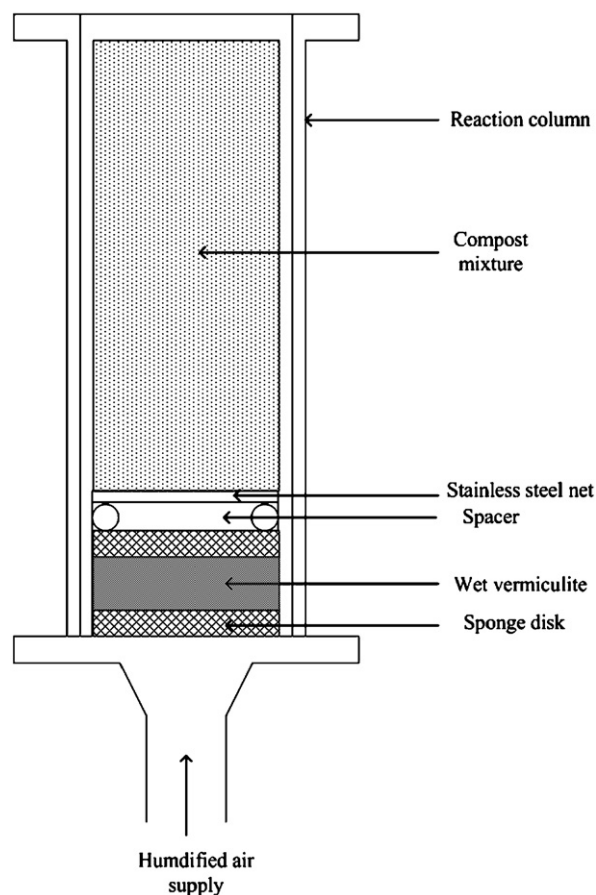


Fig. 5. Schematic of the reaction column for MODA system.

moisture removal (column 1); when the silica gel was saturated due to moisture it changed color from dark blue to colorless. Moisture removal column 2 consisted of 20% silica gel and 80% of calcium chloride (93% granular, anhydrous) obtained from

Sigma-Aldrich (St. Louis, MO) which completely removes moisture from the air. Column 3 was a carbon dioxide absorption column and contains a mixture of soda lime (cica reagent) obtained from Kanto Chemical Co. (Chuo-Ku, Tokyo) and sodium hydroxide (1.6–3 mm pellets) obtained from Merck KGaA (Darmstadt, Germany) at 1:1 ratio. This chemical reaction generated water; hence, column 4 containing calcium chloride collected the remaining water from the reaction. The CO₂ generated by biodegradation in the reaction column was measured by the weight gain seen in columns 3 and 4. The MODA system is a closed system; however, the compost mixture was taken out twice a week for manual turning to ensure proper mixing of compost and sample, and also to improve aeration and maintain accurate moisture in the mixture.

3. Results and discussion

3.1. Real composting conditions

PLA bottles were visually inspected, and right from the first day changes in color and shape were observed. The biodegradation trend is shown in Fig. 6.

The shape changes on the first day could be attributed to distortion due to higher temperatures ($65 \pm 5^\circ\text{C}$) in the compost pile relative to the glass transition temperature (T_g) of PLA ($60.6 \pm 0.3^\circ\text{C}$) [8,9]. On the fourth day, the bottles seemed tough as compared to their original condition. On the sixth and ninth days, a powdery texture was observed on the bottle surface and also the top part of bottle became brittle and started breaking apart. On the 15th day, the bottle was already in pieces and mostly consisted of parts from cap threads, neck, and bottle (bottle parts having higher thickness). On the 13th day, only a few pieces of bottle were observed and the majority were from cap threads. After that, no bottle residuals could be located through visual inspection. The variation in the molecular weight of the PLA bottles was analyzed and it is shown in Fig. 7.

A small increase in molecular weight (+11,400 Da) was observed on the first day which can be attributed to cross-linking or recombination reactions. Major fragmentation, which produces decomposition of the polymer chain into shorter oligomer chains and monomers, was observed from the fourth day onwards. PLA degradation starts by a hydrolysis reaction which follows a first order

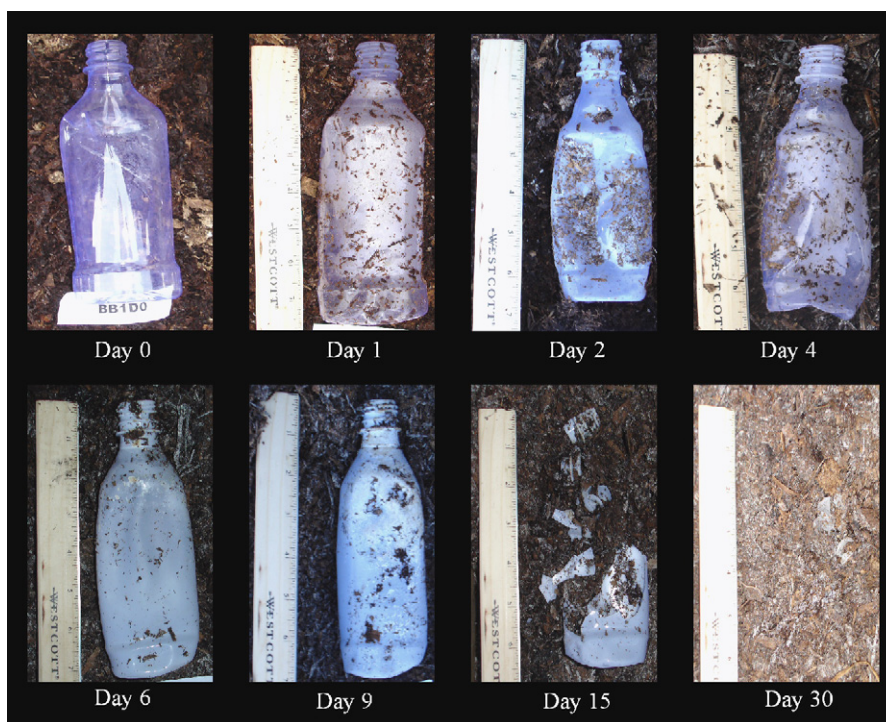


Fig. 6. Biodegradation of PLA bottles in real composting conditions. [Reprinted from G. Kale et al., Compostability of bioplastic packaging materials: an overview. *Macromol. Biosci.* 7(3) (2007) 255–277. Copyright 2007, with permission from Wiley].

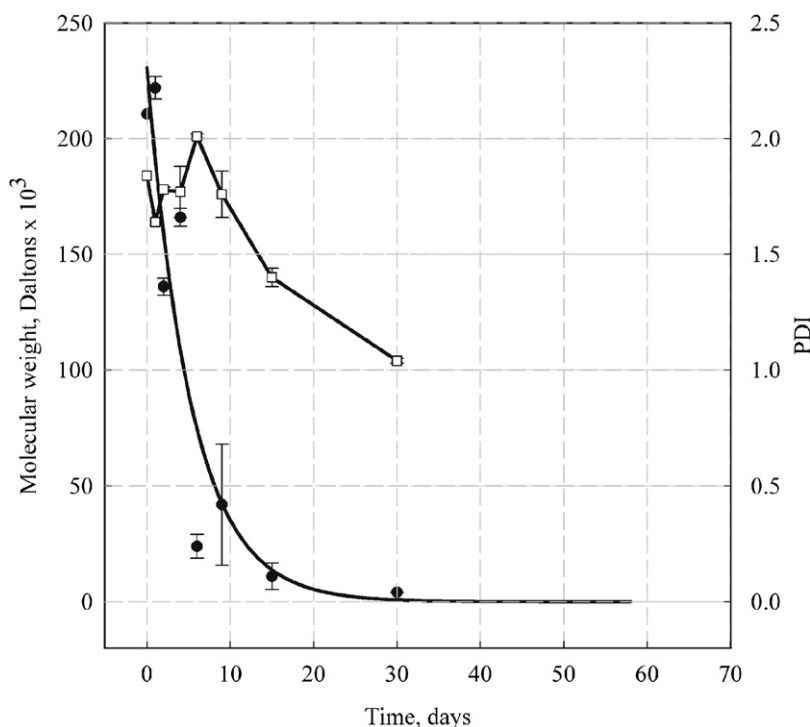


Fig. 7. Variation in molecular weight (●) and PDI (□) for PLA bottles in real composting conditions.

kinetics as previously demonstrated and fitted to Eq. (7) [8,9]:

$$M_w = a \exp^{-b \times t} \quad (7)$$

where a and b are constants and equal to $a = 229.7 \pm 28.4$ kDa, and $b = 0.1865 \pm 0.0533$ s⁻¹; t is the time in days. According to this equation, molecular weight values below 5 Da could be obtained after 57 days. Fig. 7 shows the variation in PDI on the right axis; PDI was reduced from 1.84 to 1.04, mainly because of narrowing of the molecular weight distribution due to polymer fragmentation. Initial rise in PDI could be attributed to the increase in the fragmentation process [8,9].

3.2. Cumulative measurement respirometric system

Fig. 8 shows the biodegradation of cellulose powder and PLA bottles in the CMR system at controlled temperature conditions of 58 °C. Mineralization value of 60% (requirement of ASTM D5338) was obtained on the 30th day for cellulose and on the 39th day for PLA bottle. At the end of the 58th day, cellulose reached 86% mineralization and PLA bottle was 84%. Initial slower

mineralization action in PLA is due to the fact that it first undergoes hydrolysis, which is a non-enzymatic reaction decreasing the molecular weight (as shown in Fig. 7), and later low molecular weight oligomers are consumed by microorganisms to evolve carbon dioxide.

3.3. Gravimetric measurement respirometric (GMR) system

Fig. 9 shows the biodegradation results of cellulose and PLA bottles in the GMR system. In this case, cellulose reached 70% biodegradation value on the 55th day. ISO 14855-2 recommends that this test is valid only if cellulose or positive reference control reaches 70% mineralization value before 45 days. However, ISO 14855-2 also recommends using two positive controls in the test, and it is only valid if the difference between two positive controls mineralization value is less than 20%. In our case, the system only had one positive control due to limitation of the commercial equipment.

One of the PLA bottles showed negative biodegradation in the beginning which could be due to few reasons: (a) as discussed in case of CMR system,

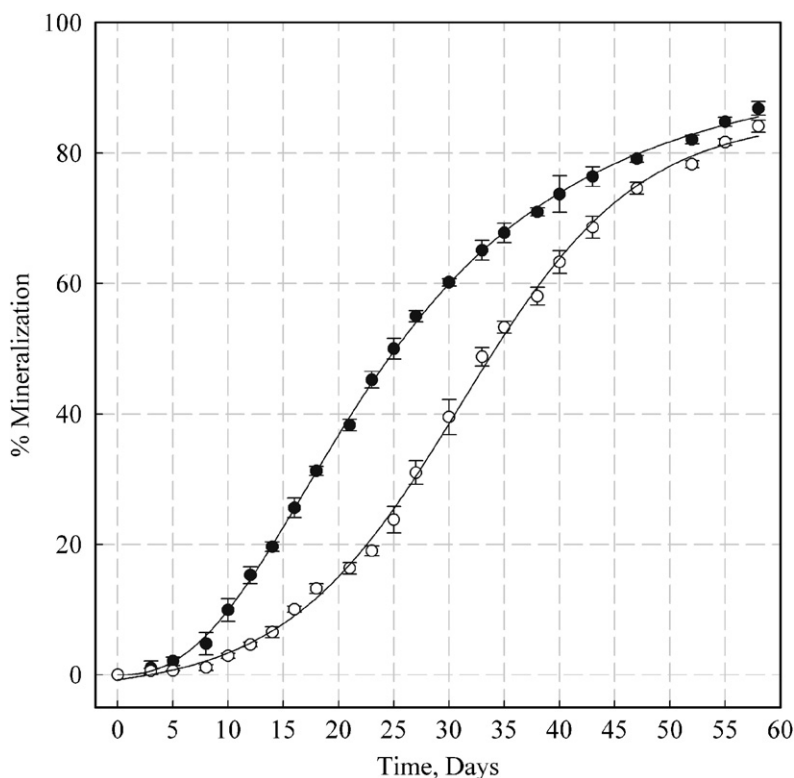


Fig. 8. Percentage mineralization as a function of time for cellulose (●) and PLA bottles (□) in CMR system.

PLA bottles first undergo hydrolysis which is non-enzymatic reaction; (b) PLA bottles consisted of a bluetone additive and also a label adhesive which may have affected the microbial activity; and (c) the homogeneity of the compost, which makes the compost generate different background of CO_2 . However, after 12 days, the lag phase for the PLA bottle was over and the average mineralization for two PLA bottle samples was 0.33% (23% in case of cellulose). On the 52nd day, one of the PLA bottles reached more than 70% of the average mineralization value so we can conclude that PLA bottles are biodegradable according to the ISO 14855-2, but only if all the ISO 14855-2 conditions of number of samples and validity criteria are met (which is not true in this case with the MODA system). At the end of the 58th day, the average mineralization of both PLA bottles was 80.9% with a variation of $\pm 10.3\%$; which is very large as compared to the CMR data. The turning activity is also shown in Fig. 9. On the 25th day, 15 g (dry weight) fresh compost was added to all reaction columns to improve the microbial activity, and an increase in mineralization value can be observed in the graph.

3.4. Comparison of all three methods

PLA bottles were tested for biodegradability in real and simulated composting conditions as previously described. The biodegradation trends for both conditions are shown in Fig. 10. The left y-axis measures the percentage mineralization for the CMR and the GMR systems, and the right y-axis measures the variation in molecular weight in real conditions.

On the 15th day, the M_w of the samples exposed under real composting conditions was reduced to 15,000 Da. If we compare this with the samples tested under laboratory simulated conditions, we can observe a very slow percentage of mineralization increase during this period. After that, when the M_w of the samples is reduced enough to allow the microorganisms to use them as carbon source, a sudden increase in the evolution of CO_2 takes place. This correlates well with the non-enzymatic hydrolysis and enzymatic reactions in the case of PLA as mentioned in previous research [8,9,13,14] and described by Eq. (7).

For both simulated conditions, CMR and GMR, the percentage mineralization value did not reach

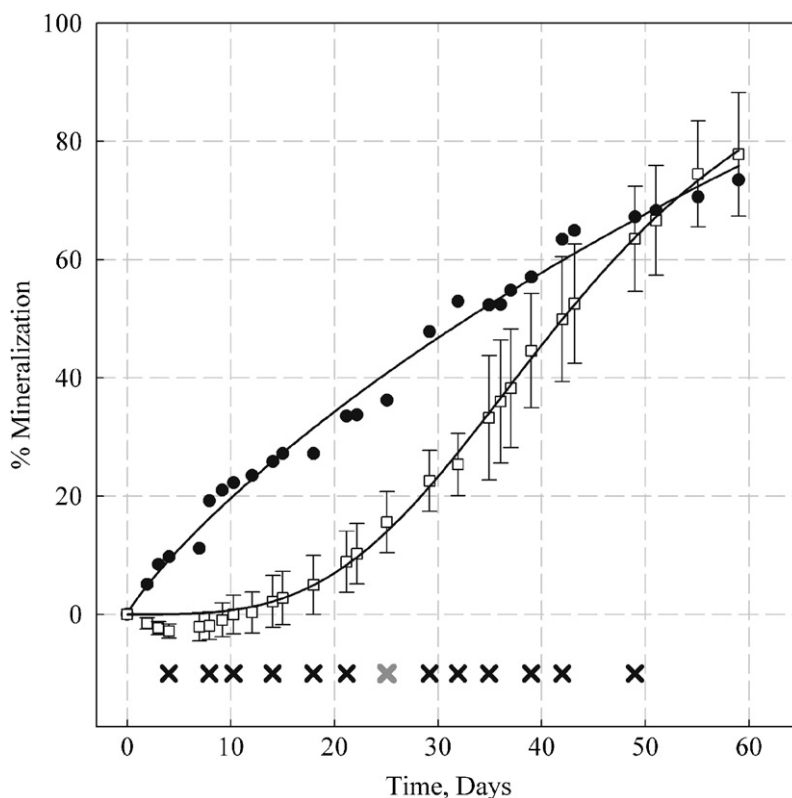


Fig. 9. Percentage mineralization as a function of time for cellulose (●) and average of PLA bottles (□) in MODA. Turning days are represented by (×).

100% at the 58th day when the test was stopped. However, the M_w of the samples in the compost pile, extrapolated according to Eq. (7), indicates that the samples would have reached 0 Da at the 58th day. Variation in the degradation time frame between the simulated and real composting conditions can be attributed to many factors, such as size of the polymer sample, sample/compost ratio, and the nature of the compost material.

In real composting conditions, the entire bottle as shown in Fig. 1 was tested, whereas in the CMR system the whole bottle (25 g) was tested but cut into $0.01\text{ m} \times 0.01\text{ m}$ pieces. Therefore, the higher surface area of the samples introduced in the CMR system should reduce the overall degradation period; however, since the ratio compost/sample was larger in the real composting conditions, a faster degradation process of the bottles was observed. In the case of the MODA system where these two factors (i.e., sample size and compost/sample ratio) were lower than the real composting conditions, an even slower degradation process was observed. Kunioka et al. conducted a biodegradation test on PLA powders in

a GMR system and also found that the size of PLA powder particles affected the biodegradation rate (i.e., smaller size samples will degrade faster due to higher surface area exposure to microorganisms attack) [15]. Hence, if a whole bottle, rather than its small pieces, is introduced in the simulated conditions, we should expect longer times to breakdown. On the other hand, it is a common practice in industrial compost facilities to shred the materials before introducing them to the mixture so that an even shorter degradation time should be expected for the bottle pieces in real conditions.

As mentioned above, the compost to PLA bottle ratio was different in both real and simulated conditions. In the case of real composting conditions, the compost/sample ratio could be considered as infinity to 1; in the case of the CMR system, it was 16:1; and in the MODA system it was 6:1. The number of microorganisms in a well-managed compost is proportional to the amount of compost and, hence, will affect the biodegradation rate [2]. For example, a large windrow compost pile would have more microbial reproduction as compared to

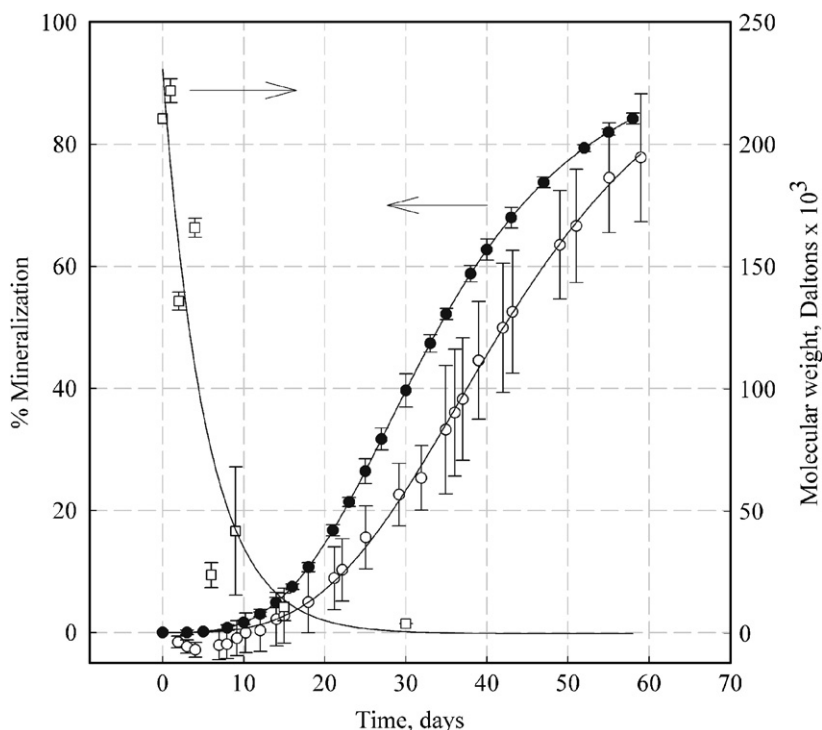


Fig. 10. Comparison of variation in molecular weight (\square) due to biodegradation and percentage mineralization values for PLA bottles in CMR (\bullet) and MODA (\circ) systems.

an in-vessel composting system, which tends to be small. Therefore, biodegradability results under simulated conditions could also be deceiving with regards to the time-frame for biodegradability if the biodegradable packages are to be disposed in compost piles or in in-vessel composting systems. Moreover, in the case of biodegradable materials whose byproducts can modify the compost environment and the microbial population, the total amount of sample which is introduced to the compost pile should be considered. In the case of PLA it was demonstrated that no more than 10% (w/w) of sample should be introduced to the compost environment to avoid acidification due to the lactic acid formation during the hydrolysis process [13].

Since composting is an aerobic process, turning of the compost mixture is essential to provide better aeration and speed up the composting process. Hence, turning is frequently done in commercial composting facilities. The frequency of turning is based on the need of aeration in the compost pile and the way of forming the compost pile (such as windrow composting, turned windrow, static windrow or in-vessel) [2]. In the current real conditions

study, the compost pile was not turned to better locate the samples. This could result in a slight reduction of the oxygen availability in the compost pile during the 30-day period so that a slower rate of degradation was achieved, even though the bottles degraded faster than in simulated conditions. To avoid channeling and to control aeration in the compost mixture in the case of the CMR system, the bioreactors were manually shaken every week. In the case of the MODA system, the compost mixture was taken out of the bioreactors twice a week and mixed to provide better aeration to the whole cross section.

The nature of the compost's raw materials plays an important role in polymers' degradation since different compost systems (i.e., manure, yard, and food waste) will produce different microbiological activity. In this study, manure waste was utilized for the real and simulated conditions. A similar study done on the same PLA bottles in a direct measurement respirometric (DMR) system using yard waste compost obtained 60% mineralization on the 53rd day, while in this study in the CMR system 60% mineralization was obtained on the 39th day [12]. Addition of vermiculite to compost in our study

might have also contributed to faster biodegradation. Therefore, the constituents of the compost should be assessed and taken into consideration.

Real composting conditions provided a good representation of the time required for the degradation of the PLA bottles, and in general this test would be helpful for commercial composting facilities to get insight of their biodegradation process. However, biodegradation in real conditions is also dependent on the compost raw materials, ambient conditions, compost mixture turning, and volume of the compost pile and compost parameters. Also as mentioned above, the size of the test samples and the compost sample ratio will impact the time-frame of biodegradation. In the case of both simulated conditions, there is a gap in the mineralization values obtained by the two techniques which again shows that it would be deceiving to derive biodegradability time-frames from these techniques.

Standards such as ASTM D5338 and ISO 14855-1 & 2 provide a traditional way of testing plastics in respirometric systems such as DMR, CMR, and GMR, but they are limited to the plastic material and not to the whole package. However, they do recommend considering the part of higher thickness from the package and evaluate its biodegradability, which can then be used to conclude if a package is biodegradable or not. There is a standard specifically developed for packaging by the European Committee for Standardization EN 13432 [6], which states that each component used in packaging should be separately tested for biodegradability for the complete package to be certified as biodegradable/compostable. These tests would give an understanding of the biodegradability of each component; however, they would not provide the time required for biodegradation of a complete package such as a PLA bottle.

4. Conclusions

PLA biodegradation tests were carried out in real composting and simulated composting conditions. Real conditions, which are governed by factors such as temperature, pH, and relative humidity of the compost pile, showed degradation of the PLA bottles and variation in their molecular weight as a result of hydrolysis plus biodegradation. The variation in molecular weight was also seen to be affected by the composting process/operation and other parameters. When shredded packages are used in real composting conditions, as used in the

CMR or the GMR systems, a faster degradation time could be expected. However, an overall conclusion cannot be exclusively derived based on the sample size, and all the variables in real composting, such as compost raw materials, enzymes, ambient atmosphere, etc. and their interaction with the biodegradable packages, should be explored for better understanding and insight of the biodegradation process. Current standard methodologies ASTM D5338 and ISO 14855-1 provide a traditional way of testing plastics in respirometric systems, but they are limited to the plastic material and not to the whole package. The new GMR system similarly has limitations of using a small quantity of compost which might extend the period of biodegradation. In short, current standards mainly answer the question: is a plastic or package biodegradable? But they do not address the final question: will the package successfully biodegrade in a commercial compost facility? Therefore, it is important to test the biodegradation of the complete package under real composting conditions for its efficient deployment in the existing composting processes as demonstrated in this work.

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