Evaluation of Compostability of Commercially Available Biodegradable Packages in Real Composting Conditions

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Abstract:

The adoption of biodegradable packaging materials is increasing in food and consumer good packaging applications. Currently, poly(lactide) (PLA) polymers are the biggest commercially available bio-based packaging material. Life cycle analyses show that the production of PLA polymers consumes around two times less energy than conventionally petroleum based polymers. Therefore, the first issue that needs to be addressed is its environmental impact. The disposal of such biodegradable polymeric packaging residues in composting facilities can be an important method of reducing the amount of packaging materials that are disposed as municipal solid waste. To the best of our knowledge, there has been no study done evaluating the compostability of a complete biodegradable package in real-time composting conditions. The real composting conditions differ from the simulated ones due to several factors such as weather, microbial growth and pH; and therefore the compostability of biodegradable packages is affected. This study addresses the compostability of two commercially available PLA packages, a bottle and a tray, in real composting conditions. The degradation of a PLA bottle composed of 96% L-lactide and 4% D-lactide with bluetone additive and a tray composed of 94% L-lactide and 6% D-lactide were evaluated in a composting pile having temperatures around 65ºC ± 5ºC (150°F ± 10°F), a relative humidity of 65% ± 5% wet weight moisture content and a pH of 8.5 ± 0.5. The packages were placed in compost in duplicate sets and were taken out on 1, 2, 4, 6, 9, 15, and 30 days. The molecular weight (M_W) and the glass transition (T_g), melting (T_m) and decomposition (T_D) temperatures were monitored to assess the changes in the packages' physical properties. The MW was assessed by gel permeation chromatography (GPC), the T_g and T_m by differential scanning calorimetry (DSC), and the T_D by thermogravimetric analysis (TGA). In addition, the packages were visually inspected for color, texture, shape and thickness changes and pictures were taken as the package configurations evolved. After 4 days of being in the compost pile, initial fragmentation of the packages were observed. At 15 days, the trays started to become a part of the compost whereas the bottles showed slower degradation and started breaking apart. After 4 days for the trays and at 6 days for the bottles, a molecular weight reduction of 77% and 85% were observed, respectively. The molecular weight of the bottles and the trays were reduced from 209,324 Daltons to 10,686 Daltons and from 176,315 to 4,708 after 15 days of being in the compost pile, respectively. At 30 days, the bottles showed a molecular weight of 4,000 Daltons, and the trays were completely degraded. Similarly the decline in T_g at 15 days for both bottles and trays were 30% and 18%, and the T_m were 2.4% and 3.9%, respectively. The initial degradation temperatures of the bottles and the trays were 396.1°C and 396.8°C, respectively; whereas after 15 days in the compost they were reduced to 358.1°C and 326.2°C. The difference between the degradation time between the PLA bottles and trays can be attributed to their initial difference in crystallinity. PLA bottles and trays degrade under real-time composting conditions much faster than in previous studies reporting simulated composting conditions.

Keywords: *poly(lactide); biopolymers; GPC; packaging; compostability*

INTRODUCTION

It is increasingly being realized that the use of long-lasting polymers as packaging materials for short lived applications is not entirely justified. Plastics packaging materials are often soiled due to foodstuff and other biological substance contents, making physical recycling of these materials impractical and normally unwanted. Hence, there is an increasing demand for biodegradable packaging materials which could be easily renewable. To date, production of packaging plastics to a large extent is based on non-renewable packaging materials. Use of biopolymer based packaging materials allows consideration of eliminating issues such as landfilling, sorting and reprocessing through availing their unique functionality, that is compostability. Composting allows disposal of biodegradable packages and is not as energy intensive compared to sorting and reprocessing for recycling, although it requires more energy than landfilling. For instance, in countries like the USA where landfilling is predominant, composting is more expensive [1].

Composting is a natural process by which organic material is decomposed into humus, a soil like substance. Decomposition is principally done by microorganisms, but also earthworms, small insects, and other soil inhabiting organisms play an important role in composting at lower temperatures. The major groups of mesophilic and thermophilic microorganisms involved in composting are bacteria, fungi, and actinomycetes. These organisms decompose the organic matter as their food source. The process requires carbon, nitrogen, water, oxygen, and heat. Organisms that decompose organic matter use carbon as a source of energy and nitrogen for building cell structures. A 30:1 carbon to nitrogen ratio is ideal for reproduction of thermophilic microorganisms [2]. Normally, a compost pile goes through two stages: an active composting stage and a curing period stage. In the first stage, the temperature raises as long as oxygen is available producing a strong microbial activity. During this stage, the temperature can rise well above 60ºC (140ºF) when many microorganisms begin to die or become dormant, and after that the temperature starts to stabilize or may even fall. In the curing stage, the materials continue to compost but at a much slower rate. The rate of oxygen consumption decreases, and the compost can be piled without turning or forced aeration. The composting process continues until the last remaining nutrients are consumed by the remaining microorganisms and until almost all the carbon is converted to carbon dioxide.

Compostability of *compostable plastic* (i.e., “a plastic that undergoes degradation by biological processes during composting to yield CO_2, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue” [6]) are commonly evaluated in simulated compost conditions and by assessing the final quality of the compost. Degradation of polymers in a compost environment occurs mainly through mechanical, thermal, and chemical degradation. Photodegradation is only present on the surface of the compost pile where the material is exposed to ultraviolet (UV) and gamma radiation. Of all the degradation mechanisms, chemical degradation is the most important for biodegradable polymers. Since biodegradable polymers have hydrolysable functional groups in the polymer backbone, the polymer chains first become susceptible to water attack and chemical degradation initiates polymer erosion (i.e., the reduction of mass of the polymer matrix due to the loss of monomers and oligomers or non-degraded polymer pieces). Standards for compostability have been developed by the American Society for Testing and Materials (ASTM), the International Standards Organization (ISO) and the European Committee for Standardization for evaluation of the compostability of biobased polymeric materials. ASTM standards (i.e., ASTM D5338-98 [3], D6003-96 [4], D6954-04 [5], D6400-99^{e1} [6], & D 6002-96 (Reapproved 2002)[1] [7]) developed by subcommittee 20.96 for assessing compostability are laboratory scale and limited to evaluation of plastic materials. [4-7] Similarly ISO standards ISO 14851 [8], ISO 14852 [9], and ISO 14855 [10] allow evaluation of materials under laboratory conditions and are based on measuring the carbon dioxide evolution and oxygen demand during degradation. The EN 13432:2000 [11] standard developed by European Committee for Standardization addresses compostability referring to ISO standards and evaluates the compost quality and toxicity. As such and until now, no standard or study has focused on the compostability of complete packages under real conditions. Degradation time of an entire package as encountered in the case of full-scale facilities that do not grind feedstock may be much longer than when the polymer pieces are grinded, representing a worst case scenario for compostability. Moreover, poor representation of actual composting conditions is a major negative aspect since mistaken conclusions could easily be drawn as biodegradation mechanisms vary among substrates.

The applications of biopolymers are growing in areas of food and consumer goods packaging and hence the first concern that needs to be addressed is environmental. Commercially available biopolymers that are biodegradable (i.e., polymers that are engineered to completely biodegrade in a microbial environment) include Natureworks^{TM} PLA developed by Cargill Dow LLC (Blair, NB). Natureworks^{TM} is producing three million pounds of PLA annually for a variety of packaging and fiber applications. Proctor and Gamble Co. (P&G) (Cincinnati, OH) have produced an aliphatic copolyester (Nodax) line of polymers that are biodegradable in aerobic and anaerobic conditions. The Nodax polymers are produced by microorganisms through a fermentation process, and the plastics are extracted from the biomass. Similar to Nodax, Eastman Chemical Company (Hartlepool, England), has developed Eastar Bio aliphatic copolyester, which is being used in lawn and garden bags, food packaging and horticultural applications worldwide. DuPont has a 200 million lb/year production facility in Tennessee for its Biomax polyethylene terephthalate copolymer hydro/biodegradable polyester, which is available both overseas and in the United States [12].

Poly (lactide) polymer (PLA) derived from starch is the main biopolymer which is commercialized as a biodegradable packaging material. PLA is fabricated by polymerizing lactic acid (LA) monomer, which is mostly produced by carbohydrate fermentation of corn dextrose. The fermentation of dextrose produces two optically active enantiomers, namely D (-) and L (+) lactic acids. Three methods are adopted to produce high molecular mass PLA of about 100,000 Daltons: a) direct condensation – polymerization, b) azeotropic dehydrative condensation currently used by Mitsui Toatsu [13], and c) polymerization through lactide formation, which was developed by Cargill Inc. in 1992 [13]. The properties of PLA such as melting point, mechanical strength and crystallinity are determined by the polymer architecture (determined by different proportions of L, D or meso-lactide) and molecular mass. The glass transition temperature (T_g) ranges from 50ºC to 80ºC while the melting temperature (T_m) ranges from 130ºC to 180ºC. PLA can be processed by injection molding, sheet extrusion, blow molding, thermoforming, and film forming. PLA is approved by the Food and Drug Administration for its intended use in fabricating articles in contact with food[13]. Currently, PLA is being commercialized and being used as a food packaging polymer for short shelf life products with common applications such as containers, drinking cups, sundae and salad cups, overwrap and lamination films, and blister packages. As PLA is a growing alternative as a green food packaging material, new applications have been claimed in the arena of fresh products, where thermoformed PLA containers are used in retail markets for fruit and vegetables. In the coming years, PLA production and package consumption are expected to increase. Therefore, there is a need to address the compostability of these packages under real composting conditions. In 2003 in the USA [1], 15 full-scale solid waste composting facilities (i.e., "one that includes the residential waste stream that arrives at the plant as mixed waste or source separated fractions [1]") were in operation. Therefore, for biodegradable polymers to be an attractive alternative, a wide range of composting facilities need to be created, or PLA will need to be composted with general yard waste.

As mentioned before, the standards mainly focus on providing information about compostability of biodegradable polymeric materials in simulated composting conditions. Simulated and real composting conditions vary due to several factors such as temperature and relative humidity, and in general simulated conditions only poorly represent real composting conditions [14-16]. Also while most of the commercialized biopolymer materials meet the standards of being biodegradable, these standards do not address compostability of a complete package in real composting conditions, which may take longer than a simple piece of polymer (i.e., worst case scenario for degradation) [14, 15]. Therefore, the aim of this paper is to provide information about compostability of commercially available biodegradable packages in real composting conditions, and to correlate the degradation process with their physical properties' breakdown. In addition, we also seek to introduce a method to assess compostability of packages in real composting conditions. Two poly(LD-lactide) packages were exposed to compost conditions and their properties' breakdown were monitored by visual inspection, gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA).

MATERIALS AND METHODS

Packages

Five hundred milliliter poly (lactide) spring water bottles commercialized by Biota brands of America (Telluride, CO) were obtained from NatureWorks™ PLA (Blair, NE). The bottles were made of 96% L-lactide and 4% D-lactide with bluetone additive and dimensions of height = 0.2 m and base diameter = 0.065 m. Poly (lactide) trays (diameter = 0.24 m, height= 0.046 m) were obtained from Wilkinson Manufacturing Company (Fort Calhoun, NE). The trays were made of 94% L-lactide and 6% D-lactide. Figure 1 (a & b) show pictures of the containers.

(a) (b)

Figure 1: PLA packages (a) bottle and (b) tray

Compost pile

A compost pile prepared at the Michigan State University Composting facility (East Lansing, MI) was used for the study. The compost pile was produced in a commercial turner manufactured by Global Earth (Ontario, Canda). Initially, 11.6 m^3 of cow manure and 7.8 m^3 of wood shaving were mixed. After that, this mix was combined with waste feed (i.e., the feed that the cows do not eat between feedings) in a proportion of 2:1. The mixture was allowed to stay in a rectangular bay of 3.6 m x 36.5 m x 1.8 m, which was turned every 3 days per week during 3 weeks. During this time the mixture heated up at around 60ºC, and it is turned up to ensure aeration and that the total volume of mixture is exposed to temperatures above 60ºC to kill the weed seeds and pathogens. After that, the mix was pulled out of the bay, and a pile of 6 x 24 x 3 meters was built up on an asphalt pad. The initial pile temperature, relative humidity, and pH was 65 ± 5ºC, 63 ± 5%, and 8.5 ± 0.5 respectively. Figure 2 shows a 2-D graph of the temperature distribution inside the compost pile at the beginning of the testing.

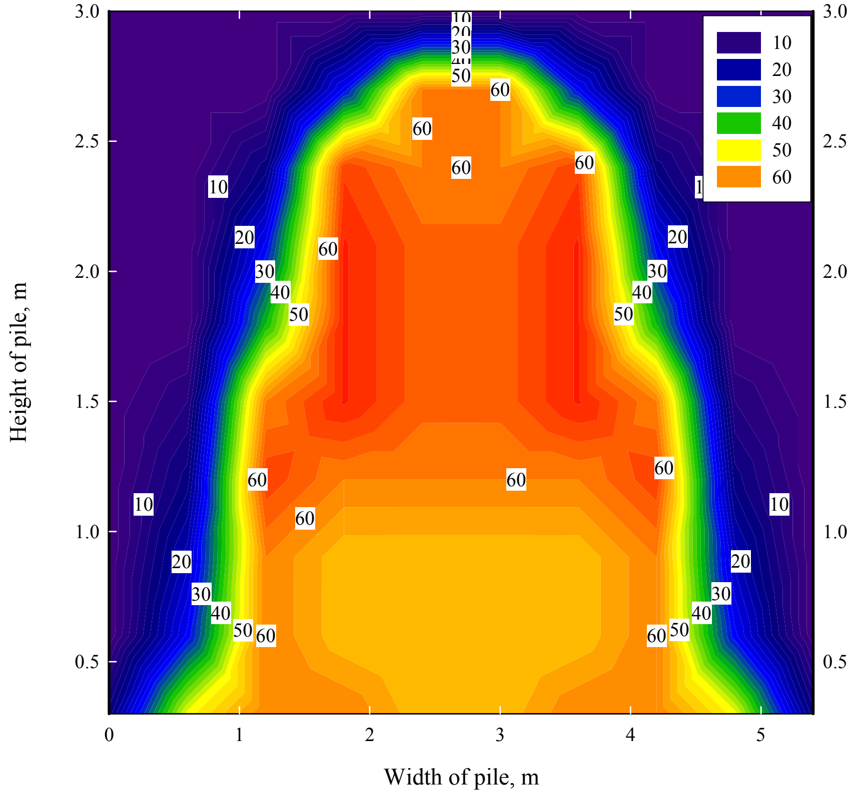


Figure 2: Temperature distribution inside the compost pile at the beginning of testing

Box

Wooden boxes having dimensions of 0.6 x 0.3 x 0.10 m were used to insert packages into the compost pile and to facilitate the actual identification of the package. A 3D image of a box is shown in Figure 3. The bottom of the box was 0.011 mesh gauge, rust and stain proof. This allows a portion of the compost and the package to be removed from the compost pile for evaluation.

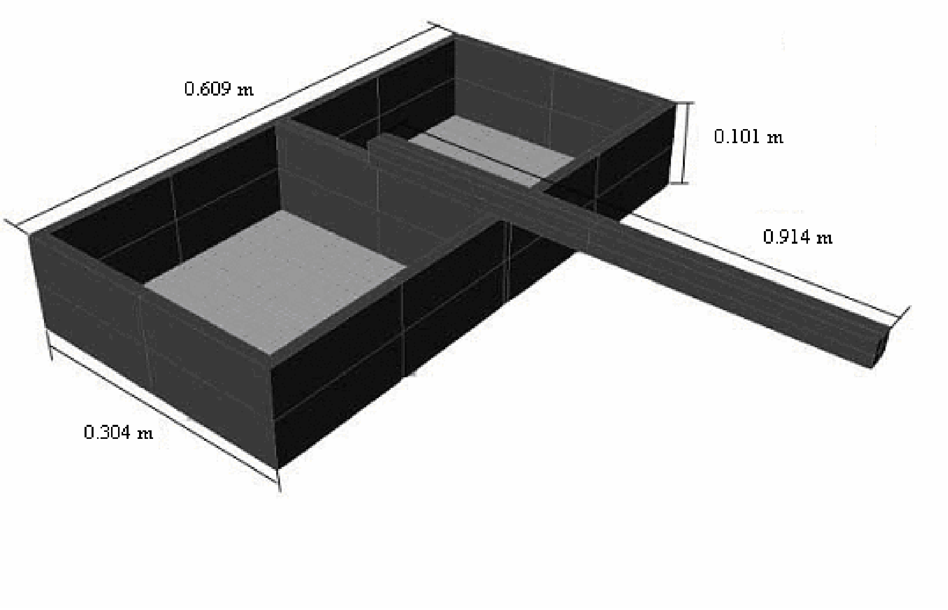


Figure 3: 3D view of the box

Placement of Packages

The packages were placed in duplicate sets in the compost pile with the help of the boxes, as mentioned above, at approximately 1.2 meters above the ground and 1 meter inside the compost pile where a uniform composting temperature was obtained during the experiment. Compost was placed over the mesh in the box and the package was placed on this compost followed by the addition of more compost. In this manner, the packages were buried in the compost pile. The handle on the box facilitated identification of the exact location of the boxes in the pile. The packages were subjected to composting for 1, 2, 4, 6, 9, 15 and 30 days.

Compost property testing

Temperature: Continuous pile compost temperatures were recorded using HOBO® brand battery operated data loggers obtained from Onset Computers (Pocasset, MA) for 6 hours intervals for the complete 30 days. Additional readings of the temperatures around the compost surrounding the packages were taken by a stainless steel thermometer (±1ºC) obtained from Reotemp (San Diego, CA).

Moisture Content: The wet weight moisture content of compost was measured using a modified version of ASTM D4643-00 [17] (previously validated using a traditional vacuum oven) [18]. A sample of the compost mix was taken out every time along with packages and checked immediately for the moisture content. The wet weight of compost was recorded and then it was subjected to microwave heating for 3 minutes. The weight drop in compost due to evaporation of moisture was recorded, and again it was subjected to microwave heating for 1 minute. The cycle of recording the weight and heating for 1 minute was continued until constant weight was obtained. The percentage wet weight moisture content is determined by the ratio of the difference between the weight of the moist and oven dried specimens to the total weight of the moist specimen.

pH: The protocol for measuring pH of compost was originally obtained from Cornell Composting [18]. The compost was dried through the microwave heating process and 5 g of specimen was weighed in a small container. 25 ml of deionized water was added and it was allowed to mix for 5 minutes. The pH of the solution was recorded using calibrated pH paper obtained from Micro Essential Laboratory Inc (Brooklyn, NY).

Visual Inspection

The packages were inspected every time they were removed from the compost and plastic containers. A Sony Cybershot DSC-P150 7.2 MegaPixel digital camera was used to take pictures. The packages were inspected for color, texture, shape, and changes in dimensions.

Physical Properties

Molecular Weight: The molecular weight was determined using a standard Gel Permeation Chromatography (GPC) technique. A Waters 600 Multisolvent delivery system equipped with Waters 717 autosampler and Waters 2410 RI detector from Waters (Milford, MA) was used to determine the molecular weight of samples after extraction. Inhibitor free tetrahydrofuran (THF) solution obtained from Sigma Aldrich (Milwaukee, USA) was transferred to 2 ml vials containing 2 mg of specimen. The vials with the specimens were manually shaken for 2 minutes. The dissolved samples were filtered with 0.2 µm pore size, 13 mm disposable PTFE (Polytetrafluroethylene) filters obtained from Whatman (Florham Park, NJ). Diluted solution was transferred to the 1 ml clear glass shell vials used in the autosampler and capped using polyethylene snap caps; both obtained from Waters (Milford, MA). Two PLgel 10µm MIXED-B 300*7.5mm columns from Polymer Laboratories (Amherst, MA) in series were used, giving a detection range of 1000 to 10,000,000 Daltons. Polystyrene obtained from Sigma Aldrich (Milwaukee, USA) was used as a standard for calibration purposes. Experiments were run at 35ºC. Sample concentrations for polystyrene and PLA samples were 1 mg/ml with a flow rate of 1 ml/min.

Glass Transition and Melting Temperature, Enthalpy of Fusion and Crystallinity: The glass transition temperature, melting temperature and crystallinity were determined using a Differential Scanning Calorimeter (DSC) Q-100 made by TA Instruments (New Castle, DE) in accordance with ASTM D 3418-97. [19] The DSC standard calibration procedures was performed according to ASTM E967-03 [20] and ASTM E968-02 [21]. Analyses of the results were done with a TA Instruments Universal Analysis 2000 (Version 3.9A). The percent of crystallinity was determined according to ASTM D3417-97 [22] and equation 1.

$$x_c(\%) = 100 \times \frac{\Delta H_c + \Delta H_m}{\Delta H_m^c} \qquad (1)$$

where ΔH_c is the enthalpy of cold crystallization, ΔH_m is the enthalpy of fusion, ΔH_m^c is the heating of melting of purely crystalline poly (lactide) PLA, 135 J/g [23, 24].

Decomposition Temperature: The decomposition temperature was obtained using a Thermogravimetric Analysis instrument (TGA) TA 2950 made by TA Instruments (New Castle, DE) in accordance with ASTM E1131-03 [25]. The specimens were heated at the rate of 20ºC from 23ºC up to 500ºC in presence of inert gas (N_2) and oxidative gas (O_2) both above 90 psi. The results were analyzed with Universal Analysis 2000 (Version 3.9A).

Statistical Analysis: All treatments were conducted in replicates of two. Statistical analyses were carried out using the General Linear Models procedure in JMP software (SAS Institute Inc. SAS Campus Drive, Cary, NC 27513).

RESULTS AND DISCUSSION

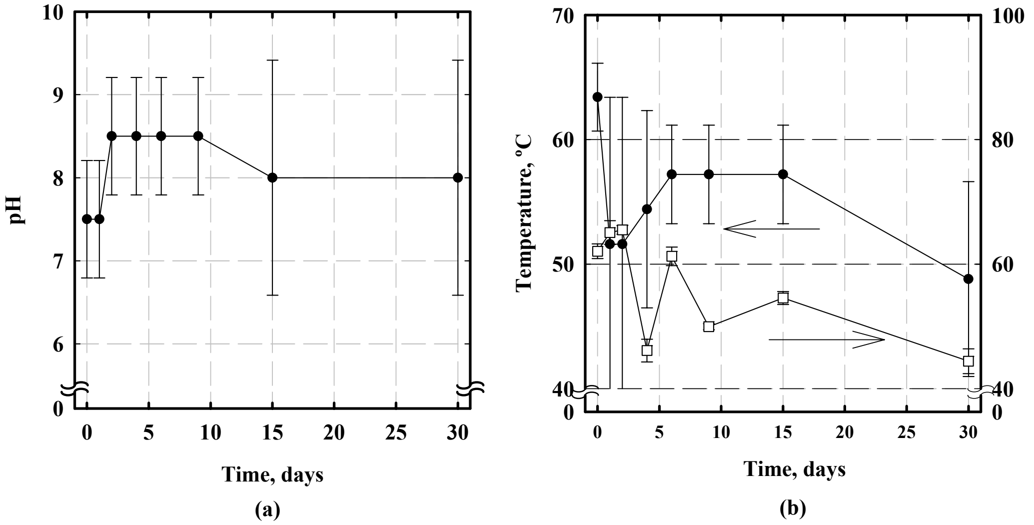
Poly(lactide) bottles and trays were introduced into the compost pile described above and composted for a period of 30 days. Table 1 shows the initial physical properties of these commercial packaging containers. PLA bottles, since they are made of 96% L-lactide, are a more highly ordered structure, which results in a higher crystallinity than PLA trays.

Table 1: Physical properties of PLA bottles and trays

Properties	Bottle	Tray
L-Lactide, %	96	94
Molecular weight	209,324	176,779
PDI	1.72	2.00
Tg, °C	60.6 ± 0.3	61.3 ± 0.6
Tm, °C	151.0±0.1	149.0±2.9
Crystallinity, %[a]	12.2±1.4	9.2±9.7

a- The percent of crystallinity was calculated according to equation 1.

The containers were introduced and located in the compost pile as described above. The temperature, relative humidity, and the pH at which the three packages were exposed during the composting conditions are shown in Figure 4 a & b, respectively. pH is one of the most important factors of hydrolytic polymer degradation since pH variations can change hydrolysis rates by few order of magnitude[26-29]. In this work, there was a slight alkalization of the pile after the second day of testing, although this difference was not statistically significant at α=0.05, P=0.91 during the 30 days of composting.

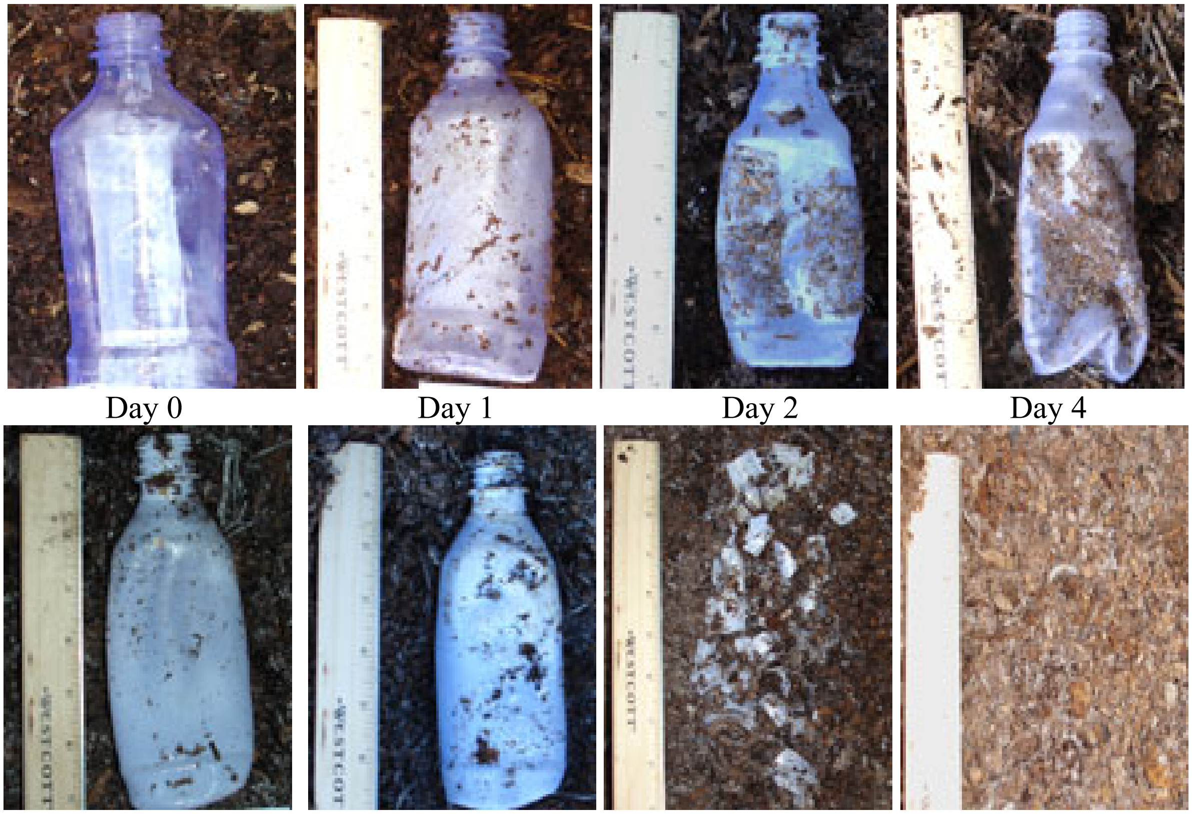


(a) (b)

Figure 4: a) Temperature and relative humidity of the compost pile at time of package removal, b) pH of the compost pile at time of package removal

Visual Inspection

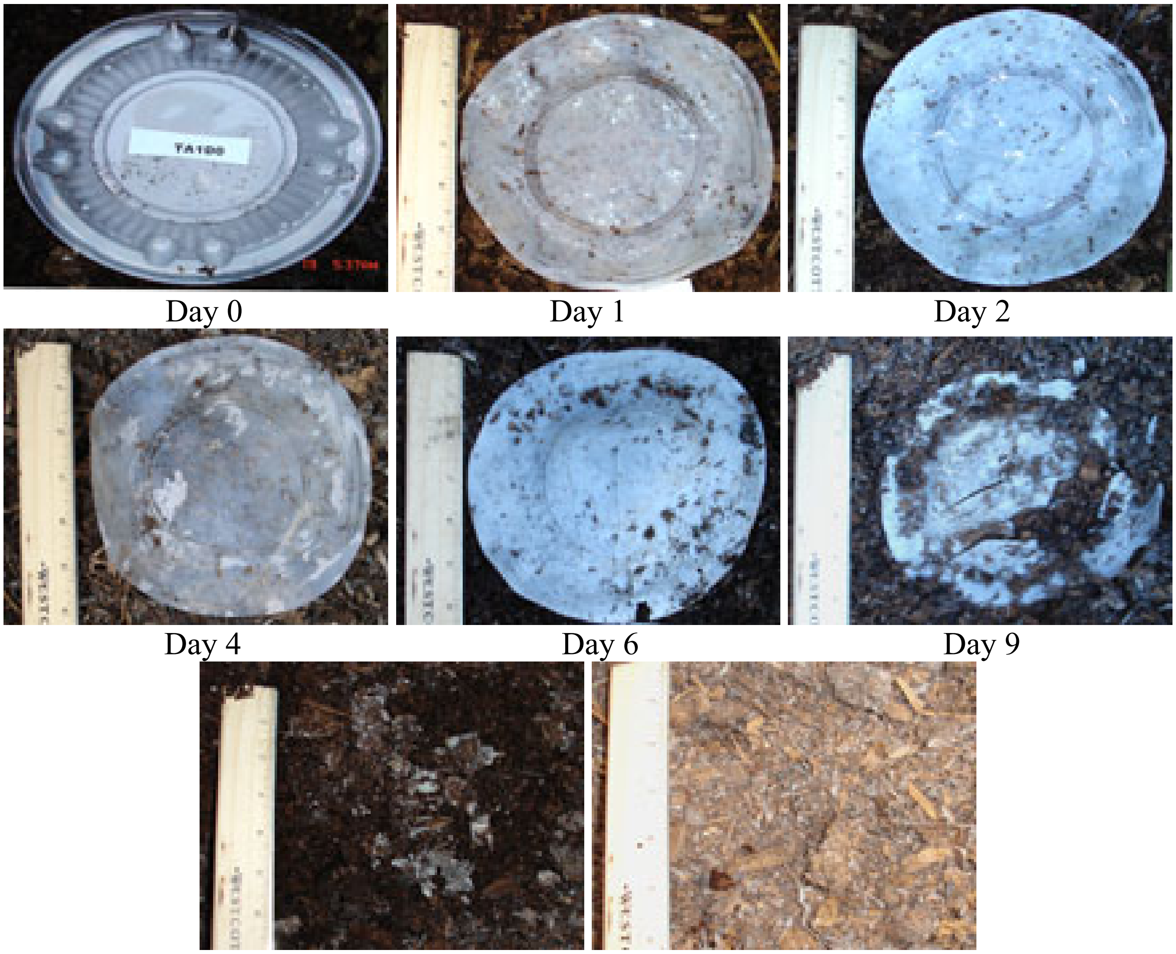
Pictures showing the degradation process of the bottles and trays are presented in Figures 5 and 6. Figure 5 shows degradation of the PLA bottles over the 30 days. Initially the bottles decreased in size and became tough. This phenomenon is attributed to the hydrolysis process that takes place in polylactide polymers. A similar degradation pathway can be seen in Figures 6 for the trays. However, the decrease in thickness and increase in fragility of the tray was much faster than for the bottles. From the first day, degradation in both packages was observed correlated to their change in shape. The dimensions of the containers before and after composting until the bottles and trays started to fragment were calculated by measuring the variation on width, length, height and thickness of the containers. Bottles dimensions reduced to 90% and trays reduced to 22.4%. Color changes were observed in the trays; significantly white at the bottom. On the fourth day, the bottle structures seemed almost the same as in the first day, but with shorter dimensions by approximately 63.4% of the original volume whereas trays started breaking apart and had same opaque characteristics at the creases and less dense areas. On the sixth day, bottle breakdown at the neck was observed and cap liners were already separated. Color change and brittleness were also observed. Trays showed almost the same rate of degradation. On the ninth day, the bottle color showed white, blue and yellow shades, a powdery texture, and was more brittle and most of the parts of the trays were already part of compost. Fifteenth day, the bottle walls and necks were almost degraded except the cap liners and bottom parts still had some residues, whereas the trays were already degraded and became part of compost. Some residuals from bottles were still observed on day 30. The residuals were mostly part of cap liners and in the form of string-like structures of very little strength.



Day 0 Day 1 Day 2 Day 4

Day 6 Day 9 Day 15 Day 30

Figure 5. Pictorial view of the PLA bottles exposed at 30 day of compost conditions.



Day 0 Day 1 Day 2

Day 4 Day 6 Day 9

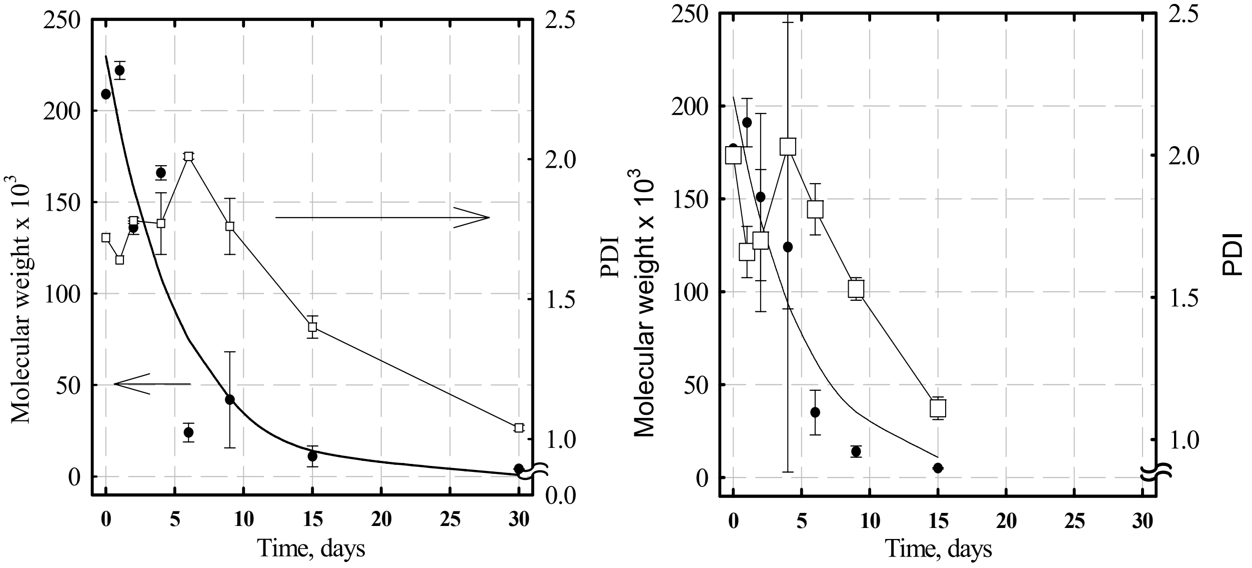
Day 15 Day 30

Figure 6. Pictorial view of the PLA trays exposed at 30 day of compost conditions.

An immediate increase in thickness of all three packages was observed after the first day in the compost pile (not shown). A doubling of the PLA wall and neck thicknesses was found in the bottles, although near the cap this variation was smaller (not shown). This increase in thickness is attributed mainly to the distortion of the containers due to high temperature levels, and the increased presence of a porous structure due to hydrolysis of the polymer.

Physical Properties

Molecular weight: The molecular weight of bottles and trays was monitored by GPC. Molecular weight variations are an indication of the degradation rate of the polymers and give information about when the main fragmentation occurs in a polymer. PLA polymers, by having – C – O – ester linkages in the polymer backbone which are hydrolysable functional groups, are susceptible to hydrolysis. In general high temperature and humidity will cause PLA to degrade rapidly. The molecular weight variation of the bottle and tray for a period of 30 days in composting is shown in figure 7 a and b. The molecular weight variation of the PLA bottles in the first 15 days of composting is much lower than the PLA trays. Major fragmentation of the bottles was observed at day 9, while trays showed similar fragmentation at day 6. At day 30, it was not possible to locate any pieces of trays for analysis.



(a) (b)

Figure 7. Comparison of the variation of the molecular weight and polydispersity index (PDI) as a function of time for a) bottles and b) trays exposed to composting conditions for 30 days.

Both PLA bottles and trays show a slight increase in the molecular weight after being exposed to the compost pile for 1 day. This molecular weight increase could mainly be attributed to crosslinking or recombination reactions. In the case of PLA, the slow degradation rate produces a loss of molecular weight over the polymer cross-section following first order kinetics. Therefore, by fitting the data of the variation of the molecular weight as a function of time, we can observe that the molecular weight degradation of the bottles and trays correlated well with a first order kinetic process as described by equation 2.

$$Mw = a * \exp^{-b*t} \qquad (2)$$

Table 2 shows the estimate of “a” and “b” values from equation (2) and their statistical level of significance for the PLA bottles and trays. Higher “b” values (the pre-exponential factor of equation 2) shown in Table 2 are an indication of faster degradation process, shown in Figure 7 (b) for the trays. So, PLA polymers in a slightly alkaline medium follow a first order hydrolysis process mainly affected by the initial crystallinity, thickness, and the shape of the samples as previously demonstrated by other researchers [26].

Figures 7 a and b, also show the change of the PDI values of the bottles and trays. Since the hydrolysis of poly (LD-lactide) occurs randomly, longer PLA chains are more susceptible to cleavage than the shorter ones. Therefore, an initial rise of the PDI after day 4 and after that for a few more days took place, and it can be correlated with an increase in the fragmentation process, which produces decomposition of the macromolecules into shorter oligomer chains and monomers. Afterwards, polymer fragmentation took place and a narrowing of the molecular weight distribution occurred with a decrease in PDI until total degradation where the PDI tends to 1.00. At this point, only oligomers of the PLA chains are present. Similar trends are observed for the three containers although PLA tray container reach final degradation much faster.

Table 2. First order equation ($M_w \times 10^3 = a^*\exp(-b^*t)$) of the degradation process of poly(lactide) bottles and trays

Properties	**L-Lactide,%**	χ_c	**a**	P_a	**b**	P_b	**Adj Rsqr**
Bottle	96	12.2±1.4	229.7±28.4	0.0002	0.1865±0.0533	0.0128	0.85
Tray	94	9.2±9.7	204.8±21.5	0.0002	0.1953±0.0470	0.0088	0.88

- P_a & P_b are the probability of being wrong in concluding that there is an association between the dependent and independent variables. The smaller the Pvalue, the greater the probability that there is an association. For this paper $\alpha=0.05$.
- Adj Rsqr is the R^2 which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.
- The “a” and “b” values are shown with their 95% confidence levels.

Glass transition and melting temperature: Examples of the glass transition and melting temperature variation of PLA bottles exposed to composting conditions for 30 days are shown in the DSC plot of Figure 8.

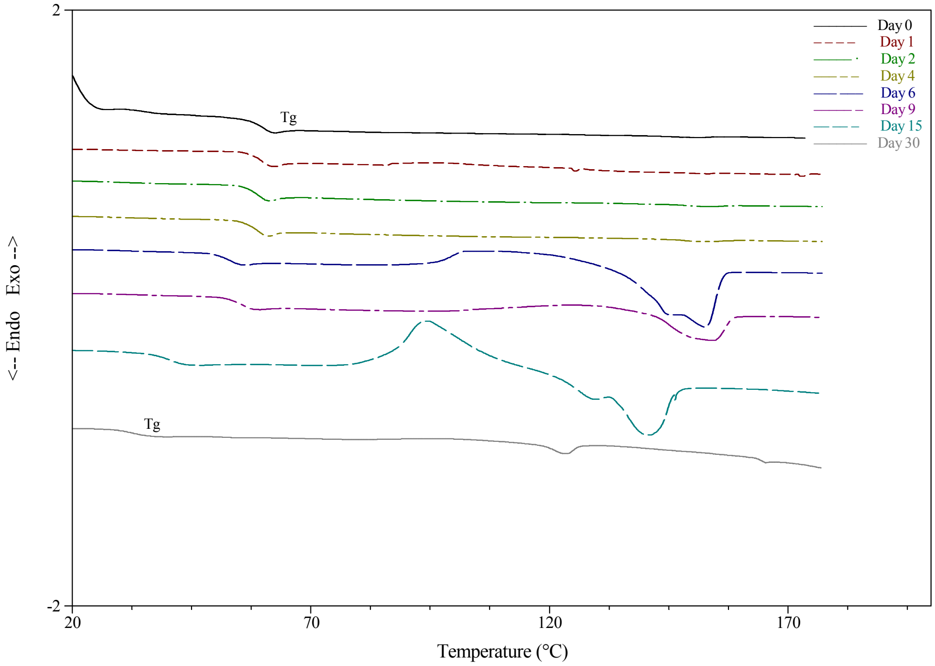
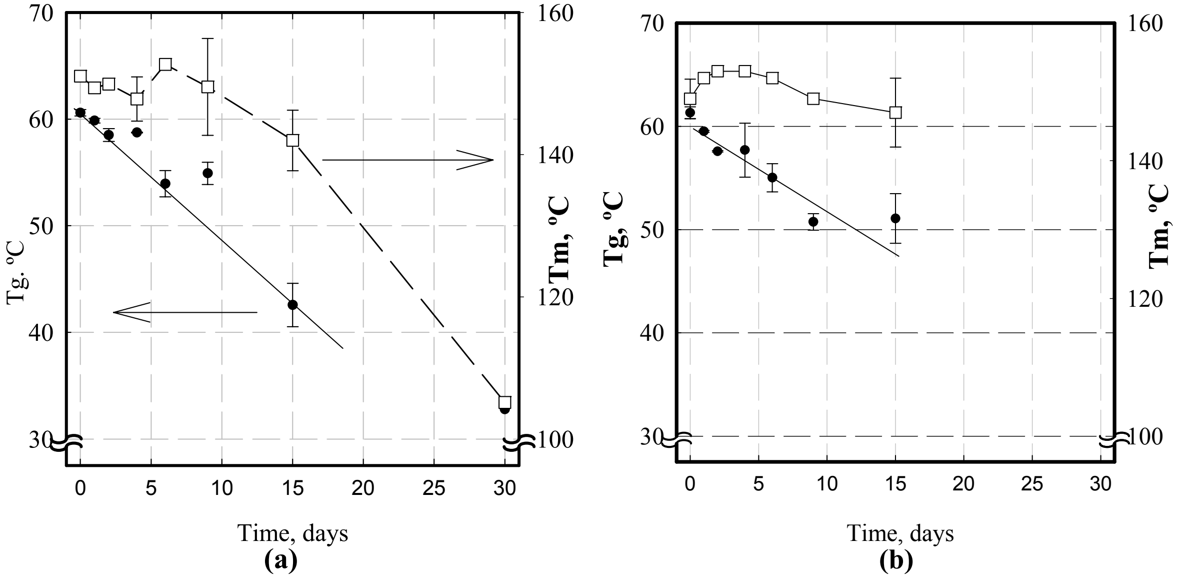


Figure 8: 2nd run of DSC showing the glass transition and melting temperature variation of the PLA bottle exposed to composting conditions for 30 days

During the first four days of composting, a slight increase of T_g is observed which is due to the short-span increment of the M_w. After that, a total reduction of T_g to around 30ºC is observed for the bottles exposed to compost conditions for 30 days. This reduction in T_g is associated with the reduction of the molecular weight of the bottles. Since the hydrolysis of PLA polymers occur at a higher rate in the amorphous region, the overall crystallinity of the containers increased as degradation of the polymer chains took place. By the preferential degradation of amorphous areas, an increase in total crystallinity was also observed during the degradation process of the partially crystalline polymers in aqueous media also noted by other researches[30]. For example, the initial crystallinity of the bottles χ_c = 12.2±1.4 increased to values of around 16% until the last degradation day (First run of the DSC not shown). During the second run, the crystallinity of the samples decreased because the heating of the samples over the melting temperature erased all the previous thermal story of the samples, and the cooling cycle did not allow crystallization.

The variation of T_g and T_m of the packages exposed to composting conditions for 30 days are shown in Figures 9 a and b.



(a) (b)

Figure 9 Glass transition and melting temperature variation of a) bottles and b) Trays exposed to composting conditions for 30 days

The reduction of the T_g for the PLA packages subjected to compost conditions follows a linear trend. Table 3 shows the results of fitting equation 3 to Figure 9's values

$$T_g = T_{g(0)} + d^*t \qquad (3)$$

where "$T_{g(0)}$" is the glass transition temperature at time zero, and "d" is the reduction of the T_g as a function of time. Table 3 and Figure 9 a) show that a reduction of T_g= 0.97ºC/day took place in the bottles exposed to composting. For the trays a reduction of T_g= 0.70ºC/day was observed, respectively. Table 3 shows that a good fit to equation 3 is found for the PLA bottles and trays.

Table 3. Variation of glass transition $T_g = T_{g(0)} + d*t$ as a function of time for poly(lactide) bottles and trays containers

Properties	**L-Lactide,%**	χ_c	$T_{g(0)}$	$P_{Tg(0)}$	**d**	P_d	**Adj Rsqr**
Bottle	96	12.2±1.4	60.86±1.01	<0.0001	-0.97±0.08	<0.0001	0.95
Tray	94	9.2±9.7	59.87±0.95	<0.0001	-0.70±0.13	0.0031	0.82

- $P_{Tg(0)}$ & P_d are the probability of being wrong in concluding that there is an association between the dependent and independent variables. The smaller the Pvalue, the greater the probability that there is an association. For this paper α=0.05.
- Adj Rsqr is the R^2 which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.
- The "$T_{g(0)}$" and "d" values are shown with their 95% confidence levels

Decomposition temperature: PLA polymers in an open system such as the TGA degrade by melt hydrolysis or thermal degradation. Melt hydrolysis is the reverse of the condensation esterification of lactic acid which is important for articles stored in air at room temperature and composting conditions. Thermal decomposition occurs by depolymerization and random degradation. Depolymerization is characterized by a rapid reduction in polymer mass with a slow reduction in molecular weight, while random degradation is characterized by a slow loss of polymer mass with an exponential decrease in molecular weight. These two processes are important during resin processing without water at relatively high temperature.

A TGA plot of the variation of weight as temperature increased for the bottles exposed at different composting times is shown in Figure 10. It is possible to observe that the major change in variation of the decomposition temperature (T_D) happened between days 15 and 30 when the M_W of the bottles decreased from around 11,000 to 4,000 Daltons.

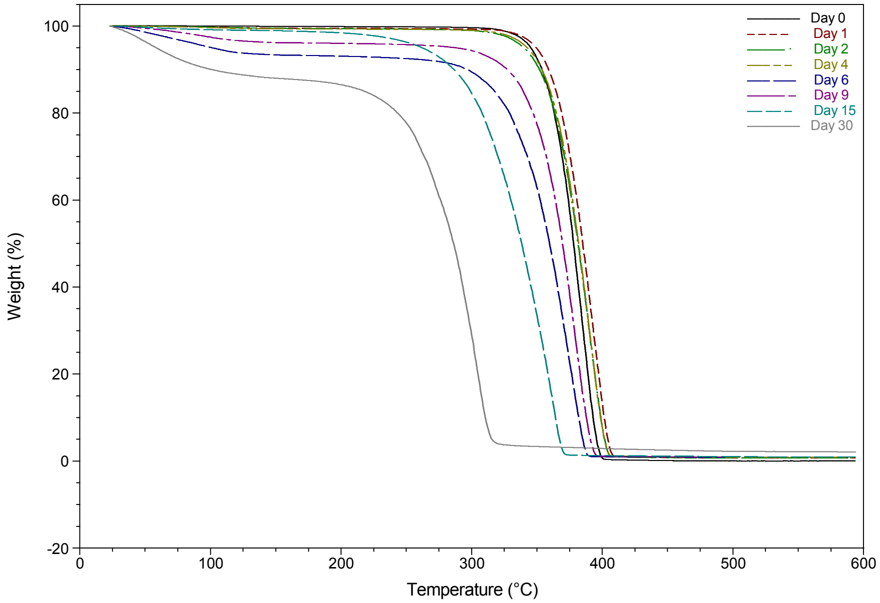


Figure 10. Weight percent reduction vs temperature

A reduction of T_D was observed for all the samples exposed to compost conditions. Figure 11 shows the variation in decomposition temperature for bottles and trays. The variation of T_D with time is a linear variation. Table 4 shows the values obtained from fitting equation 4 to the data shown in Figure 20:

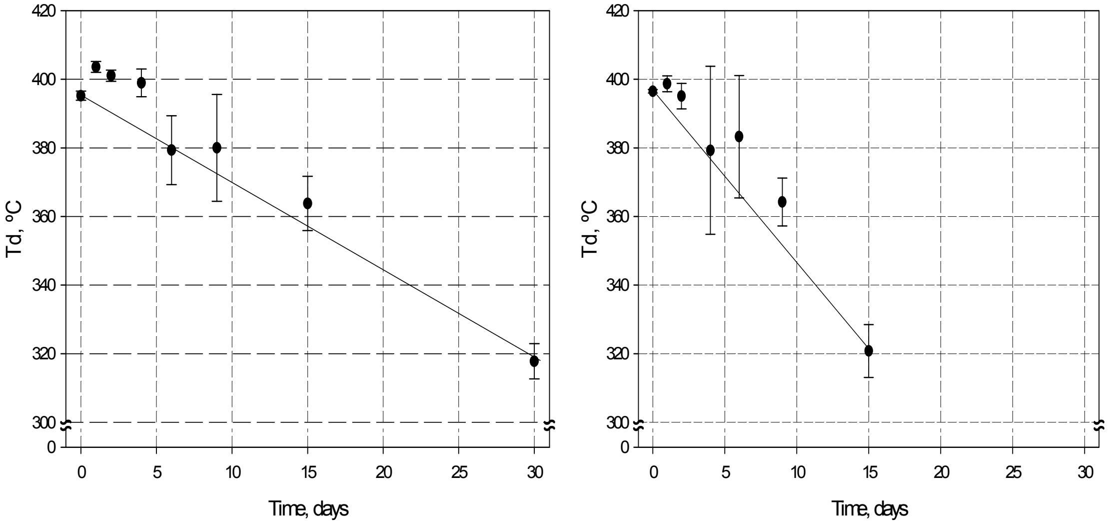
$$T_D = T_{D0} + e^*t \qquad (4)$$

where "T_{D0}" is the decomposition temperature at t=0 day, and "e" is the variation of T_D as a function of time. Table 4 also shows the variation of T_D vs M_n for equation 5:

$$T_D = T_{D(\infty)} - B/M_n \qquad (5)$$

where "$T_{D(\infty)}$" is the T_D for very high M_n , and "B" is a constant term. The variation of T_D vs time and the correlation with the number average molecular weight show that PLA bottles presented a lower reduction of T_D as they were exposed to compost conditions than the trays.

Table 4 shows that a good adjustment of equation 4 & 5 are obtained for the bottles, and trays (see Adj Rsqr values).



(a) (b)

Figure 11. Decomposition temperature a) bottles and b) trays composting conditions for 30 days

Table 4. Variation of decomposition temperature $T_D = T_{D0} + e^*t$ as a function of time (equation 6) and Molecular number for poly(lactide) bottles and tray containers. Variation of decomposition temperature $T_D = T_{D(\infty)} - B/M_n$ as a function of M_n

Equation 4: $T_D = T_{D0} + e^*t$

Properties	**L-Lactide,%**	χ_c	T_{D0}	$P_{T\,D0}$	**e**	P_e	**Adj Rsqr**
Bottle	96	12.2±1.4	403.4±2.7	<0.0001	-2.8±0.2	<0.0001	0.95
Tray	94	9.2±9.7	403.5±3.9	<0.0001	-5.1±0.5	0.0003	0.93

Equation 5: $T_D = T_{D(\infty)} - B/M_n$

Properties	L-Lactide,%	χ_c	$T_{D(\infty)}$	$P_{TD(\infty)}$	B	P_B	Adj Rsqr
Bottle	96	12.2±1.4	402.2±2.3	<0.0001	-327,501±21,647	<0.0001	0.97
Tray	94	9.2±9.7	397.8±3.3	<0.0001	-342,941±35,267	0.0002	0.94

- P_{TDO}, P_e, $T_{D(\infty)}$, & P_B are the probability of being wrong in concluding that there is an association between the dependent and independent variables. The smaller the Pvalue, the greater the probability that there is an association. For this paper α=0.05.
- Adj Rsqr is the R^2 which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.
- The "T_{D0}," $T_{D(\infty)}$, and "B" values are shown with their 95% confidence levels.

In summary, PLA polymers absorb water resulting in the hydrolysis of the ester linkages, which produces the breakdown of the long macromolecular chains. PLA 94% L-lactide packages degraded faster than those of 96% L-lactide. The rate of degradation is mainly affected by the L-lactide content and the crystallinity of PLA, and the temperature, relative humidity, and pH of the pile. The change of the degradation rate with respect to the initial crystallinity of the containers should be considered when samples are introduced in compost piles; however, the two packages did not take more than a month to completely degrade even though the packages were not ground (worst case scenario) before they were introduced to the compost pile. Similar compost studies, but with PLA samples and not complete packages, were carried out by Weber [31] by storing PLA samples in biodegradation chambers. As a result, they recommended that a maximum of 10% PLA be used in compost piles to prevent pH reduction of the pile. In this study, this concern was not a problem due to the ratio of polymer to compost. Thus, the present work addressed the degradation time of the physical properties of two commercially available PLA packages and gives information on the compostability and the reduction of the physical properties under real compost conditions. Further studies are being carried out to simulate the real degradation process in simulated conditions in order to establish reliable tests to evaluate degradation under real compost conditions. This work found that the degradation time of PLA trays in a commercial facility was not more than 30 days, and in the case of the bottle was not more than 45 days. Packages made of PLA will compost in municipal/industrial facilities, but they may be difficult to completely compost in backyard composting since PLA degradation is driven by hydrolysis which needs higher temperatures to take place. Further research is necessary to find methods and techniques that can assess the degradability of biodegradable packages under real composting conditions before they are degraded in commercial composting operations.

CONCLUSION

Two PLA compostable packages, a bottle and a tray were used to determine the degradation process under compost conditions. A novel method was used to identify and keep track of the degradation of the PLA packages on a real compost facility. The degradation of the PLA containers was monitored by visual inspection, GPC, DSC, and TGA. PLA trays degraded before 30 days under composting conditions (T>60 ºC, >65%RH, ph~8.5). First order degradation kinetics was observed for both packages. A T_g reduction of 1ºC/day was found for bottle, and a T_g reduction of around 0.6 ºC/day was found for trays. A method to study the compostability of biodegradable packages under real compost conditions has been outlined.

Further studies are being carried out to address the compostability of biodegradable packages under simulated conditions, and to establish a standard that can address the compostability of biodegradable packages under real and simulated compost conditions.

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