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Title: Comparing the degradability of commercially available biodegradable packages in composting and ambient exposure conditions

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ABSTRACT

The adoption of biodegradable polymeric materials is increasing in food and consumer good packaging applications due to the concerns of disposing of petroleum based polymers. Currently Poly (lactide) (PLA) polymers are the biggest commercially available bio-based polymeric packaging materials. Life cycle analyses show that PLA polymers consume around two times less energy than conventional petroleum based polymers. As the main concern in regards to PLA adoption is environmental, there is a need to address the degradability and environmental performance of these biodegradable packages. This study focuses on comparing the degradability of two commercially available biodegradable packages, a PLA bottle composed of 96% L-lactide and 4% D-lactide with bluetone additive and a PLA deli container composed of 94% L-lactide and 6% D-lactide in composting and ambient environments. Both composting and ambient exposure degradability mechanisms were carried out in real conditions governed by weather, microbial growth and pH of compost, distinct from the simulated ones in which the parameters are controlled. The packages were placed in duplicates in the compost pile and similarly they were exposed in duplicates to the ambient environment; and they were taken out on days 1, 2, 4, 6, 9, 15 and 30 for analyzing their property changes. When taking out the packages these were inspected for shape, texture, color changes and material breakdown. The molecular weight (MW) 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.

The degradation of packages subjected to composting conditions was observed right from the first day in correlation to their dimensions, shape, thickness and color changes. The deli container was completely composted on the 30th day, while the bottle still had some residues. Molecular weight of bottles was reduced by 98.5% on the 30th day of being in the compost and that of deli container was reduced by 97.4% on the 15th day. No such changes were observed for both packages subjected to ambient exposure conditions. When exposed to ambient conditions, bottles molecular weight was reduced by 4.2% and deli containers' was increased by 2.4%. DSC analysis show that bottles exposed to compost conditions showed a T_g reduction of 46% and a T_m reduction of 30% of the initial values on the 30th day. Deli containers showed a reduction of T_g of 12% and 3% of T_m respectively on the 15th day. In the case of the packages subjected to ambient exposure conditions, bottles showed an increase in T_g of 1.2% and a reduction of 0.7% in T_m ; deli containers showed an increase of 1.2% in T_g and a 0.5% reduction in T_m . A reduction of the decomposition temperature of the samples exposed to compost conditions was also observed. First order degradation kinetics were observed for both packages subjected to composting conditions. It was verified that the degradability of PLA is mainly affected by the L-lactide content, initial crystallinity and degradation conditions or parameters.

In summary, a distinction between two degradation processes, compost and ambient, and for distinct packages was addressed. Thus a novel technique was used to identify and compare the degradation of two complete packages in two different real environments.

Comparison of the Degradability of Commercially Available Biodegradable Packages in Composting and Ambient Exposure Conditions

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ABSTRACT

The adoption of biodegradable polymeric materials is increasing in food and consumer good packaging applications due to concern of disposal of petroleum based polymers and the increasing cost of petroleum based polymer resins. Currently, poly (lactide) (PLA) polymers are the biggest commercially available bio-based polymeric packaging materials. As the main motivation for adopting biopolymers is environmental, there is a need to address the degradability and environmental performance of biodegradable packages. The aim of this work was to study the degradation of two commercially available biodegradable packages made of PLA under real compost conditions and under ambient exposure by visual inspection, gel permeation chromatography, differential scanning calorimetry, and thermal gravimetric analysis. A novel technique to study the degradability of these packages, to identify and to track the degradation rate under real compost conditions was used. Both packages were subjected to composting and ambient exposure conditions for 30 days, and the degradation of the physical properties was measured at 1, 2, 4, 6, 9, 15 and 30 days. PLA bottles made of 96% L-lactide exhibited lower degradation than PLA deli container made of 94% L-lactide, mainly due to their highly ordered structure, therefore, higher crystallinity. The degradation rate changed as the initial crystallinity and the L-lactide content of the packages varied. Temperature, relative humidity, and pH of the compost pile played an important role in the rate of degradation of the packages. First order degradation kinetics and linear degradation trend were observed for both packages subjected to composting conditions.

[Keywords: *biopolymers; compostability; degradation; GPC, hydrolysis; poly(lactide)*]

1. INTRODUCTION

There is an increasing demand of biopolymers based packaging materials which could be easily renewable providing enhanced environmental performance. Till now, the majority production of packaging plastics is based on non-renewable materials. Plastics packaging materials are often landfilled due to foodstuff and other biological substance contents, making physical recycling of these materials impractical. 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. Hence, compostability has, so far, been the main focus of applications of biobased packaging materials, which is the natural outcome for a vast amount of food and pharmaceutical packaging materials and waste. Composting permits 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 at this time is more expensive [1].

Composting is the controlled and natural decomposition of organic materials by microorganisms. The organic materials are decomposed into a soil like substance called humus. The major groups of microorganisms involved in composting are fungi, bacteria and actinomycetes. Microorganisms need food in form of carbon, nitrogen, oxygen and water.

Organisms decompose the organic matter by utilizing carbon as source of energy and nitrogen for building cell. A 30:1 carbon to nitrogen ratio is an ideal proportion for reproduction of thermophilic microorganisms [2]. A compost pile goes through two composting stages, first a composting stage and a curing stage. In the first stage, temperature rises up to around 60°C as long as oxygen, carbon and nitrogen are available in the ideal proportion and promotes strong microbial activity. In the later stage, the decomposition continues at a smaller rate till last remaining nutrients are consumed by remaining microorganisms and until almost all the carbon is converted to carbon dioxide.

Compostability of *compostable plastics* (i.e., “ a plastic that undergoes degradation by biological processes during composting to yield CO₂, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leave no visible, distinguishable or toxic residue” [3]) are commonly evaluated in simulated compost conditions and by assessing the final quality of the compost. While evaluating the compostability, plastic is subjected to mechanical, thermal and chemical degradation out of which chemical degradation is the most important. Biodegradable polymers first become susceptible to water attack and chemical degradation initiates the polymer erosion since they have hydrolysable functional groups in the polymer backbone. Standards have been developed for evaluating the degradation and compostability of a biopolymer by the American Society for Testing and Materials (ASTM), the International Standards Organization (ISO) and the European Committee for Standardization. ASTM standards (i.e., ASTM D5338-98 [4], D6003-96 [5], D6954-04 [6], D6400-99^{e1} [3], & D 6002-96 (Reapproved 2002)^{e1} [7]) developed by subcommittee 20.96 for assessing compostability are laboratory scale and limited to evaluation of plastic materials [3, 5-7]. Similarly ISO standards such as ISO 14851 [8], 14852 [9], and 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. The above mentioned standards mainly focus on addressing the compostability of a polymer or a material, but not that of a package in 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 adoption of biodegradable polymeric materials is increasing in food and consumer goods packaging applications due to concern of disposal of petroleum based polymers. Currently, poly(lactide) (PLA) polymer developed by Cargill Dow LLC (Blair, NB) and currently under the name of NatureWorks[®] LLC is the biggest commercially available bio-based polymeric packaging materials. NatureWorks[®] LLC is producing three hundred million pounds of PLA annually for a variety of packaging and fiber applications. 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. Similar to Eastar, 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. 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].

PLA polymer, the predominant biopolymer in the market for packaging applications, can be manufactured by carbohydrate fermentation or chemical synthesis. Lactic acid (2-hydroxy propionic acid) is the simplest hydroxyl acid with an asymmetric carbon atom, and it exists in two optically active configurations, the L(+) and D(-) isomers. The majority of lactic acid is made

by bacterial fermentation of carbohydrates. The fermentation processes to obtain lactic acid can be classified according to the type of bacteria used. High molecular weight PLA can be obtained using different methods; a) direct condensation polymerization [13]; b) azeotropic dehydrative condensation polymerization currently used by Mitsui Toatsu [13] and c) polymerization through lactide formation developed by Cargill Inc. in 1992 [13]. The properties of high molecular weight PLA are determined by the polymer architecture (i.e. stereochemical makeup of the backbone) and the molecular mass, which is controlled by addition of hydroxylic compounds. The ability to control the stereochemical architecture permits precise control over the speed of crystallization and finally the degree of crystallinity, the mechanical properties and the processing temperature of the material. In addition, the degradation behavior strongly depends on the crystallinity of the PLA. The glass transition temperature (T_g) ranges from 50°C to 80°C while the melting temperature (T_m) ranges from 130°C to 180°C. 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]. Life-Cycle Assessment (LCA) and economic studies indicated that PLA polymers are more energy efficient than PP and PS polymers [14-17], which is mainly because PLA consumes almost no feedstock energy. Currently, PLA is being commercialized and being used as a food packaging polymer for short shelf life products with common applications such as containers [18], drinking cups, sundae and salad cups, overwrap and lamination films, blister packages, and bottles. As the PLA consumption is increasing, there is a need to address its compostability in real composting conditions and its potential recyclability. 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. Hence for PLA to be considered as an alternative for conventional polymers, a wide range of composting facilities needs to be developed, or PLA will need to be composted with general yard waste. Looking at PLA potential recyclability, NatureWorks® LLC instituted a large volume “buy-back” program in North America for post-consumer of PLA bottles in mixed plastic waste recycling streams [19]. PLA can be sorted from other plastics using near infrared technology. However, as mentioned before, recyclability is not an alternative for containers with foodstuff contents.

As previously described, the standards developed so far mainly address the compostability of plastic in simulated conditions and correlated to evolution of CO₂. There are several parameters which differentiate the real and simulated or controlled composting conditions. According to ASTM D 6002-96(2002)e1 [7] and the Federal Trade Commission (FTC) [20], a “compostable claims would be appropriate on products or packages that will break down, or become part of usable compost, in a safe and timely manner in home compost piles [20],” where “time manner” means the time necessary for leaves, grass, and food stuff take to compost. Some of the commercially available “*biopolymer materials*” comply with the standards of compostability, but generally package or containers were not evaluated. According to ASTM D 6400-04 [3] “products and finished articles should be tested in the same form as they are intended to be used.” Therefore, if the packages show different chemical composition or structure, it is necessary to test them to evaluate their compostability.

The aim of this paper is to provide information about comparison and compostability of two commercially available biodegradable packages in real composting and ambient environments further correlating and comparing their degradation through visual inspection and analysis of physical properties. The physical properties analyzed were molecular weight using gel permeation chromatography (GPC), glass transition (T_g) and melting temperature (T_m) using differential scanning calorimetry (DSC) and decomposition temperature (T_D) using a thermogravimetric analysis (TGA).

2. MATERIALS AND METHODS

Packages

Poly (lactide) bottles were obtained from NatureWorks® LLC (Blair, NB) and commercialized by Biota brands of America (Telluride, CO) with 96% L-lactide and bluetone additive; dimensions of height = 0.2 m and base diameter = 0.0065 m (Volume = 500 ml). Deli containers were obtained from Wilkinson Manufacturing Company (Fort Calhoun, NB) with 94% L-lactide; dimensions of height = 0.07 m and base diameter = 0.09 m (Volume = 600 ml). Figure 1, (a) and (b) shows pictures of these containers.

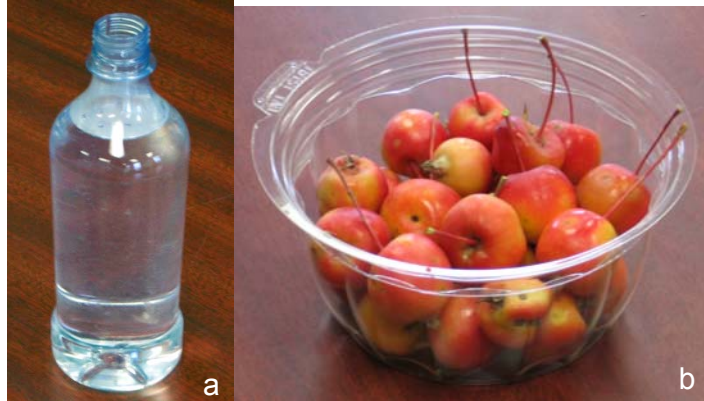


Figure 1. PLA packages (a) bottle and (b) deli container

Compost pile

A compost pile made up of cow manure and wood shavings was prepared at the Michigan State University Composting facility (East Lansing, MI) and was used for the study. Initially, 11.6 m³ of cow manure and 7.8 m³ of wood shaving were mixed. This mixture 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 such made that the carbon to nitrogen ratio was approximately 30:1.

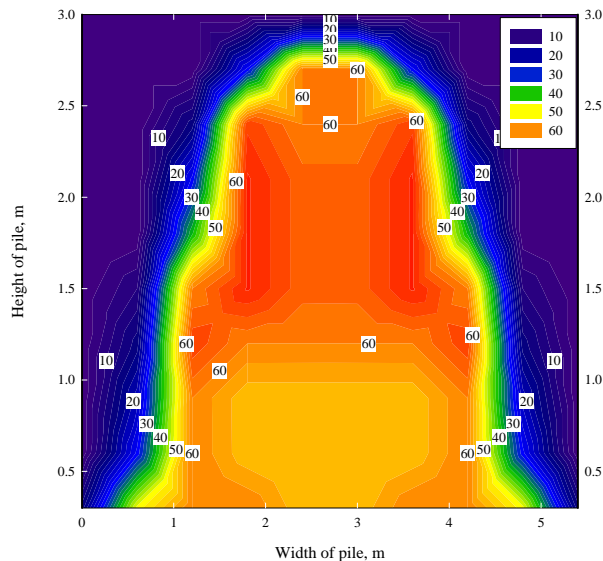


Figure 2. Temperature distribution inside the compost pile at the beginning of the testing

It was allowed to stay in a rectangular bay of 36.5 x 3.6 x 1.8 meters, which was turned using a commercial turner manufactured by Global Earth (Ontario, Canada) every 3 days per week during 3 weeks. Due to turning, the mixture got heated up to 60°C under the presence of aeration. This temperature was enough to kill weed seeds and pathogens. Later, the mixture was pulled out of the bay, and a pile of 24 x 6 x 3 meters was built up on an asphalt pad. Initially the compost parameters such as temperature, moisture and pH were measured and determined. A temperature of $65 \pm 5^\circ\text{C}$, moisture of $63 \pm 5\%$, and a pH of 8.5 ± 0.5 was observed. Figure 2 shows a 2-D graph of the temperature distribution inside the compost pile at the beginning of the testing.

Box

Wooden boxes of dimensions 0.6 x 0.3 x 0.1 meters were produced using treated wood and were used for subjecting packages into the compost pile. Those boxes facilitated the exact location and identification of package in the compost pile; and also the removal of package and portion of compost for analysis. A mesh of 0.011 gauge was fitted at the bottom of the boxes. A 3D image of a wooden box is shown in Figure 3.

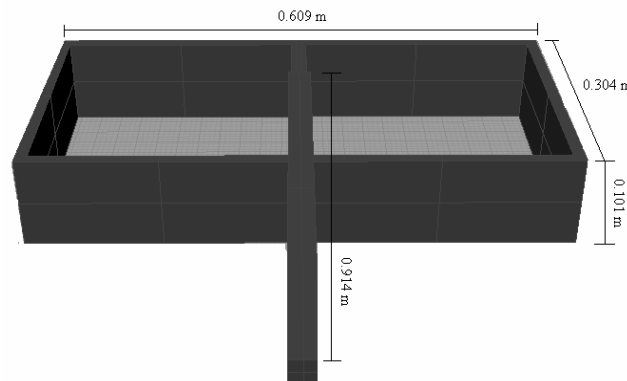


Figure 3. 3D image of box

Plastic Containers

Foldable reusable plastic containers obtained from CHEP-USA (Orlando, FL) of dimensions 0.6 x 0.4 x 0.4 meters were used to expose the packages to ambient conditions.

Placement of Packages

Composting exposure: Both bottles and deli containers were placed in duplicate sets in the compost pile with the help of 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. Initially, the compost was placed over the mesh in the box, later a package was placed followed by addition of compost completely over the box. The handle on the box facilitated identification of the exact location of the boxes in the pile.

Ambient exposure: The packages were placed in the plastic containers mentioned above in duplicate set as in case of composting exposure. The packages were taken out at 1, 2, 4, 6, 9, 15 and 30 days from both compost pile and plastic containers.

Compost Parameters

Temperature: Temperatures were recorded every time packages were removed from the compost pile using stainless steel thermometer ($\pm 1^\circ\text{C}$) obtained from Reotemp (San Diego, CA). Also the temperatures were continuously recorded using HOBOTM brand battery operated data loggers obtained from Onset Computers (Pocasset, MA) for 6 hours intervals for the complete 30 days.

Moisture Content: The wet weight moisture content of compost was measured using a modified version of ASTM D4643-00 [21] (previously validated using a traditional vacuum oven) [22]. A sample was obtained whenever packages were taken out of compost pile and checked immediately for the moisture content. Initially the wet weight of compost was recorded and then heated in microwave for 3 minutes. The weight drop in compost due to evaporation of moisture was recorded, and it was again 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 was 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 [22]. 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).

Ambient Parameters

Hourly data for ambient parameters such as temperature, relative humidity and solar radiation were obtained from the Michigan Automated Weather Network (East Lansing, MI) located at 42.6734 degree latitude, -84.4870 degree longitude and 264 m elevation for the complete 30 day period. The air temperature measurements were taken above 1.5 meters above ground level. Figure 4 a) shows the maximum and minimum ambient temperatures, Figure 4 b) shows the maximum and minimum relative humidity during the 30 day testing period, and Figure 4 c) shows the average daily solar radiation during the same period.

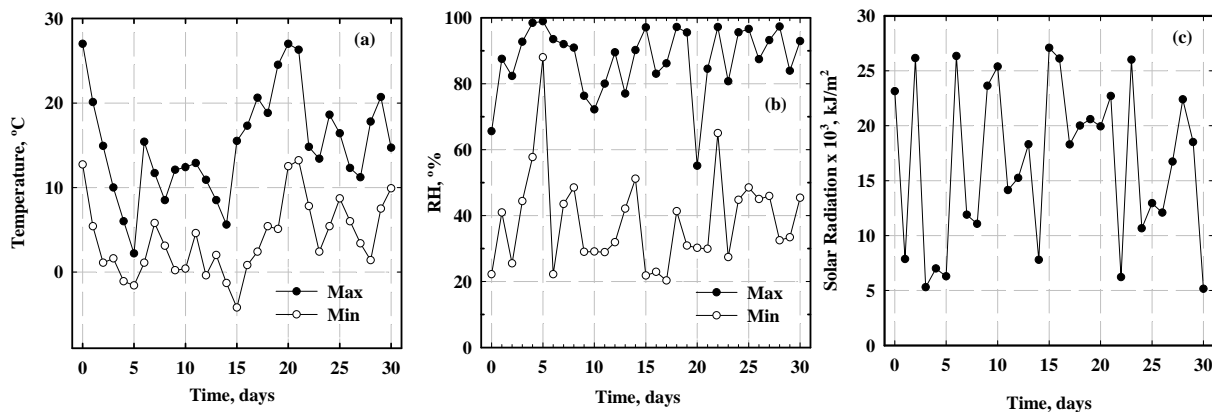


Figure 4: a) 30 days maximum and minimum temperature data; b) 30 days maximum and minimum relative humidity data; c) 30 days average total solar radiation

Visual Inspection

Both 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

Thickness: The thickness of packages was determined using a Magna Mike 8000 thickness gauge manufactured by Panametrics (Japan) according to ASTM D4166-99(2004)^{e1} [23].

Molecular Weight: The molecular weight was determined using a standard GPC technique. A Waters 600 Multisolvant 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 (Polytetrafluoroethylene) 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 10 μm MIXED-B 300*7.5mm columns from Polymer Laboratories (Amherst, MA) in series were used, giving a detection range of 1,000 to 10,000,000 Daltons. Polystyrene obtained from Sigma Aldrich (Milwaukee, USA) was used as a standard for calibration purposes. Experiments were run at 35°C. 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 DSC Q-100 made by TA Instruments (New Castle, DE) in accordance with ASTM D 3418-03 [24]. The DSC standard calibration procedure was performed according to ASTM E967-03 [25] and ASTM E968-02 [26]. Analyses of the results were done with Universal Analysis Software (Version 3.9A). The percent of crystallinity was determined according to ASTM D3417-99 [27] and equation 1.

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

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 PLA, 135 J/g [28, 29].

Decomposition Temperature: The decomposition temperature was obtained using a TGA TA 2950 made by TA Instruments (New Castle, DE) in accordance with ASTM E1131-03 [30]. The specimens were heated at the rate of 20°C from 23°C up to 500°C in presence of inert gas (N_2) and oxidative gas (O_2) both above 90 psi. The results were analyzed with Universal Analysis Software (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).

3. RESULTS AND DISCUSSION

Poly (lactide) bottles and deli containers were subjected to composting and ambient exposure conditions for a period of 30 days. Table 1 shows the initial physical properties of these packages. The PLA bottles, made up of 96% L-lactide, are a more highly ordered structure resulting in higher crystallinity than the deli containers with 94% L-lactide. PLA derived from greater than 93% L-lactic acid can be semicrystalline [13, 31]. Meso- and D- lactide induce twists in the otherwise very regular poly(L-lactide) molecular architecture. Molecular imperfections are responsible for the decrease in both the rate and extent of poly(L-lactide) crystallization. In this study, the deli containers had higher molecular weight than the bottle and a lower initial PDI.

Table 1. Physical properties of the poly(lactide) bottles and deli containers

Properties	Bottle	Deli
L-Lactide, %	96	94
Molecular weight, daltons	209,324	222,700
PDI	1.72	1.66
T _g , °C	60.6 ± 0.3	62.6 ± 4.3
T _m , °C	151.0±0.1	149.0 ± 1.1
Crystallinity, % ^a	12.2±1.4	1.4 ± 0.3

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 5 (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[32-35]. 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 $\alpha = 0.05$, $P=0.91$ during the 30 days of composting.

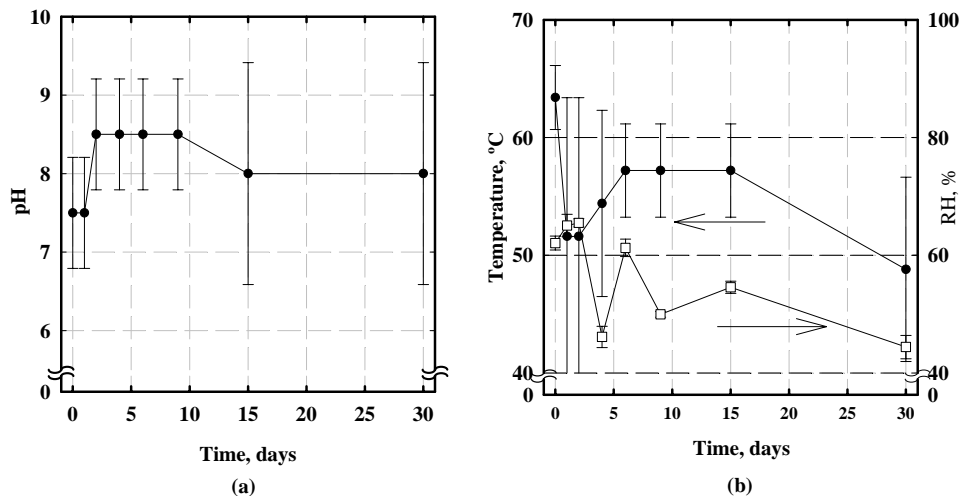


Figure 5. a) pH of the compost pile at time of package removal and b) Temperature and relative humidity of the compost pile at time of package removal

Visual Inspection

Pictures showing the degradation process of the bottles and deli containers in the compost pile are presented in Figures 6 & 7. Figure 6 shows the degradation of the PLA bottles over the 30 days. Initially the bottles decreased in size and became tough. The change in shape is because of distortion due to the higher temperatures in the compost pile.

A similar degradation process can be seen in Figure 7 for deli containers. 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 deli containers started to fragment were calculated by measuring the variation on width, length, height and thickness of the containers. Variation in thicknesses and shapes were observed on both packages from day 1. On first day, bottle dimensions reduced to 90% and that of deli container reduced to 22.22%.

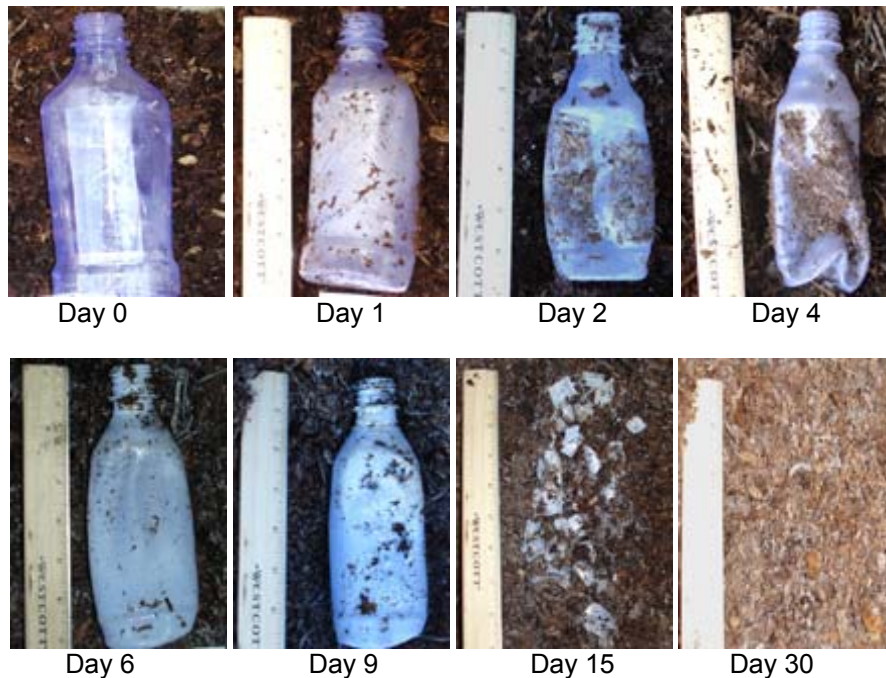


Figure 6. Pictorial view of the PLA bottles exposed at 30 day of compost conditions

Color changes were observed in the deli containers; significantly white at the bottom. On the fourth day, the bottle structures seemed almost the same as on the first day, but with shorter dimensions by approximately 63.4% of the original volume whereas deli containers showed toughness in the material. On the sixth day, bottle breakdown at the neck was observed and cap threads were already separated. Color change and brittleness was also observed. Deli containers 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.

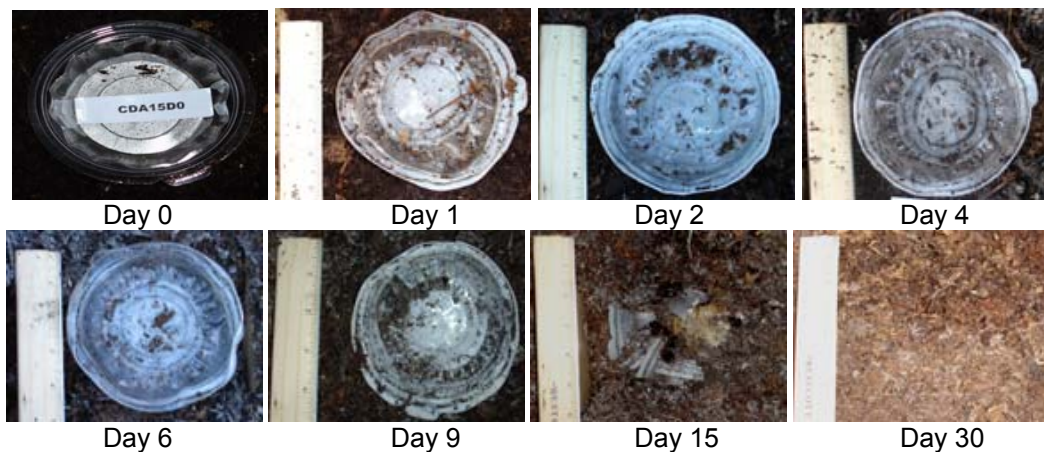


Figure 7. Pictorial view of the PLA deli container exposed at 30 day of compost conditions.

Deli containers started breaking apart, had powdered structure, and were very brittle. Fifteenth day, the bottle walls and necks were almost degraded except the part of cap threads and bottom parts still had some residues, whereas the deli containers showed some residues in form of yellowish film and could not be identified whether it was from walls or bottom of the deli containers. Some residuals from bottles were still observed on day 30. The residuals were mostly part of cap threads and in the form of string-like structures of very low strength. The

bottles and deli containers exposed to ambient conditions were also inspected through the visual inspection. Pictures showing the degradation process of the bottles and deli containers in ambient environments are presented in Figures 8 & 9. The packages faced different atmospheric conditions such as solar radiation, rain, snow, wind and variable atmospheric pressures (Figure 4: a, b, & c). Not much visible difference was observed in any of the containers for 30 day period.

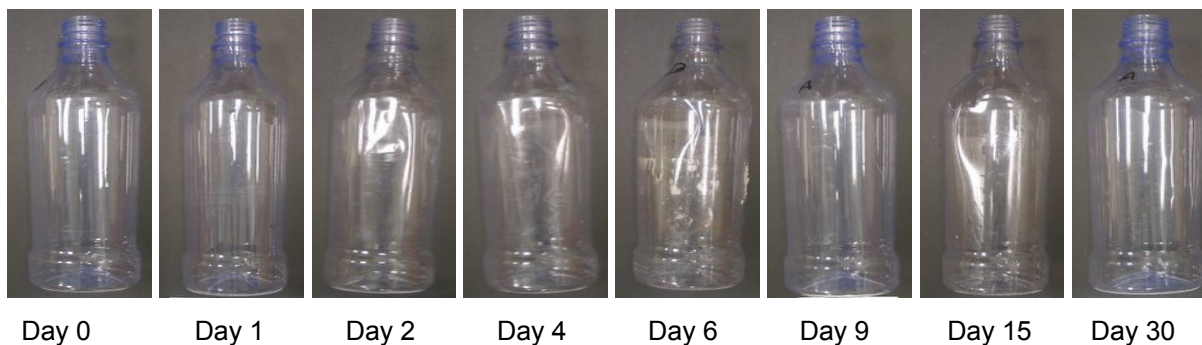


Figure 8. Pictorial view of the PLA bottles exposed for 30 days under ambient conditions

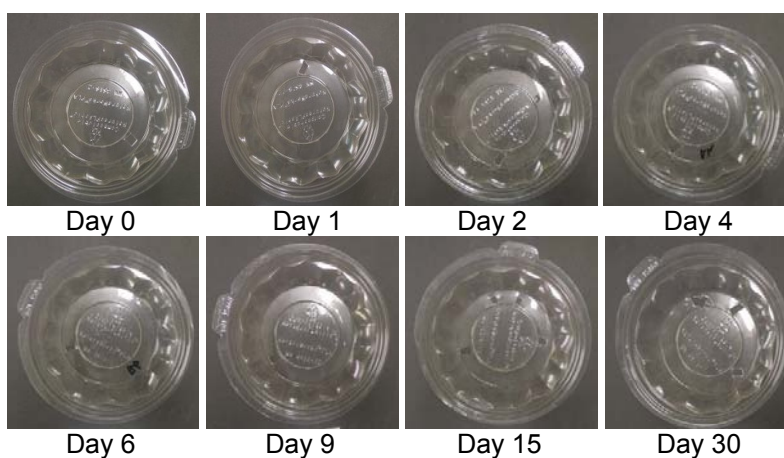


Figure 9. Pictorial view of the PLA deli containers exposed for 30 days under ambient conditions

Physical Properties

Molecular weight. The molecular weight was monitored using standard GPC technique as previously described. The molecular weight degradation gives information about 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.

Initially, random non-enzymatic chain scission of the ester groups leads to a reduction in molecular weight and is accelerated by acids or bases, affected by temperature and moisture levels [13]. Embrittlement of polymers occurs with reduction of molecular weight to around 50,000 Daltons. The PLA degradation is driven by the hydrolysis and cleavage of the ester linkages in the polymer backbone, autocatalyzed by the carboxylic acid end groups. This part of process follows a first order kinetics.

Secondly, low molecular weight PLA ($M_n < 10,000$) or low molecular weight oligomers are metabolized by microorganisms to yield carbon dioxide and water. In general, high temperature and humidity (50°C to 60°C , and $\text{RH} > 60\%$) will cause PLA to degrade rapidly [36]. Mainly, the

polymer degradation rate is determined by the nature of the functional group and the polymer reactivity with water and catalysts. Although the degradation process in PLA is a simple hydrolysis, any factor which affects the reactivity and the accessibility such as particle size and shape, temperature, moisture, crystallinity, isomer percentage, residual lactic acid concentration, molecular weight, molecular weight distribution, water diffusion, and metal impurities from the catalyst, will affect the PLA degradation rate [13, 37, 38].

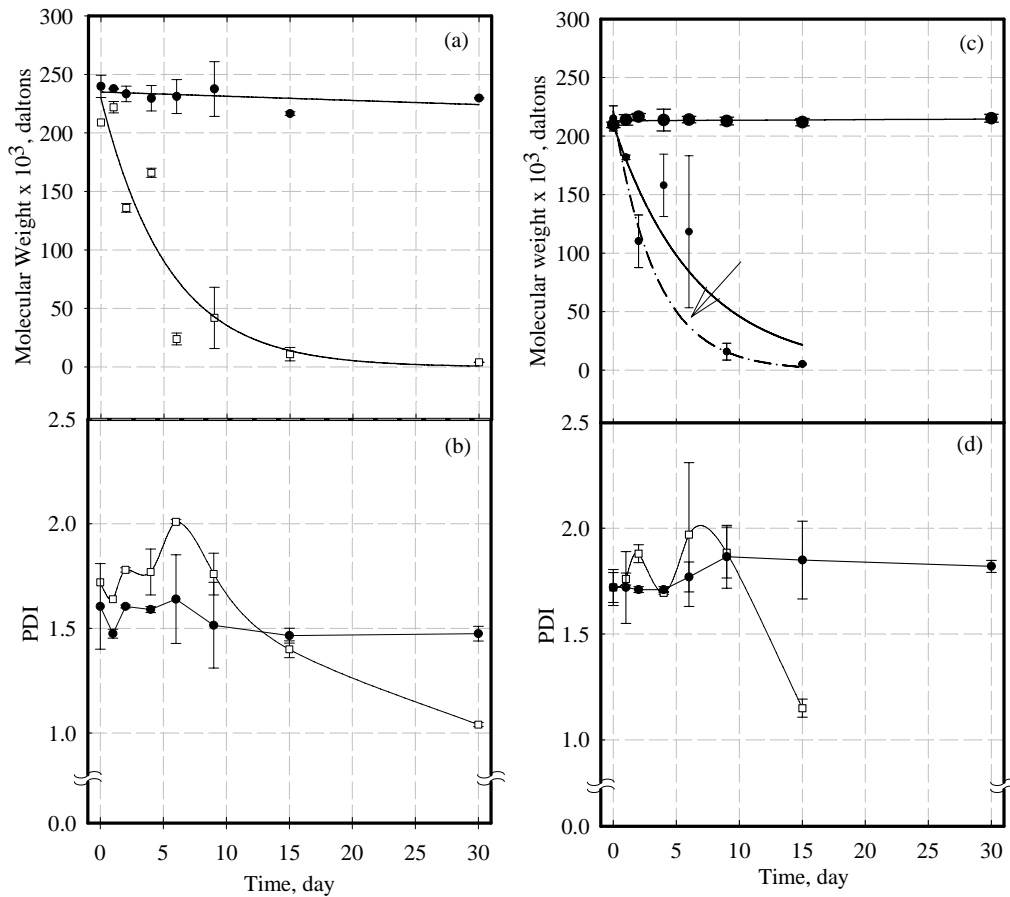


Figure 10. Variation of the molecular weight and polydispersity index (PDI) as a function of time for a) and b) bottles exposed to composting (□) and ambient (●) conditions for 30 days and c) and d) deli containers exposed to composting (□) and ambient (●) conditions for 30 days. (---) dot line in Figure 10 c indicates the fitting of equation 2 without considering the M_w values at day 4 and 6)

The variation in molecular weight of bottles and deli containers is shown in Figure 10. PLA bottles and deli containers exposed to ambient conditions for 30 day do not show significant M_w variation as a function of time at $\alpha = 0.05$ level ($P > 0.01$) (Figure 10-a & c). Also, the variation of PDI for the bottles and deli containers were not statistically significant at $\alpha = 0.05$ level ($P > 0.01$ for the bottle and deli containers). Kai-Lai and Pometto, (1999) showed that the exposure of poly(lactide) films to ultraviolet light (UV) for 8 weeks enhances the degradation rate and the deterioration of the mechanical properties of these polymers [39]. In this study, the bottles and deli containers were exposed for 4 weeks to ambient conditions and compare with the time that took the packages to degrade in compost environment. Figures 10 (a) and (c) show the molecular weight change of the packages that were exposed to compost conditions for

30 days. Figure 10 (a) shows that the molecular weight variation of the PLA bottles at the first 15 days of composting is much lower than the PLA deli containers as shown in figure 10 (c). Major fragmentation of the bottles was observed at day 9. At day 30 it was not possible to locate any residues of deli containers. The PLA bottles (figure 10 a) show a small increase in the molecular weight after being exposed to the compost pile for 1 day. This increase in molecular weight 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 [40]. The higher M_w values obtained at day 4 and 6 for the deli containers could be mainly attributed to the temperature variations on those days in the position that the deli containers were located, and to local variation in the compost pile. 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 [32].

Figures 10 (b) and (d) show the variation in PDI for both bottles and deli containers subjected to composting and ambient conditions. Longer PLA chains are more susceptible to cleavage than the shorter ones as the hydrolysis of PLA occurs randomly. Hence, an initial rise in PDI for both packages subjected to composting conditions was observed on day 4 which could be correlated to the fragmentation process, which produces decomposition of the macromolecules into shorter oligomer chains and monomers. Later narrowing of the molecular weight distribution was observed with decrease in PDI until the complete degradation. At this point, only oligomers of the PLA chains are present. In case of both packages subjected to ambient conditions, no significant changes of M_w at $\alpha = 0.05$ level and $P > 0.01$ were observed.

Glass transition and melting temperature: The glass transition temperature and melting temperature was analyzed using differential scanning calorimetry as mentioned above. A decrease of around 30°C was observed in bottles on 30th day whereas it was 8°C for deli containers on 15th day. 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 observed during the degradation process of the crystalline PLA polymers in aqueous media by other researches [41]. In this work, the initial crystallinity of the bottles ($\chi_c = 12.2 \pm 1.4$) increased to values of around 16% until the last degradation day and in case of deli containers $\chi_c = 1.40 \pm 0.3$ it was observed to increase to 27. 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 recrystallization.

The variation in T_g and T_m for both packages subjected to composting and ambient environments are shown in Figure 12. Figures 12 (a) and (b) show the T_g and T_m variations for bottles respectively and Figures 12 (c) and (d) shows T_g and T_m variations for deli containers, respectively. A slight increase in T_g for both bottles and deli containers was observed for the samples exposed to composting which can be correlated to the increase in molecular weight at the early stages due to recombination reactions. A linear degradation trend in case of PLA packages subjected to composting conditions was observed.

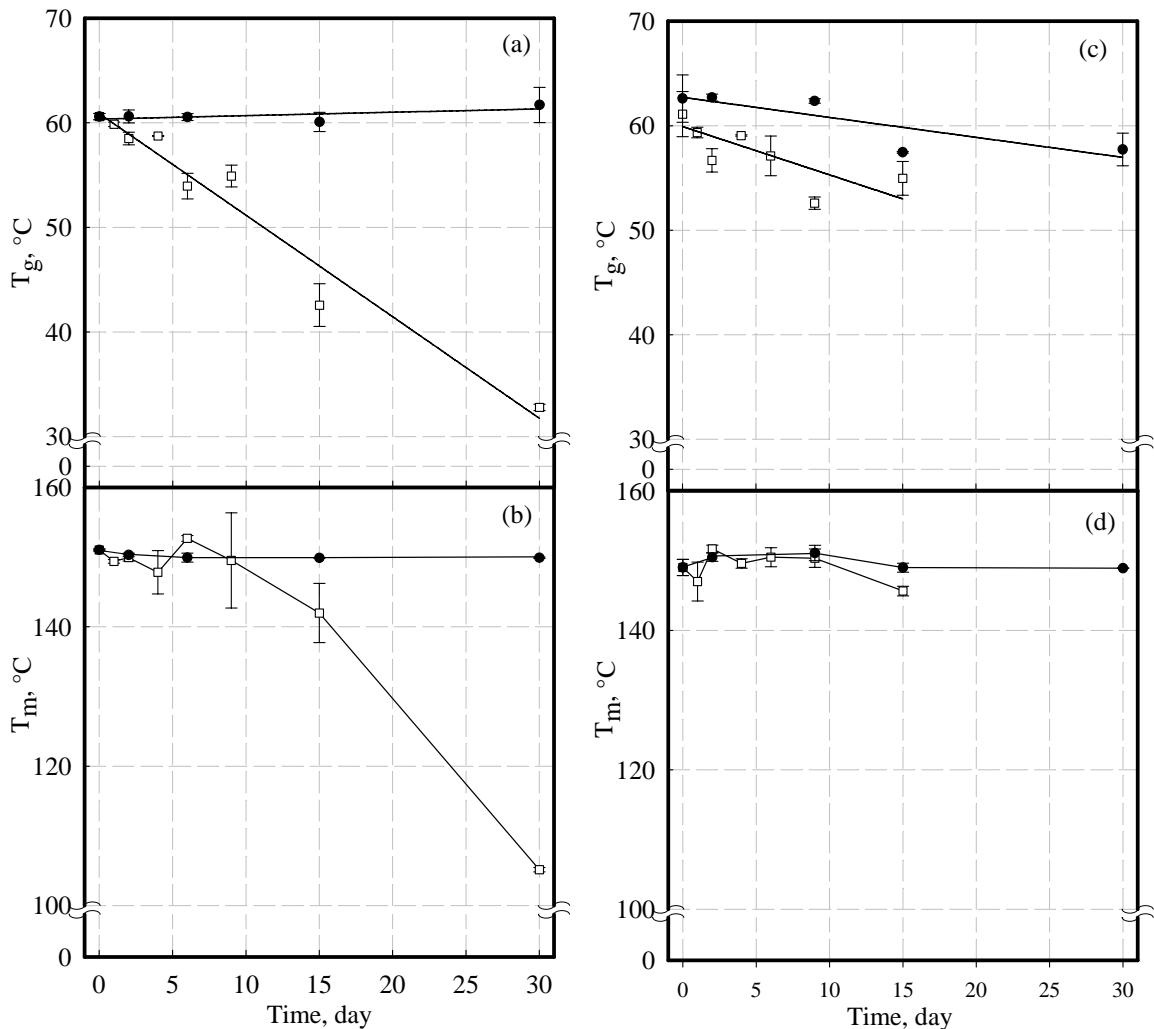


Figure 11. Variation of the glass transition and melting temperature as a function of time for a) and b) bottles exposed to composting (□) and ambient (●) conditions for 30 days and (c) and (d) deli containers exposed to composting (□) and ambient (●) conditions for 30 days

Decomposition temperature: Decomposition temperature of PLA packages was analyzed using TGA. A plot obtained from TGA showing variation of weight as a function of temperature and variation of derivative weight as function of temperature for bottles are shown in Figure 12 (a) and (b) and that for deli containers in Figure 12 (c) and (d). It can be seen that a major variation was observed on 15th and 30th day for the bottles and on 15th day for deli containers subjected to composting conditions. Also a major variation in molecular weight of bottles was observed on 15 and 30 day which was from around 11, 000 to 4, 000 Daltons and can be correlated to the decomposition temperature discussed above.

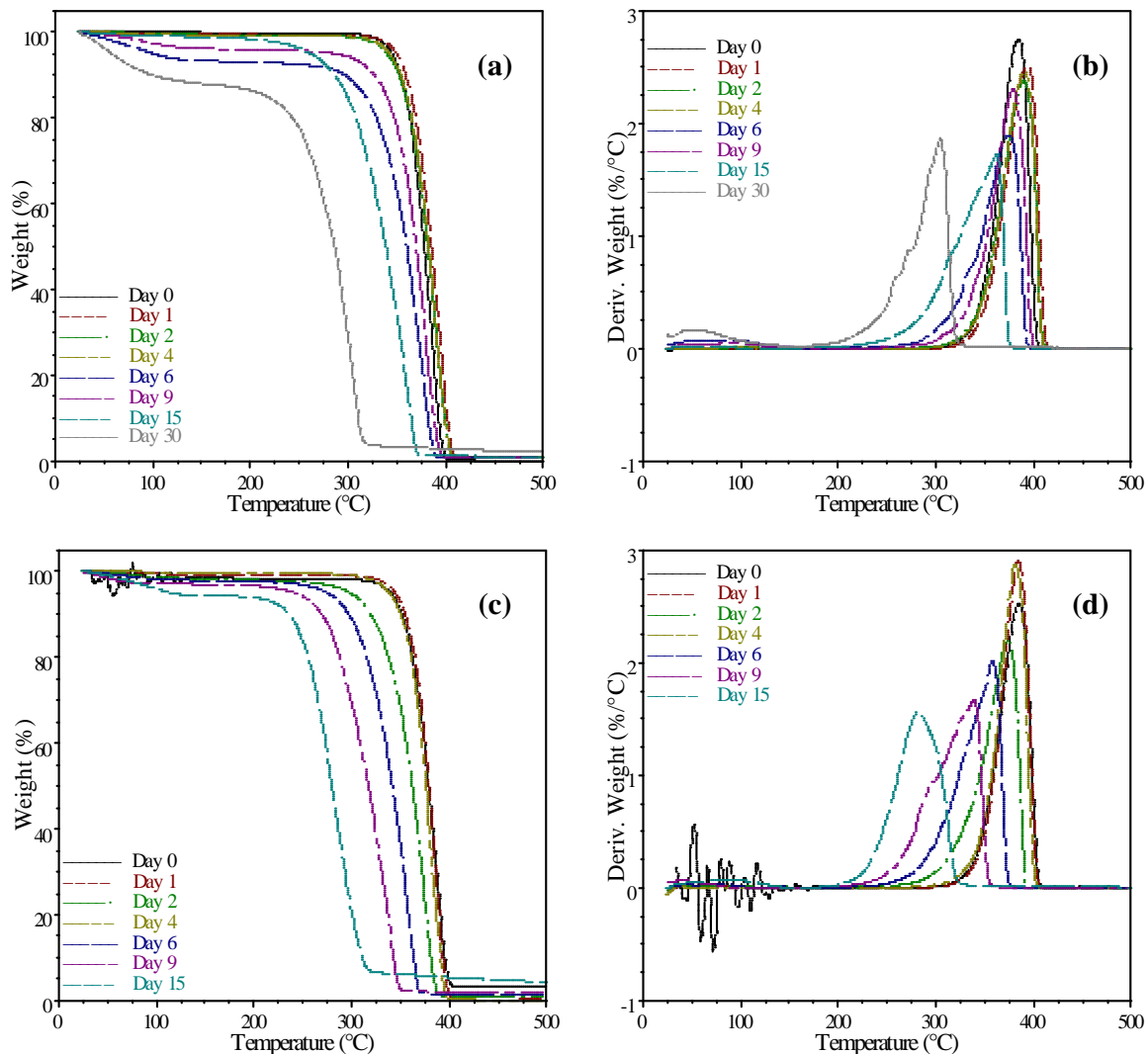


Figure 12. a) Weight percent reduction vs temperature, b) first derivative vs temperature of PLA bottles and c) weight percent reduction vs temperature, d) first derivative weight vs temperature of PLA deli containers exposed to composting conditions for 30 days

The variation of T_D as a function of time for both package and for both environments is shown in Figure 13 (a) and (b). A linear variation was observed for packages subjected to composting conditions whereas no significant changes were observed for the packages subjected to ambient conditions at $\alpha = 0.05$ level ($P > 0.01$), mainly due to the small number of values.

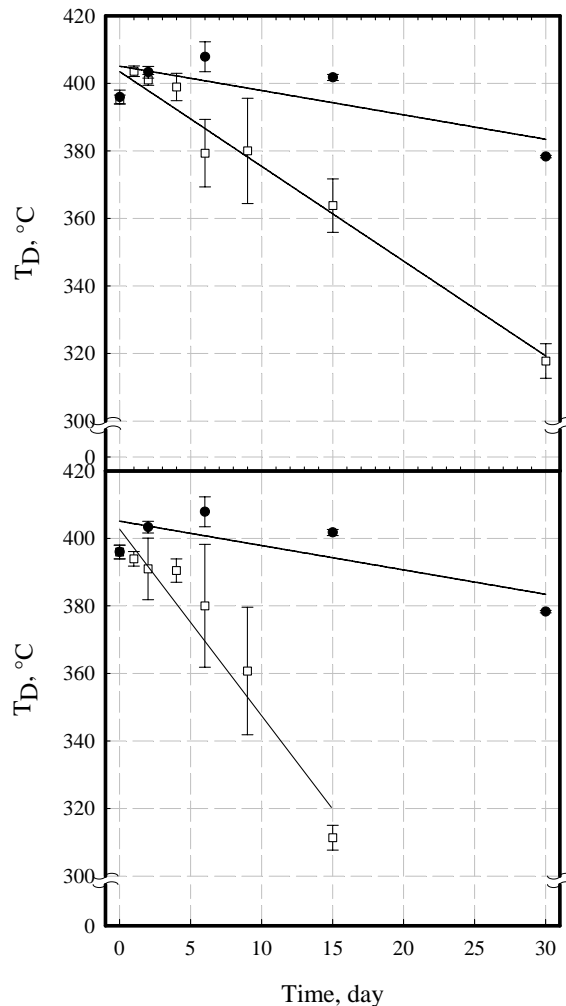


Figure 13. Variation in decomposition temperature as a function of time for a) bottles exposed to composting (□) and ambient (●) conditions for 30 days and (b) deli containers exposed to composting (□) and ambient (●) conditions for 30 days

A graphical decrease in T_D was observed in case of both packages subjected to ambient conditions. Bottle's T_D decreased from 395°C to 378°C, however no statistical significance was observed at $\alpha = 0.05$ level ($P=0.0130$). Similarly the decrease in case of deli containers was from 396°C to 378°C and no statistical significance was observed at $\alpha = 0.05$ level ($P= 0.0118$). In this case, however the decrease and linearity was observed but no statistical significance could be due to lesser number of samples analyzed.

In summary, PLA polymers break down due to the absorption of water resulting in the hydrolysis of the ester linkages. The rate of degradation is highly affected due to the temperature, moisture and pH conditions of the compost. Considering the PLA package, the rate of degradation was observed to be affected by the initial crystallinity and the percentage L-lactide content. The 94% L-lactide content packages disappear fast from the compost than the 96% L-lactide packages. Hence initial crystallinity and L-lactide content of the PLA packages should be considered for estimation of required time for decomposition in composting environment. Similar compost studies, but with PLA samples and not complete packages, were carried out by Weber [42] 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. Some comparisons between laboratory and field exposure degradation have been carried out by Pometto and collaborators [36, 39, 43-45]. They exposed PLA films in banana fields in Costa Rica, and found that these PLA plastic films lost their mechanical properties faster than during exposure in simulated conditions in the laboratory [44]. They also found that degradation of PLA is enhanced by an increase in temperature and relative humidity [36]. Most of the studies and research carried out before was based on assessing degradability of plastic samples and not complete packages. Hence, the present work assessed and addressed the degradation time, physical properties and comparison of two commercially available PLA packages and gives information on the compostability and the reduction of the physical properties under real compost as well as ambient exposure conditions. This work found that the degradation time of PLA deli containers in a commercial facility was not more than 30 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 ($T > 50^{\circ}\text{C}$). Further research is being carried out to simulate the real degradation process in simulated or controlled conditions in order to establish a standard laboratory scale test for evaluation of packages under real compost conditions. Furthermore, more research is necessary to find methods and techniques that can assess the degradability of biodegradable packages under real composting conditions before they are introduced and degraded in commercial composting operations.

4. SUMMARY

Two PLA packages, a bottle and a deli container, were used to determine the degradation process under ambient exposure and compost conditions. A novel method was used to identify and keep track of the degradation of the PLA packages in a real compost facility. The degradation of the PLA containers was monitored by visual inspection, GPC, DSC, and TGA. PLA deli containers degraded before 30 days under composting conditions ($T > 60^{\circ}\text{C}$, $\text{RH} > 65\%$, $\text{pH} \sim 7.5$). First order degradation kinetics was observed for the bottles. A T_g reduction of $1^{\circ}\text{C}/\text{day}$ was found for PLA bottles with 96%L-lactide. 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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