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BIODEGRADATION OF COMMERCIALLY AVAILABLE BIODEGRADABLE PACKAGES IN REAL AND SIMULATED COMPOSTING CONDITIONS

presented by

GAURAV KALE

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BIODEGRADATION OF COMMERCIALLY AVAILABLE BIODEGRADABLE PACKAGES IN REAL AND SIMULATED COMPOSTING CONDITIONS

Ву

Gaurav Kale

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

School of Packaging

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ABSTRACT

BIODEGRADATION OF COMMERCIALLY AVAILABLE BIODEGRADABLE PACKAGES IN REAL AND SIMULATED COMPOSTING CONDITIONS

By

Gaurav Kale

There is currently incentive and growth for the adoption of biodegradable polymers for packaging applications. Standards developed so far address the biodegradability of these polymers in simulated controlled composting conditions but they are limited to the assessment of plastic material and not whole package. As a result, it is necessary to assess biodegradability performance of biodegradable packages. The first part of this thesis presents a review of: 1) the current standards and methodologies used for evaluating biodegradability; 2) the commonly employed composting processes and the actual biodegradation environments; and 3) the certifications process used for biodegradable plastics. In the second part, biodegradation studies of polylactide (PLA) based packages were carried out in real composting and ambient exposure conditions using a novel technique. In the third part, biodegradation of PLA bottles was investigated in simulated composting conditions as prescribed by ASTM D5338, ISO 14855-1 (titration method) and a new method based on ISO 14855-2 (gravimetric method). Finally, in the fourth part, the biodegradation of poly(butylene adipate terephthalate) films and its blends was carried out in real composting conditions. PLA packages disintegrated very fast in real composting conditions based on visual inspection and variation in physical properties. The comparison of both simulated laboratory methods and real composting conditions for PLA bottles showed that much variability occur in biodegradation in real composting conditions.

DEDICATION

To my Parents and their more than 20 years of dedicated service in Packaging

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CHAPTER 1 - INTRODUCTION

There has been a recent growth in adoption of biodegradable polymers for packaging applications due to concerns of growth in municipal solid waste (MSW) and the contribution of polymeric packaging waste in it. For example, in 2005 in United States; 6.55 million tons of plastics packaging waste was generated, out of which 0.58 million tons was recovered through recycling [1]. The common recycled products were carbonated beverage bottles, milk bottles and water bottles which has a good waste collection infrastructure in many states in USA; due to the bottle bill first introduced in Vermont in 1953. The rest of plastic packaging material went to landfill and could not be recycled mainly because of the contamination caused due to the food and other biological substances in it.

Also recently sustainable packaging systems has gained lot of attention and according to Sustainable Packaging Coalition (USA); one of the criteria of definition of sustainable packaging is that the "packaging should be sourced, manufactured, transported and recycled using a renewable energy". Currently many commercially available biodegradable polymers like polylactide (PLA), polyhydroxybutyrate (PHB), etc. come from renewable sources and the consumption of same for packaging applications can go up due to the packaging sustainability initiatives. Chemical nature of those renewable biodegradable polymeric materials are discussed in detail in the literature review.

As those new biodegradable polymers are emerging for packaging applications, it is necessary to address its biodegradability, and avail its unique functionality to reduce the waste generation problem. Standards are developed by ASTM and ISO (International

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Standards Organization) for evaluation of biodegradability of plastic materials in simulated controlled composting conditions. Those standards, their scope and comparison are also discussed in detail in the literature review. It also become essential to study various systems where those biodegradable polymeric packages could be successfully biodegraded, hence commonly used composting processes and materials are discussed in literature review.

As mentioned above, the standards provide guidelines for testing plastic materials for biodegradability in simulated externally controlled composting conditions. There is a need to develop a testing procedure which can test a complete biodegradable package and report its biodegradability which can be useful and applied in successful biodegradation/composting operations. At the same time, it is also necessary to address the degradation performance of those packages in ambient conditions as opposed to composting conditions (where microorganisms are involved). Chapter 3 and 4 discusses one such procedure of testing biodegradable packages based on polylactide (PLA) in real composting conditions and ambient conditions.

Although the simulated composting conditions are operated with externally controlled parameters, but are difficult to resemble the real composting conditions due to the variability's associated with it. Those variability's need to be investigated and proper comparison report of biodegradation performance in both real and simulated composting conditions is necessary. A PLA based bottle was used for this comparison and is discussed in chapter 5.

Polymeric flexible packaging materials such as LDPE are used in variety of packaging applications in food and consumer goods. At the end of its life cycle, those

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flexible packages end up in landfill as no known waste management initiatives are deployed in this case. Also majority of flexible packaging materials are blend or laminations used for property enhancement of package, hence recycling of those packages becomes difficult due to its non-uniformity. Some biodegradable resins such as Ecoflex[®] commercialized by BASF has desirable properties needed for some flexible packaging applications. Biodegradability of such materials was carried out in real composting conditions and discussed in detail in chapter 6.

Chapter 7 discusses the future recommendations derived based the results obtained in this study.

In short, the main objectives of this study were:

- 1. To review and compare the current methodologies and standards associated with biodegradable testing of plastic materials; and its scope in regards with the packaging.
- 2. To develop a method of testing whole packages and polymeric films in real composting conditions; which can give a correct representation of its biodegradation performance.
- To evaluate biodegradation of biodegradable polymeric package on basis of existing standards and standards under development; and comparison of its results with real composting conditions.

Rł 1.

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CHAPTER TWO

Gaurav Kale, Thitisilp Kijchavengkul, Rafael Auras, Maria Rubino, Susan E. Selke, Sher Paul Singh. (2006). An overview of compostability of bioplastic packaging materials; <u>Macromolecular Bioscience</u>, 7 (3): 255-277

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CHAPTER 2 - LITERATURE REVIEW

SUMMARY

Annually, packaging waste accounts for 78.81 million tons (31.6% of the total municipal solid waste, MSW) in 2003 in the USA, 56.3 million tons (25% of MSW) in 2005 in Europe, and 3.3 million tons in 2004 (10% of MSW) in Australia. Currently, in the USA the dominant method of packaging waste disposal is landfill, followed by recycling, incineration, and composting. Since landfill occupies valuable space and results in generation of greenhouse gases and contaminants, recovery methods such as reuse, recycling or composting are encouraged as a way of reducing packaging waste disposal. Most of the common materials used in packaging (i.e., steel, aluminum, glass, paper and paperboard, plastics and wood) can be efficiently recovered by recycling; however, if packaging materials are soiled with foods or other biological substances, physical recycling of these materials may be impractical. Therefore, composting of some of these packaging materials is a promising way to reduce MSW. As biopolymers are developed and increasingly used in applications such as food, pharmaceutical, and consumer goods packaging, composting could become one of the prevailing methods for disposal of packaging waste provided that industry, governments, and consumers encourage and embrace this alternative.

The main objective of this article is to provide an overview of the current situation of packaging compostability, to describe the main mechanisms that make a biopolymer compostable, to delineate the main methods to compost these biomaterials, and to explain the main standards for assessing compostability, and the current status of biomaterial labeling.

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Biopolymers such as poly(lactide) and poly(hydroxybutyrate) are increasingly becoming available for use in food, medical and consumer goods packaging applications. The main claims of these new biomaterials are that they are obtained from renewable resources and that they can be biodegraded in biological environments such as soil and compost. Although recycling could be energetically more favorable than composting for these materials, it may not be practical due to excessive sorting and cleaning requirements. Therefore, the main focus is to dispose them by composting. So far, there is no formal agreement between companies, governments and consumers as to how this packaging composting will take place; therefore, the main drivers for their use have been green marketing and pseudo environmental consciousness related to high fuel prices. Packaging compostability could be an alternative for disposal of biobased materials as long as society as a whole is willing to formally address the challenge to clearly understand the cradle-to-grave life of a compostable package, and to include these new compostable polymers in food, manure, or yard waste composting facilities.

2.1 INTRODUCTION

Packaging waste is a major contributor in generation of municipal solid waste (MSW). In the USA, containers and packaging waste accounted for 74.81 million tons (31.6% of the total MSW) in 2003 [1]; 56.3 million tons (25% of the total MSW) generated in Europe [2] in 2005; and 3.3 million tons (10% of the total MSW) in Australia [3] in 2004. Currently in the USA, the most dominant method of packaging waste disposal is landfill, followed by recycling, incineration and composting. However, landfilling results in generation of greenhouse gases and takes up or may contaminate

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land that composti materials and wood can also compostir Сс soil-like s microorga actinomyc CO_2 , and jcarbon, ni and nitroge reproduction [4]. A com a curing p ^{oxy}gen is decreases does not s nutrients a been conve ^{oxy}gen; if digestion is land that could be used in the future. Hence, recovery methods like recycling or composting could be more desirable ways of packaging waste disposal. The common materials used in packaging are steel, aluminum, glass, paper and paperboard, plastics and wood, all of which could be efficiently recovered through recycling. Paper and wood can also be recovered through composting; biodegradable polymers also provide composting as a waste disposal option.

Composting is a natural process by which organic material is decomposed into a soil-like substance, called humus, a soil conditioner. Decomposition is mainly done by microorganisms (mesophilic and thermophilic), including bacteria, fungi and actinomycetes. These microorganisms use organic matter as their food source, generate CO_2 , and produce humus as an end product. This natural process requires availability of carbon, nitrogen, water and oxygen. Microorganisms use carbon as a source of energy and nitrogen for building cell structures. A 30:1 carbon to nitrogen ratio (C:N) is ideal for reproduction of thermophilic microorganisms, and makes the composting process faster [4]. A composting process goes through two main stages, an active composting stage and a curing period. In the first stage, the temperature rises and remains elevated, provided oxygen is available, resulting in strong microbial activity. In the later stage, temperature decreases but the materials continue to compost, at a slower rate. The compost process does not stop at a particular point; rather it continues slowly until the last remaining nutrients are consumed by the remaining microorganisms and almost all the carbon has been converted to carbon dioxide [5]. Aerobic composting takes place in the presence of oxygen; if oxygen is absent then the process changes to anaerobic digestion. Anaerobic digestion is also a naturally occurring process of decomposition and decay, by which

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organic matter breaks down into simple chemical components, producing biogas and digestate (a relatively stable soil residue similar to compost). Biogas is a mixture of gases, mainly methane, which can be used for production of heat and electricity, and carbon dioxide. The digestate can be used as a soil amendment, much like humus, for applications like farming or landscaping. The quality of compost produced in aerobic conditions is different from that produced in anaerobic digestion conditions, as different microorganisms are active [5].

The majority of packaging materials used for food and medical packaging applications are disposed by landfill, in part because of contaminants that are difficult to separate and may produce complications in recycling. In 2003, in the USA, 11.9 million tons of plastics packaging was generated, out of which only 1.06 million tons (8.9%) was recovered through recycling. Composting provides a viable option for recovering waste packages by returning them to nature.

According to ASTM, a biodegradable plastic is a plastic which degrades due to the action of naturally occurring microorganisms such as bacteria, fungi and algae. There is a difference between a biodegradable and a compostable plastic. 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. Therefore all compostable plastics are biodegradable, but the reverse is not true.

Biodegradation of plastics depends on both the environment in which they are placed and the chemical nature of the polymer. Biodegradation is an enzymatic reaction; hence it is very specific to the chemical structures and bonds of the polymer. There are

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different mechanisms of polymer biodegradation. One common mechanism is hydrolysis, in which random non-enzymatic chain scission of ester groups leads to reduction in molecular weight. The hydrolysis process is affected by the rate of diffusion of water through the polymer. As mentioned before, the biodegradation of plastics depends on both environmental factors (i.e., temperature, moisture, oxygen, pH) and the chemical structure of the polymer. Biodegradable polymers usually contain ester, amide or carbonate hydrolyzable bonds in the polymer backbone. The presence of these hydrolyzable functional groups increases the susceptibility to biodegradation. Other factors that affect biodegradability are crystallinity, molecular weight, and, in the case of copolymers, the copolymer composition [6].

Standards have been developed by ASTM and ISO (International Standards Organization) for assessment of the biodegradability of polymers in different environments such as composting, anaerobic digestion, and wastewater treatment. According to ASTM standard D6400 [7], a product is compostable if it passes the tests of disintegration, biodegradation, and terrestrial and aquatic safety in controlled laboratory scale composting. Similarly, there is a standard developed by ISO (EN 13432) [8] specifically for packaging, which assesses packaging compostability based on characterization, biodegradation, disintegration, and quality of compost or ecotoxicity. Characterization of packaging includes analysis of the composition of package materials, heavy metals, organic carbon content, total dry solids and volatile content. Detailed procedures and their harmony with other standards are discussed later.

A number of certification systems which provide compostable packaging labels have been established worldwide for certification of compostable plastics. Some of these

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labels are based on standards developed by ASTM, ISO, DIN (Deutsches Institut für Normung) and JIS (Japanese Industrial Standards). These certification systems include DIN CERTCO based on DIN V54900, OK Compost by AIB Vincotte (Begium) based on EN 13432[8], Compostable by the U.S. Composting Council based on ASTM D6400 [7], and GreenPla certification by the Biodegradable Plastics Society (Japan) based on JIS K6953, to mention a few. JIS K6953 is reported by the Japanese Industrial Standards Committee to be identical to ISO 14855 [9].

Currently, biodegradable bags that are certified by the U.S. Composting Council as compostable are being used in San Francisco for transportation of compostable materials to the composting facility and composted along with other materials [10]. According to the American Forest & Paper Association (AF&PA) in America, about 6.5 million tons of postconsumer paper and paper products are produced annually that may be better suited for composting than recycling. This includes paper yard bags, waxed corrugated containers, milk cartons, paper plates, cups, napkins, and towels. In 1999, 300,000 to 325,000 tons of postconsumer paper was composted [11]. In the case of plastics, non-biodegradable plastics still dominate packaging applications and hence eliminate the option of composting.

Compostable polymers are being promoted as environmentally beneficial, especially if they can be derived from renewable resources and recovered through organic recycling. To evaluate the environmental performance of biobased products, a standard practice has been developed and presented in ASTM D7075 [12] and ISO 14000 using life cycle assessment (LCA). LCA is a cradle-to-grave analysis tool developed for assessment of the total environmental performance of a product (or process) and the

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system used for manufacturing, use and disposal (or recovery) of that product. Currently, LCA studies of biobased polymers generally show reduced environmental impact and energy use when compared to petroleum based polymers. For example, PLA derived from starch utilizes 0 GJ/ton of feedstock energy and 53 GJ/ton of processing energy, as compared to PET which utilizes 39 GJ/ton of feedstock energy and 38 GJ/ton of processing energy [13]. Furthermore, if PLA is disposed through composting and the compost is used in agriculture, significant emission and energy credits can accrue due to the value of the compost in sustainable agriculture practices, which can improve even further the sustainability of this biobased polymer.

The objective of this paper is to explore the current status of compostability of bioplastic packaging based on compostability mechanisms, the current status of composting, standards relevant to the compostability of packaging materials, and life cycle analysis of the performance of biodegradable packages based on composting as a disposal option.

2.2 COMPOSTABLE PACKAGES

Packaging materials, as previously mentioned, can be divided into 4 groups: paper/paperboard, plastic, metal, and glass packages. Only paper/paperboard, and some plastic packages are biodegradable and, hence, compostable. ASTM defines a compostable plastic as a plastic that undergoes degradation by biological processes during composting at a rate consistent with other known compostable materials [7]. Therefore, only materials that biodegrade in composting environments and match the composting period of known compostable materials can be considered as "compostable." Not all biodegradable materials are compostable [7].

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2.2.1 COMPOSTABLE MATERIALS

There are two main factors that make a material compostable: the material itself and the microorganisms in the compost. The material must be biodegradable, such as paper/paperboard and biodegradable polymers, which can be consumed by microorganisms as food sources. A compost pile is a great source of microbial activity, because it has a high moisture content and temperature, so it is a suitable environment for a variety of microbes, such as bacteria and fungi, to live and reproduce, providing a tremendous amount and variety of organisms able to attack and digest compostable materials. Bacteria can be either aerobic or anaerobic, while fungi are strictly aerobic. In both cases, the degradative reaction proceeds via production of enzymes that break down organic substrates providing nutrients [14]. The enzymatic mechanisms can be divided into 2 categories: enzymatic oxidation (by aerobic microorganisms only), and enzymatic hydrolysis (by either aerobic or anaerobic microbes). The biodegradation mechanisms of the main packaging materials differ. Therefore, in this overview, the degradation mechanisms are described by material, and it will mainly concentrate on the degradation of bioplastics.

2.2.2 BIODEGRADABLE POLYMERS AND DEGRADATION MECHANISMS

Since biodegradation is an enzymatic reaction, it is very specific to chemical bonds and structures of particular functional groups. Microorganisms can attack only specific functional groups at specific sites, and the polymer chain also has to be conformationally flexible enough to fit into the active site of the enzyme. The meaning of conformational flexibility is defined later. There are various types of biodegradable

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polymers, with differing degradation mechanisms, so we will separately discuss them: (1) natural polymers, (2) carbon chain polymers, and (3) hetero chain polymers [14].

2.2.2.1 Natural Polymers

As mentioned earlier, microorganisms can directly consume natural polymers like starch, cellulose, and polymers based on starch, since enzymatic reactions can reduce their molecular weight in extracellular environments - outside the microorganisms' cells. The polymer chains are enzymatically cleaved, and the portions that are small enough are transferred into the cells and consumed. The biodegradation rate of these polymers can be accelerated by hydrolysis involving random chain scission, which results in rapid molecular weight reduction. The resulting smaller molecules are much more susceptible to enzymatic attack, making the polymer degrade much faster.

Another of is type natural polymer "bacterial polyester", poly(hydroxyalkanoates), or PHA. These natural polyesters are produced by bacteria as "intercellular reserve materials" when they are fed carbon sources such as sugar or lipids but nutrients are restricted. The polymers are then extracted from the bacterial cells [14]. PHAs are aliphatic polyesters; the most common are $poly(\beta-hydroxybutyrate)$ or PHB, and poly(hydroxybutyrate-valerate) or PHBV, see Figure 2.1. The degradation mechanism starts with rapid enzymatic hydrolysis to cleave the ester bonds present in the polymer structure via extracellular depolymerases, such as those produced from Psuedomonas lemoignei and Alcalignes faecalis [15].

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2.2.2.2 Carbon Chain Polymers

Vinyl polymers, such as poly(ethylene), poly(propylene), and poly(vinyl chloride), with carbon-only backbones, are normally not susceptible to hydrolysis or to biodegradation. An exception is poly(vinyl alcohol) or PVOH, which is biodegradable because of its high hydrolizability. The enzymatic oxidation of hydroxyl groups (-OH) forms carbonyl groups (C=O) in the polymer backbone, and hydrolysis of two carbonyl groups (-CO-CH₂-CO-) causes polymer chain cleavage leading to a decrease in molecular weight [14, 16]. Microbes will then consume those low molecular weight portions.

2.2.2.3 Hetero Chain Polymers

Hetero chain polymers are polymers that have atoms other than carbon, such as oxygen and nitrogen, in their backbones. Those atoms make the polymers susceptible to hydrolysis (i.e., in which random non-enzymatic chain scission of ester groups leads to reduction in molecular weight), and therefore can make them susceptible to biodegradation. Most synthetic hetero chain polymers, such as polyesters, nylons, polycarbonates, etc., do not biodegrade to any significant extent.

Currently, the most common hetero chain biodegradable polymers are poly(lactide) (PLA), poly(glycolic acid) (PGA), and poly(ϵ -caprolactone) (PCL). The bacterial polyesters such as Polyhydroxyalkanoate (PHA) also fit in this category. The higher the rate of hydrolysis is, the more available sites there are for microbes to attack, and hence the faster is the biodegradation. Polymer hydrolysis is controlled in part by the rate of diffusion of water in the amorphous regions of the polymer [6]. Water diffusion

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through crystalline regions is negligible. Some plastics, such as PLA, will not biodegrade without prior hydrolysis.

The biodegradable polymers that have a promising future for packaging applications are mainly alighatic polyesters, such as PLA, PCL, and PHA [14, 15] (see Figure 2.1), and also include poly(tetramethylene adipate/terephthalate) (PTMAT), poly(butylene succinate) (PBS), poly(butylene succinate adipate) (PBSA), and some polyesteramides, since their properties are comparable to petroleum-based polymers commonly used in the packaging industry. For example, PHBV is hydrophobic and also provides excellent gas barrier [14, 15]. Temperature stability and processability of PLA are comparable to those of poly(styrene); oil and grease resistance and flavor barrier properties are comparable to PET; and sealing temperature is lower than poly(ethylene) and poly(propylene) [17, 18]. Almost all of these polymers contain in the polymer backbone at least one of the following hydrolyzable bonds: ether, ester, amide or carbonate [6]. While C-C linkages increase stability, the presence of hydrolyzable functional groups in the polymer backbone dramatically increases the susceptibility to biodegradation [19] (see Figure 2.2), since it not only increases the vulnerable sites for hydrolysis but also the polymer flexibility [20], so that the polymer chains can more easily arrange themselves to fit into the active sites of the enzymes.

The performance of hydrolyzable biodegradable polymers is primarily dependent on their erosion mechanisms, especially if they are intended for use in medical applications, such as drug delivery agents, or in agricultural applications, such as nutrient releasing agents in fertilizer [6].

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Figure 2.2 Hydrolyzable functional group commonly found in biodegradable polymers

There are two modes of erosion: surface erosion and bulk erosion. Enzymatic degradation caused by microbes occurs only at the polymer surface, while non-enzymatic hydrolysis can occur throughout the polymer's bulk because water can diffuse through the amorphous regions of the polymer. Both reactions usually happen at the same time, and compete with each other. If water-induced hydrolysis is faster than the enzymatic degradation, then the polymer tends to degrade throughout its cross section, in "bulk erosion" [6, 17, 21]. On the other hand, if the enzymatic degradation is faster, then "surface erosion" predominates [6, 17]. These erosion mechanisms play a very important role in determining the applications of a biopolymer. For instance, if a polymer is used as a drug delivery agent and the active ingredient is located in the polymer surface,

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polymers that mostly undergo surface erosion will release the compound faster; on the other hand for a slow release drug, a polymer that undergoes bulk erosion will be more suitable so the active ingredient contained in the polymer matrix can be released over a longer period of time [6].

2.2.3 FACTORS AFFECTING THE RATE OF BIODEGRADATION

Factors affecting biodegradation rates can be categorized as: (1) the exposure conditions, and (2) the polymer itself [20].

2.2.3.1 Exposure conditions

Water or moisture

Water or moisture can affect the biodegradation of polymers in two ways. First, water is needed for microorganisms to grow and reproduce. Therefore, when moisture is plentiful, there should be more microbial activity, and polymers should degrade faster. Second, since hydrolysis plays a fundamental role in biodegradation for some polymers, in moisture-rich environments hydrolysis reactions should increase, producing more chain scission reactions and increasing the available sites for microorganisms to attack. Kai-Lai et al [22] found that degradation rates increased tremendously as the relative humidity of the exposure conditions increased. They determined that the molecular weight loss of PLA films exposed to 10%, 50%, and 100% RH in an environmental chamber at 55°C was 3,972, 61,947, and 121,836 Daltons per week, respectively. Therefore, it can be expected that polymers will biodegrade faster in moisture-rich environments than in dry conditions.

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For hydrolyzable polymers, the rate of hydrolysis reactions can also be altered by pH, since reactions can be either acid or base catalyzed. For instance, it was found that the hydrolysis rate of PLA capsules was slowest at a pH of 5.0 and increased in more acidic and more alkaline solutions [17, 21]. Degradation products, such as water-soluble lactic acid from PLA, can change the pH of the exposure environment. Changes in pH affect not only the rate of hydrolysis, but also the growth of microorganisms.

Temperature

Temperature is a significant factor in controlling polymer biodegradation since both hydrolysis reaction rates and microbial activity increase as temperature increases; however, if temperatures are too high, microbial activity decreases or even stops. Kai-Lai et al [22, 23] reported that the average degradation rate of PLA films at 25, 40, and 55°C and 100% RH in an environmental chamber was 4,691, 40,634, and 91,892 Daltons per week, respectively. Therefore, moderately increasing the exposure temperatures enhances the degradation rate of PLA, at least in part due to increasing the rate of hydrolysis. A study done by Cargill Dow LLC also showed that the hydrolysis rate of PLA increased dramatically above the glass transition temperature (T_g) [21]. Further, different microorganisms can grow and reproduce at their best at different temperatures. In general, the rate of biodegradation increases with temperature, as long as it is not high enough to kill the microorganisms.

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Aerobic or anaerobic conditions

In aerobic biodegradation, the microorganisms use oxygen and consume carbon from the polymer as a food source; as a result carbon dioxide and water are produced and released. This corresponds to enzymatic biological oxidation. This reaction predominates if a high oxygen concentration (not less than 6%, as described in ASTM D 5338 [24]) is available. If the oxygen supply is depleted, aerobic microorganisms will change their metabolism rate, causing a reduction of the biodegradation rate. On the other hand, in anaerobic biodegradation, anaerobic microorganisms consume carbon from the polymer and release methane and carbon dioxide. Each kind of microorganism may consume carbon from polymers at a different pace; therefore, biodegradation of polymers in aerobic conditions may be totally different than that in anaerobic conditions. For example, as reported by Gartiser et al [25], PCL did not biodegrade, and PLA was found to biodegrade at a minor level (less than 10%) under anaerobic conditions based on ASTM D 5511 [26] and ISO 14853 [27] test methods.

Enzyme specific

Different enzymes may have differently shaped active sites and therefore are more able to biodegrade certain polymers. For example, the fungi *Aspergillus niger* and *Aspergillus flavus* produce enzymes that more readily degrade aliphatic polyesters derived from diacid monomers with 6-12 carbon atoms than those derived from other monomers [14]. It was found that extracellular PHB depolymerases - enzymes that depolymerize PHB - degrade PHB by different mechanisms depending on the specific bacteria specific 2.2.3.2 Polyme 1 much en closer to flexible, easily fit rate. Tw groups that Sic polytelyco because th inhibits cha the polyme: Doubl

Doubl adjacent sing) bacteria producing those enzymes [15]. Therefore, different microorganisms consume specific polymers at different rates.

2.2.3.2 Polymer factors

Polymer structure and chain flexibility

The "flexibility" (conformational flexibility) of a polymer chain indicates how much energy it takes to rotate molecules around bonds and how easy it is to move atoms closer to or further away from others. If a polymer chain is more conformationally flexible, more sites will be accessible to water for hydrolysis, and the polymer will more easily fit into the active sites of enzymes; both of these will increase the biodegradation rate. Two factors that affect the polymer's conformational flexibility are bulky side groups that limit chain movement and certain types of linkages in the polymer backbone.

Side groups increase the energy required for chain rotation. For example, poly(glycolic acid), Figure 2.3 (left), degrades faster than poly(lactide), Figure 2.3 (right), because the poly(lactide) chain is less flexible due to the methyl (-CH₃) side group that inhibits chain movement [20]. The methyl side group reduces the water accessibility of the polymer chain as well as the biodegradation rate.



Figure 2.3 (Left) Poly(Glycolic acid), (Right) Poly(Lactide)

Double bonds in the backbone increase flexibility by easing rotation around adjacent single bonds, as illustrated by the fact that the rotational barrier (energy required

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Crystallinity

As mentioned earlier, hydrolytic reactions are controlled in part by the rate of water diffusion into the polymer bulk in the amorphous regions, since water cannot diffuse through crystalline regions and amorphous regions are more flexible. Therefore, amorphous regions are more susceptible to both hydrolysis and biodegradation than crystalline regions [6]. For polymers like PHB, biodegradation occurs mainly via surface erosion due to enzymatic hydrolysis, and the main factors that control the rate of biodegradation were found to be the degree of crystallinity [15] and accessibility of the polymer chain to microorganisms. PLA with different degrees of crystallinity, due to different contents of L-lactide and D-lactide, has different degradation rates, due to the effect on the rate of hydrolysis [17, 28]. PLA polymers with higher contents of D-lactide degrade much faster since D-lactide induces twists in the otherwise very regular poly(L-lactide) molecular architecture, reducing crystallinity.

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Molecular weight

Generally, plastics are immune to microbial attack if their molecular weights are high (e.g., for PLA, $M_w \ge 20,000$ Daltons) because their molecules are too large to allow their entrance into the microorganisms' cells. Microorganisms can degrade only low molecular weight portions, which are taken into the cells and then converted into metabolites [14]. For natural polymers, such as starch and cellulose, microorganisms can attack the molecules directly since they can produce enzymes to cleave, or depolymerize, the natural polymer backbones, and consequently molecular weight reduction can happen outside the microbial cells [14]. For other biodegradable polymers, before being utilized by microorganisms, the molecular weights have to be reduced to a point at which the molecules can enter the microbial cells by other means of degradation, such as hydrolysis or photodegradation. The upper limit of molecular weight that microbes can metabolize differs by polymer; for example, a critical molecular weight (M_w) for PLA is 10,000-20,000 Daltons [17, 21], and for PHB is approximately 13,000 Daltons [14].

The molecular weight of a polymer affects the biodegradation rate in two different ways. As the molecular weight increases, the polymer's T_g also increases, making the polymer glassier and less flexible. Furthermore, a higher molecular weight polymer also has a longer chain length, which means that there are more bonds that must be cleaved in order to release the water soluble oligomers or monomers that are small enough to be consumed by microorganisms [6]. Consequently, a polymer with a higher molecular weight biodegrades more slowly than the same polymer with a lower molecular weight.



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Copolymer composition

Introducing comonomers into a polymer structure will increase irregularity of the polymer chains, which generally will reduce the polymer's crystallinity and thus may increase biodegradability. However, the effect also depends on the type of comonomer [6]. If the comonomer contains hydrolyzable groups, the biodegradability should be increased. On the other hand, if the comonomer contains aromatic structures, or other groups that provide rigidity to the polymer chain, and no hydrolyzable groups, the copolymer will generally have lower biodegradability or may not even biodegrade at all. Chiellini and Corti [29] reported that graft copolymerization of lignin with PCL was found to increase the biodegradability from 10% mineralization with pure lignin to 60% mineralization during a 100 day incubation period in mature compost at 55°C.

Size and Shape

The size and shape of the exposed polymer also play an important role in biodegradation. Polymers with higher surface areas will degrade faster than those with lower ones, other factors being equal, since a larger fraction of the polymer is in contact with moisture and microorganisms for hydrolysis and enzymatic degradation. Both ASTM [7] and ISO [9] standards for biodegradability require control of size and shape during biodegradation testing.

2.3 COMPOSTING

Composting is a biological process in which microorganisms convert organic materials such as manure, sludge, leaves, paper and food waste into a soil-like substance called compost. Composting is an aerobic process (in the presence of oxygen) as

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discussed earlier. Compost can be produced by commercial techniques involving turning mechanisms, sorting and shredding on a large scale; and also in small scale backyard composting. Commercial composting is typically a much faster process than backyard composting, as it is managed more intensively and optimal conditions are maintained.

2.3.1 WASTE MATERIALS

2.3.1.1 Yard waste

Yard waste can be defined as the vegetative waste resulting from the care and maintenance of landscaped areas, lawns and gardens. It may include leaves, grass clippings, garden wastes, tree trunks and prunings from trees or shrubs. The C:N (carbon to nitrogen) ratio of yard waste ranges from 9 to 80 (grass clippings 9-25, leaves 40-80, shrub trimmings about 53, tree trimmings about 16) [5]. Sometimes, yard wastes are composted in passive piles (a method of composting in which there is little management and manipulation of the materials after they are mixed and piled). Yard waste is mostly generated from municipalities and landscapers.

In the USA, yard waste is commonly collected at curbside or via public drop-off sites. Public drop-off sites are specified locations where residents and businesses can take their yard trimmings. In curbside collection, the municipality or concerned agency picks up yard trimmings that residents have placed outside of their homes [30]. Yard waste can be composted in either Commercial composting facilities or by backyard composting. Environmental Protection Agency (EPA) of United States estimates that 3,800 yard waste composting facilities were in operation in 2000 in USA [31].

In Canada, leaf and yard trimmings are the most common materials composted, with 182 facilities in operation. Collection methods range from drop-off by private

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haulers and residents (135 facilities) to curbside residential programs (77 facilities, with the vast majority being either source-separated or wet-dry programs) [32].

In 2003 in Europe, 1800 composting plants were in operation, 40% of which only included yard waste [33]. Victoria, Australia has contracts with composting companies to recycle green organic materials from yards and gardens with a capacity of over 100,000 metric tons per year. New South Wales diverts over 300,000 metric tons per year of organic materials with an estimate of 800,000 metric tons still to be diverted [34].

New Zealand has undertaken a zero waste initiative with the goal of minimizing and eventually eliminating waste. There are growing numbers of composting facilities in New Zealand, and in 1999 approximately 23,000 cubic meters of material was composted. In Christchurch, New Zealand, 70% of households recycle each week and about 60% compost at home or take green waste to the council's composting plant [34].

According to the Japan Organics Recycling Association (JORA) the annual production of wood residuals such as bark, sawdust and wood chips was about 5.34 million tons in 2001; about 95% of these residuals were utilized effectively. Yard waste due to pruning trees or trimming grass represented 6% (2.47 million tons) of total municipal solid waste in 2001 [35].

2.3.1.2 Food waste

Food wastes mostly consist of uneaten food and food preparation wastes from residences, commercial establishments like restaurants, institutional sources like school cafeterias, and industrial sources like factory lunchrooms. The C:N ratio of food wastes ranges from 14 to 80 (garbage food waste 14-16, and refuse 34-80) [5]. The main source of food waste is usually garbage and refuse (mixed food and packaging) that results from

mixed will cc sorting comes out, inc generat noncon prepara homes c ł normally waste is quantitie compost I and 11 m ³⁸]. In (sector [3] was food the dome processin scraps. E developm mixed MSW. MSW is extremely heterogeneous in size, moisture and nutrient content and will contain varying degrees of non-compostable and possibly hazardous wastes. Hence, sorting of MSW, using mechanical or manual techniques, plays an important role when it comes to composting of food waste. While some composting of mixed MSW is carried out, increasingly composting of food waste is dependent on source separation – the waste generator separating food (perhaps along with other compostable wastes) from noncompostables. The food wastes may be pre-consumer, such as food processing or preparation wastes from institutional or industrial sources, or post-consumer, wastes from homes or from restaurant or institutional meals [36].

Food waste has a high moisture content and little physical structure; hence normally it is mixed with a bulking agent such as yard waste for composting. Also, food waste is very susceptible to odor production (ammonia) and tends to generate large quantities of leachate. Hence, normally a well aerated pile is recommended for composting food scraps [36].

In 2005, in the USA there were16 mixed MSW composting facilities in operation and 11 more that compost residential source separated food wastes were in operation [37, 38]. In Canada, there are 54 facilities composting food residues from the residential sector [32]. Around 39% of the total 200 million tons MSW generated in Europe in 2000 was food scraps or food waste [33]. In Australia, food residuals comprise up to 41% of the domestic waste stream and 17% of the commercial/industrial stream. A food residuals processing facility was set up in the Melbourne metropolitan area that composts food scraps. EcoRecycle Victoria provided almost \$1.2 million to support infrastructure development for green organics and food residuals collection and processing [34]. JORA

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has estimated an annual production of food residuals based on the supply basis by the Ministry of Agriculture, Forestry and Fisheries and food intake calculated on nutrition demand basis on the Ministry of Health and Welfare which was 18 million tons in June 2001 out of which only 0.1 percent was used for composting and majority was either landfilled or incinerated [35].

2.3.1.3 Manure waste

Manure is the fecal and urinary excretion of livestock and poultry. Manure waste may contain bedding, spilled feed, water, and soil as well as livestock excreta. It can be classified as liquid, semi-solid, slurry or solid. Manure waste used in composting normally involves broiler litter, cattle manure, horse manure, laying hens, sheep, swine and/or turkey litter or a combination of these. The C:N ratio ranges from 3 to 56. Most of the animal manures are rich in nitrogen content and hence are normally mixed with materials with higher carbon content to achieve an optimized C:N ratio for composting. Commercial composting is a more suitable way for handling manure waste than home/backyard composting [5]. In Canada, 39 facilities compost manure or animal waste. In 1998, finished compost production was around 845,400 tonnes, which included composting of manure waste, food waste and yard waste [32]. In Japan, annual production of animal waste was around 94 million tonnes: 65 million tonnes of feces and 29 million tonnes of urine. According to JORA, in 2001 94% of total animal excretion was recycled to farmland and grassland after drying or composting [35]. Table 2.1 shows the total amount of yard and food waste generated and composted in the U.S.A. during 2003.

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Waste	Generated	Composted
Food, million tons	25.1	0.7
Yard, million tons	26	14.6
Total	51.1	15.3

Table 2.1 Food and yard waste generated during 2003 in the USA

2.3.1.4 Packaging waste

Packaging waste is generated due to disposal of packaging materials such as paper and paperboard, plastics, steel, aluminum, glass and wood. Steel, aluminum and glass cannot be composted and must be separated prior to composting. A substantial amount of the paper and plastics in MSW come from packaging of food and consumer goods and is normally recycled, landfilled, or incinerated. In the USA, in 2003, 56.4% of paper and paperboard packaging was recycled while only 9% of plastics packaging was recycled.

Upon introduction and certification of compostable plastics, composting plants have started accepting compostable liner bags. For example in San Francisco, the composting facility accepts "compostable liner bags" containing food scraps. The compostable liner bags (commercially available and produced from corn starch) make it easier for residents to separate food scraps for compost collection [39]. In Massachusetts, the Massachusetts Department of Environmental Protection (MADEP) is encouraging composting of items such as spoiled fruits and vegetables, floral and deli wastes, and waxed cardboard from supermarkets through the Massachusetts Supermarket Organics Recycling Network. The main goal of this program is to divert to compost facilities the commercial food waste generated by supermarkets. MADEP identified supermarkets as a major generator of waste organics. They estimated that there are 400 supermarkets in the state generating around 90,600 tons of organics per year. Compostable liner bags that biodegrade quickly and safely are being used in this program to transport the materials from collection containers to the commercial composting facility [40, 41]. Some commercial compostable bag brands are Bio-Bag (Canada), Cereplast (CA, USA) and EcoFilm and EcoWorks by Cortec Corporation (MN, USA).

Currently, researchers are demonstrating that compostable packages can be composted in facilities handling yard waste and manure as well as in those handling food wastes. Therefore, more options to compost biopolymers could be available if compostable biopolymers used in packaging applications were accepted by these compost facilities. Figures 2.4 and 5 show the degradation of PLA bottles and EcoflexTM films under compost conditions (58°C, 60%RH) after 30 days and 60 days, respectively [42-45].



Figure 2.4. Pictorial view of PLA bottles exposed at 30 day of compost conditions

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Figure 2.5. Pictorial view of Ecoflex films exposed at 60 day of compost conditions.

As market incentives are created for green and environmental friendly polymers, there is also interest in developing new compostable materials from petroleum resources [46]. As previously defined, a compostable material must completely biodegrade under standard compost conditions. Currently, some manufacturers are claiming compostability for polyolefin plastics containing additive technologies that are reported to work in a twostep process that accelerates oxidation and then biodegrades. The manufacturers claim the prodegradant additives control these processes in a highly predictable and manageable manner in all conditions with a source of oxygen and naturally occurring microorganisms (air, soil, landfill, compost, litter). The process is commonly referred to as "oxobiodegradation". The main market for these polymers is biodegradable mulch film, but these need to be collected after the harvesting season if composting is the intended option for their disposal. According to manufacturers, these polymers are engineered to degrade and totally fragment in 90 to 120 days. After that they will 60% mineralize/biodegrade in



a further 12 to 24 months when disposed of in a commercial compost facility and in subsequent soil application [46]. Figure 2.6 shows commercially available LDPE film with the oxo-biodegradation additive exposed to composting conditions for 60 days at $48^{\circ}C \pm 5^{\circ}C$ and $52 \pm 16\%$ RH. After 60 days in the compost pile, no visual fragmentation was observed. Therefore, further study of these polymers is necessary to determine whether the compostability claims can be substantiated.



Figure 2.6. Pictorial view of LDPE with oxo-additive exposed at 60 day of compost

conditions (48°C±5°C, 52±16%RH).

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2.3.2 COMPOSTING TECHNIQUES

2.3.2.1 Commercial Composting

Commercial or municipal composting is a large scale composting operation which generally employs turning and active aeration, except static pile and some in-vessel composting systems. Since waste materials have different characteristics, operational parameters such as moving, mixing and manipulation differ.

Composting begins with collection of suitable organic materials, followed by mixing to achieve the desired C:N ratio, moisture content and pore space. Usually one material is primary and then one or more amendments are added [5]. Raw material sorting is essential, especially if it is a mixed waste stream. Shredding or grinding is optionally employed if the raw materials include newspaper, corrugated cardboard, brush, tree stumps or other large yard wastes. Grinding or shredding may use shear shredders (rotary or belt), hammer mills or tub grinders [5]. In some of the in-vessel methods, the mixing step is built into the system. The material needs to be loaded into the silo, hopper or vessel using conventional materials handling equipment such as conveyors, augers or bucket loaders. Subsequent turning mixes the materials more thoroughly.

Frequent turning improves consistency and diminishes the importance of the initial mixing in windrow systems, relative to a static-pile system, where organic waste is formed into rows of long piles and aerated by turning the pile periodically. Bucket loaders play a very versatile role in composting operations by allowing mixing and pile/windrow formations. Mixing can be simply done by repeatedly bucketing the ingredients together. Windrows and passive piles can be mixed and formed in a single step by depositing the raw materials on the composting site in layers, forming a crude

pile. The loaders then mix the materials together and work them into the desired shape until the materials are well mixed. Other equipment used in mixing includes batch mixers in which amendments are placed in the mixer and then the manure added on top. The mixture can be discharged through the side delivery elevator directly into the windrow, or onto an aerated pile as the mixer is pulled forward parallel to the air distribution pipe.

After the active composting phase, compost requires a curing period of at least one month to finish the process and allow the compost to develop the desired characteristics for its intended use.



Figure 2.7 Commercial composting system and operations

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After curing, screening of compost separates materials of different sizes and/or shapes. Screening is nearly always performed after curing either to improve compost quality or recover bulking agents. Different type of screens are available, including trommel screens, shaker screens, vibrating screens, flexing belt screens, disc screens, auger and trough screens and rotary (spinning disc) screens [5].

Drying follows after screening to lower the moisture content of the compost. It typically involves extra aeration or an extended composting period.

Figure 2.7 shows a flowchart of a complete commercial composting process.

2.3.2.2 Advances in composting techniques

Currently source separated composting has gained lot of attention in USA, Canada and Europe in which the waste is separated by the consumers at the residential level. In the USA, 11 residential source separated composting projects were active in the states of California, Michigan, Minnesota and Washington in 2003 [38]. The residential sorting and collection methods differ based on the composting facility; for example in San Francisco, CA, residential 3 source separation cart collection is employed which consists of organics, single stream recyclables, and trash [38]. Similarly in Canada, source separating MSW into wet and dry streams is a popular way to achieve waste diversion objectives, as it offers great flexibility in classification of waste streams, collection methods, collection frequency and waste processing. About 98% of the consumers in Guelph, Canada, participate in the wet-dry 2 stream program [47]. In Europe, composting of mixed MSW is becoming rare due to growing recognition of the benefits of source separated MSW composting. In 1998, around 85% of home composted or separately collected MSW was being recovered in Austria, Belgium, Denmark,

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Germany and Netherlands [48]. Those five nations have finalized their organic waste policies based on source separated MSW diversion and have achieved better recovery rates [48].

In the case of mixed MSW, sorting is necessary. Goldstein [38] explained a typical composting process for a mixed MSW stream. Initially MSW is sorted to remove the oversized items and then passed by conveyor through a manual sorting step to remove inappropriate materials for composting. A bag breaker machine is used to remove wastes from the bags. This automated system consists of different diameter drums which rotate at different speeds. They are equipped with hooks which grab the bags and elongate them as the drums spin to spill out the contents from the bags. Next the waste is screened through a debris (disk) roll screen. The waste material obtained through the screen goes to an auger mixer, and the remaining material on the screen is moved to an optional sorting station where more recyclables can be removed. The mixer auger is equipped with knives which help in reducing the particle size without shredding or grinding. Later, water is added to the mixture in vessels to improve the moisture content. The vessels' aeration system is designed to minimize evaporation and maintain temperature levels. The vessels are later unloaded to form the aerated static piles. After the compost is ready, it is screened to remove any foreign materials contained in the final product.

Savage et al [52] provide an overview of screening and introduction to air separation based on material density. Air separation uses an air current to classify the waste materials; a typical air classification system consists of introduction of MSW materials through a chute into an upward flowing stream of air. The lighter materials are carried out with the air and the heavier materials fall onto a conveyor or into a bin. The

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lighter particles next enter into an air cyclone where they settle out. Air separation is a function of density, shape and size of the particles and can be efficiently used in separation of plastic particles and film from the compost [52].

Turning equipment is used for the mechanical agitation of piles to manage the temperature and oxygen levels. The Windrow turners commonly used in commercial composting can be categorized by turning mechanisms, orientation to the windrow, power source and mode of travel [49, 50]. Some categories of turners based on their mechanical agitation are straddle type, auger equipped turner, elevating face and trapezoid turners [49, 50]. Some improvements in recently produced turners (as reviewed by Diaz et.al. [49, 50]) include better efficiency, increased durability, less maintenance, ability to accommodate large or different sizes of windrows, and increased ease of travel and transportation. Turner manufacturers are stressing improving the turning equipment for larger windrow sizes which will help in larger production of compost. More details regarding turning equipment and the turning process can be found elsewhere [49, 50].

The last step after the compost is produced is screening to remove foreign matter (FM) (undesirable materials such as plastic, metal or glass). A recent study by Page et.al. [51] compared three different screening methods for finished compost. One pass through a ball screen (resulting in 0.26% FM) and two passes through a trammel screen (0.53% FM) gave the best results.

2.3.2.3 Home composting (back yard)

Home composting is handled on a small scale using small piles or composting bins. Turning is usually done manually unless the bins are equipped with rotating drums. Home composting usually involves lower temperatures than commercial composting,

with r Yard v manag anima take u Comm revolv there h many o compos Bokash process increasi within t some sy with stir househol rate of 25 approxim diventing 2.3.3 PLA Syı and hence with much of the decomposition taking place at mesophilic temperatures (10°C to 46°C). Yard waste and food waste normally go into home composting systems [5], but improper management of food scraps can cause odors and also might attract unwanted insects or animals [31]. In back yard composting, conversion of organic matter to compost may take up to two years, but manual turning can decrease this time to 3 to 6 months [31]. Commercial backyard composting bins are typically either open or closed cylinders, revolving drums, or orbs that can be rolled along the ground to turn the pile. Recently there have been many developments in commercial indoor and outdoor composing bins, many of which are specifically designed to compost food scraps. An indoor kitchen composter developed in Japan anaerobically ferments food scraps using the patented Bokashi method [53] of beneficial microbial inoculation which speeds up the microbial process. Some other systems have bins containing three compartments which allow increasing or decreasing the volume and classifying fresh and mature compost or humus within the same bin. Also, as ventilation is important to maintain the aerobic process, some systems continuously circulate air throughout the bin. Some bins are also equipped with stirrers and screens which turn and screen the compost [53]. In Seattle, Washington, households doing back yard composting of yard waste had an annual household recovery rate of 254 kgs and those who composted food waste recovered 131 kgs [53]. In Canada, approximately 27% of homeowners in Edmonton are composting in their back yards, diverting 10,224 tonnes of organic waste from landfill each year [32].

2.3.3 PLASTICS IN COMPOST

Synthetic plastic waste or particles in compost is a major contamination problem and hence plastic separation in compost is an important factor for both the compost

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feedstock and the compost end product. As mentioned above, different screening and separation mechanisms can be used to separate plastics from compost.

A case study on plastic-wrapped industrial food residuals was done in California, USA in 2005 [38]. The composting facility received industrial food waste contained in plastics packaging which was then ground with the green feedstock, composted, and foreign matter was subsequently screened out through a trammel screen. Plastics present in the compost floated through the trammel and were ejected over a belt equipped with an air knife. The plastic particles were sucked up through the air knife, leaving behind the bulking agents, which could be used again in the composting process.

Rynk [54] reported case studies about contamination of compost due to plastics and other foreign particles. In one study, samples of MSW compost were inspected after repeated sieving, drying and weighing; it was found that plastics (average 1.9% of compost dry weight) remained in the compost even after repeated sieving with seive sizes of 1 mm to 4 mm. For larger compost size ranges (4 mm to <25 mm) the plastics contamination percentage ranged from 3.5 to 6.6 % of compost dry weight [54]. Another study comparing the presence of plastics contamination in sieved and non-sieved samples found similar results for plastics contamination in sieved (1.875 mm) and non-sieved compost [54].

De Baere [54] evaluated the replacement of biodegradable with synthetic polymers and their composting in commercial composting facilities, including cost analysis. The first case study was for a 50,000 ton/year Belgium-based source separated composting facility which had 80% of its organic waste delivered in plastic bags. The system included prescreening to remove the plastic material to avoid plastics

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contamination in the composting process and end product. According to De Baere [54], use of 500 tons of compostable biopolymer per year rather than non-compostable plastics would eliminate 2000 tons/year of overs for pre-screening since biodegradable plastic does not need this step.

2.3.4 USES OF COMPOST

Compost is a very valuable soil amendment which improves plant growth. Compost-enriched soil can also reduce erosion, alleviate soil compaction and help control disease and pest infestation in plants. In addition to common agricultural and horticultural applications, compost is used in some building and construction projects. On steep embankments along roads and highways, compost can be more effective than traditional hydromulch at reducing erosion and establishing turf because compost forms a thicker, more permanent growth due to its ability to improve the infrastructure of the soil. Due to the ability of compost to retain moisture, it also helps protect soil from wind erosion and during droughts. Compost is also used to remediate turf grasses that are extensively used for recreational activities such as golf, football, soccer, etc. Often the wear and tear on such turf results in disease, pests and soil compaction. Use of compost increases resistance to growth of turf diseases, such as snow mold, brown patch and dollar spot. Compost is an effective landscape mulch; when placed over the roots of plants, compost mulch conserves water and stabilizes soil temperatures. It also helps keep plants healthy by controlling weeds, providing a slow release of nutrients, and preventing soil loss through erosion [55, 56].

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2.3.5 ENVIRONMENTAL IMPACTS OF THE COMPOSTING PROCESS

Leachate

Leachate is the liquid that results when water comes in contact with a solid and extracts material, either dissolved or suspended, from it [5]. Leachate differs from other water that may accumulate on a compost site due to precipitation or flooding since leachate may contain a combination of nutrients, soluble chemicals, and organic matter. Hence, good drainage at composting sites is necessary.

Leachate management can be achieved in different ways, including by providing a slope for easy run off, maintaining sufficient and recommended distances between compost and ground water facilities, maintaining the moisture content of compost below the maximum recommended level, and encouraging effective drainage by orienting windrows with the slope of the compost pad rather than across it.

In Canada, leachate is either disposed through local waste water systems, released to engineered wetlands to purify it, or released through natural purification systems [57]. In Europe, leachate is used for watering the composting mass or is discharged [58]. In Australia, containment of leachate within the composting area is required. It can be used for irrigation of piles, disposed of in existing slurry lagoons, or be treated adequately before discharge. The drainage and collection system has to be able to handle heavy rainfall [59].

2.4 STANDARDS

In order to determine whether certain packaging materials, i.e. plastics and papers, are compostable, standards organizations, such as ASTM and ISO, have published their

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own series of standards for compostability and/or biodegradability of materials in different exposure environments. In general, these standards describe terminology and definitions, testing guidelines, procedures, conditions, significance, limits, and results interpretation. In this overview, the standards are separated into two groups, ASTM and ISO standards, as these are the two main standards organizations.

2.4.1 ASTM STANDARDS

The current ASTM standards involving materials compostability and biodegradability can be categorized into three groups based on exposure environments: (1) composting, (2) anaerobic digestion and wastewater treatment, and (3) others (see Table 2.2). Only standards involving composting of plastics will be included in this overview and the discussion mainly will focus on standards for compostable plastics.

According to ASTM D 6400 [7], to claim that a certain material is compostable (see Figure 2.8), it must meet requirements that include satisfactory disintegration, biodegradation, and terrestrial and aquatic safety in a controlled laboratory scale composting test. In this test, described in guide D 6002 (Tier 2) [60] and test method D 5338 [24], the test materials are exposed to the compost mixture in closed vessels. At least 12 vessels must be used: 3 blanks, 3 negative controls such as LDPE, 3 positive controls such as cellulose, and 3 for the test material. CO_2 -free humidified air is supplied for a test period of no less than 45 or more than 180 days, at a constant 58°C temperature (thermophilic phase), or using a desired temperature profile (e.g., 35°C for 1 day, 58°C for 4 days, 50°C for 23 days, and 2 days for 35°C).

Table 2.2 List of current ASTM Standards sorted by category

Composting Environment
D 6400 "Standard Specification for Compostable Plastics"
• D 6002 "Standard Guide for Assessing the compostability of Environmentally Degradable Plastics"
• D 5338 "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions"
• D 5988 "Standard Test Method for Determining Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials After composting"
• D 5929 "Standard Test Method for Determining Biodegradability of Materials Exposed to Municipal Solid Waste Composting Conditions by Respirometry"
• D 6954 "Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation"
• D 6340 "Standard Test Methods for Determining Aerobic Biodegradation of Radiolabeled Plastic Materials in an Aqueous or Compost Environment"
Anaerobic Digestion and Wastewater Treatment
• D 5210 "Standard Test Method for Determining the Anaerobic Biodegradation of Plastic Materials in Presence of Municipal Sewage sludge
• D5271 "Standard Test Method for Determining the Aerobic Biodegradation of Plastic Materials in an Activated-Sludge-Wastewater-treatment system"
• D 5526 Standard for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions
• D 5511 Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions
Other Standards
 D 5951 "Standard Practice for Preparing Residual Solids Obtained After Biodegradability Standard Methods for Plastics in Solid Waste for Toxicity and Compost Quality Testing" D 5075 "Standard Test Method for Determining the Stability of Convert here
• D 5975 "Standard Test Method for Determining the Stability of Compost by Measuring Oxygen Consumption"

The amount of carbon dioxide gas evolved is measured using either a cumulative method (titration method), or direct measurement from the exhaust air, using an infrared (IR) detector or gas chromatography (GC). Figure 2.9 (a) and (b) shows systems for biodegradation evaluation by the cumulative method and by direct measurement,

respective weight is material Disinte ____ <1(Weig
respectively [61]. At the end of the test period, if no more than 10% of the original dry weight is found to remain after sieving the final compost with a 2 mm sieve, then the test material shows satisfactory disintegration.



Figure 2.8 Compostable materials identification flowchart



(a)



(b) Figure 2.9 a & b. Accumulative and direct method to measure biodegradation [61]

car val (ho cop me the Bra gio [27 mat the mu the alga biop mec plas be e vagı To achieve satisfactory biodegradation, the cumulative percentage of organic carbon converted to carbon dioxide gas, or mineralization, compared to the theoretical value for the test polymer must be at least 60% for a material containing a single polymer (homopolymer or random copolymer), and 90% for a material containing a block copolymer, segmented copolymer, blend, or low molecular weight additives.

For determination of terrestrial and aquatic safety, the concentration of heavy metal in plastic must be lower than 50% of the amount listed in 40CFR§503.13 [62], and the final compost must pass the toxicity test, including aquatic toxicity test with rotifer Brachionus (Guide E 1440) [63], the plant germination with cress seed test, the plant growth test (OECD Guideline 208) [64], and the earthworm test (OECD Guideline 207) [27]. In order to pass the toxicity test, the results from the compost containing the test materials must have no significant differences compared to the blank compost. Prior to the toxicity test, the final compost from the controlled laboratory scale composting test must be prepared in accordance with test method D 5951 [65].

ASTM D 6400 also defines biodegradable plastic as a degradable plastic in which the degradation results from the actions of microorganisms such as bacteria, fungi and algae [7]. Therefore, based on this definition, for example, PLA, a commonly used biopolymer, would not qualify as a biodegradable material since the main degradation mechanism is hydrolysis. Another definition needing more explanation is compostable plastic. D 6400 defines this term without including the types of compost the plastic will be exposed to, or the time limit required for material to become fully degraded. This vague definition gives room for materials to claim they are compostable even if they will

not com paper. T Tier 1, c sample a desiccato stored in carbon d or 90° o polymer biodegrad negative T that are r test met biodegrac determine reactor fo by dividin theoretica ^{compare} a combined ^{compost} w not compost as fast as natural materials such as yard trimmings, food wastes, and kraft paper.

Test method D 5988 [66] or the "soil contact test", as described in guide D 6002 Tier 1, can be used as a rapid screening test prior to test method D 5338. In this test, the sample and reference materials are mixed with a soil mixture in air sealed vessels, such as desiccators, with each vessel containing only one test material. The test vessels are stored in the dark at 21°C (mesophilic phase) for 30-60 days. The amount of evolved carbon dioxide is quantified by titration. A positive result, which means more than 60% or 90% of the total organic carbon converted to carbon dioxide (depending on the polymer composition as described above), indicates that the test material will also biodegrade in the composting environment, which has a higher temperature. However a negative result should be confirmed by test method D 5338.

There are some standards involving exposing materials to a compost environment that are not listed in specification D 6400 for compostable materials identification, e.g. test method D 5929 [67], and guide D 6954. In test method D 5929 [67], the biodegradability of the test material exposed to the MSW composting condition (40°C) is determined by measuring the oxygen uptake and carbon dioxide production from each reactor for a test period of 45 days. Then, the percentage of biodegradation is calculated by dividing the total cumulative oxygen uptake and carbon dioxide production by the theoretical value. Guide D 6954 [68] is a tier based framework, similarly to D 6002, to compare and rank the degree of degradation of polymers by thermal- and photo-oxidation combined with biodegradation in disposal environments such as soil, landfill, and compost with other tested polymers chosen for that application. Tier 1 involves exposing

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the test applicati such as disposal 60% and to this g which a 2.4.2 EI . compos EN 134 packagi instead standard quality three cr compos content, must ha example least 50 values 1 the test material to the thermal- or photo-oxidation conditions, based on its intended application. In tier 2, the residual fragments from tier 1 are subjected to a "biometer test" such as D 5338 or D 5988, to measure the carbon dioxide evolution in the simulated disposal environment; soil (20-30°C), landfill (20-35°C), or compost (30-65°C). The 60% and 90% organic carbon conversion described in specification D 6400 also applies to this guide. In tier 3, the residue from the biometer test is subjected to toxicity tests which are similar to those listed in guide D 6002 tier 2.

2.4.2 EUROPEAN AND ISO STANDARDS

There are only a few European and ISO standards involving packaging and composting environments. The specification, test scheme, and guidelines are detailed in EN 13432 [8]. Unlike the ASTM standards, this standard can be applied to any packaging or packaging component, and is not limited to plastic materials. Moreover, instead of three criteria for plastic compostability, there are four criteria in the EN 13432 standard: (1) characterization, (2) biodegradability, (3) disintegration, and (4) compost quality or ecotoxicity. However, these four criteria cover the same scope as ASTM's three criteria.

In characterization, the packaging materials are analyzed to determine the composition, the presence of hazardous substances (e.g. heavy metals), organic carbon content, and total dry and volatile solids. To pass this criterion, the packaging material must have those values within specifications listed in Annex A.1 of EN 13432. For example, packaging, packaging materials, and packaging components should contain at least 50% of volatile solids, and the concentration of heavy metals should not exceed the values listed in Table 2.3. The volatile solids mean the materials that become volatile at

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high temperatures; a temperature of 550±50°C is used for an ignition test as described by ASTM D 5338 [24] and the American Public Health Association (APHA) standards 2540 E [69].

Element	mg/kg on dry substance	Element	mg/kg on dry substance
Zn	150	Cr	50
Cu	50	Mo	1
Ni	25.0	Se	0.75
Cd	0.5	As	5
Pb	50	F	100
Hg	0.5		

 Table 2.3 Maximum heavy metal content of packaging material and whole packaging from EN 13432 Annex A.1 [8].

The biodegradation test is described in ISO 14855 [9], and is similar to the test method in ASTM D 5338, with a few differences. First, the ISO test method does not require the negative control vessels; therefore, only 9 vessels are required instead of 12. Second, ISO 14855 also includes the determination of percentage of biodegradation based on weight loss as an optional result to support the value determined from carbon dioxide evolution. Third, the acceptance level of percentage of biodegradation of the test material is at least 90% in total or 90% of the maximum degradation of the reference material after a plateau stage for both reference and test materials has been reached. For disintegration, the European and ISO standard suggest testing the materials in controlled pilot-scale tests, as described in ISO 16929 [70], instead of using the controlled laboratory-scale test in ASTM D 6400. But the rest is similar, i.e. the final compost is screened with a 2 mm screen, and the material needs to pass the disintegration criterion (i.e. no more than 10% of the original dry weight is recovered after 12 weeks of composting).

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For the compost quality or ecotoxicity test, physical and chemical parameters such as density, total dry and volatile solids, salt content, and pH, have to be determined to show that the test packaging does or does not have negative effects on the compost quality. Only the plant growth test, based on OECD guideline 208 [64], is included in EN 13432 for ecotoxicity. The results (germination numbers and plant biomass) of the compost with test material and the blank compost are compared. Figure 2.10 shows a detailed flowchart of the evaluation of organic recoverability of packaging according to EN 13432. As shown in Figures 2.9 and 2.10, the procedure to have any package certified as "compostable" is very elaborate. It involves not only the package passing the test method ASTM 5338 [24] or ISO 14855 [9], but also meeting various other requirements, such as passing the disintegration test, having levels of heavy metals within limits, and passing the plant growth test by having no significant difference between the compost containing test material and the blank compost. For example, Figure 2.11 shows the percentage of mineralization of the PLA bottles previously tested in the compost facility and shown in Figure 2.5, compared with PET bottles (negative control) and corn starch (positive control), according to ASTM D 5338 and ISO 14855 [61]. This test will comply with the first and second requirements of ASTM D6400 and EN 13432, characterization and biodegradability. However, this test does not certify that the material is compostable according to these standards. Further studies assessing the complete disintegration and the compost quality or ecotoxicity of the bottles are required. Therefore, the PLA bottle could not be labeled as compostable just by passing ASTM D5338 and ISO 14855.

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Figure 2.10 Flowchart of evaluation of organic recoverability of packaging



Figure 2.10 Flowchart of evaluation of organic recoverability of packaging



Figure 2.10 Flowchart of evaluation of organic recoverability of packaging

80 70 **6**0 %Mineralization 05 05 05 20 10 0 Fig 2.5 LA 1 composi [71]. To be a lat ^{such} as Compos centification certificat



Figure 2.11 Percentage of mineralization of PLA and PET bottles and corn starch measured according ASTM D 5338 [24] and ISO 14855 [9].

2.5 LABELING AND CERTIFICATION

Currently, there is confusion about conventional plastics and biodegradable and compostable plastics throughout the U.S., since they are hardly physically distinguishable [71]. To succeed in recovering these materials and properly composting them, there must be a labeling system that separates them from conventional materials. Organizations such as the Biodegradable Products Institute (BPI) located in New York City; the U.S. Composting Council (USCC), located in Holbrook, NY; and DIN CERTCO, the certification organization of DIN, the German Institute for Standardization, offer certification programs that award a compostable logo to approved products.

Iı there sho are comp due to di temperat consider certificat products P which ca that certi to have recogniz with the Specific Compos products approve website cenifies ^{tests} of and the these st. In order to claim or label a product or package as compostable, or biodegradable, there should be reliable scientific evidence supporting this claim [72, 73]. Packages that are compostable in institutional facilities may not be compostable in home composting, due to different composting conditions, such as the waste mixture, moisture content, and temperature. Therefore, the claim must be clarified enough to avoid deception, especially considering the limited availability of compost facilities [72]. These are reasons for certification; therefore concrete evidence must be submitted to organizations to have any products certified.

Packaging manufacturers can have their products certified as "compostable", which can be used as a marketing advantage. Also, composting facilities can be ensured that certified products are definitely compostable. Therefore, certification is the first step to have compostable packages accepted by composting facilities. Two of the most recognized certification organizations are BPI and DINCERTCO. BPI, in cooperation with the USCC, uses the ASTM specifications D6400 [7] and D6868 [74] "Standard Specification for Biodegradable Plastics Used as Coatings on Paper and Other Compostable Substrates" [8]. The compostable logo, see Figure 2.12(a), is given to products that are compliant with ASTM specifications based on testing results from any approved laboratory. A list of the approved laboratories can be found online at the BPI website: http://bpiworld.org/BPI-Public/Program/Labs.html. Similarly, DINCERTCO certifies compostable products made from biodegradable materials based on laboratory tests of either ASTM specification D 6400 [7], or the European standard EN 13432 [8], and the "compostable" logo, see Figure 2.12(b), is awarded to products that meet one of these standards [75]. Many other organizations also certify compostable materials based



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on ASTM D 6400 [7], EN 13432 [8], or both. For example, AIB Vincotte (AV), located in Belgium, awards the "OK compost" logo, see Figure 2.12(c). Other certification bodies award certificates (not compostable labels) to products that meet ASTM, ISO, or CEN standards, similar to the ISO 9000 series certification. For example, SGS offers biodegradability and ecotoxicity testing based on ISO standards.

Currently, approved BPI and DIN CERTCO compostable products include compostable bags and films; packaging, such as water bottles, ovenable and microwavable trays; dishes and bowls; disposable utensils; and resins, such as EcoflexTM from BASF, PLA from NatureWorks[®] LLC, and Mater-Bi from Novamont [8, 75].



(a)



Figure 2.12 (a) BPI compostable logo, (b) DIN CERTCO compostable logo, (c) AV OK

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In 2006, Assembly Bill No. 2147 "Solid waste: Compostable plastic food and beverage containers" was introduced by Harman in California. This bill prohibits selling plastic food and beverage containers labeled "degradable", "biodegradable", or "compostable" unless the containers meet current ASTM standards [76], in contrast to the existing law which applies only to plastic bags. However, the bill does not specify the ASTM standards, and it does not address which standards the packages have to comply with, for example D5338 or D6400. The purpose of the bill is to stop food and beverage packaging manufacturers or distributors from using mislabeling, because there have been erroneous uses of the words "degradable", "biodegradable", and "compostable" in marketing. Therefore, there must be a system to label the packages that is reliable and scientifically based.

2.6 LIFE CYCLE ANALYSIS

As discussed earlier, LCA is an evaluation technique which compares the performance of alternative systems and products; and quantifies the environmental consequences of a product, system or process over its entire life. As delineated in ASTM D7075 [12], the LCA methodology for biobased products involves distinct stages such as goal setting, inventory analysis, impact assessment and interpretation. Goal setting defines the reasons for and scope of the study, including its breadth and depth. The inventory analysis identifies and quantifies the environmental inputs (water, energy, raw material, land and other resources) and outputs (releases to air, land, and water) associated with the product over its entire life cycle. Impact assessment characterizes the inventory input-output flows in relation to a set of environmental impacts (such as resource depletion, global warming, ozone depletion, human toxicity, ecotoxicity,

photoche landscap describes The prac used in I T compost importar biobased land app value of studies o A should in cycle of (2) the e material used to r Bohlmar biodegra ^{have} bec associate photochemical oxidant, acidification, eutrophication and degradation of ecosystems and landscapes). The final interpretation step combines the environmental impacts and describes the results in a manner and in accordance with the goals of the LCA study [13]. The practice stated in ASTM D7075 is in accordance with the terminology and concepts used in ISO Standards 14040 – 14043 [77-80].

The waste management stage for the compostable packages may include composting, combustion, landfilling or recycling. The final disposal system has an important role in the overall ecobalance, especially for biodegradable materials. If biobased materials are disposed through composting, and the compost is further used in land application, then significant emission and energy credits can accrue, because of the value of the compost to sustainable agriculture. Impact factors emphasized in earlier LCA studies of biodegradable packaging include eutrophication, ecotoxicity, and land use [81].

According to EPA, evaluating greenhouse gas emissions of a polymer system should include analysis of three factors: (1) greenhouse gas emissions throughout the life cycle of the polymer, including utility emissions and emissions from the disposal option; (2) the extent to which carbon sinks are affected by manufacturing and disposing of the material; and (3) the extent to which the management option recovers energy that can be used to replace electricity, thus reducing utility greenhouse gas emissions. According to Bohlmann [81], there is considerable uncertainty in estimating the impact of biodegradable polymers such as PLA on emissions of greenhouse gases, and few studies have been published that address greenhouse gas emissions and carbon sequestration associated with landfilling.

I Wales, A the total reduction conditior equivaler A managem compostin benefits o and uses could not fertilizer u pesticide manufactu Ko solid wast production experiments considers th ^{that} the odo the total cap ^{than 90%} of LCA studies have been done on composting at the University of New South Wales, Australia. However, they reported some limitations of LCA as a tool to evaluate the total environmental impact assessment of a compost operation, since a number of reductions in agricultural inputs (such as fertilizers and water) and improvement in soil conditions could not be evaluated due to the unavailability of required characterization or equivalency factors [82].

Another LCA study evaluated the environmental impacts of solid waste management alternatives, concluding that if organic waste is diverted from landfills to composting, there is reduction in the energy recovery and greenhouse gas emissions benefits of the waste management system. The composting process increases emissions and uses energy. Again, in this study; the environmental consequences of composting could not be characterized completely due to lack of data. Offsets could include reduced fertilizer use, conservation of nutrients in compost-amended soil, less irrigation, reduced pesticide application, avoided harvest and transportation of peat, or avoided manufacturing of erosion control products [83].

Komilis and Ham developed a life cycle inventory (LCI) model for municipal solid waste composting and yard waste facilities [84]. Their model considers the production of compost as a high and low value product, and was based on laboratory experiments to determine selected emissions which were not available. The model considers three organic streams: food waste, mixed paper, and yard waste. They found that the odor control system and the building were the largest capital cost (around 77% of the total capital cost) for these types of operation. In addition, they reported that more than 90% of the emitted CO_2 was due to solid waste decomposition. Further research

charact necessa 2.7 CO and pol consum is an ava these bi renewabl refinery p composti materials Therefore addition, claims. Alı many of t requiremen ^{system} in p green marke ^{is that} we h Packaging so ^{to} formally characterizing the emissions and determined that indicators for composting facilities are necessary in order to systematically evaluate and compare composting facilities.

2.7 CONCLUSION

As new biopolymers obtained from renewable resources such as poly(lactide), and poly(hydroxybutyrate) are increasingly becoming available for food, medical and consumer goods packaging applications, disposal of these polymers through composting is an available alternative. However, until now the main focus of companies promoting these biomaterials is the claim that they are obtained from environmentally-friendly renewable resources and reduce petroleum consumption (even though only about 5% of refinery production goes to chemical products, including polymers). Since recycling and composting programs for these materials are generally not available, these "green" materials mostly end up in landfill, along with many other packaging materials. Therefore, a better approach to the disposal of these new biomaterials is needed. In addition, state or federal regulations are necessary to avoid improper compostability claims.

Although recycling could be energetically more favorable than composting for many of these new biopolymers, it may not be practical due to sorting and cleaning requirements. A viable alternative is composting. However, since at present there is no system in place for collection and composting these materials, their main benefit is just green marketing based on pseudo environmental benefits. The risky point of these claims is that we have really created a new packaging waste problem, rather than a sustainable packaging solution. Compostable packages can be a valuable alternative if we are willing to formally address the challenge of clearly understanding the cradle-to-grave life of

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these materials. Including compostable polymers in existing food, manure, or yard waste composting facilities is a promising approach. Canada and Germany are among the countries in the forefront of this initiative, positioning them to take full advantage of adopting these new materials.

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CHAPTER THREE

Gaurav Kale, Rafael Auras, Sher Paul Singh. (2006). Degradation of Commercial Biodegradable Packages under Real Composting and Ambient Exposure Conditions. Journal of Polymers and the Environment. 14: 317-344

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CHAPTER THREE - DEGRADATION OF COMMERCIAL BIODEGRADABLE PACKAGES UNDER REAL COMPOSTING AND AMBIENT EXPOSURE CONDITIONS

SUMMARY

The use of long-lasting polymers as packaging materials for short lived applications is not entirely justified. Plastic packaging materials are often soiled due to foodstuffs and other biological substances, 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. Use of biopolymer based packaging materials allows consideration of eliminating issues such as landfilling, sorting and reprocessing through taking advantage 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. The aim of this work was to study the degradation of three commercially available biodegradable packages made of poly(LD-lactide) (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 and to track the degradation rate under real compost conditions was used. The packages were subjected to composting for 30 days, and the degradation of the physical properties was measured at 1, 2, 4, 6, 9, 15 and 30 days. PLA packages made of 96% L-lactide exhibited lower degradation than PLA packages 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

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the compost pile played an important role in the total degradation of the packages. A first order degradation of the molecular weight as a function of time was observed for the three packages.

3.1 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 ł carbon, nit carbon as a nitrogen ra compost p stage. In th strong mic (140°F) wł temperatur to compost compost c continues microorgan Co by biologi and bioma ^{visible}, dis conditions a composi degradation the materia mechanism Since bioc ^{backbone,}

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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 60°C (140°F) 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 CO₂, 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

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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)^{ϵ 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

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engineered to completely biodegrade in a microbial environment) include Natureworks[™] PLA developed by Cargill Dow LLC (Blair, NB). Natureworks[™] 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 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]. 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

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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. Three 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).

3.2 MATERIALS AND METHODS

3.2.1 Packages

Five hundred milliliter poly (lactide) spring water bottles commercialized by Biota brands of America (Telluride, CO) were obtained from NatureWorksTM 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) and deli containers (0.195 m x 0.17 m x 0.04 m) were obtained from Wilkinson Manufacturing Company (Fort Calhoun, NE). The tray and deli containers both were made of 94% L-lactide and 6% D-lactide. Figure 3.1 a, b & c show pictures of the containers.





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(c) Figure 3.1. PLA containers a) bottle; b) tray; c) deli



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3.2.2 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, Canada). Initially, 11.6 m³ of cow manure and 7.8 m³ 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 60°C, and it is turned up to ensure aeration and that the total volume of mixture is exposed to temperatures above 60°C 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 $65 \pm 5^{\circ}$ C, $63 \pm 5^{\circ}$ 6, and 8.5 ± 0.5 respectively. Figure 3.2 shows a 2-D graph of the temperature distribution inside the compost pile at the beginning of the testing.

3.3.3 Box

Wooden boxes having dimensions of $0.6 \ge 0.3 \ge 0.10$ 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 3.3. 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 3.2: Temperature distribution inside the compost pile at the beginning of the



Figure 3.3: 3D view of Box

3.3.4 Placement of Packages

Composting exposure: 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. Each package was labeled for easy identification.

Ambient exposure: The packages were placed in open foldable reusable plastic containers obtained from CHEP (Orlando, FL) of dimensions $0.6 \ge 0.4 \ge 0.4 \ge 0.4$ meters, and they were exposed to ambient conditions. Two packages were evaluated at each condition.

3.3.5 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 ($\pm 1^{\circ}$ C) 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).

3.3.6 Ambient Conditions

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 3.4 a) shows the maximum and minimum ambient temperatures, Figure 3.4 b) shows the maximum and minimum relative humidity during the 30 day testing period, and Figure 3.4 c) shows the average daily solar radiation during the same period.



Figure 3.4: a) 30 days maximum and minimum temperature data; b) 30 days maximum and minimum relative humidity data; c) 30 days average total solar radiation

3.3.7 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.

3.3.8 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}. [19]

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 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 Differential Scanning Calorimeter (DSC) Q-100 made by TA Instruments (New Castle, DE) in accordance with ASTM D 3418-97. [20] The DSC standard calibration procedures was performed according to ASTM E967-03 [21] and ASTM E968-02 [22]. 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 [23] and equation 1.

$$x_{c}(\%) = 100 \times \frac{\Delta H_{c} + \Delta H_{m}}{\Delta H_{m}^{c}}$$
(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 [24, 25]. *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 [26]. The specimens were heated at the rate of 20°C from 23°C up to 500°C in presence of inert gas (N₂) and oxidative gas (O₂) 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).

3.4 RESULTS AND DISCUSSION

Poly(lactide) bottles, trays, and deli containers were introduced into the compost pile described above and composted for a period of 30 days. Table 3.1 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 and deli containers. The deli containers had a higher molecular weight than the bottles and trays.

Properties	Bottle	Tray	Deli
L-Lactide, %	96	94	94
Molecular weight	209,324	176,779	215,466
PDI	1.72	2.00	1.70
Tg, °C	60.6 ± 0.3	61.3 ± 0.6	62.1±3.4
Tm, °C	151.0±0.1	149.0±2.9	149.1±0.3
Crystallinity, % ^ª	12.2±1.4	9.2±9.7	2.7±1.8

Table 3.1. Physical properties of the poly(lactide) bottles, trays, and deli containers

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 3.5 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[27-30]. 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.



Figure 3.5. 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

3.4.1 Visual Inspection

Pictures showing the degradation process of the bottles, trays, and deli containers are presented in Figures 3.6, 3.7, & 3.8. Figure 3.6 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 3.7 and 3.8 for the trays

and deli containers. However, the decrease in thickness and increase in fragility of the tray and deli containers was much faster than for the bottles. From the first day, degradation in all packages was observed correlated to their change in shape. The dimensions of the containers before and after composting until the bottles, trays, and deli containers started to fragment were calculated by measuring the variation on width, length, height and thickness of the containers. Bottles dimensions reduced to 90%, trays to 22.4% and deli to 38%. Color changes were observed in the tray and deli containers; both were 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. The deli container showed increased degradation on the fourth day. 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 and deli containers showed almost the same rate of degradation with deli containers having almost 70% breakdown. On the ninth day, the bottle color showed white, blue and yellow shades, a powdery texture, and was more brittle. Most of the parts of the trays were already part of compost and approximately 98% of the deli containers were composted. Fifteenth day, the bottle walls and necks were almost degraded except the cap liners and bottom parts still had some residues, whereas the trays and deli containers 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. All other packages were degraded by the thirtieth day.



Figure 3.6. Pictorial view of the PLA bottles exposed at 30 day of compost conditions.



Day 1

Day 2



Day 4

Day 6



Figure 3.7. Pictorial view of the PLA trays exposed at 30 day of compost conditions.


Figure 3.8. Pictorial view of the PLA deli exposed at 30 day of compost conditions.

Although a major difference between the molecular weight of the trays and deli container was measured at time zero, this difference was not a reason for the longer degradation time of the deli containers. These will be expanded later in the paper.

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.

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3.4.2 Physical properties

Molecular weight: The molecular weight of bottles, trays, and deli containers exposed to ambient exposure and to composting conditions were 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 (see Scheme 3.1), are susceptible to hydrolysis.

First, randon non-enzymatic chain scission of the ester groups leads to a reduction in molecular weight. This step is accelerated by acids or bases and is affected by temperature and moisture levels[13]. Embrittlement of the polymers occurs in this step with a reduction of the molecular weight to around 50,000 Daltons. Second, low molecular weight PLA (M_n<10,000) can diffuse out of the bulk polymer and be used by microorganisms, yielding carbon dioxide, water, and humus. In the first step, PLA degradation is driven by the hydrolysis and cleavage of the ester linkages in the polymer backbone, autocatalyzed by the carboxylic acid end groups (Scheme 3.1). This part of the process follows first order kinetics[31]. In the second step, the molecular weight is reduced by the diffusion of the bulk polymer, and the lactic acid and low molecular weight oligomers are naturally metabolized by microorganisms to yield carbon dioxide and water.

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Scheme 3.1. PLA hydrolysis and molecular weight loss

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 polymer degradation rate[13, 32, 33]. In general, high temperature and humidity (50°C to 60°C) will cause PLA to degrade rapidly[34]. The molecular weight variation of the bottle, trays, and deli containers exposed to ambient and composting conditions for a period of 30 days can be seen in Figure 3.9 a to f. PLA bottles show a small increase of

molecula these var lower nu statistical first 15 d variation (P>0.01). significan to ambien the contai cleavage a increase i poly(lactid deterioratio in the mole glass transi degradation Figu were expose weight varia the PLA tray 9, while the t was not possi molecular weight due to the exposure to ambient conditions (Figure 3.9-a); however, these variations were not significant at the α =0.05 level (P>0.01), mainly due to the lower number of samples tested (six). In the case of the trays (Figure 3.9-b), a statistically significant increase in the molecular weight of ~28% was observed during the first 15 days (P<0.01). In the case of the deli containers (Figure 3.9-c), no significant variation of the molecular weight as a function of time was found at the α =0.05 level (P>0.01). However, the variation of the polydispersity index (PDI) was statistically significant at the α =0.05 level (P<0.01). The increase of the M_w for the sample exposed to ambient conditions could be due to recombination which occurs during the exposure of the containers to UV or gamma radiation. The electromagnetic radiation produces chain cleavage and subsequent recombination, which can result in crosslinking and hence an increase in the M_w. Kai- Lai and Pometto, (1999) showed that the exposure of poly(lactide) films to ultraviolet light (UV) enhances the degradation rate and the deterioration of the mechanical properties of these polymers [35]. However, the increase in the molecular weight, in case of the bottles and the trays, produces an increase in the glass transition temperature (shown later in Figure 3.11 a, b, &c) and leads to slower degradation since glassy polymers degrade more slowly than rubbery ones.

Figures 3.9 d, e, and f show the molecular weight change of the packages that were exposed to compost conditions for 30 days. Figure 3.9 d) shows that the molecular weight variation of the PLA bottles in the first 15 days of composting is much lower than the PLA trays and deli containers. Major fragmentation of the bottles was observed at day 9, while the trays and deli containers showed similar fragmentation at day 6. At day 30, it was not possible to locate any pieces of the tray and the deli container for analysis. The

PLA bot after bei attribute degradat followin molecula degradat kinetic p Table 3.2 level of s (the pre-e degradatic PLA bottles and trays (Figure 3.9 d & e) show a small increase in the molecular weight after being exposed to the compost pile for 1 day. This M_w 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[31]. Therefore, by fitting the data of the variation of the molecular weight as a function of time (equation 2), we can observe that the M_w degradation of the bottles, trays, and deli containers correlated well with a first order kinetic process as described by equation 2.

$$Mw = a * \exp^{-b^*t} \tag{2}$$

Table 3.2 shows the estimate of "a" and "b" values from equation (2) and their statistical level of significance for the PLA bottles, trays, and deli containers. Higher "b" values (the pre-exponential factor of equation 2) shown in Table 3.2 are an indication of faster degradation process, shown in Figure 3.9 e and f for the deli containers and the trays.



1

Figure 3.9 (P t



Figure 3.9. Comparison of the variation of the molecular weight and polydispersity index (PDI) as a function of time for a) bottles, b) trays, c) deli containers exposed to the ambient for 30 days; and d) bottles, e) trays, f) deli containers exposed to composting conditions for 30 days.

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Properties	L- Lactide, %	Xc	a	Pa	b	Pb	Adj Rsqr
Bottle	96	12.2±1.4	229.7±28.4	0.0002	0.1865±		0.85
					0.0533	0.0128	
Tray	94	9.2±9.7	204.8±21.5	0.0002	0.1953±	0.0088	0.88
					0.0470		
Deli	94	2.7±1.8	195.0±42.0	0.0056	$0.2401 \pm$	0.0911	0.64
					0.1149		

Table 3.2. First order equation $(M_w \times 10^3 = a^* \exp(-b^*t))$ of the degradation process of poly(lactide) bottles, trays, and deli containers

• $P_a \& P_b$ 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 R² 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.

The lower adjusted R values for the deli container is mainly due to a smaller reduction in the M_w of the samples extracted at day 4, credited mainly to the lower compost temperature in this part of the compost pile. 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[27]. Figures 3.9 d, e, and f also show the change of the PDI values of the bottles, trays and deli containers. 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 th Similar t reach fin Glass tre temperat shown in increase a total re condition molecula rate in t degradati amorphou degradatio other rese increased shown). [heating of of the sam and T_m of shown in F when the P the recombin 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 and deli containers reach final degradation much faster.

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 3.10. 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 30°C 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[36]. For example, the initial crystallinity of the bottles $\chi_c = 12.2 \pm 1.4$ 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 ambient and composting conditions for 30 days are shown in Figures 3.11 a, b, c, d, e, and f. The T_g of the bottles and the trays slightly rose when the PLA containers were exposed to ambient conditions for 30 days mainly due to the recombination process which increases the molecular weight and the T_g .



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Figure 3.10. 2nd run of DSC showing the glass transition and melting temperature variation of the PLA bottle 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 3.3 shows the results of fitting equation 3 to Figure 3.11's values

 $T_{g} = T_{g(0)} + d^{*}t$ (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 3.3 and Figure 3.11 d) show that a reduction of T_g = 0.97°C/day took place in the bottles exposed to composting. For the trays and the deli container a reduction of T_g = 0.70°C/day and T_g = 0.53°C/day were observed, respectively. Table 3.3 shows that a good fit to equation 3 is found for the PLA bottles and trays.





Figure 3.11. Glass transition and melting temperature variation of a) bottles b) trays c) deli containers exposed to the ambient conditions for 30 days; d) bottles e) trays f) deli containers exposed to composting conditions for 30 days

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In the case of the deli containers the fitting of equation 3 does not show a good agreement (AdsRsq= 0.67).

Table 3.3. Variation of glass transition $T_g = T_{g(0)} + d^*t$ as a function of time for poly(lactide) bottles, trays, and deli containers

Properties	L- Lactide, %	Xc	T _{g(0)}	P _{Tg(0)}	d	P _d	Adj Rsqr
Bottle	96	12.2±	60.86±1.01	< 0.0001	-0.97±	< 0.0001	0.95
Tray	94	9.2± 9.7	59.87±0.95	<0.0001	-0.70±	0.0031	0.82
Deli	94	2.7± 1.8	59.15±1.04	<0.0001	-0.53± 0.14	0.0143	0.67

• $P_{Tg(0)}$ & 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 $\alpha = 0.05$.

• Adj Rsqr is the R² 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.

If we plot the reduction of T_g as function of the number average molecular weight

 (M_n) , where $M_n = M_w$ / PDI (Figure 3.12 a, b, and c), we can observe that T_g decreases as the M_n decreases, which translate into a reduction of PLA degradation rate when M_n decreases. The influence of M_n on T_g can be expressed by an equation of the type:

$$T_g = T_{g(\infty)} - A/M_n \tag{4}$$

where " $T_{g(\infty)}$ " is the T_g for very high M_n , and "A" is a constant term. Table 3.4 shows the results of fitting equation 4 to the data of Figure 3.12. There is a slight difference between the best fit of equation 4 for the bottles, the trays, and the deli containers. The PLA bottles have a better fit to equation 4 (Adj-Rsqr=0.95). However, the trays and the deli containers show a poor correlation. This lack of correlation of T_g against M_n for the trays and deli containers is mainly because it was not possible to analyze samples after 15 days of being in the compost (i.e., lower M_n), and due to the variation in temperature at day

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four for the trays. The variation of T_m as a function of time does not follow a linear relationship. A slight increase of T_m is found for the samples submitted to compost conditions at the beginning of the composting process.

Table 3.4. Variation of glass transition $T_g = T_{g(\infty)} - A/M_n$ as a function of average
molecular weight number for poly(lactide) bottles, trays, and deli containers

Properties	L- Lactide, %	Xc	T _{g(∞)}	₽ _{T g(∞)}	Α	P _A	Adj Rsqr
Bottle	96	12.2±	60.42±	< 0.0001	-112,972±	< 0.0001	0.95
		1.4	0.94		8,968		
Tray	94	9.2±	58.83±	< 0.0001	-44,435±	0.0147	0.67
		9.7	1.14		12,166		•
Deli	94	2.7±	58.66±	< 0.0001	-32,643±	0.0289	0.58
		1.8	1.12		10,750		

• $P_{Tg(\infty)} \& P_A$ 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 R² which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.

• The " $T_{g(\alpha)}$ " and "A" 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.



Figure 3.12. $T_g vs M_n$ of the a) bottles b) trays, and c) deli containers exposed to compost conditions for 30 days



Figure 3.13. a) Weight percent reduction vs temperature

A TGA plot of the variation of weight as temperature increased for the bottles exposed at different composting times is shown in Figures 3.13 a & b. 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.

The variation of T_D as a function of time for the packages exposed to ambient and composting conditions is shown in Figure 3.14. Figures 3.14 a, b, & c show the variation of T_D versus time for PLA bottles, trays, and deli containers exposed to ambient conditions and to composting conditions, respectively. As shown in Figure 3.14, no variation of the T_D as a function of time was observed for the samples exposed to ambient

conditions. However, a reduction of T_D was observed for all the samples exposed to compost conditions.

The variation of T_D with time is a linear variation. Table 3.5 shows the values obtained from fitting equation 6 to the data shown in Figure 3.20:

$$T_D = T_{D0} + e^{t} t$$
 (6)

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 3.5 also shows the variation of T_D vs M_n for equation 7:

$$T_{\rm D} = T_{\rm D(\infty)} - B/M_{\rm n} \tag{7}$$

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 and the deli.



Figure 3.14. Decomposition temperature a) bottles b) trays c) deli containers exposed to (□) ambient and (•) composting conditions for 30 days

Table 3.5 shows that a good adjustment of equation 6 & 7 are obtained for the

bottles, trays, and deli containers (see Adj Rsqr values).

Table 3.5. Variation of decomposition temperature $T_D = T_{D0} + e^*t$ as a function of time (equation 6) and Molecular number for poly(lactide) bottles, trays, and deli containers. Variation of decomposition temperature $T_D = T_{D(\infty)} - B/M_n$ as a function of M_n

<u>Equation o</u> :	$T_D = T_{D0} + e^*$	t					
Properties	L- Lactide,%	Xc	T _{D0}	P_{T D0}	e	Pe	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
Deli	94	2.7±1.8	398.4±9.5	< 0.0001	-6.2±1.3	0.0057	0.77
Equation 7:	$T_{\rm D} = T_{\rm D(\infty)} - E$	B/M _n					
	T		The second secon	D	D	D	4 11
Properties	L- Lactide,%	Xc	T _{D(∞)}	₽ _{TD(∞)}	В	P _B	Adj Rsqr
Bottle	L- Lactide,% 96	Xc 12.2±1.4	T _{D(∞)} 402.2±2.3	P _{TD(∞)} <0.0001	B -327,501± 21,647	Р _в <0.0001	Adj Rsqr 0.97
Bottle	L- Lactide,% 96 94	Xe 12.2±1.4 9.2±9.7	T _{D(∞)} 402.2±2.3 397.8±3.3	P _{TD(∞)} <0.0001 <0.0001	B -327,501± 21,647 -342,941± 35,267	P _B <0.0001 0.0002	Adj Rsqr 0.97 0.94

 P_{TDO}, P_e, T_{D(∞)}, & 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 R² 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 three 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 [37] 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 [34, 35, 38-40]. 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 [39]. They also found that degradation of PLA is enhanced by an increase in temperature and relative humidity [34]. However, no comparison or methods of assessing the degradation of complete packages were carried out.

Thus, the present work addressed the degradation time of the physical properties of three 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. 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 and deli containers 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.

3.5 CONCLUSIONS

Three PLA packages, a bottle, a tray, and a deli container, were used to determine the degradation process under ambient exposure and 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 and deli containers degraded before 30 days under composting conditions (T>55 °C, >65%RH, ph~7.5). First order degradation kinetics was observed for the bottle and tray. A Tg reduction of 1°C/day was found for PLA containers with 96%L-lactide, and a Tg average reduction of around 0.6 °C/day was found for PLA containers with 94% 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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CHAPTER FOUR

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CHAPTER FOUR - COMPARISON OF THE DEGRADABILITY OF POLY (LACTIDE) PACKAGES IN COMPOSTING AND AMBIENT EXPOSURE CONDITIONS

ABSTRACT

The adoption of biodegradable polymeric materials is increasing in food and consumer goods packaging applications, due to concerns about the disposal of petroleumbased 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 study was to investigate and compare the degradation of two commercially available biodegradable packages made of PLA under real compost conditions and under ambient exposure, using visual inspection, gel permeation chromatography, differential scanning calorimetry and thermal gravimetric analysis. A novel technique to study and track the degradability of these packages 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 delicatessen ('deli') containers made of 94% L-lactide, mainly due to their highly ordered structure and, therefore, their 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 trends were observed for both packages subjected to composting conditions.

4.1 INTRODUCTION

There is an increasing demand for biopolymer-based packaging materials that are easily renewable, providing enhanced environmental performance. Until recently the majority of the production of packaging plastics was based on non-renewable materials. Plastic packaging materials are often landfilled due to their content of foodstuffs and other biological substances, making physical recycling of these materials impractical. Use of biopolymer-based packaging materials reduces concerns such as landfilling, sorting and reprocessing by taking advantage of their unique functionality, i.e. compostability. Hence, compostability has 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 as sorting and reprocessing for recycling, although it requires more energy than landfilling. For example, 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 the form of carbon, nitrogen, oxygen and water. Organisms decompose the organic matter by utilizing carbon as a source of energy and nitrogen for building cells. A 30:1 carbon:nitrogen ratio is an ideal proportion for the reproduction of thermophilic microorganisms.² A compost pile goes through two composting stages. In the first stage, the temperature rises up to around 60°C, so long as oxygen, carbon and nitrogen are available in the ideal proportions, and promotes strong microbial activity. In the second 'curing' stage, the decomposition continues at a slower rate and the last remaining nutrients are consumed by microorganisms and until almost all the carbon has been converted to carbon dioxide.

The compostability of a *compostable plastic* (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 leaves no visible, distinguishable or toxic residue³) is commonly evaluated in simulated compost conditions and by assessing the final quality of the compost. While evaluating the compostability, plastics are subjected to mechanical, thermal and chemical degradation, of which chemical degradation is the most important. Biodegradable polymers first become susceptible to water attack and chemical degradation initiates the polymer erosion as a result of 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. The ASTM standards (i.e. ASTM D5338-98,⁴ D6003-96,⁵ D6954-04,⁶ D6400-99,³ and D 6002-96 (reapproved 2002)^{ϵ 1,7}) developed by subcommittee 20.96 for assessing compostability, are laboratory-scale and limited to the evaluation of plastic materials.^{3,5–7} Similarly ISO standards, such as ISO 14851,⁸ 14852⁹ and 14855,¹⁰ allow evaluation of

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materials under laboratory conditions and are based on measuring the carbon dioxide evolution and oxygen demand during degradation. The EN 13432:2000¹¹ standard developed by the European Committee for Standardization addresses compostability referring to ISO standards and evaluates the compost quality and toxicity. The abovementioned standards mainly focus on addressing the compostability of a polymer or a material, but not that of a package in real conditions. The 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 ground, 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 about the disposal of petroleumbased polymers. Currently, poly(lactide) (PLA) polymer developed by Cargill Dow LLC (Blair, NE) and at this time under the name of NatureWorks[®] LLC, is the biggest commercially available bio-based polymeric packaging material. NatureWorks[®] LLC is producing 300 million lb PLA annually for a variety of packaging and fibre applications. Eastman Chemical Company (Hartlepool, UK), has developed Eastar Bio aliphatic co-polyester, 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) has produced an aliphatic co-polyester (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 co-polymer hydro/biodegradable polyester, which is available both overseas and in the USA.¹²

PLA polymer, the predominant biopolymer in the market for packaging applications, can be manufactured by carbohydrate fermentation or chemical synthesis. Lactic acid (2-hydroxypropionic 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. the stereochemical make-up of the backbone) and the molecular mass, which is controlled by addition hydroxylic compounds.¹³ 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.¹³ In addition, the degradation behaviour strongly depends on the crystallinity of the PLA.¹³ The glass transition temperature (T_g) is in the range 50-80°C, while the melting temperature (T_m) is in the range 130-180°C. PLA can be processed by injection moulding, sheet extrusion, blow moulding, 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 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. 'ones that include the residential waste stream that arrives at the plant as mixed waste or source separated fractions¹) were in operation. Hence for PLA to be considered as an alternative to 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's potential recyclability, NatureWorks[®] LLC instituted a large volume 'buy-back' programme in North America for post-consumer treatment of PLA bottles in mixed plastic waste recycling streams.¹⁹ PLA can be sorted from other plastics using near-infrared technology. However, as already mentioned, 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 CO_2 . There are several parameters which differentiate the real and simulated or controlled composting conditions. According to ASTM D 6002-96(2002),⁷ and the Federal Trade Commission (FTC),²⁰ 'compostable claims would be appropriate on products or packages

that will break down, or become part of usable compost, in safe and timely manner in home compost piles',²⁰ where 'timely manner' means the time necessary for leaves, grass and foodstuffs to compost. Some of the commercially available 'biopolymer materials' comply with the standards of compostability, but generally packages or containers made from these materials 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 the comparison of degradability 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 analysed 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).

4.2 MATERIALS AND METHODS

4.2.1 Packages

Poly(lactide) bottles were obtained from NatureWorks[®] LLC (Blair, NE) and commercialized by Biota brands of America (Telluride, CO) with 96% L-lactide and bluetone additive, height = 0.2 m and base diameter = 0.0065 m (volume = 500 ml). Delicatessen ('deli') containers were obtained from Wilkinson Manufacturing Company

(Fort Calhoun, NE) with 94% L-lactide; height = 0.07 m and base diameter = 0.09 m (volume = 600 ml). Figure 4.1a, b shows these containers.







(b)

Figure 4.1. PLA containers a) bottle & b) deli container

4.2.2 Compost pile

A compost pile used for this study was composed of cow manure and wood shavings prepared at the Michigan State University Composting Facility (East Lansing, MI) and was used for the study. Initially, 11.6 m³ cow manure and 7.8 m³ wood shavings 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 allowed a carbon:nitrogen ratio of 30:1. The mixture was kept in a rectangular bay of $36.5 \times 3.6 \times 1.8$ m, which was turned using a Marvel model of a commercial turner manufactured by Global Earth (Ontario, Canada) 3 days/week for 3 weeks. Due to turning, the mixture was heated to 60°C in 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 $24 \times 6 \times 3$ m was built up on an asphalt pad. Initially the compost parameters, such as temperature, moisture and pH, were measured and determined. A temperature of $65 \pm 5^{\circ}$ C, moisture of $63 \pm 5\%$ and pH of 8.5 ± 0.5 was observed. Figure 4.2 shows a two-dimensional graph of the temperature distribution inside the compost pile at the beginning of the testing.



Figure 4.2: Temperature distribution inside the compost pile at the beginning of the

testing

Wooden boxes of dimensions $0.6 \times 0.3 \times 0.1$ m were manufactured using treated wood and were used for subjecting packages into the compost pile. Those boxes facilitated the exact location and identification of the package in the compost pile; and also the removal of the package and portion of compost for analysis. A mesh of 0.011 gauge was fitted at the bottom of the boxes. A three-dimensional image of a wooden box is shown in Figure 4.3.



Figure 4.3: 3D view of Box

4.2.4 Plastic containers

Foldable reusable plastic containers obtained from CHEP-USA (Orlando, FL) of dimensions $0.6 \times 0.4 \times 0.4$ m were used to contain and expose the packages to ambient conditions.

4.2.5 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 m above the ground and 1 m 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 with the 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 sets, as in case of composting exposure. The packages were taken out at 1, 2, 4, 6, 9, 15 and 30 days from both the compost pile and plastic containers.

4.2.6 Compost parameters

Temperature: Temperatures were recorded every time the packages were removed from the compost pile, using a A60FR fast response windrow stainless steel thermometer (\pm 1°C) obtained from Reotemp (San Diego, CA). Temperatures were continuously recorded using H12 Type J HOBO[®] brand battery-operated data loggers obtained from Onset Computers (Pocasset, MA) at 6 h intervals for the duration of the study.

Moisture content:. The wet weight moisture content of the compost was measured using a modified version of ASTM D4643-00²¹ (previously validated using a traditional vacuum oven).²² A sample of compost was obtained whenever packages were taken out of the compost pile and checked immediately for the moisture content. Initially the wet weight of compost was recorded and then heated in a 600 W microwave, Model MW8625W, obtained from Emerson Radio Corporation (Parisppany, NJ) for 3 min. The weight reduction in the compost due to evaporation of moisture was recorded, and the sample was again subjected to microwave heating for 1 min. The cycle of recording the weight and heating for 1 min 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 After the compost was dried through the microwave heating process, 5 g of the specimen was added to 25 ml deionized water. This mixture was stabilized for 5 min before the pH of the solution was recorded using a calibrated pH paper (150AB pHydrion paper dispenser), obtained from Micro Essential Laboratory Inc. (Brooklyn, NY).

4.2.7 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° latitude, -84.4870° longitude and 264 m elevation, for the complete duration of the study. The air temperature measurements were taken 1.5 m above ground level. Figure 4.4a shows the maximum and minimum ambient temperatures; Figure 4.4b shows the maximum and minimum relative humidity during the 30 day testing period; and Figure 4.4c shows the average daily solar radiation during the same period.



Figure 4.4: a) 30 days maximum and minimum temperature data; b) 30 days maximum and minimum relative humidity data; c) 30 days average total solar radiation

4.2.8 Visual inspection

Every time that the packages were removed from the compost and ambient exposure conditions they were visually inspected by the authors. A Sony Cybershot DSC-P150 7.2 MegaPixel digital camera was used to take pictures. The packages were inspected for colour, texture, shape and changes in dimensions.

4.2.9 Physical properties

Thickness. The thickness of the packages was determined using a Magna Mike 8000 thickness gauge, which utilizes a magnetic method manufactured by Panametrics (Japan) according to ASTM D4166-99 (2004).²³

Molecular weight. The molecular weight was determined using a standard GPC technique. A 600 Multisolvent delivery system equipped with 717 autosampler and 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, WI) was transferred to 2 ml vials containing 2 mg of specimen. The vials with the specimens were manually shaken for 2 min. The dissolved samples were filtered with 0.2 μ m 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 PL gel 10 μ m MIXED-B 300 \times 7.5 mm i.d. columns from Polymer Laboratories (Amherst, MA) in series were used, giving a detection range of 1000–10 000 000 Da. Polystyrene obtained from Sigma Aldrich (Milwaukee, WI) 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 at 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 (Newcastle, DE) in accordance with ASTM D 3418-03.²⁴ The DSC standard calibration procedure was performed according to ASTM E967-03²⁵ and ASTM E968-02.²⁶ Analyses of the results were made using Universal analysis software (version 3.9A). The percentage crystallinity was determined according to ASTM D3417-99²⁷ and equation 1:

$$x_{c}(\%) = 100 \times \frac{\Delta H_{c} + \Delta H_{m}}{\Delta H_{m}^{c}}$$
(1)

where ΔH_c is the enthalpy of cold crystallization, ΔH_m is the enthalpy of fusion, and 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 (Newcastle, DE) in accordance with ASTM E1131- $03.^{30}$ The specimens were heated at a rate of 20°C/min from 23°C to 500°C in the presence of inert gas (N₂) and oxidative gas (O₂), both > 90 p.s.i. The results were analysed using Universal analysis software (version 3.9A).

4.2.10 Statistical analysis

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

4.3 RESULTS AND DISCUSSION

Poly(lactide) bottles and deli containers were subjected to composting and ambient exposure conditions for a period of 30 days. Table 4.1 shows the initial physical properties of these packages. The PLA bottles, made of 96% L-lactide, are a more highly ordered structure, resulting in a higher crystallinity than the deli containers, with 94% L-lactide. PLA derived from > 93% L-lactic acid can be semi-crystalline.^{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 container had a higher molecular weight than the bottle and a lower initial polydispersity index (PDI).

Properties	Bottle	Deli
L-Lactide (%)	96	94
Molecular weight (kDa)	209.3 ± 1.06	222.7 ± 9.20
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

Table 4.1. Physical properties of the poly(lactide) bottles and deli containers

^aPercentage 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 pH to which the three packages were exposed during the composting conditions are shown in Figure 4.5a, b.



Figure 4.5. 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

pH is one of the most important factors of hydrolytic polymer degradation, since pH variations can change hydrolysis rates by a few orders of magnitude.³²⁻³⁵ In this

study, there was a slight alkalization of the pile after the second day of testing, although this difference was not statistically significant at the $\alpha = 0.05$ level (p = 0.91) during the 30 days of composting.

4.3.1 Visual inspection

Pictures showing the degradation process of the bottles and deli containers in the compost pile are presented in Figures 4.6, 4.8. Figure 4.6 shows the degradation of the PLA bottles over the 30 days. Initially the bottles decreased in size. The change in shape is because of distortion due to the higher temperatures in the compost pile.



Figure 4.6. Pictorial view of the PLA bottles exposed at 30 day of compost conditions.





A similar degradation process can be seen in Figure 4.8 for deli containers. From the first day of being in the compost pile, shape changes were observed in both packages. The dimensions of the containers before and after composting until the bottles and deli containers started to fragment were calculated by measuring the variations in width, length, height and thickness of the containers. Variation in thicknesses and shapes were observed on both packages from day 1, when the bottle dimensions reduced to 90% and those of the deli container reduced to 22.22% of their original volumes. Colour changes were observed in the deli containers, which became white at the bottom. On day 4, the bottle structures seemed the same as on the first day, but with shorter dimensions by approximately 63.4% of the original volume, whereas the deli containers showed toughness in the material. On day 6, bottle breakdown at the neck was observed and bottle threads were already separated.



Figure 4.8. Pictorial view of the PLA deli container exposed at 30 day of compost conditions.



Figure 4.9. Pictorial view of the PLA deli containers exposed for 30 days under ambient conditions

Colour change and brittleness were also observed. The deli containers showed a similar rate of degradation. On day 9, the bottle colour showed white, blue and yellow shades and a powdery and more brittle texture; the deli containers started breaking apart, had powdered structure, and were very brittle. By day 15, the bottle walls and necks were almost degraded except for the parts of the bottle threads and bottom that still had some residues, whereas the deli containers showed some residues in the form of a yellowish film, although it could not be identified whether the residue was from the walls or bottom of the containers. Some residuals from the bottles were still observed on day 30. The residuals were mostly part of bottle threads and in the form of string-like structures. Bottles and deli containers exposed to ambient conditions were also examined by visual inspection. Figures 4.7, 4.9 show the degradation process of the bottles and deli containers in ambient environments. The packages faced different atmospheric conditions such as solar radiation, rain, snow, wind and variable atmospheric pressures (Figure 4.4ac). No visible difference was observed in either of the packages exposed to ambient exposure conditions for the duration of the study.

4.3.2 Physical properties

4.3.2.1 Molecular weight

The molecular weight was monitored using the standard GPC technique, as previously described. The molecular weight degradation gives information about the main fragmentation which occurs in a polymer. PLA polymers, by having -C-O- ester linkages in the polymer backbone that are hydrolysable functional groups (see Scheme 1), are susceptible to hydrolysis.



Scheme 4.1. PLA hydrolysis and molecular weight loss

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 Da. The PLA degradation is driven by the hydrolysis and cleavage of the ester linkages in the polymer backbone, autocatalysed by the carboxylic acid end-groups. This part of the process follows 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 (50–60°C and 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 that affects the reactivity and 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} The variation in molecular weight of bottles and deli containers is shown in Figure 4.10. PLA bottles and deli containers exposed to ambient conditions for 30 days did not show significant M_w variation as a function of time at the $\alpha = 0.05$ level (p > 0.01) (Figure 4.10a, c). Also, the variations of PDI for the bottles and deli containers were not statistically significant at the $\alpha = 0.05$ 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 compared with the time taken by the packages to degrade in the compost environment.

Figure 4.10a, c, shows the molecular weight change of the packages that were exposed to compost conditions for 30 days. Figure 4.10a 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 4.10c.



Figure 4.10. 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 4.10 c indicates the fitting of equation 2 without considering the M_w values at day 4 and 6)

Both high molecular weight polymers are reduced to low molecular weight polymer by a combination of chain scission and removal of repeat units from the chain ends of the polymer. This leads to fragmentation or dissolution of the polymer. Major fragmentation with $M_w < 10000$ of bottles and deli were observed at day 15. At day 30 it was not possible to locate any residues of the deli containers. Further enzymatic action yields oligomeric fragments and simple organic compounds that are intermediates of the biodegradation process. The PLA bottles (Figure 4.10a) 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 cross-linking 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 Therefore, by fitting the data of the variation of the molecular weight as a function of time (equation 2), we can observe that the M_w degradation of the bottles and deli containers correlated well with a first-order kinetic process:

$$Mw = a * \exp^{-b^*t} \tag{2}$$

Table 4.2 shows the estimate of *a* and *b* values from equation (2) and their statistical level of significance for the PLA bottles and deli containers. The *b* (the pre-exponential factor of equation 2) values indicate the degradation rate. Higher *b* values denote higher degradation rates. We can observe that PLA bottles have a higher *b* value $(b = 0.18 \pm 0.05)$ than deli containers $(b = 0.15 \pm 0.04)$ (solid line in Figure 4.10c). However, if the M_w values for the deli containers at days 4 and 6 are not taken in consideration when fitting equation 2, the degradation rate of the deli containers $(b = 0.29 \pm 0.04)$ is higher than that of the bottles $(b = 0.18 \pm 0.05)$. Also, a higher adjusted *R* value is obtained in the second case for the deli containers $(Adj Rsqr_{Deli} = 0.991)$. The higher M_w values obtained at days 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 variations 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

Properties	χc	<i>a</i> ³	p_a^{-1}	b^3	p_b	Adj Rsqr ²
Bottle	12.2 ± 1.4	229.7 ± 28.4	0.0002	0.18 ± 0.05	0.01	0.867
Deli	1.4 ± 0.3	209.6 ± 27.8	0.0010	0.15 ± 0.04	0.03	0.823
Deli $()^4$	1.4 ± 0.3	221.2 ± 11.7	0.0003	0.29 ± 0.04	0.008	0.991

Table 4.2. First-order equation $[M_w \times 10^3 = a^* \exp(-b^*t)]$ of the degradation process of poly(lactide) bottles and deli containers

 p_a and p_b are the probability of being wrong in concluding that there is an association between the dependent and independent variables. The smaller the *p* value, the greater the probability that there is an association. For this study, $\alpha = 0.05$.

²Adj Rsqr is the R^2 which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.

 $a^{3}a$ and b values refer to equation 2. These values are shown with their 95% confidence levels. ⁴Second line fitted in Figure 4.10c.

Figure 4.10b, d, shows 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 compositing 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. After day 15, narrowing of the molecular weight distribution was observed with decrease in PDI until complete degradation. At this point, only oligomers of the PLA chains are present. When both packages were subjected to ambient conditions, no significant changes of M_w at the $\alpha = 0.05$ level (p > 0.01) were observed.

4.3.2.2 Glass transition and melting temperature

The second run DSC plots for PLA bottles and deli containers exposed to composting conditions are shown in Figure 4.11. A decrease of 28°C was observed in bottles on day 30, whereas it was 8°C for deli containers on day 15. Initially, a short increase of T_g is observed, which can be attributed to the short span increment of the molecular weight. The later reduction in T_g is associated with the reduction of the molecular weight for both packages. Since the hydrolysis of PLA polymers occurs 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 researchers.⁴¹ In this study, the initial crystallinity of the bottles ($\chi_c = 12.2 \pm 1.4$) increased to values of 16% until the last degradation day, and in the case of the deli containers $\chi_c = 1.40 \pm 0.3$ it was observed to increase to 27% higher (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 history of the samples and the cooling cycle did not allow recrystallization.



Figure 4.11. 2nd run of DSC showing the glass transition and melting temperature variation of the PLA (a) bottle and (b) deli container exposed to composting conditions

for 30 days

The variation in T_g and T_m for packages subjected to both composting and ambient environments is shown in Figure 4.12. Figure 4.12a, b, shows the T_g and T_m variations, respectively, for bottles and Figure 4.12c, d, shows T_g and T_m variations, respectively, for deli containers.



Figure 4.12. 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

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 in the early stages, due to recombination reactions. A linear degradation trend in case of PLA packages subjected to composting conditions was observed. Values in Figure 4.13 for equation 3 are shown in Table 4.3:

$$T_g = T_{g(0)} + d^*t$$
 (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 4.3 and Figure 4.13a show that a reduction of $T_g = 0.97^{\circ}$ C/day took place in the bottles exposed to composting. For the deli containers, a reduction of $T_g = 0.46^{\circ}$ C/day was observed, but a good correlation was not obtained (*Adj Rsqr* = 0.47). Higher adjustment *R* values were observed for bottles than for deli containers.

Table 4.3. Variation of glass transition $T_g = T_{g(0)} + d^*t$ as a function of time for poly(lactide) bottles and deli containers

Properties	Xc	$T_{g(0)}^{3}$	$P_{Tg(0)}^{1}$	d^3	p_d	Adj Rsqr ²
Bottle	12.2 ± 1.4	60.86 ±	< 0.0001	-0.97 ±	< 0.0001	0.954
Deli	14 ± 03	1.01 59 90 ±	< 0.0001	0.08	0.0516	0 477
2 VII	= 0.5	1.30		0.18	0.0010	0/

 ${}^{1}p_{T_{g(0)}}$ and p_{d} are the probability of being wrong in concluding that there is an association between the dependent and independent variables. The smaller the *p* value, the greater the probability that there is an association. For this study, $\alpha = 0.05$.

 $^{2}Adj Rsqr$ is the R^{2} which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.

 ${}^{3}T_{g(0)}$ and d values refer to equation 3. These values are shown with their 95% confidence levels.

No significant changes in T_g and T_m were observed in case of both packages subjected to ambient conditions at $\alpha = 0.05$ level (p > 0.01). However, a slight reduction of the T_g values is graphically observed (Figure 4.12c).

4.3.2.3 Decomposition temperature

The variation of T_D as a function of time for both package and for both

environments is shown in Figure 4.13 a, b.

A linear variation was observed for packages subjected to compositing conditions, whereas no significant changes were observed for the packages subjected to ambient conditions at $\alpha = 0.05$ level (p > 0.01).

Table 4.5 shows the values obtained from fitting equation 4 to the data shown in Figure 4.14:

$$T_D = T_{D0} + e^* t \tag{4}$$

where T_{D0} is the decomposition temperature at day t = 0, and e is the variation of T_D as a function of time. Table 4.5 also shows the variation of T_D vs. M_n , number average molecular weight for equation 5:

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

where $T_{D(\infty)}$ is the T_D for very high M_n , and B is a constant term. The R^2 values obtained for fitting equation 5 to both packages are shown in Table 4.4. An inverse decay (as shown in equation 5) was observed in correlation of T_D with the number average molecular weight for both the packages.



Figure 4.13. 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. T_D for bottles decreased from 395°C to 378°C; however, no statistical significance was observed at the $\alpha = 0.05$ 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 the $\alpha = 0.05$ level (p = 0.0118).

Table 4.4. Variation of decomposition temperature $T_D = T_{D0} + e^*t$ as a function of time (equation 4) and molecular number for poly(lactide) bottles and deli 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	χc	T_{D0}^{3}	<i>p</i> _{TD0}	e^{3}	p_{e}	Adj Rsqr ²	
Bottle	12.2 ± 1.4	403.4 ± 2.7	< 0.0001	-2.8 ± 0.2	< 0.0001	0.960	
Deli	1.4 ± 0.3	404.1 ± 4.8	< 0.0001	-5.6 ± 0.6	< 0.0001	0.918	

Equation 5: $T_D = T_{D(\infty)} - B/M_n$							
Properties	Xc	$T_{D(\infty)}^{3}$	$p_{TD(\infty)}$	B^3	p_{B}^{1}	Adj Rsqr²	
Bottle	12.2 ± 1.4	402.2 ± 2.3	< 0.0001	-327 501.0 ± 21 647.0	< 0.0001	0.97	
Deli	1.4 ± 0.3	394.0 ± 2.5	< 0.0001	-403 956.8 ± 30 589.1	< 0.0001	0.97	

 ${}^{1}p_{TDO}$, p_c , $T_{D(\infty)}$ and p_B are the probability of being wrong in concluding that there is an association between the dependent and independent variables. The smaller the *p* value, the greater the probability that there is an association. For this study, $\alpha = 0.05$.

²Adj Rsqr is the R^2 which measures the proportion of the variation in the dependent variable accounting for the number of explanatory variables.

 ${}^{3}T_{D0}$ refers to equation 4; and $T_{D(\infty)}$ and B refer to equation 5. These values are shown with their 95% confidence levels.

In summary, PLA polymers break down due to the absorption of water, resulting in 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 affected by the initial crystallinity and the percentage Llactide content. The 94% L-lactide content packages disappear more rapidly from the compost than the 96% L-lactide packages. Hence, the initial crystallinity and L-lactide content of the PLA packages should be considered for estimation of the time required for decomposition in the composting environment. Similar compost studies, but with PLA samples and incomplete packages, were carried out by Weber⁴² by storing PLA samples

in biodegradation chambers. Weber⁴² 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 in various studies.^{36,39,43-} ⁴⁵ They exposed PLA films in banana fields in Costa Rica, and found that these PLA plastic films lost mechanical properties and degraded faster in composting conditions than during exposure in soil conditions (3 weeks and 6 months, respectively).⁴⁴ These studies also found that degradation of PLA is enhanced by an increase in temperature and relative humidity.³⁶ Previous studies have been based on assessing the degradability of plastic samples and not complete packages. This study has assessed and addressed the degradation time, physical properties and comparison of two commercially available PLA packages. It also gives information about the compostability and reduction of the physical properties under real compost as well as ambient exposure conditions. 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 in order to take place ($T > 50^{\circ}$ 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 the evaluation of packages under real compost conditions. Furthermore, future 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.

4.4 CONCLUSIONS

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 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 in < 30 days under composting conditions ($T > 60^{\circ}$ C, RH > 65%, pH \approx 7.5). First-order degradation kinetics were observed for the bottles. A T_g reduction of 1°C/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 will aid in the development of a reliable laboratory test that can address the compostability of biodegradable packages resembling real conditions.

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CHAPTER 5 - BIODEGRADABILITY OF POLYLACTIDE BOTTLES IN REAL AND SIMULATED COMPOSTING CONDITIONS

5.1 INTRODUCTION

According to the 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 composting (ASTM D5338), anaerobic digestion (ASTM D5511 and D5526), and wastewater treatment (ASTM D5210 and D5271) [2]. In order to justify a cradle to cradle approach, one of the most attractive alternatives would have biodegradable plastics be composted at the end of their useful life and later used in sustainable agricultural practices; hence, in 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 (CO₂ 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

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biodegradable and further ecotoxicity tests are carried out in accordance with ASTM D6400 to certify that it is compostable. ISO 14855-1 [5, 6] 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 references [4-6].

ASTM and ISO standards guidelines are limited to the biodegradability evaluation of plastic material or a plastic material from a package; however, the European Committee for Standardization (CEN) has developed a standard EN 13432 [7], which provides detailed guidelines for evaluation of packaging and packaging components' biodegradability and compostability based on their characterization, biodegradability, disintegration and compost quality/ecotoxicity. The biodegradability test methods are mainly based on the ISO 14855-1 and somewhat similar to the ASTM D5338 standard [2].

ISO has a standard under development, ISO 14855-2, which measures mineralization of a polymer by a gravimetric method. ISO 14855-2 [8] 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. Also 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 have been reported and correlated to visual changes and variation in physical properties of the materials [9, 10]. 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 packaging compostable 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; and 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 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.

5.2 MATERIALS AND METHODS

5.2.1 Samples

PLA bottles (500 mL) used for packaging of spring water and commercialized by Biota brands of America (Telluride, CO) were obtained from NatureWorks[™] PLA (Blair, NE). The PLA bottles were composed of 96% L-lactide with bluetone additive and dimensions of 0.2 m height and 0.065 m in base diameter. The organic carbon content of the PLA bottle was 49.5% which was determined by elemental analysis (Organic Elemental Analysis, PerkinElmer, Shelton, CT) A picture of the PLA bottle is shown in figure 5.1.



Figure 5.1 PLA Bottle

5.2.2 Real composting conditions

A compost pile made of cow manure, wood shaving and waste feed (i.e., the feed that the cows do not eat between feedings) 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 meters in width, 24 meters long, and 3 meters in height, and it was built up on

asphalt pad. The initial temperature, relative humidity and pH of pile were $65 \pm 5^{\circ}C$, $63 \pm$ 5%, and 8.5 ± 0.5 , respectively, and it 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 composting process were recorded through the Michigan Automated Weather Network (East Lansing, MI) for the entire period of the study [9, 10]. A novel method was developed to track and trace the PLA bottles in the compost pile. A wooden box of dimensions 0.6 x 0.3 x 0.1 meters was built with a mesh attached at its bottom to retain and easily identify the samples and the surrounding compost for further analysis. Initially, compost was added on the bottom of the mesh, and later the PLA bottle was placed on it and completely covered with compost. The box was placed at approximately 1.2 meters above the ground and 1 meter 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 references [9, 10]. Figure 5.2 shows how the packages were located in the compost pile. After the packages were covered with compost soil, 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.



Figure 5.2 Placement of packages in compost pile

5.2.3 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 [9, 10].

5.2.4 Cumulative Measurement Respirometric (CMR) System

A CMR system based on ASTM D5338 [4] and ISO 14855-1 [6] 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 Michigan State University composting facility was used for biodegradation purpose. The preparation of

the compost was previously discussed. The compost was sieved through a 5 mm sieve and inert materials such as glass, stones and metal were removed. Fine particle of vermiculite grade number 4 soil conditioner manufactured by Therm-O-Rock (New Eagle, PA) was used for mixing with compost to provide better aeration and retain of moisture. Dry compost (400 grams) was mixed with 100 grams of dry weight vermiculite, and the moisture level was adjusted so that the mixture retains moisture of its 90% water holding capacity [11]. PLA bottles were cut into 0.01 m x 0.01 m pieces, except the part of neck and cap threads. These cut PLA bottle samples were used as a sample 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 and should be in 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 recommends using a negative control for this experiment, a negative control was neglected in this study. The current system comprised of 9 bioreactors; 3 blanks, 3 positive control (cellulose) and 3 samples (PLA bottles) placed in a temperature controlled system. An environmental controlled room manufactured by Lab-Line Instruments Inc (Melrose Park, IL) was used to place the bioreactors in the temperature controlled environment. A schematic of CMR system is shown in Figure 5.3.



Figure 5.3 Schematic of CMR system

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 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 mounted 2 mm screen at the bottom of bioreactor and above the air inlet were introduced to equally distribute the air in the compost and avoid channeling, as previously proposed by Kijchavengkul et.al [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 mL 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:

$$NaOH + CO_2 \longrightarrow NaHCO_3$$
 (1), then

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O \tag{2}$$

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

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$
 (3), then

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$
(4)

Initially, few drops of phenolphthalein indicator were added to the 10 mL NaOH aliquot and further titrated till 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:

$$gCO_2 = \frac{V.C.44}{1000}$$
(5)

where gCO_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:

$$\% Mineralization = \frac{gCO_2 - gCO_2b}{g_{material} \cdot \frac{\% C_{material}}{100} \frac{44}{12}} \times 100$$
(6)

where gCO_2 is the amount of evolved carbon dioxide in grams in the sample and the positive control; gCO_2b is the amount of evolved carbon dioxide in grams in blank; $g_{material}$ is the mass of the bottle or sample; $%C_{material}$ is the percentage organic carbon content of the bottle/sample.

Gravimetric Measurement Respirometric (GMR) System

The GMR system construction is based on ISO 14855-2 [8] which is an standard under development phase and differs from ISO 14855-1 and ASTM D5338. Some of the differences are; 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 2 blanks, 2 positive reference material and 2 samples to be analyzed for the biodegradation measurement. ASTM D5338 and ISO 14855-1 recommends to use compost and sample in a ratio of 6:1 and commonly used quantity is 600 grams of compost to 100 grams sample, whereas in ISO 14855-2 one tenth of compost/sample ratio is used. A GMR system according to some of these specifications has been built by Hissan Trading Co. Ltd. (Japan), and it 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 4 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. Further, air is passed through each bioreactor and later through an ammonia eliminator, moisture remover and finally to a CO_2 trap column. A schematic of the MODA system with a single bioreactor and column connections is shown in Figure 5.4.



Fig 5.4 Schematic of MODA system

The standard test soil for the MODA system is a mixture of mature compost (60 grams dry weight) and vermiculite (60 grams dry weight) and initially the moisture is adjusted up to 90% of its water holding capacity. Mature compost (three months old) was obtained from Michigan State University composting facility and vermiculite grade number 4 fine particle soil conditioner was obtained from Therm-O-Rock (New Eagle, PA). Vermiculite (18 grams dry weight) was also added at the bottom of 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 Figure 5.5.



Figure 5.5 Schematic of the reaction column for MODA system

Initially, a sponge disk was placed at the bottom of reaction column followed by wet vermiculite (18 grams dry weight) and again 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 Figure 5. The compost mixture was added on top of the stainless steel disk and finally the reaction column was closed with a lid attached with the thermosensor which stayed all the time 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 was also generated from the reaction column which was eliminated by passed the output of the reactors through 2 N sulfuric acid (H_2SO_4) in the ammonia absorption flask, and the neutralization of H_2SO_4 by ammonia was monitored by methyl red. Later the air was passed through moisture removal column 1 and 2 as shown in figure 4. Silica gel (type 3) obtained from Sigma Aldrich (St. Louis, MO) was used for

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 mm -3 mm pellets) obtained from Merck KGaA (Darmstadt, Germany). Both soda lime and sodium hydroxide were mixed in 1:1 ratio. This chemical reaction generated water and hence column 4 containing calcium chloride collected the remaining water from the reaction. The carbon dioxide generated by biodegradation in the reaction column was measured by the weight gain seen in column 3 and column 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. While turning the entire mixture was collected in an aluminum bowl, except the divider sponge and stainless steel disks. The reaction column was immersed in water to completely wet the vermiculite at the bottom. Compost mixture was turned properly manually and appropriate amount of water was added to adjust moisture upto 90% water holding capacity of mixture.

5.3 RESULTS AND DISCUSSION

5.3.1 Real composting conditions

PLA bottles were first visually inspected in the compost pile for changes in their shape, texture and color. Right from the first day, changes in color and shape were observed [9, 10]. The biodegradation trend is shown in Figure 5.6.

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Figure 5.6 Biodegradation of PLA bottles in real composting conditions

The shape changes on the first day could be attributed to distortion due to higher temperatures ($65 \pm 5^{\circ}$ C) in the compost pile and also because the glass transition temperature (Tg) of PLA bottle was $60.6 \pm 0.3^{\circ}$ C [9, 10]. On fourth day, the bottles seemed tough as compared to its original configuration. 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 fifteenth day, the bottle was already in pieces and mostly consisted parts from cap threads, neck and bottle (bottle parts having higher thickness). On the thirtieth day, only few pieces of bottle were observed and were

majority from cap threads. After that, no bottle residuals could be located through visual inspection.

In case of PLA, the presence of -C=O- in the ester linkages in the polymer backbone makes it susceptible to hydrolysis. Initially, random non-enzymatic chain scission of ester groups results in reduction of molecular weight, and then lower molecular weight PLA was consumed by microorganisms which yields CO₂ and humus [13, 14]. Apart from hydrolysis, there are certain parameters which govern the biodegradation rate of PLA, for example higher temperatures and humidity results in rapid biodegradation of PLA [15]. Other factors which can govern the degradation rate are size and surface area of polymer/package, crystallinity, isomer percentage, residual lactic acid concentration, molecular weight, number average molecular weight and water diffusion [13, 14, 16]. As mentioned before, the temperature, relative humidity and pH of compost surrounding the containers were monitored every time the PLA bottles were taken out from the compost pile. Along with that, the atmospheric conditions such as temperature, relative humidity and solar radiation were also monitored for the duration of the study [9, 10]. The compost parameters may change with atmospheric changes which can affect the biodegradation. During the duration of study, atmospheric temperature varied from -4.2°C to 27°C; and atmospheric relative humidity from 20.3% to 98.9% which might have affected the composting process [9, 10].

Variation in physical properties of PLA bottles such as molecular weight was also analyzed. Molecular weight gives representation of the fragmentation process in PLA and also their degradation trend. Figure 5.7 shows the variation in molecular weight for PLA bottles for a period of 30 days.

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Figure 5.7 Variation in molecular weight (●) and PDI (□) for PLA bottles in real composting conditions; (-) solid line indicated fitting of equation 7.

Small increase in molecular weight (+11,400 Daltons) was observed on first day and it can be attributed to cross-linking or recombination reactions [9, 10]. Major fragmentation, which produces decomposition of the polymer chain into shorter oligomer chains and monomers, was observed on the fifteenth day when molecular weight was reduced from 210,600 to 11,000 Daltons. On the ninth day, large difference in the molecular weight was observed ($42,000 \pm 26,000$ Daltons), and this could be attributed to the differences in the compost parameters and/or the atmospheric conditions. PLA degradation starts by a hydrolysis reaction which follows a first order kinetics as shown by Kale et. al. [9, 10], which fitted the variation of molecular weight as a function of time to a first order kinetic process as expressed by equation (7).

$$Mw = a * \exp^{-b^*t} \tag{7}$$

where "a" and "b" are constants and equal to $a= 229.7\pm28.4$ kDaltons, and $b=0.1865\pm0.0533$ s⁻¹; t is the time in days. According to this equation, molecular weight values below 5 Daltons could be obtained on 57 days as shown in Figure 7. Figure 7 also 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 [9, 10]. For a detail study of the correlation between molecular weight and glass transition, melting and decomposition temperatures for PLA bottles in real composting conditions the readers can refer to references [9, 10]

5.3.2 Cumulative Measurement Respirometric System

Figure 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 30th day for cellulose and on 39th day for PLA bottle. At the end of 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 figure 7) and later low molecular weight oligomers are consumed by microorganisms to evolve carbon dioxide. A similar study was done by Kijchavengkul et.al. [12] on the same type of PLA bottles, but in a direct measurement respirometric (DMR) system and with yard waste compost showed that PLA bottles reached 60%

mineralization value on around 55th day. However, the size of PLA bottle sample used was lesser (18.86 grams) as compared to the 25 grams used in CMR system. The amount of compost used was 300 grams wet weight as compared to 400 grams dry weight compost used in this study. The higher is the quantity or surface area of compost regarding the sample the more is the chance to have enough microorganisms to biodegrade the samples. Also, the nature of the compost used as in this case yard waste compost will play an important role in the rate of the biodegradation since different amount of microorganism will be present.





bottles (\Box) in CMR system.

Gravimetric Measurement Respirometric (GMR) System

Figure 5.9 shows the biodegradation results of cellulose and PLA bottles in the GMR system. In this case, cellulose reached 70% biodegradation value on 55th day. ISO 14855-2 recommends that this test is valid only if cellulose or positive reference control reached 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.





of PLA bottles (\Box) in MODA. Turning days are represented by (**x**).

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, PLA bottles first undergo hydrolysis which is non-enzymatic reaction and (b) PLA bottles consisted of a bluetone additive and also a label adhesive which may have affected the microbial activity; c) the homogeneity of the compost, which make the compost generate different background of CO₂. 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 52nd day, one of the PLA bottles reached more than 70% of the average mineralization value which 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 MODA system). At the end of 67th day, the average mineralization of both PLA bottles was 80.9% with a large variation of $\pm 10.3\%$; which is very large as compared to the CMR data. The compost mixture in all reaction columns was turned twice a week; each time during turning moisture was adjusted to sustain microbial activity. The turning activity is also shown in Figure 9. On the 25th day, 15 grams (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. A similar test was carried out by Kunioka et.al [17] on PLA and the mineralization value reached more than 80% in just 50 days; however, the difference was that PLA powder (size of 92.5µm) was used, whereas PLA bottle pieces of 0.01 x 0.01 m was used in this case. PLA powder provides more surface area in the reaction column and can be more uniformly distributed with the compost than the PLA bottle pieces (mainly because of the label adhesive which tends pieces to adhere to each other).

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 Figure 5.10. The left y-axis measures the % mineralization for the CMR and the GMR systems and the right y-axis measures the variation in molecular weight in real conditions.



Figure 5.10. Comparison of variation in molecular weight (□) due to biodegradation and % mineralization values for PLA bottles in CMR (●) and MODA (○) systems

On the 15^{th} day, the M_w of the samples exposed under real composting conditions was reduced to 15,000 Daltons. 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 CO₂ takes place. This correlates well with the non-enzymatic hydrolysis and enzymatic reactions in the case of PLA as mentioned in previous research [9, 10, 13-15] and described by equation 7.

For both simulated conditions, CMR and GMR, the % mineralization value did not reach 100% at the 58th day when the test was stopped. However, the M_w of the samples in the compost pile, extrapolated according to equation 7, indicates that the samples would have reached zero Daltons 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 Figure 1 was tested, whereas in the CMR system the whole bottle (25 grams) was tested but cut into 0.01 x 0.01m pieces. Therefore, the higher surface area of the samples introduced in the CMR system should reduce the overall degradation period; however, since the relation compost / sample were 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) [17]. Hence,

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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 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% wt/wt 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 very 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 twice a week from bioreactors and mixed properly also 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 using yard waste compost obtained 60% mineralization value on the 53rd day while in this study in the CMR system with manure waste compost the 60% mineralization value was obtained on the 39th day [12]. Addition of vermiculite to compost in our study might have also contributed to a faster biodegradation. Hence, the nature of compost raw materials such as food, manure or yard waste could impact the biodegradation time-frame of PLA bottles and other biodegradable packages planned for composting. Therefore, this 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 timeframes 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 [7], 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 like a PLA bottle.

Thus, 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? Consequently, tests should be carried out to fully understand the whole and real package degradation process.

CONCLUSION

A PLA biodegradation test was 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 similar to the CMR has limitations of using a small quantity of compost which might extend the period of biodegradation. In short, standards mainly answer the question if a plastic or package piece is biodegradable, but they are not addressing the final question if these new biodegradable packages will 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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CHAPTER 6 - BIODEGRADABILITY OF PACKAGING FILMS IN REAL COMPOSTING CONDITIONS

6.1 INTRODUCTION

In United States, almost 245.7 million tons of municipal solid waste (MSW) was generated in 2005 with a decrease of 1.6 million tons from 2004. MSW recycled through recycling and composting increased to 32.1 percent in 2005 from 31.4 percent in 2004 which shows growing potential of recycling in United States [1]. Out of the total MSW of 245.7 million tons, plastics packaging comprised of 13.7 million tons out of which only 1.28 million tons (9.4%) was recovered through recycling and mainly included carbonated drink, milk and water bottles because of the bottle bill introduced in Vermont in 1953 [1]. Plastics packaging films and other plastic containers were mostly land filled and comprised of a huge volume due to light weight of films; for example shopping bags, wrapping materials, etc. As a result new class of polymers are developed that could be biodegraded and completely mineralized in microbial mediums such as in composting. The biodegradable polymers commercially available for packaging applications are mainly aliphatic polyesters (Polylactide (PLA), Polycaprolactone (PCL), Polyhydroxyalconates (PHA)) and aliphatic aromatic co-polyesters such as PBAT (Ecoflex[®] by BASF). Ecoflex[®] is based on terephthalic acid, adipic acid, 1,4-butanediol modular units. Certain desired packaging functionalities as well as biodegradation are achieved by synthesis of customized molecular structures obtained through statistical copolyester units, including 1-4 butanediol and dicarbonic acids, adipic acid and terephthalic acid linkages. For example, biodegradation is obtained by introducing ester units in carbon chain in the polymer structure. Common applications of Ecoflex[®] are

compost bags for organic waste, mulch films, coated and laminated materials and oriented films [2].

The monomer unit of Ecoflex[®] is shown in Figure 6.1. Ecoflex[®] polymer is built up of incorporation of hydrophilic components of monomers with branching resulting in higher molecular weight and chain-lengthening. The glass transition temperature (T_g) of Ecoflex[®] is -30°C and melting temperature (T_m) of 110-115°C. The properties of Ecoflex[®] are comparable to those of LDPE such as tear resistance and flexibility. However, Ecoflex[®] also has some limitations such as moderate water vapor permeability which can be adjusted using different masterbatches or additives [2]. One of such additive or masterbatch is antiblocking agent (i.e. fine talc) which is used to reduce surface friction during film extrusion of Ecoflex[®] and in further processes such as printing or bag making [3].

Figure 6.1. Monomer unit of Ecoflex

Ecoflex[®] passes the test of biodegradability according to DIN EN 13432, ASTM D6400-99 and Japanese GreenPla standard [2]. In many cases and especially for aliphatic polyesters primary degradation step is caused due to hydrolysis, whereas pure aromatic polyesters like polyethylene terephthalate (PET) are very resistant to any hydrolytic degradation and microbial attack. Only under drastic chemical conditions (e.g sulfuric acid at 150°C) hydrolysis of such polymers can be used for recycling purposes. Hence many attempts have been made to increase hydrolytic susceptibility of those polymers by adding aliphatic constituents to it (such as PBAT); and it was found that by varying the

amount of aromatic constituents, the biodegradation rate is affected. More the amount of aliphatic constituent, higher is the susceptibility of biodegradation[4].

Studies have been done till now to assess the biodegradability of PBAT in simulated composting conditions as per recommended in ASTM, DIN and JIS standards. However as per author's knowledge, no study has been done to evaluate its biodegradability in real composting conditions correlating to its loss in molecular weight. This paper investigates the biodegradability of PBAT based commercially available copolyester Ecoflex[®] and Ecoflex[®] with antiblocking agent (talc) for a period of 60 days.

6.2 MATERIALS AND METHODS

6.2.1 Samples

PBAT (P) and PBAT with talc additive (P_T) were provided by Northern Technologies International Corporation (Circle Pines, MN) with thickness of 20 μ m and 27 μ m respectively. The films were cut into 4" x 4" pieces and were subjected in compost pile in four replicates and hence 6 such sets for 5, 10, 18, 26, 45 and 60 days. The molecular weight of P and P_T was 66,293±2041 Daltons and 90,126±1649 Daltons respectively.

6.2.2 Compost pile

A compost pile was built at Michigan State University composting facility (East Lansing, MI). This compost pile was used to test the PBAT films biodegradability. The composition of pile was 40-45% of cattle manure, 40-45% of horse barn shavings and 10-20% of waste feed (that is the food that cattle's do not consume). The dimension of the

pile was 6 x 12 x 3 meters and the initial temperature, relative humidity and pH of the pile was 60°C±1.1°C, 60.5%±1.3% and 8.5 respectively.

6.2.3 Compost parameters

Compost parameters which plays essential role in biodegradation such as temperature, relative humidity (%RH) and pH was recorded everytime the films were taken out from the compost pile on 5, 10, 18, 26, 45 and 60 day. Temperature, %RH and pH are shown in Figure 6.2 (a,b,c).

- (a) Temperature: The temperature of the compost pile at the samples place was recorded using a stainless steel thermometer (±1°C) obtained from Reotemp (San Diego, CA).
- (b) Relative humidity (RH): Wet weight moisture content of the compost was calculated using microwave heating method previously used by Kale et.al. [5, 6].
- (c) pH: 5 grams of compost sample was dissolved in 25 ml of deionized water and pH was determined using calibrated pH paper obtained from Micro Essential Laboratory Inc (Brooklyn, NY).
- 6.2.4 Ambient conditions

The ambient air conditions which may also affect the composting conditions were recorded at the Michigan Automated Weather Network (East Lansing,MI). During the 60 days duration of study , the ambient air temperature varied from -13.1° C to 26.6° C, the relative humidity from 20.3% to 98.8% and the total solar radiation from 2043 kJ/m² to 25565 kJ/m². Figure 6.2 (d,e,f) shows the ambient temperature, %RH and solar radiation for the duration of study (60 days).



Figure 6.2. (a) Temperature (\bullet), (b) %RH (\Box) and (c) pH (\blacktriangle) of compost pile; and (d) ambient maximum(\bullet) and minimum(\Box) temperatures, (e) ambient maximum(\bullet) and minimum(\Box) %RH and (f) solar radiation (Δ) as a function of time for 60 day period.
6.2.5 Placement of films in compost pile

A wooden box was built with mesh attached to its bottom to test films in composting conditions. The box was placed in the compost pile where optimum temperatures (i.e. $60^{\circ}C_{+}$) were found. Initially compost was added on the mesh and later films were placed in 4 replicates in one box. The films and the box were later covered with compost over it. The position of box in the compost pile was at 1.2 m above ground and 1 m inside compost pile from surface. For more information about the methodology, readers can refer to references [5, 6].

6.2.6 Visual inspection

The films were visually inspected everytime each set of box was taken out from compost pile on respective day. The films were inspected for their changes in the color, breakdown or cracks and impact on each of 4 pieces of films due to different position in compost pile. Digital pictures were taken by digital camera manufactured by Cannon (Model A530).

6.2.7 Molecular weight analysis

Molecular weight determination was carried out using gel permeation chromatography (GPC). Multisolvent delivery system, autosampler and RI detector; all manufactured by Waters (Milford, MA) were used for determination. Inhibitor free Tetrahydrofuran (THF) solution was used to dissolve samples and was obtained from Sigma Aldrich (Milwaukee, USA). PBAT biodegraded samples (15 grams each) were dissolved in 10 ml of THF solution and later it was filtered through a PTFE (polytetrafluroethylene) filters obtained from Whatman (Florham Park, NJ). The diluted samples in THF were transferred to 1 ml vials obtained from Waters (Milford, MA).

6.3 RESULTS AND DISCUSSION

6.3.1 Visual inspection

The pictorial representation of PBAT films biodegradation in real composting conditions is shown in Figure 6.3. The samples shown in figure are one of the four samples tested for biodegradation. On eighteenth day some breakdown in the film can be seen in the Figure 3. The breakdown part could not be traced in the compost pile and could be consumed by microorganisms. A similar breakdown can also be seen on the 26th and 45th days where even more quantity of film is disintegrated on each day. All the four samples of PBAT films on 60th day are shown in Figure 6.4. Samples A and D were towards exterior of the pile, whereas samples B and C were more towards the interior of the pile. Slow degradation can be seen in case of samples A and D as compared to samples B and C. This could be due to the higher reproduction of microorganisms, and higher temperature and humidity. One of the PBAT films (out of four) was disintegrated in the compost pile on 60th day in this study. However this could be governed due to many factors as well, for example there was much variability in the temperature and relative humidity of the compost pile. Similarly PBAT with talc additives was also tested for biodegradation for period of 60 days in real composting conditions. Pictorial representation of the same is shown in Figure 6.5.



Figure 6.3. Visual inspection of PBAT films in real composting conditions



Figure 6.4. Pictorial representation of four samples of PBAT films on 60th day. Samples B and C were more towards interior of the pile.



Figure 6.5. Visual inspection of PBAT + talc films in real composting conditions

PBAT with talc additive films (P_T) shows similar trend as of PBAT films (P) in the beginning, however no significant changes could be observed till 26th day. On 45th day some breakdown can be seen and on 60th few residuals of the P_T films could be seen. This slow biodegradation in P_T as compared to P could be due to its higher molecular weight (which is almost 25,000 Daltons more) and also due to the presence of talc (antiblocking agent) in it. As mentioned before, as per authors knowledge there has been no study done to PBAT films in real composting conditions and hence it becomes difficult to correlate the disintegration trend obtained in this study. The variation in temperature and %RH in the compost pile during study period could be determining factors in the disintegration of PBAT films. For example the temperature was reduced upto 37°C which could involve mesophilic microorganisms (0-40°C) in the composting process, rather than thermophilic microorganisms (40-55°C) which are essential for efficient composting processes. Composting piles are usually turned frequently for providing better aeration to compost and hence speeding up the composting process. In this study, the compost pile was not turned at all which might have also leaded to decrease in temperatures and hence variability in the disintegration. However this case scenario shows some insight of the difficulty of real composting studies.

Molecular weight

The variation in molecular weight for PBAT films is shown in Figure 6. One of the four samples was degraded on 60^{th} day in compost pile, hence 60^{th} day molecular weight data shown is an average of 3 samples; whereas others are average of four samples. Initial rise in molecular weight on 5^{th} and 10^{th} day can be attributed to the cross linking or recombination process occurred in films due to degradation. The solid line shown is a linear fitted line as a function of time based on the molecular weight data for four samples for each day (Adj R square=0.72).

Also after 10th day, major variation can be seen on the 18th, 26th, 45th and 60th day. It was observed that the films which were close to the interior of compost pile showed greater decrease in molecular weight, whereas the ones near exterior showed very less decrease in molecular weight. For example, on 60th day, the molecular weight of three available samples was 62,672 Daltons, 46,460 Daltons and 61687 Daltons respectively which can be comparable to the molecular weight of PBAT films on zero day. Out of the three, the sample for which 46,460 Daltons molecular weight was obtained was towards the interior of the pile which might be the reason for the further decrease in molecular weight. PBAT films has aliphatic and aromatic sequences in it and aromatic sequences are quite resistant to microbial attack as can be seen in case of polyethylene terephthalate (PET). Hence, unlike polylactide which is an aliphatic polyester, there is no hydrolysis reaction occurred in PBAT which would decrease the molecular weight drastically to be able to be consumed by microorganisms.



Figure 6.6. Variation in molecular weight for PBAT films (●) and PBAT with talc additive (□) films in real composting conditions.
* 60th day data point shows average of 3 points for PBAT films.

In case of aliphatic polyesters, the degradation occurs due to the diffusion of water into the polymer bulk. In case of PBAT, the degradation of polymer bonds is faster than diffusion of water and hence the polymer will be consumed by hydrolysis on its surface. This phenonmenon is known as surface erosion as the degradation occurs on the surface. Hence, no significant changes could be observed in the physical shape of the polymer as polymer is slowly decomposed on the surface [7, 8]. A degradation test on PBAT powder was carried out by U.Witt et.al. [9] in the synthetic medium with

actinomycete strain T.fusca DSM 43793 at 55°C in shaking vessels. This test in mineral salt medium and inoculum was carried out and 94% solubilization of polymer was observed in 21 days. However, this is a type of simulated composting test where microorganisms and temperature are controlled and which could give clear understanding and idea of favorable conditions for biodegradation of PBAT. According to U.Witt et. al. [9], test microorganism T.fusca DSM 43793 has a very good ability to depolymerize PBAT but not able to readily metabolize monomers and oligomers formed. In our study, the molecular weight could not been seen comparable to monomers or oligomers. The least molecular weight obtained for P was 46,460 Daltons and for P_T was 66,340 Daltons on 60th day. According to Gopferich A. [8], molecular weight loss in polymers such as poly (anhydrides) shows no change in molecular weight or physical geometry in the course of degradation. The microorganisms involved in this study were not analyzed, which could have given idea of how matrix of microorganisms affects the biodegradability. However, it cannot be just concluded in one study or one replicate of it, and more repetitions are essential for concluding the biodegradation of PBAT in real composting conditions.

A similar biodegradation trend for PBAT with talc additives is shown in Figure 6.6. Unlike PBAT, as discussed before in visual inspection the biodegradation and breakdown in P_T can be seen after 26th day. Similar to PBAT, an initial rise due to recombination reactions or crosslinking can be seen for the first two days. The molecular weight increase is also seen till 45th day. However on 60th day, the average molecular weight was below the molecular weight on zero day. The solid line represents the linear fitting for molecular weight data points as a function of time (adj R square value of

0.45). The consecutive variability in the molecular weight could be again due to the position of films in either interior or exterior of the pile. For example on the 60th day, 88,821, 66,340, 73,022 and 83,514 Daltons was the respective molecular weight for four film samples; as compared to 90,126±1,649 Daltons on zero day. Talc is commonly used as an antiblocking agent in improving the processing of Ecoflex[®] film production. Ecoflex[®] batch AB1 (60% fine talc) is one such antiblocking agent in film production [10]. Hence, it is very much likely that additives such as talc would be incorporated for efficient film production and which would eventually affect the biodegradation property. For successful biodegradation of polymer, it is necessary to have a proper time representation of its biodegradation in real conditions. As per Witt U et.al [11], Ecoflex[®] reached 60% mineralization value in controlled composting conditions on 45th day, however the conditions are controlled where thermophilic microorganisms are active, unlike real conditions where characterization of microorganisms may change with change in the compost variable parameters. To make a more clear representation of the biodegradation mechanism in case of PBAT, Witt U et.al [11] exposed PBAT using microorganisms (isolated from compost) in aqueous medium. After degradation, only water soluble intermediates were found through GC/MS which showed that those isolated microorganisms were able to degrade polymer chains into monomers. Later the metabolism of monomers was achieved through adding a mixed culture of microorganisms which did not show any residues in the GC analysis. These two steps of degradation are referred as a "symbiosis process" by Witt U et.al in which "individual organisms are able to perform only one degradation step, and other organisms the next." However, it cannot be proved that the PBAT copolyester structure actually went through this symbiosis process because of possibility of indigestion of soluble fragments in their cells.

In summary, it can be concluded through visual inspection that biodegradation can be seen by breakdown in films. This trend can't be seen in variation of molecular weight, mainly because of the presence of aromatic sequences which are resistant to microbial attack and the surface erosion phenomenon. Müeller et.al. [4] showed that the biodegradation of (1,4 butanediol, adipic acid, terephthalic acid) BTA is affected by the increasing percentage of terephthalic acid.

CONCLUSION

It has already been proven according to the simulated conditions that aliphatic aromatic copolyester such as Ecoflex[®] is biodegradable. Looking at the current trend of waste generation in United States, usages of such biodegradable films would be beneficial in eliminating municipal solid waste. As per the author's knowledge and current literature, the biodegradability of PBAT powder/films is mostly reported for testing in simulated microbial conditions where either compost parameters are controlled or enzyme specific aqueous mediums are used. It is also essential to match this information with the actual film testing in real microbial environments such as composting. This study gave an understanding of how films biodegradation could get affected due to location and environmental factor changes in the compost pile. This variability in the exposure of film surface area and microbial medium parameters is an important consideration in successful biodegradation of those films; otherwise it will create another plastic waste problem. Also based on limited knowledge on enzymatic

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attack on complex structures present in copolyesters, work has to be done to evaluate biodegradability of those films in novel evaluation methods such as in real conditions which would give good representation of biodegradation performance in different environments.

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CHAPTER 7 – FUTURE RESEARCH RECOMMENDATIONS

The following topics are recommended for future research work:

- 1. Variability's in the biodegradation of packages in real composting conditions should be investigated through more replicates of the study.
- 2. Commonly used compostable materials such as food, manure and yard waste in composting processes and their interaction with biodegradable packages should be studied.
- Accurate correlation between the biodegradation performance of packages in simulated and real composting conditions should be established. A more detailed information and timely representation can provide better guidelines in biodegradation processes such as composting.
- 4. Study on microorganisms involved in composting (depending on the compostable materials used) and its interaction with packages would be helpful in determining the degree of biodegradation efficiency with respective microorganisms.
- 5. For biodegradable packaging, a focus on biodegradation testing of a whole package should be made to have the idea of how packaging components and its association with the main package might affect the biodegradability.
- 6. As per the results obtained in PBAT study, the location of films in compost pile makes difference to its biodegradability. A study on location of package/film in compost and its biodegradability should be investigated.

7. A pilot scale study on waste management of biodegradable packages and its composting at commercial level would be helpful in determining the probability of packages getting disintegrated in it.

