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BIODEGRADABILITY OF POLYHYDROXYBUTYRATE-VALERATE BY WEIGHT-CHANGE METHOD IN A SIMULATED DISPOSAL SYSTEM

A Thesis

Presented to

The Faculty of the Department of Nutrition and Food Science

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Li-Sa Vui-Sim Kon

May 1998
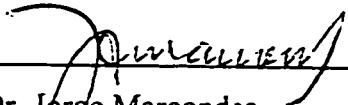
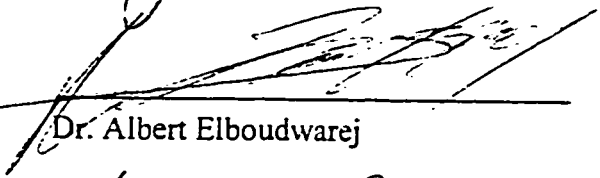**UMI**
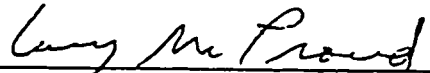300 North Zeeb Road
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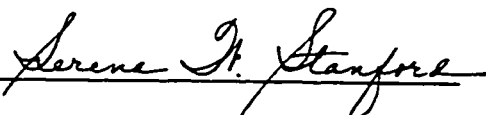
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Dr. Albert Elboudwarej

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ABSTRACT

BIODEGRADABILITY OF POLYHYDROXYBUTYRATE-VALERATE BY WEIGHT-LOSS METHOD IN A SIMULATED DISPOSAL SYSTEM

by Li-Sa Vui-Sim Kon

The biodegradability of polyhydroxybutyrate-valerate (PHBV) under aerobic simulated landfill conditions was estimated from the absolute value of weight change. PHBV is a microbially synthesized polyester. Depending on the soil conditions in which PHBV pellets were placed, weight change varied between 0% to 27% from dry weight loss. Biodegradability of plastic resin was influenced by soil microbial activity. Use of chicken manure as a soil medium caused the highest percentage of weight loss regardless of its moisture condition. Sterilized sand due to the lack of microbial activity generated the least degradation. Results of the experiments showed a positive correlation between microbial activity of soil and biodegradation of PHBV plastic resins. In the U.S, yard and food waste represent 28%, by volume of municipal solid waste. From the composition of MSW and results of this experiment, it could be postulated that PHBV be used as packaging materials without adverse effects on the environment and landfill.

ACKNOWLEDGEMENTS

PREFACE

The following is a publication style thesis. The second chapter is written in journal format and will be submitted to *Packaging Technology and Science.* Chapter I and III are written according to guidelines outlined in the *Publication Manual of the American Psychological Association*, 4th edition, 1994.

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3.   SUMMARY AND RECOMMENDATIONS

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List of Acronyms and Abbreviations

CB	combination by weight of half chicken manure and sterilized sand
CM	chicken manure
CO_2	carbon dioxide gas
HB	hydroxybutyrate
HM	high moisture
HV	hydroxyvalerate
LM	low moisture
O_2	oxygen gas
PHA	polyhydroxyalkanoates
PHBV	polyhydroxybutyrate-valerate
PS	potting soil
SS	sterilized sand

CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

Introduction

The need for proper disposal of solid waste is one of the dilemmas created by the

many benefits of our modern lifestyles. Packaging gets a lot of attention because we

bring packages into our home, and they turn up as litter. Packaging has an image

problem and is consistently portrayed as an environmental assault to the waste stream.

Mostly of course, plastic packaging is targeted because when we look around us,

packaging materials are very often made out of plastics of various types. Plastic

materials are indispensable because of many desirable properties including durability and

resistance to degradation. In many applications, such as the polystyrene clamshell for

take-out fast foods, the long lasting properties are not required. The food will be

consumed within minutes, but the container in which the food was packaged will last for

decades in the landfills. The United States leads the world in waste production,

producing an average of 3.6 pounds of solid waste per day, almost twice as much as the

average German (United States Environmental Protection Agency, EPA). Three and one

half pounds might not seem like much of a problem, but if each of us is just one of 240

million Americans making this daily contribution to a growing garbage heap, that

amounts to nearly 160 million tons per year (Lee, Pometto, Fratzke, & Bailey, 1991).

Plastic materials account for about 20 percent by volume of materials in

municipal solid waste, third behind paper and yard clippings (Franklin Associates

Limited, 1989). Franklin Associates is an independent research group under contract to

the EPA to estimate composition of municipal solid waste based on volume for the

Council for Solid Waste Solutions, Washington, DC (Anonymous, Dow Plastic Brochure,

1997). Since plastics are made from a wide range of natural gas and petroleum formulae,

thus do not mix easily in remaking them into new products. As a result, the United States

recycles only two percent if plastics with the exception of soft-drink bottles and standard

milk jugs, which are made out of polyethylene terephthalate and high-density

polyethylene respectively (Grove, 1994). The four major waste management methods

that the EPA recommends for the solid waste industry are source reduction, recycling,

incineration, and landfills (Anonymous, GARBAGE Magazine, 1993).

The most fundamental way to reduce waste is to prevent it from ever becoming

waste in the first place. Examples of source reduction are using less material when

making a product, or converting thicker gauge materials to thinner gauge alternatives as

in aluminum beverage cans and plastic soft drink bottles (Hosford & Duncan, 1994).

Increasing public awareness of what materials are recyclable and stimulating the demand

for recycled products requires strong partnerships with government at all levels, industry,

and the public. Many businesses signaled their compliance by marking their products

with a green dot, which signifies a container's recyclability. However, lack of and/or

insufficient enforcement and incentives has caused packaging to pile up beyond

recyclers' ability to process it (Grove, 1994). Aside from its high cost in comparison to

other forms of waste management, incineration with state of the art emission control

devices to handle pollution for heat and power generation, may be the most effective

method of disposal (Leaversuch, 1987). The waste management dilemma facing

Americans today centers squarely on economic and environmental factors (Kelsey,

1989). Landfills as places to hide our garbage until it disappears through decomposition

or it may indeed never disappears, continue to play a key role in solid waste management.

Moisture is the most important environmental variable of degradation, and landfills are

kept at a low moisture level to prevent excessive groundwater contamination from

runoffs (Rathje, 1992).

Over the past decades, the intrinsic resistance of plastic materials to degradation

has been increasingly regarded as a source of environmental and waste management

problems. Solutions to the growing waste management problems posed a challenge to

material scientists and industry leaders to come up with polymers that have good short-

term properties. Many industry leaders work hand in hand with material scientists

towards innovations to prove that they are environmentally correct. In other words, there

is a fine line between positive environmental impact, and image enhancement adopted

due to environmentally conscious consumer demand.

Among the candidates for biodegradable plastics, polyhydroxyalkanoates (PHAs)

has been drawing much attention. PHAs are reserve polyesters that are accumulated as

intracellular inclusions in a variety of bacteria (Anderson & Dawes, 1990). Of these

polymers, polyhydroxybutyrate (PHB) is the most common. Physical properties vary

with the hydroxyvalerate (HV) units incorporated randomly throughout the polymer

chain (Howells, 1982). Since the physical properties of PHB resemble those of

polypropylene, and polyethylene, the commercial production of PHAs is of considerable

interest (Hangii, 1995). One such commercial PHA is a random copolymer, p(HB-co-

HV), of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV), produced by the

bacterium *Alcaligenes eutrophus* from glucose and propionic acid over a period of

fermentation (Lindsay, 1992). In addition to being compatible with conventional waste

disposal systems such as recycling, incineration and landfill, these PHAs are fully

biodegradable and compostable (Lee & Chang, 1995).

There are four primary degradation mechanisms that are often mistaken to be

synonymous. They are biodegradation, photodegradation, chemical degradation, and

macroorganism degradation. Biodegradation is defined as the conversion of the

constituents of a polymer to carbon dioxide, methane, and other natural products in an

aerobic and anaerobic environment by microorganisms such as bacteria and fungi

(Raghavan, 1995). The extent to which a certain mechanism influences the degradation

of a plastic is dependent on the nature of the plastic, processing conditions, performance

requirements, and method of disposal (Shin, Myung, & Kim, 1997).

Photodegradation is the process by which the polymer is degraded when exposed

to sunlight. Ultraviolet radiation in sun rays lead to photo-initiated radical reactions,

which may result in chain scission and degradation of the polymer (Raghavan, 1995).

The polymer embrittles and molecular weight decreases depending on the concentration

of photo-initiating additives in the material.

Chemical degradation usually occurs independently of the microbial activity.

When reactive chemical species in the material form free radicals and eventually cause

chain scission, and bond breakage, this form of degradation is known as chemical

degradation (Raghavan, 1995).

When a polymer is degraded by insects, animals, and other living creatures, due to mastication, digestion, and post-ingestion, this form of degradation is classified as macroorganism degradation (Raghavan, 1995).

Objectives

The objective of this study is to determine the biodegradability of PHBV samples in the form of pellets when exposed to simulated waste disposal conditions in the laboratory.

Significance of the Study

Until recently, much of the assessment of biodegradable plastics was done in accordance with American Standard of Testing and Materials (ASTM) procedures developed in the 1960s and 1970s (Coma, Couturier, Pascat, Bureau, Guilbert, & Cuq, 1993). Literature of ASTM in the 60s and 70s was based on qualitative visual observation of the microbial growth on the material used by measuring colony diameter (ASTM, 1976). Qualitative tests permitted an initial classification of materials according to their potential degradability, and allowed the identification of the microbial species, particularly fungi, most likely to grow on the materials being studied (Kestelmann, Yaravenko, & Melnikova, 1972).

Due to the increasing demand for the use of biodegradable materials, as well as for the fact that landfills will continue to play a key role in solid waste management, an evaluation of biodegradability of PHBV, based on the weight loss method in simulated landfill conditions is needed.

Review of Literature

Back to Nature and Working with Nature

Production of PHBV requires sunlight, and starts with crops such as sugar beets

and cereal crops (Alderete, Karl, & Park, 1993). During photosynthesis, crops convert

carbon dioxide from the atmosphere into carbohydrates. These carbohydrates which

serve as the carbon source are the raw materials from which PHBV resin is made. The

naturally occurring soil bacterium *Alcaligenes eutrophus* accumulates large quantities of

PHBV as discrete intercellular granules when grown on glucose under deprived nutrient

conditions (Alderete, et al., 1993). Just like mammals that store fat, bacteria accumulate

PHBV as an energy source. At the end of the fermentation, the microorganisms have

accumulated up to 80% of their dry weight as PHBV resin (Lopez, Pozo, Toledo,

Rodelas, & Salmeron, 1996). It is then harvested by breaking open the cells and

extracting and purifying the polymer. The chemical structure of PHBV copolymer is

shown in the Appendix A.

Physical properties vary with the HV content of the polymer (Howells, 1992).

The homopolymer PHB is relatively stiff and brittle, but flexibility and toughness can be

introduced by increasing the HV content (Doi, Mukai, Kasuya, & Yamada, 1994). This

allows a variety of copolymers to be produced with flexibility and tensile strength in

ranges encompassing those of polyethylene and polypropylene. In addition to being

compatible with conventional waste disposal systems such as recycling, incineration, and

landfill, they are fully biodegradable and compostable (Doi, et al., 1994).

In the presence of oxygen, the final biodegradation products of PHBV were carbon dioxide and water, exactly equivalent to the final decomposition products of any other organic matter (Doi, et al., 1994). PHBV also biodegrades under anaerobic conditions. The by-products as a result of biodegradation were carbon dioxide, water and methane (Coma, Guilbert, & Couturier, 1994). PHBV can be incinerated safely, yielding an energy value comparable with traditional plastic materials such as polypropylene which generates about 19,850 BTU per pound (Mergaert, Anderson, Wouters, & Swings, 1994).

Testing of Biodegradable Plastics

The biodegradation of PHBV was observed under a variety of waste disposal systems such as sewage sludge, landfills, compost, and soil. The significance of burying PHB resins in the mentioned environment was important because most of society's waste, in reality, eventually becomes a part of landfills, compost, soil or sludge (Coma, et al., 1994). Just as naturally occurring microorganisms produce PHBV as an energy food store, a wide variety of living organisms in the environment can consume PHBV resin as a source of carbon. Biodegradation is initiated by the action of microorganisms growing on the surface of the polymer, and secreting enzymes which degrade PHBV resin into individual molecular fragments of HB and HV (Coma, et al., 1994). Fragments of HB and HV are immediately transported into the colonizing cells where they are used as a carbon source for growth (Coma, et al., 1994).

In a true experiment, degradation studies were performed on PHBV resins according to ASTM D5209 in activated sewage sludge under aerobic conditions (Coma,

et al., 1994). The aerobic biodegradation test method proposed by ASTM is modeled on the Sturm test, which was originally developed for determining the biodegradation of soluble solvents in an aqueous environment (Wool, Raghavan, Billieux, & Wagner, 1991). This test is perceived by most scientists as being the most reliable test method for evaluating the biodegradability of a polymer in an active microbial environment (Phillips & Axelrod, 1991).

The rate of degradation was determined by measuring CO_2 evolution relative to a control at 25 ± 0.5 °C (80 °F) (Coma, et al., 1994). After 40 days, gas evolution was found to be equivalent to 85% of the theoretical value of carbon dioxide evolution. The theoretical value is defined as the amount of carbon dioxide that was taken up during photosynthesis at the beginning of the cycle (Mergaert, Anderson, Wouters, & Swings 1994). In a separate experiment conducted in the absence of oxygen, carbon dioxide evolution was reported to be 78% of the theoretical value (Coma, et al., 1994). Results led the researchers to conclude that PHBV could biodegrade under aerobic or anaerobic conditions. While the measurement of CO_2 production as a function of time provided information about the degradation of a polymer, it was a limited view of the overall biodegradation process. Microorganisms utilizing a carbon substrate (biodegradable plastics) are known to convert the degradable polymeric carbon to biomass and soluble carbon (Shin, et al., 1997). Thus, to provide a complete analysis of the extent of degradation of biodegradable plastics, a carbon balance of the polymer would be essential.

Biodegradation tests were performed under aerobic conditions at room temperature using two varieties of soil: a sandy loam soil and a high content organic matter (Lee, Pometto, Fratzke, & Bailey, 1991). Results indicated that PHBV resins that were buried in both types of soil underwent up to 90% biodegradation at 7-8 months (measured by CO_2 evolution). In a separate microscopic analysis test, PHBV films were buried for 72 days at 25 ^{0}C. Scanning Electron Microscopy (SEM) micrographs, which retained a three-dimensional appearance of the sample, were used to aid in the microscopic analysis. Micrographs showed that the surface has become pitted and eroded as a result of degradation (Lee, Pometto, Fratzke, & Bailey, 1991).

In a time series study, both bottles and strips from PHBV resins were buried in active wastewater under aerobic conditions. At room temperature, both bottles and strips degraded over a period of weeks such that after 25 weeks, a 50% weight loss was observed (Mukai, Kasuya, & Yamada 1994). However, when data of weight percentage change versus time on both forms of PHBV were plotted, strips of PHBV showed a linear weight loss, whereas weight loss of bottles illustrated a decreasing trend, but cyclical in pattern. Since both forms of PHBV samples were buried in identical soil and temperature conditions, the factor that may have been responsible for the difference in weight loss pattern was the shape of the specimens.

PHBV bottles that were buried in an industrial composting plant under aerobic conditions at 70 ^{0}C (158 ^{0}F) for 15 weeks became very brittle and fragmented (Doi, et al., 1992). As the experiment progressed, it was noted that the rate of weight change was more pronounced. Turning of the compost heap, which mechanically broke up the

bottles, further increased the surface area for microbial attack. Weight losses of up to 80% were observed over 15 weeks (Doi, et al., 1992). The high temperatures present in the study may have contributed to the brittleness of the PHBV bottles, which aided the increased rate of degradation.

PHBV bottles tested under managed landfill conditions at a temperature of 35 ^{0}C (95 ^{0}F) underwent a downward linear weight loss of approximately 50% over a period of 40 weeks (Guillet, Huber, & Scott, 1991). Despite extensive research done to determine a definable rate of biodegradation of PHBV, it appeared that the rate is influenced by a number of factors including: temperature, difference in bury mediums and shapes in which the PHBV was formed in; whether specimens are in the form of film, pellets, or bottles.

There are three methods to determine weight change of biodegradable plastics: after soil burial procedures, agar culture or tests in bioreactors (Krupp, 1991). The weight loss method is especially adapted to materials containing biodegradable compounds. Its is easy and rapid to use, and capable of determining the low levels of biodegradation that can appear in the first stages of incubation (Wendt, Kaplan, & Greenberger, 1970). However, the weight of microorganisms and of soil residues not eliminated during the cleaning leads to errors in the weight loss calculation. The method based on the weight loss could not by itself prove the biodegradation of materials, but negative results constitute proof of non-biodegradability (Krupp, 1991). The main difficulty with the weight loss method is the recovery of samples. It was difficult to separate and retrieve the PHBV material being studied from the variety of waste disposal

systems (Doi, et al., 1994). Unretrieved or missed portions of compounds might be overestimated and calculated as weight loss. This will contaminate the results of the research.

Research in France reported a similar study, but noted some disparities in the percentages of carbon dioxide gas evolved, and weight loss (Anderson & Dawes, 1995). Most of the other research lead by Doi and colleagues was conducted in Japan. Comparison of results in similar studies among researchers from different geographical areas led to the conclusion that microorganisms from different species and genera were present in a complex biological environment (Anderson, et al., 1995). Disparities in their studies provided data to suggest that a polymer's degradation rates depended upon the disposal environment. There appeared to be unanimous agreement among the researchers that rates of biodegradation were influenced by a number of factors.

Shin, Kim, and Kim (1997), determined the biodegradability of plastic under anaerobic conditions using ASTM (D5210-91). In this method, anaerobic sludges in wastewater treatment plants were used as microbial sources. The biodegradabilities of various plastics by anaerobic digested sludge were measured and compared with the biodegradabilities under simulated landfill conditions. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate), the natural aliphatic polyester, degraded nearly to completion within 2 days of cultivation by anaerobic digested sludge, while synthetic aliphatic polyester such as polylactic acid, polybutylene succinate and polybutylene succinate-co-ethylene succinate did not degrade at all in 100 days (Shin, et al., 1997). Cellophane, which was

used as a control material, was reported to have exhibited a similar degradation behavior to PHBV.

Based on experimental literature, it appeared that more research was done on PHBV polymer under aerobic conditions. This may be due to the fact that waste disposal systems, without exceptions, were exposed to oxygen from the atmosphere.

Outlook on Biodegradable Plastic

At present, PHAs production of P(3HB) and P(3HB-co-3HV) which rely on efficient bacterial fermentation are the only members of PHAs that are produced on a commercial scale (Lee, 1996). The production of PHBV on a commercial scale is about 1000 tons per year and this figure is scheduled to be several thousand tons by the late 1990's (Byrom, 1994). Currently, production of PHBV is at about 11 thousand tons per year (Ryan, Hartmam, & Nangerone, 1998). Even though PHBV has been recognized as a good candidate for biodegradable plastics, its high costs in development and isolation, coupled by high demands in excess of supply has limited its use in a wide range of applications. The price of PHBV is still too high to be used as a bulk plastic material if we consider the cost of synthetic plastics (Lee, 1996).

Alcaligenes eutrophus is considered the most economical due to the bacteria's ability to accumulate large amounts of PHBV (Alderete, et al., 1993). Conditions leading to the accumulation of PHAs have been studied extensively in the wild type bacteria currently in use, *Alcaligenes eutrophus*. Recently, transgenic plants harboring *Alcaligenes eutrophus* PHA biosynthesis genes have been developed (Poirier, Nawrath,

& Somerville, 1995). Researchers expect that the production and use of metabolically engineered types of bacteria will surpass the wild type that is currently in use.

Many companies worldwide are developing products for PHBV. At present the German hair-care company, Wella, marketed a shampoo bottle (SANARA) made from PHBV (Lee, Yim, & Chang, 1994). Berlin Packaging Corporation, an American company is currently supplying bottles made from PHBV to Marshal Fields Superstore in Chicago for containment of cosmetic products (A. Elboudwarej, personal communication, February 18, 1998). A biodegradable single-serve yogurt cup with heat-seal foil lid is available on store shelves in Germany (Anonymous, 1998). Danone, the German company that manufactures the yogurt product, claimed that the ecologically correct cup decomposes under commercial composting conditions within approximately 60 days. The thermoformed biodegradable cup is derived from sugar beets grown in Spain that provide the carbon substrate for the production of PHBV. Other possible applications for PHBV are limited to high cost and low volume pharmaceutical/surgical products such as blood vessel and bone replacements. (Brandl, Gross, Lenz, & Fuller, 1990).

Environmental differences abound, making interpretation of biodegradability of data complex. As evidence has shown, problems resulting from the disposal of synthetic polymer packaging have created a need to obtain biodegradable products from biological bacterial fermentation. Continued research and development is required to develop packaging materials composed entirely of renewable sources such as agricultural

products and that are affordable for more widespread usage. This is essential to ensure

environmental protection and create a new outlet for agriculture crops.

CHAPTER 2

JOURNAL ARTICLE

Author's Title Page

BIODEGRADABILITY OF POLYHYDROBUTYRATE-VALERATE BY WEIGHT-LOSS METHOD IN SIMULATED DISPOSAL SYSTEM

Li-Sa Vui-Sim Kon, Albert Elboudwarej*, Jorge Marcondes, and Lucy McProud

Department of Nutrition and Food Science

San Jose State University

1 Washington Square

San Jose, Ca 95192

*Address question and comments to: Dr. Albert Elboudwarej

Department of Nutrition and Food Science, San Jose State University,

1 Washington Square, San Jose, CA 95192-0058, 408-924-3124

ABSTRACT

The biodegradability of polyhydroxybutyrate-valerate (PHBV) under aerobic simulated landfill conditions was estimated from the weight change absolute value. Carbohydrate is converted into PHBV by a specific microorganism via a fermentation process. PHBV is a microbially synthesized polyester. Depending on the soil conditions in which PHBV pellets were placed in, weight change varied between 0 % to 27 % from dry weight basis. Results show that the biodegradability of plastic resin was influenced by soil microbial activity. Use of chicken manure as a soil medium caused the highest percentage of weight loss regardless of its moisture conditions. Sterilized sand due to the lack of microbial activity generated the least degradation. Results also showed a positive correlation between microbial activity of soil and biodegradation of PHBV plastic resins. In the U.S, yard and food waste represent 28 %, by volume of municipal solid waste. From the composition of MSW and results of this experiment, it could be postulated that PHBV could be used as packaging materials without adverse effects on the environment and landfill.

Keywords: biodegradable resin, packaging application, biodegradation, weight change, soil conditions

Running headline: weight change of biodegradable plastic

INTRODUCTION

The need for proper disposal of solid waste is one of the dilemmas created by the many benefits of our modern lifestyles. Packaging gets a lot of attention because we bring it into our home, it turns up as litter, and very often it is made out of plastics. Plastic materials are indispensable because of their many desirable properties including durability and resistance to degradation. In many applications, such as the polystyrene clamshell for take-out fast foods, the long lasting properties are not required. The food will be consumed within minutes, but the container in which food was packaged, will last for decades in the landfills. The United States leads the world in waste production, producing an average of 3.6 pounds of solid waste per day, almost twice as much as the average German [1]. Three and a half pounds might not seem like much of a problem but if each of us is just one of 240 million Americans making this daily contribution to a growing garbage heap, that amounts to nearly 160 million tons a year [2].

Plastic materials account for about 20 percent by volume of materials in municipal solid waste, third behind paper and yard clippings [3]. Made from a wide range of natural gas and petroleum formulae, plastics do not mix easily for remaking into new products. As a result, the United States recycles only two percent of plastics with the exception of soft-drink bottles and standard milk jugs, which are made out of polyethylene terephthalate and high-density polyethylene respectively [4].

The four major waste management methods that the EPA recommends for the solid waste industry are source reduction, recycling, incineration and landfills [5].

The most fundamental way to reduce waste is to prevent it from ever becoming waste in the first place. The waste management dilemma facing Americans today centers squarely on economic and environmental factors [6]. Landfills as places to hide our garbage until it disappears through decomposition or may never, continue to play a key role in solid waste management. Moisture is the most important environmental variable of degradation, and landfills are kept at a low moisture level to prevent excessive groundwater contamination from runoffs [7].

Over the past decades, the intrinsic resistance of plastic materials to degradation has been increasingly regarded as a source of environmental and waste management problems. Solutions to the growing waste management problems posed a challenge to material scientists and industry leaders to come up with polymers which have good short-term properties. Many industry leaders work hand in hand with material scientists towards innovations to prove that they are environmentally correct.

This study was undertaken to determine the biodegradability of PHBV resins in the form of pellets when exposed to a simulated waste disposal conditions in the laboratory. Objective was achieved via weight change method, carbon dioxide evolution, and dissolved oxygen depletion in water.

BACKGROUND

Among the candidates for biodegradable plastics, polyhydroxyalkanoates (PHAs) has been drawing much attention. Biodegradation is defined as the conversion of the constituents of a polymer to carbon dioxide, methane, and other natural products in an

aerobic and anaerobic environment by microorganisms such as bacteria and fungi [8].

PHAs are reserve polyesters that are accumulated as intracellular inclusions in a variety

of bacteria [9]. Of these polymers, polyhydroxybutyrate (PHB) is the most common.

Physical properties vary with the hydroxyvalerate (HV) units incorporated randomly

throughout the polymer chain [10]. Since the physical properties of PHB resemble those

of polypropylene,and polyethylene, the commercial production of PHAs is of

considerable interest [11]. One such commercial PHA is a random copolymer, p(HB-co-

HV), of 3-hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV), produced by the

bacterium *Alcaligenes eutrophus* from glucose and propionic acid over a period of

fermentation [12] In addition to being compatible with conventional waste disposal

systems such as recycling, incineration and landfill, these PHAs they are fully

biodegradable and compostable [13].

Until recently, much of the assessment of biodegradable plastics was done in

accordance to an American Standard of Testing and Materials (ASTM) procedure

developed in the 1960s and 1970s [14]. Literature of ASTM in the 60s and 70s was

based on qualitative visual observation of the microbial growth on the material used by

measuring colony diameter (ASTM, 1976). Qualitative tests permitted an initial

classification of materials according to their potential degradability, and especially

allowed the identification of microbial species, particularly fungi, most likely to grow on

the materials being studied [15]. Due to the increasing demand for the use of

biodegradable materials as well as for the fact that landfills will continue to play a key

role in solid waste management, an evaluation of biodegradability of biodegradable

plastics (PHBV), based on a weight loss method in simulated landfill conditions is

needed.

MATERIALS AND METHODS

Research Experimental Design

The degradation rate of the PHBV polymer was assessed by the weight change method, and by the amount of carbon dioxide gas that was evolved throughout the 60 days of each trial of experiment. The two variables in the experiments were moisture content, and bacteria loading of the different soil mediums (simulated disposal conditions).

High moisture (HM) groups were watered once every 10 days with 10 milliliters of San Jose City water. Low moisture (LM) groups were watered with 10 milliliters of San Jose City water only once at the beginning of the experiment.

Plastic Samples

All samples were in the form of pellets. There are about 6 different grades of PHBV plastic resins. Grade differentiation was based upon the ratio of HB and HV. Experiments were conducted using grade D400G from batch number W/429205.

Polymer pellets/granules were weighed in 5-gram portions. Each experimental trial required thirty, 5-gram portions. To ensure that all pellets were recovered during the retrieval process, the number of pellets in each 5-gram portion was counted. Each pellet varied slightly in size and hence every 5-gram portion consisted of a different number of pellets. The number of pellets varied between 83 to 89 per 5-gram portion.

Simulated Disposal Conditions

The various simulated landfill mediums were chicken manure (CM), sterilized sand (SS), potting soil (PS), and an equal combination, by weight of half sterilized sand and chicken manure (CB). CM was chosen for its high content in organic matter, and presence of microorganisms. Construction grade sand from Home Depot was sterilized by placing it in an oven (heated up to 212° F) for 48 hours. SS represented the absence of organic matter and microorganisms. PS was used for its compost content and wide usage in gardens by the general public. A combination of half-chicken manure and half (by weight) sterilized sand was an attempt to simulate the moderate presence of organic matter and microorganisms.

Controls

There were separate control groups for both the high and low moisture set-ups. Control groups for the high moisture set-up consisted of PHBV pellets being submerged in San Jose City water. PHBV pellets in the control low moisture set-ups were exposed to moisture present in the surrounding air.

Instruments

Carbon dioxide gas (CO_2) production was measured with the Mocon Dual Head Space Analyser, model Pac Check 650. An electrical digital scale, Mettler PE 3600 Delta Range was used to weigh out 5-gram portions of PHBV pellets. The same electrical scale

was used for detecting possible weight changes that may have occurred after each set time retrieval session. YSI Model 51B Dissolved Oxygen Meter and YSI 5730 Oxygen probe were used to measure the amount of oxygen (O_2) in water in the high moisture control groups.

Tray Set-up for Weight Change Measurement

In the first two trials of the experiment, the laboratory was maintained at a temperature of 70 ± 5 ^{0}F, and at 50 ± 5 % relative humidity throughout the duration of the experiment (summer). PHBV pellets buried in various soil mediums were contained in polypropylene trays.

Each tray had six holes at the bottom for drainage, and individual trays upon completion of set up of the experiment were covered with perforated aluminum foil. There were three compartments in each tray. Each tray contained one particular soil medium. Within each tray, a polystyrene divider separated each compartment. Each individual compartment held five grams of PHBV pellets that were buried in 1.5 pounds of soil medium (Figure 1).

Contents from the first compartment of each tray were retrieved after 20 days. Forty days after the beginning of the experiment, PHBV pellets and soil mediums of each tray from the second compartment were unearthed. The contents from the third compartment were retrieved after 60 days.

Glass Jar Set-up for Carbon Dioxide Gas Measurement

The last trial was conducted during the fall semester in the same laboratory but the temperature was maintained at $60 \pm 2\ ^0F$ and at 40 ± 3 % relative humidity. PHBV pellets together with their designated bury mediums were contained in glass jars with perforated lids.

Thirty glass jars were used in the third trial of the experiment. Both pellets and their designated bury mediums were contained in glass jars with screw-on perforated metal lids. Lids were punctured with two holes, one quarter inch in diameter (Figure 2). There were two drainage holes at the bottoms of all of the glass jars, except for six jars that were to be used for controls. High moisture control jars consisted of PHBV pellets that were submerged in San Jose City water. Hence, these bottles could not have holes at the bottom. Low moisture controls consisted of pellets that were placed in jars with perforated lids; no drainage holes were necessary.

Change in choice of containment for the third trial was necessary to facilitate attachment of the rubber tubing and septum. A blue rubber septum 0.5 inch in diameter was secured over one of the two holes on each lid with silicon gel. The other hole was fitted with rubber tubing seven inches in length. The diameter of rubber tubing was a quarter of an inch. Silicon gel was used to secure and seal the area around the point of insertion of the rubber tubing.

The rubber tubing and septum were attached to perforations on each lid to facilitate CO_2 accumulation and measurements. The rubber tubing for each bottle was clamped shut for 2 hours each day prior to measuring the amount of CO_2 in the bottle.

The needle of Dual Head Space Analyser was inserted into each bottle via the blue septum to measure the amount of CO_2 in the bottle.

The labeling of glass jars was identical to the tray set-up. The difference lied in having each compartment being contained in a jar instead of being separated by dividers.

Dissolved Oxygen Gas Measurement

Dissolved O_2 is indicated in mg/L (milligrams per liter) on a 0-15 mg/L scale. Solubility of O_2 in water at 21 ^{0}C and 760 mm Hg is 8.90 ± 0.2 mg/L (Standard Materials for the Examination of Water and Wastewater). The machine was calibrated to register readings at 760 mm Hg since City of San Jose is situated at sea level.

For the control, the probe was submerged in 1 liter of San Jose City water for 72 hours. Water was contained in a glass jar. The experimental group consisted of five grams of PHBV pellets that were submerged in one liter of San Jose City water. The probe was again inserted and left in the glass jar that contained the PHBV pellets and San Jose City water, for 96 hours. Readings of dissolved O_2 were manually registered every 24 hours for both the control and experimental groups.

Retrieval and Cleaning Process of Pellets

Samples in all three trials were retrieved and cleaned in the same order and manner. The steps were as follows:

- Empty contents of compartment or jars onto metal tray

- Separate pellets from soil/bury mediums

- Inventory pellets to make sure that the number of pellets retrieved is equal to the number of pellets present at the beginning of experiment

- Place pellets in a fine mesh strainer and rinse under running water to remove dirt residue caked onto pellets

- Dry specimens by exposing pellets to air for 3 hours

- Weigh dried pellet on electronic scale

Best Fit Linear Regression

Weight change of PHBV pellets after having been exposed to different soil conditions were computed, and analyzed statistically using Microsoft Excel. Respective best fit linear regressions and correlation coefficients were plotted and calculated.

RESULTS AND DISCUSSION

The results of experiments conducted are reported in three sections:

1. Weight change of PHBV pellets after having been exposed to different soil conditions;

2. Amount of carbon dioxide gas (CO_2) that evolved from soil mediums and plastic resins;

3. Amount of dissolved oxygen (O_2) that was present in the water in which the plastic resin pellets were submerged.

Effects of soil conditions with high microbial activity – chicken manure

Figure 3 showed the best fit linear regressions and actual weight change for PHBV pellets that were exposed to CMHM and CMLM. Correlation coefficients of CMHM and CMLM are 0.976 and 0.988, respectively. Results implied that actual weight change was very close to predicted values. Note that both graphs of CMHM and CMLM were linear, but graphs CMHM exhibited a steeper slope than CMLM. A weight loss of approximately 27% was observed over a period of six weeks for PHBV plastic pellets that were located in CMHM. On the contrary, only 8% weight loss was measured for the pellets that were located in CMLM. Results suggested that higher moisture content in soil of high concentration of microbial activity encouraged a more rapid weight change. With an adequate amount of moisture, microbes underwent less stress

and consequently could concentrate on propagation, which in turn contributed to the weight loss.

Effects of soil conditions with minimum/lack of microbial activity – sterilized sand

Figure 3 also shows weight change of PHBV pellets that were placed in the SSHM and SSLM. SS is the extreme opposite of CM with respect to lack of microbial content and activity. Correlation coefficient of SSHM and SSLM are 1.0 and 0.948 respectively. At the end of the six-week period, pellets that were exposed to SSHM did not show any weight change. However, pellets located in SSLM showed a 3.6% loss in weight. Weight loss shown by PHBV pellets in both trials for the experiment in SSLM might have been due to coincidental contamination of the sterilized sand. Occurrence of weight loss of PHBV resin pellets that were in SSLM may have also been due to oxidation of resin itself.

Effect of soil conditions with moderate amount of microbial activity

Two soil mediums represented moderate content of microbial activity in soil; PS, and CB. PHBV resin pellets that were exposed to CBHM experienced a 15% lost in weight versus 8% for pellets that were in PSHM. Under low moisture conditions, PHBV pellets degraded such that after 6 weeks, a weight loss of 11.6% and 6.2% were observed in CBLM and PSLM, respectively. Results of the experiment indicated that the presence of CM caused a higher weight loss in pellets, for both high and low moisture conditions.

Under both high and low moisture levels, CB caused more weight loss on the PHBV resin pellets than PS. Correlation coefficients for PS and CB in both high and low moisture conditions were all above 0.90. The difference among all the best-fit linear regressions in Figure 4 lied in their gradients. The steeper the gradient, the higher the weight change. Results suggested that microbial activity from only half the amount of chicken manure (by weight) in the CB soil medium exerted a faster weight loss in PHBV pellets than potting soil. Moisture level appeared to have less of an influence on weight loss for both soil mediums.

Results on controls for low and high moisture levels

Figure 5 shows the actual weight change and best-fit linear regressions for both the controls under different moisture conditions. The PHBV resin pellets in both the controls did not show any change in weight. Correlation coefficients for both the controls were 1. Best fit linear regressions for both the controls has no gradient. Results may suggest that packaging materials such as bottles and film made out of PHBV plastic resins are stable and durable under normal conditions of storage and use.

Evidence from weight change experiments indicated that while the PHBV plastic resin could biodegrade when deposited in microbially active environments, pellets were also moisture resistant, durable and stable in use. The rate of degradation was influenced by a range of environmental and material parameters and is particularly dependent on the microbial activity of the environment.

Evolution of carbon dioxide gas

The amount of CO_2 evolved is a direct indicative measurement of microbial activity. The higher the microbial activity, the more CO_2 is generated and as a result, PHBV pellets will experience more weight loss. The normal atmospheric gas composition of CO_2 and O_2 are 0.03% and 21%, respectively. The range and comparison of CO_2 evolution and O_2 consumption in jars that contained the different soil mediums, at two different moisture levels, and PHBV pellets that were buried in it are shown in Table 1.

Jars that contained CMHM generated 59% of CO_2 versus 27% in CMLM. Results also indicated that lower amounts of O_2 were registered in high moisture jars of the same content, except for the control jars and SS jars. Lower O_2 readings may have suggested that there was higher microbial activity in CMHM.

Jars that contained SSHM and SSLM did not show any change in CO_2 and O_2 levels. Thus the weight change experiment that showed a weight loss in SSLM was not due to cross contamination. Possibility of cross contamination is presently ruled out because there was no evidence of respiration, which would have been indicated by an increased in CO_2 gas measurement. A difference of 1% higher O_2 reading in jars that contained PHBV resins in SSHM is insignificant, since atmospheric oxygen fluctuates between two to three percent of the norm, which is 21%.

Data on CBHM and CBLM in Figure 1 shows CO_2 evolution peaked at 29% and about 27% respectively. There was higher microbial activity in jars of CBHM than CBLM. CO_2 evolution in both CBHM and CBLM jars were the average of CM and SS for both moisture levels. Propagation of microbes in CB soil under low moisture conditions may have been decreased by a lack of moisture. This is because O_2 readings appeared to be much higher in LM than in the HM level. A higher O_2 reading implied less microbial activity.

Potting soil data in Figure 1 did not show much variation in O_2 consumption and CO_2 evolution between low and high moisture levels. The lower range of CO_2 evolution was 60% higher in the CBHM jars than PSHM jars. Results suggested that microbial activity from only half of the amount (in weight) of CM is more influential in degradation than the full weight of potting soil. However, CO_2 for PS in both moisture levels peaked at approximately the same level as in the CB soil medium

There was no difference in readings between both the LM and HM control jars; PHBV resins are stable and durable under normal use and are especially so when there is an absence of microbial activity from various soil types. A non-sterile medium of any sort is indeed the key to degradation of PHBV plastic resins.

Results from dissolved oxygen gas meter

Readings from both control and experiment groups hovered around 7.8 to 8.0 mg/L. Readings were not exactly close to 8.90 ± 0.2 mg/L as listed on the chart by Standard Materials for the Examination of Water and Wastewater. Deviations may have been due to fluctuations in the barometric pressure of the atmosphere at the time of reading. Dissolved O_2 readings from both groups were so identical that results strongly indicate that PHBV pellets would not deplete dissolved O_2 content of water. Results further suggest that if by chance packaging materials that were made of PHBV plastic resins were washed into the ocean, they would not jeopardize marine life.

Conclusion

The soil medium to which the PHBV plastic pellets were exposed has a significant influence on their rate of degradation (illustrated in Figures 3, 4 and 5). The results presented in this paper showed that soil types had a higher influence on weight loss in PHBV pellets, than the amount of moisture that was present. However, weight loss occurred at a faster and higher rate when PHBV resins were exposed to soil that contained the most microbial activity, such as manure. The higher the presence of microorganisms the soil contained, the faster the degradation rate, which was measured by weight loss and carbon dioxide evolution. This was further proven in trays that held the combination soil and potting soil. Both soil types contained organic matter, but microbial content was the influential factor. The experiment proved that a fixed rate of

degradation could never be determined on PHBV plastic resins because the rate of degradation is determined by a range of environmental and material parameters. Rate is particularly dependent on the microbial activity of the environment.

In all trials of this research, temperature and humidity were maintained at approximately the same level. Also the same grade of PHBV plastic resins were used in each trial. As mentioned earlier, PHBV plastic resins come in different grades based upon the amount of hydroxyvalerate that was introduced into the structure of hydroxybutyrate. Therefore the molecular structure and weight may influence the rate of biodegradation.

Results from the dissolved O_2 experiment verified that degradation of PHBV pellets would not deplete water of its dissolved O_2. This is crucial because most aquatic life is extremely dependent on O_2 for respiratory activities and propagation of species.

The weight loss method is appropriate to determine the rate of degradation of PHBV plastic resins. Confined to a laboratory situation and not having to conduct a study in various landfills, the weight loss method was sufficient to prove that PHBV resins do biodegrade, but are very much environmentally controlled.

ACKNOWLEGMENTS

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Table 1. Comparison of CO_2 evolution and O_2 consumption in different soil mediums and moisture levels

Soil Medium	Low moisture (LM)			High moisture (HM)		
	CO_2 (%)	O_2 (%)	Jar #	CO_2 (%)	O_2 (%)	Jar #
Chicken Manure (CM)	21 to 27	0.8 to 1.9	28	21 to 59	0.02 to 0.3	13
	21 to 27	0.8 to 1.9	29	21 to 59	0.02 to 0.3	14
	21 to 27	0.8 to 1.9	30	21 to 59	0.02 to 0.3	15
Sterilized sand (SS)	0.9 to 1.4	21 to 22	22	0.9 to 1.4	21 to 23	7
	0.9 to 1.4	21 to 22	23	0.9 to 1.4	21 to 23	8
	0.9 to 1.4	21 to 22	24	0.9 to 1.4	21 to 23	9
Equal in wt. of SS & CM (CB)	13.7 to 26.8	4.5 to 14	19	21.5 to 29	0.1 to 3	4
	13.7 to 26.8	4.5 to 14	20	21.5 to 29	0.1 to 3	5
	13.7 to 26.8	4.5 to 14	21	21.5 to 29	0.1 to 3	6
Potting soil (PS)	13 to 27	1.0 to 0.8	25	13 to 28.5	1 to 0.8	10
	13 to 27	1.0 to 0.8	26	13 to 28.5	1 to 0.8	11
	13 to 27	1.0 to 0.8	27	13 to 28.5	1 to 0.8	12
Control	0.9 to 1.3	21.1 to 1.7	16	0.9 to 1.3	21.1 to 21.7	1
	0.9 to 1.3	21.1 to.21.7	17	0.9 to 1.3	21.1 to 21.7	2
	0.9 to 1.3	21.1 to 21.7	18	0.9 to 1.3	21.1 to 21.7	3

Titles of figures:

Figure 1. Tray set-up for weight change experiment

Figure 2. Components of glass jar set-up for carbon dioxide gas monitoring

Figure 3. Weight change and linear best-fit in chicken manure and sterilized sand

Figure 4. Weight change and linear best-fit in combination soil and potting soil

Figure 5. Weight change and linear best fit in controls

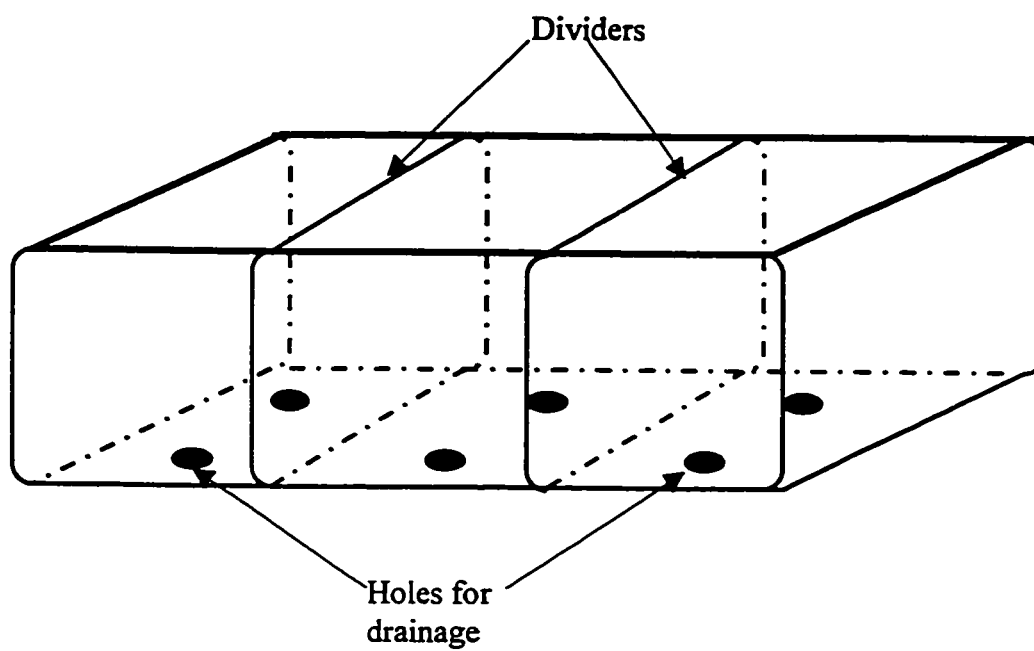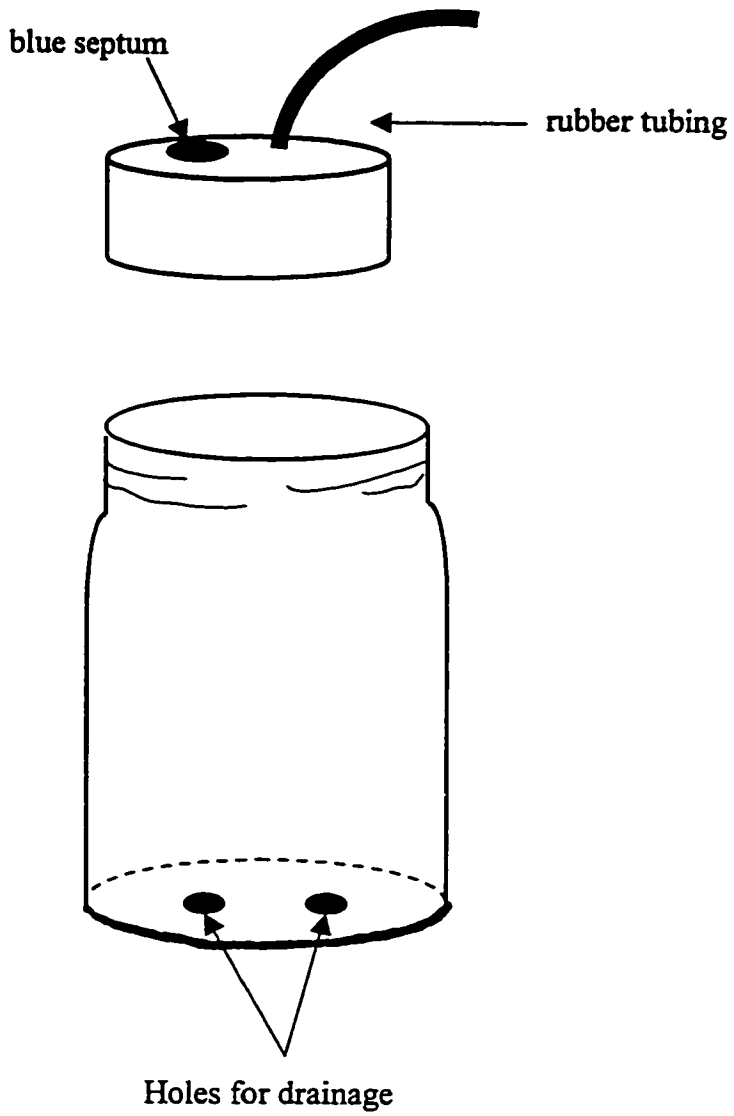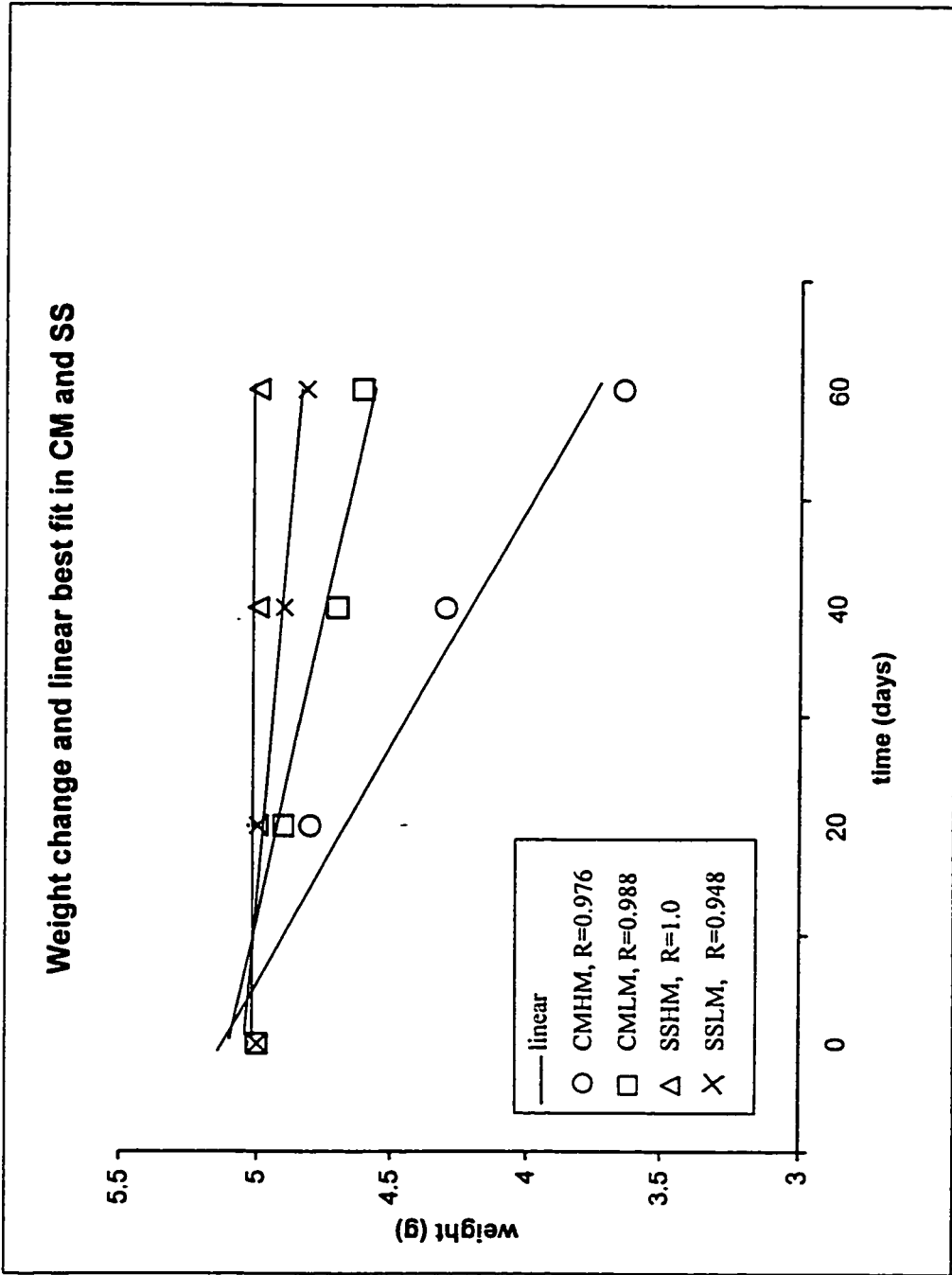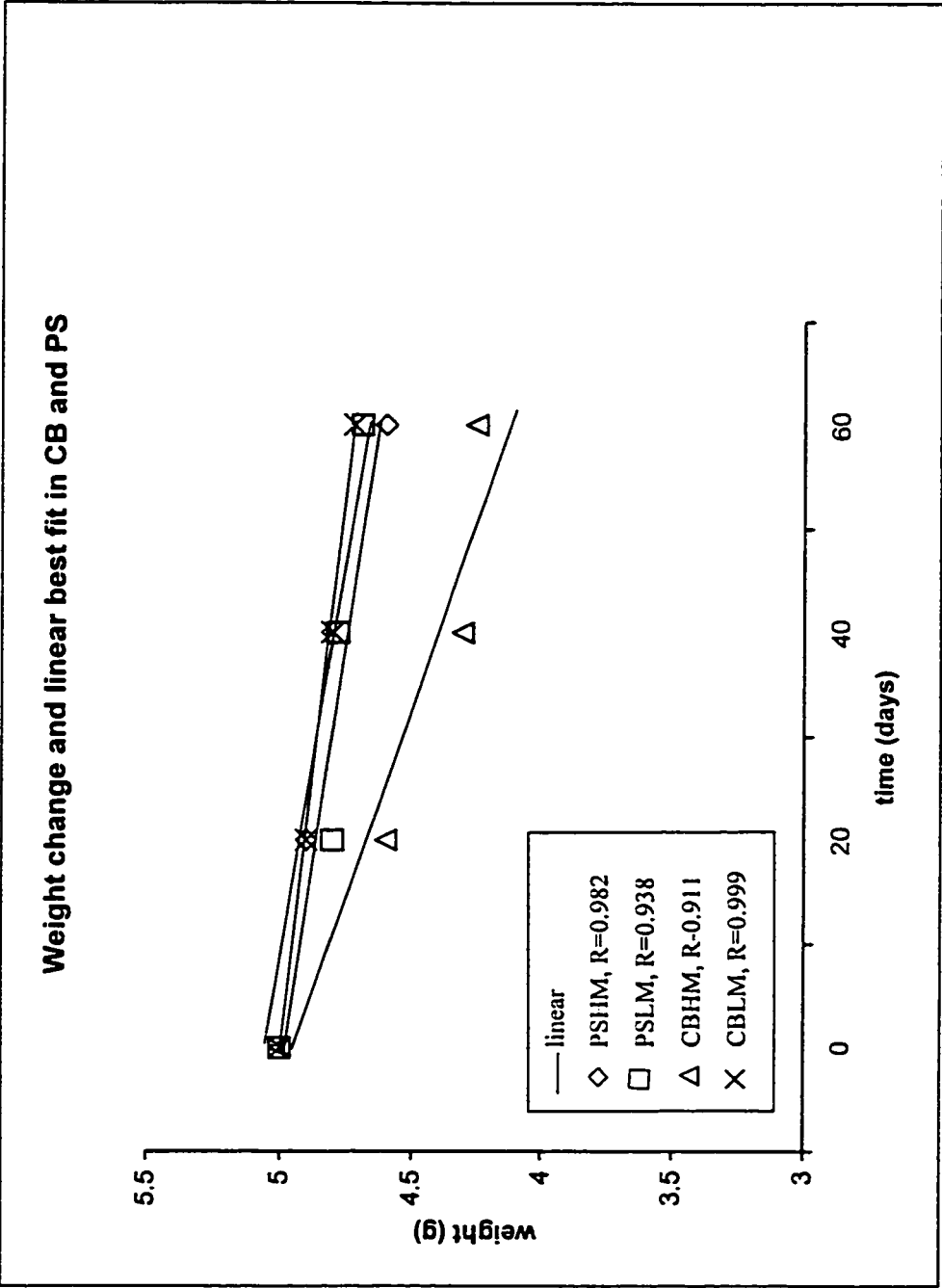Figure 1. Tray set-up for weight change experiment

Figure 2. Components of glass jar set-up for carbon dioxide gas monitoring

blue septum

rubber tubing

Holes for drainage

Weight change and linear best fit in CM and SS

Weight change and linear best fit in CB and PS

weight (g)

time (days)

linear
PSHM, R=0.982
PSLM, R=0.938
CBHM, R-0.911
CBLM, R=0.999

Weight change and linear best fit in controls
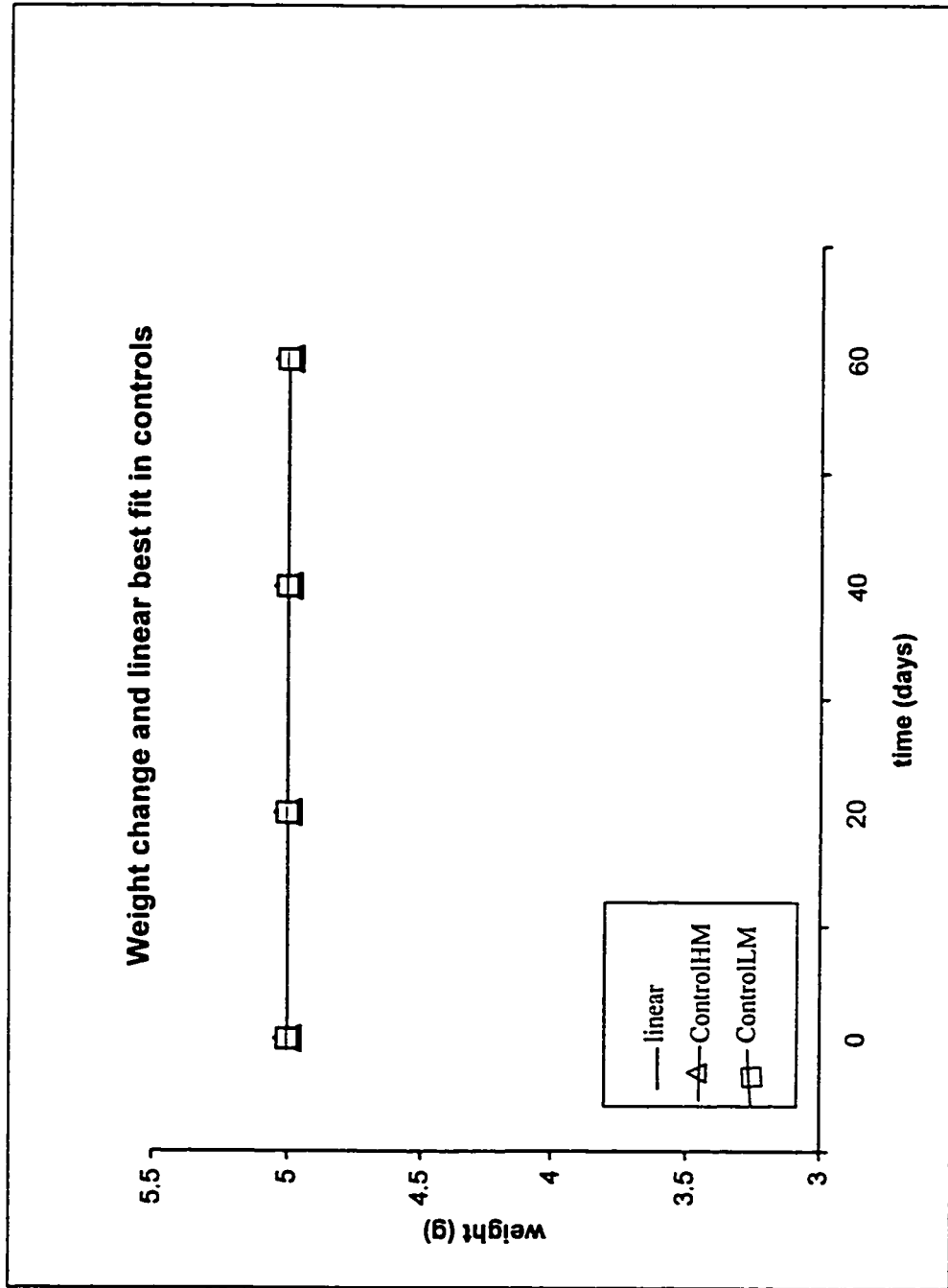
CHAPTER 3

SUMMARY AND RECOMMENDATIONS

Summary

Quantitative determination of biodegradability of PHBV plastic resins was estimated by the weight change method in an aerobic simulated disposal system. All data on weight change shown in PHBV pellet were computed on a dry basis, and statistically analyzed using Excel. Indicative measurements of microbial activity and respiration such as evolution of carbon dioxide were conducted by comparing the amount that was present in the enclosed jar and atmospheric carbon dioxide composition.

The soil medium in which the PHBV plastic pellets were exposed has a significant influence on its rate of degradation. The results showed that soil types had a higher influence on weight loss in PHBV plastic pellets than the amount of moisture that was present. However, weight loss occurred at a faster and higher percentage when PHBV resins were exposed to soil that contained the most microbial activity, such as manure. The higher the presence of microorganism that soil contained, the faster the degradation rate, which was measured by weight loss and carbon dioxide evolution. This was further proven in trays that held the combination soil and potting soil by itself. Both soil types contained organic matter, but microbial content was the influential factor. The experiment showed that a fixed rate of degradation could never be determined on PHBV plastic resins because the rate of degradation is determined by a range of environmental and material parameters. Rate is particularly dependent on the microbial activity of the environment.

Temperature and humidity were maintained at approximately 70 ^{0}F and 50% respectively in all trials of this research. PHBV plastic resins come in different grades based upon the amount of hydroxyvalerate that was introduced into the structure of hydroxybutyrate. Therefore the molecular structure and weight may influence the rate of biodegradation. The same grade of PHBV plastic resin was used in each trial.

Results from the dissolved oxygen experiment verified that degradation of PHBV pellets would not deplete water of its dissolved oxygen. This is crucial because most aquatic life is extremely dependent on oxygen for respiratory activities and propagation of species.

The weight loss method is appropriate to determine the rate of degradation of PHBV plastic resins. Confined to a laboratory situation and not having to conduct a study in various landfills, the weight loss method was sufficient to show that PHBV resins do biodegrade, but are very much environmentally controlled.

<div align="center">Recommendations and Suggestions</div>

Packaging exists solely to perform four basic functions: protection, containment, information, and utility of product use. If packaging is to perform effectively, it must respond to continuous changes in the cost, function, availability of materials, and changes in consumer needs. Consumer needs for packaging vary from physical use to environmental concerns. Petro-chemical plastics are extensively used in manufacturing of packaging materials. After the package has served its purpose, the problem of disposing of the material can be a challenge. Products made out of petro-chemical

plastics do not degrade. Packaging is conspicuous, and constitutes a large portion of the municipal solid waste.

Material scientists with their innovative knowledge and technology could hopefully one day use biodegradable plastics for all types of packaging materials. Application of various copolymers of PHBV plastic resins that are compatible to geographically different waste disposal systems would certainly help to ease problems in MSW. Think of the vast amounts of disposable items that are currently made out of petro-chemical plastics such as utensils, diapers, or feminine hygiene products. There would be great economic justification for making these items out of PHBV resins to reduce the MSW.

Biodegradable carriers such as bags, films, drums for insecticides, herbicides or fertilizers and other agricultural activities, though not as conspicuous to the general public, would also help to reduce waste and increase usage of PHBV. Agricultural plastic films made out of PHBV plastic resins for frost protection and mulching would save farmers the hassle and time of having to gather up the brittle and fragmented sheets of currently in use petro-chemical based films.

Medical devices such as surgical pins, sutures, staples, wound dressing and swabs, when accumulated from all medical facilities constitute a tremendous volume of "trash". Recycling of these products is very controversial for health reasons. Therefore medical devices made out of PHBV would also help to alleviate MSW.

With increase in demand of PHBV based products, more advance production and recovery methods of PHBV, it is likely that PHBV will become a major biodegradable

plastic. Applications in a wide range of products such as toothbrushes, toys, and casings for computers could all be gathered for composting. The meaning and horizon for composting programs may have to be redefined.

Future research should be done on finished products that are made out of the PHBV resins. Plasticizers that are incorporated into the PHBV resin during manufacturing of an item may bring about a different effect on PHBV degradation. Finished products manufactured by different methods of production such as lamination, co-extrusion and blending should be evaluated separately. Degradation evaluations for products made from different methods are needed because lamination, which involves gluing of separate layers of plastic films, may be different from simultaneous layering of films, as in co-extrusion process. Similarly, blending of PHBV resins together with other types of resin, or another copolymer of PHBV resin could effect the rate of degradation of an item. It would be beneficial for the next graduate student to conduct a similar study as a follow up using bottles that are made out of PHBV resins, instead of just the resin pellets.

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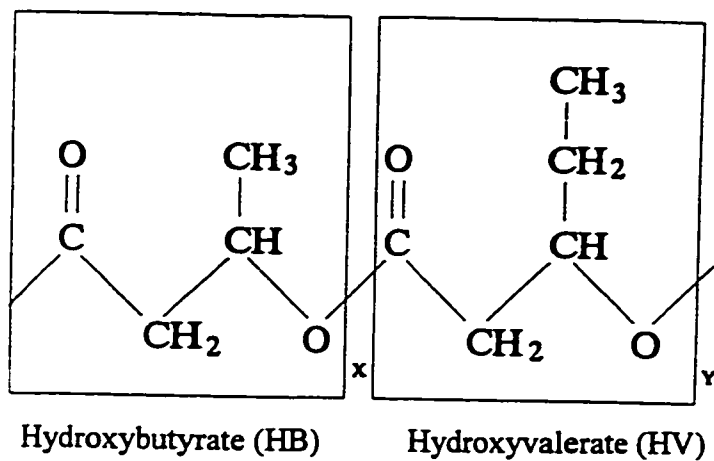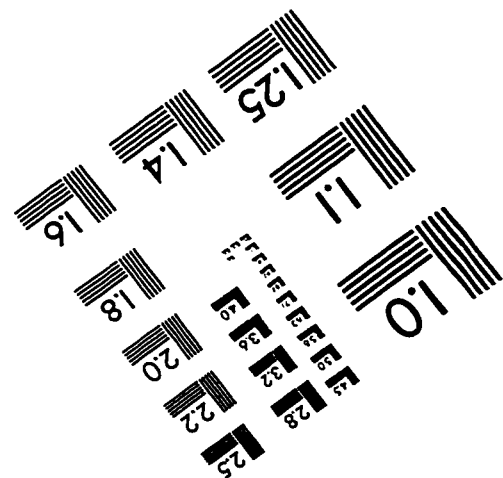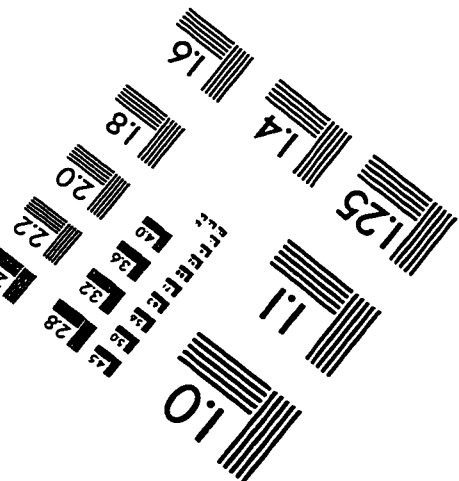Appendix A
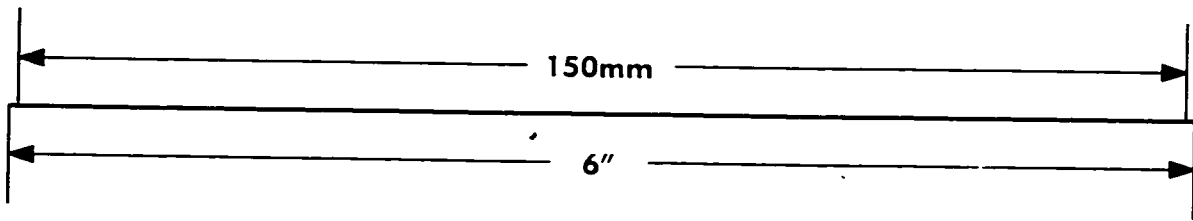
Chemical structure of PHBV copolymers .

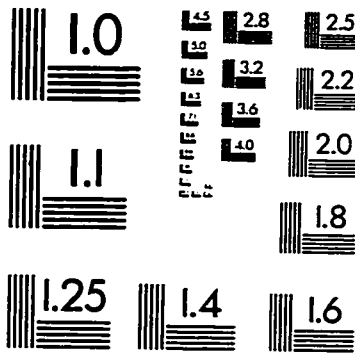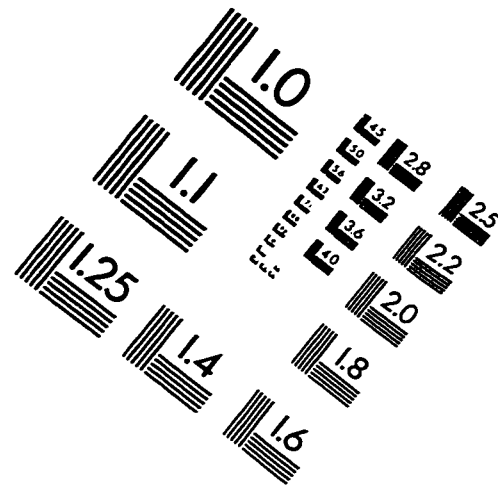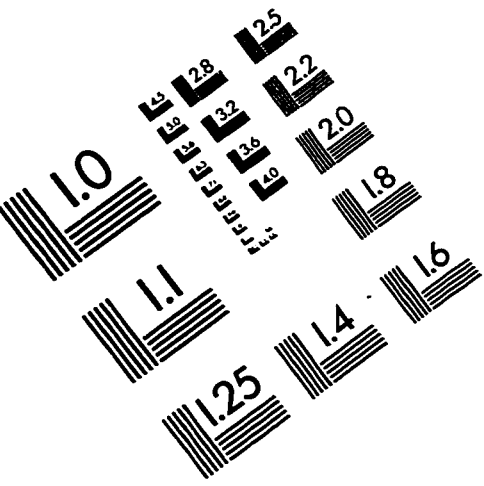Hydroxybutyrate (HB)   Hydroxyvalerate (HV)

IMAGE EVALUATION
TEST TARGET (QA-3)

150mm

6"

APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989