Biodegradation of high density polyethylene and poly(L-lactic acid) blends

Dissertation submitted in partial fulfillment for the requirement of degree of

Master of Technology

in

Environmental Science and Technology

By

Onam Khare

(Roll No. 601101029)

under the supervision of

Dr. Pramod K. Bajpai
Distinguished Professor

Department of Chemical Engineering

Dr. Haripada Bhunia

Associate Professor

Department of Chemical Engineering

SCHOOL OF ENERGY AND ENVIRONMENT

THAPAR UNIVERSITY, PATIALA 147 004 PUNJAB, INDIA

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DECLARATION

I hereby declare that the work embodied in thesis entitled **"Biodegradation of high density polyethylene and poly(L-lactic acid) blends"** submitted in the **"School of Energy And Environment"**, Thapar University, Patiala, is a record of the work carried out by me under the guidance of Dr. Pramod K. Bajpai, Distinguished Professor, ChED and Dr. Haripada Bhunia, Associate Professor, ChED. The matter presented in this dissertation has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

Date: _____ (**Onam Khare**)

Roll No: 601101029

CERTIFICATE

This is to certify that the dissertation entitled **"Biodegradation of high density polyethylene and poly(L-lactic acid) blends"** is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology (M. Tech.) in Environmental Science and Technology from Thapar University, Patiala, under the guidance of Dr. Pramod K. Bajpai, Distinguished Professor, ChED and Dr. Haripada Bhunia, Associate Professor, ChED during July 2012 to June 2013.

Date: 8/7/13

Onam Khare (18/6/2013)
(Onam Khare)
Roll No: 601101029

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

(Pramod K. Bajpai)
Distinguished Professor
Department of Chemical Engineering
Thapar University, Patiala

(Haripada Bhunia)
Associate Professor
Department of Chemical Engineering
Thapar University, Patiala

Countersigned by

(A. S. Reddy)
Head, School of Energy and Environment
Thapar University, Patiala

(Prof. S. K. Mohapatra)
Dean of Academic Affairs
Thapar University, Patiala

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(Onam Khare)

Roll No: 601101029

ABSTRACT

The blends of HDPE-PLLA in different ratios were tested for the degree of biodegradation as per ASTM D 5338 (2003) standard, which is the "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions". The samples (along with their composition and tensile strength) were provided by the Department of Chemical Engineering. A total of six bioreactors (containing one 'blank' and five film samples of blends of HDPE/PLLA in ratios 100/0, 95/5, 90/10, 80/20 and 75/25 respectively) were used. The CO_2 free air was supplied to the bioreactors (under pressure) through six rotameters, one for each of the bioreactors. The temperature of the bioreactors was maintained at 37°C by placing them in an air circulated incubator. The carbon of the polymer samples got converted into CO_2 by its aerobic degradation with the help of microorganisms present in the composted municipal solid wastes (ued as inoculums). The amount of CO_2 evolved was calculated at the time intervals of 12 hr, 24 hr, 48 hr, and 96 hrs by using phenophthelein indicator and titration against HCl solution. The blend PB5 (HDPE/PLLA = 75/25) showed the maximum biodegradation, which may be due to the reason that it contained the highest amount of the biodegradable polymer PLLA. The sample PB1 (HDPE/PLLA = 100/0) showed the minimum biodegradation.

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ABBREVIATIONS

ASTM	American Society for Testing and Material
CEN	European Committee for Standardization
HDPE	High Density Polyethylene
ISO	International Organization for Standardization
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
PE	Polyethylene
PLA	Polylactic acid
PLLA	Poly(L-lactic acid)
ChED	Chemical Engineering Department
PP	Polypropylene

CHAPTER: 1

INTRODUCTION

A polymer is a chemical compound or mixture of compounds consisting of repeating structural units bonded by covalent chemical bonds created through a process of polymerization **[1]**. A monomer is a low molecular weight compound that can be connected together to give a polymer and an oligomer is a short polymer chain **[2]**. Polymers are categorized into two broad categories: natural polymers (e.g. proteins, carbohydrates, natural rubber) and synthetic polymers (e.g. plastics, fibres, elastomers).

Plastics are typically organic polymers of high molecular mass, but they often contain other substances. They are usually synthetic, most commonly derived from petrochemicals, but many are partially natural. Plastics are divided into two groups: thermoplastics and thermo-set plastics **[3]**. In thermoplastics, the atoms and molecules are joined end-to-end into a series of long, sole carbon chains. These long carbon chains are independent of the others **[4]**. This kind of structure in which the backbone is solely built of carbon atoms makes thermoplastics resistant to degradation or hydrolytic cleavage of chemical bonds. Consequently, thermoplastics are considered as non-biodegradable plastics. Distinguished from the linear structure of thermoplastics, thermoset plastics have a highly cross-linked structure **[5]**. Since main chain of thermoset plastics is made of hetero atoms, it is possible that they are potentially susceptible to be degraded by the hydrolytic cleavage of chemical bonds such as ester bonds or amide bonds **[6]**. Thermoplastics are widely used in packaging and fabrication of bottles and films (Table 1.1). The major types of thermoplastic material include linear low density polyethylene (LLDPE), high density polyethylene (HDPE), polyvinyl chloride (PVC), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and other resins. Thermoset plastics include polyesters, one of which is polyethylene terephthalate (PET); and polyurethane **[7]**.

Table 1.1: Types of plastics and their applications

Plastic(s)	Applications
Low density polyethylene (LDPE), linear low density polyethylene (LLDPE), polyvinylchloride (PVC)	Films and Packaging
Polyethylene terephthalate (PET), PVC, high density polyethylene (HDPE)	Bottles, tubes, pipes, insulation molding
Polystyrene (PS), polypropylene (PP), PVC	Tanks, jugs, containers
LDPE, LLDPE	Bags
Polyurethane (PUR)	Coating, insulation, paints, packing

Primarily, there are seven commodity polymers in use – polyethylene, polypropylene, polyvinylchloride, polyethylene-terephthalate, polystyrene, polycarbonate, and poly (methyl methacrylate) (Plexiglas). These make up nearly 98% of all polymers and plastics encountered in daily life. Each of these polymers has its own characteristic modes of degradation and resistances to heat, light and chemicals. Polyethylene, polypropylene, and poly (methyl methacrylate) are sensitive to oxidation and UV radiation, while PVC may discolour at high temperatures due to loss of hydrogen chloride gas, and become very brittle. PET is sensitive to hydrolysis and attack by strong acids, while polycarbonate depolymerises rapidly when exposed to strong alkalis. For example, polyethylene usually degrades by *random scission* - that is by a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When this polymer is heated above 450°C, it becomes a complex mixture of molecules of various sizes that resemble gasoline. Other polymers - like poly-alpha-methyl-styrene - undergo 'specific' chain scission with breakage occurring only at the ends; they literally unzip or depolymerize to become the constituent monomers **[8]**.

1.1 Polyethylene

Polyethylene (abbreviated as PE) or polythene (IUPAC name polyethene or poly(methylene)) is the most common plastic (Fig. 1.1). The annual production is approximately 80 million metric tons. Its primary use is within packaging (plastic bag, plastic film, geomembranes, containers including bottles, etc.). Many kinds of polyethylene are known, but they almost always have the chemical formula $(C_2H_4)_n$. Thus PE is usually a mixture of similar organic compounds that differ in terms of the value of n **[9]**.

Figure 1.1: Polyethylene

1.2 High-density polyethylene (HDPE)

It is a type of polyethylene thermoplastic made from petroleum. It takes 1.75 kilograms of petroleum (in terms of energy and raw materials) to make one kilogram of HDPE. HDPE is

commonly recycled, and has the number "2" as its recycling symbol. In 2007, the global HDPE market reached a volume of more than 30 million tons **[10]**.

HDPE films are widely used for packaging applications because of their high processibility and good mechanical properties, e.g. high tensile strength (Fig. 1.2).

Figure 1.2: HDPE film

Typical properties and applications of HDPE Films

- Thickness 0.0005" to 0.030" (width restrictions may apply).
- Available in translucent or opaque colours (standard colours: red, white, shades of blue, shades of green, shades of yellow, orange, gray, black, etc.)
- Striping applications (to produce colour coded vacuum formed storage trays and plastic pallets).
- Also available with anti-static, flame retardant and ultraviolet additives.
- High moisture barrier properties (WVTR of 0.50 to 0.80 g/100 sq.in/mil/24 hours)
- High temperature resistance (Melting temperature of approximately 260 °F)
- Non-abrasive, non-scratching film and high resistance to acids. good release property without silicone coating.
- Used as release liners and interleaving sheeting, foam in place, box liners.
- Upon corona treating, film is printable with flexographic, offset, hot stamping or silk screening processes.
- Polyethylene films used in packaging applications, protecting products such as powder, cheese, frozen foods, and electronic parts **[11]**.

One of the main problems of polyethylene is that without special treatment it is not biodegradable, and thus accumulates. This ‘plastic waste’ creates approx. 18% (by volume) of the total waste worldwide per year **[12]**. It is estimated that approximately 10,000 tons per day (TPD) of plastics waste is generated in India only, i.e., 9% of 0.12 million TPD of total municipal solid waste (MSW) in the country resulting in widespread littering on landscape, which not only affects environment

but also human beings. Asia's top plastic waste market is India's National Capital Delhi, in which the daily handling and trading is over 1000 tones, whereas the generation of plastic waste is only 300 tonnes per day **[13]**. Amongst all the plastic wastes, the disposable packaging materials used to protect fragile items and that used in food and drinks share the largest amount.

Recyclable plastic wastes is collected and recycled mainly through unorganized sectors located in non-conforming areas. Waste plastics are recycled under very unhealthy, unscientific and unhygienic conditions **[14]**. These are resistant to degradation, and consequently their disposal are fuelling national as well as international drive for the development of biodegradable polymers **[15]**. According to senior official from CPCB, BIS standards are rarely adopted by the manufacturers, hence, the Environment Ministry needs to issue a notification banning ordinary plastic bags and promoting biodegradable plastic bags **[16]**. In the year 2010, specifications (consisting of 10 standards) on biodegradable plastics are notified by the Bureau of Indian Standards **[17]**.

The development of innovative biodegradable or environmentally friendly polymers (or biopolymers) is in progress for a number of years, and continues to be an area of interest for many scientists. The use of biodegradable polymers and their final method of biodegradation are dependent on the composition and processing method employed **[18]**. As biodegradable polymers materials are thought to help the environment by reducing waste, many countries have begun to accept these materials. The biodegradable plastics (BDPs) must also be microbially and environmentally degraded upon disposal, without any adverse environmental impact **[19]**. The various routes and types of polymer degradation are depicted in Fig. 1.3.

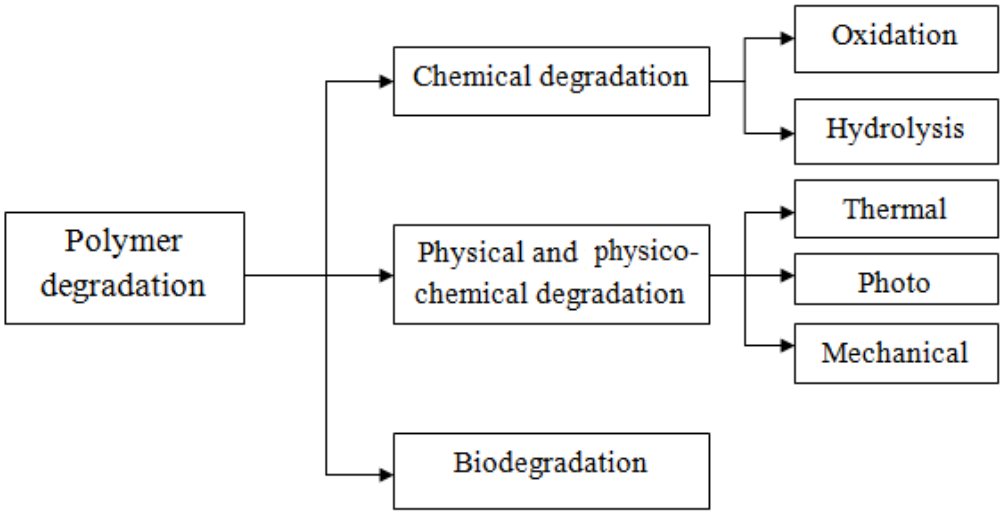

Figure 1.3: Overview of degradation of polymers

The biodegradability of BDPs can be estimated by many methods. The extent to which a polymer is available for attack by microorganisms is the biodegradability of that polymer. Although a wide range of biodegradable polymers exists, but those which aren't biodegradable, pose a problem to

the environment. Depending on their origins, BDPs may be classified as being either bio-based or petrochemical-based. The formers are mostly biodegradable by nature and produced from natural origins (plants, animals or micro-organisms) such as polysaccharides (e.g. starch, cellulose, lignin and chitin), proteins (e.g. gelatine, casein, wheat gluten, silk and wool) and lipids (e.g. plant oils and animal fats). Natural rubber as well as certain polyesters either produced by micro-organism/ plant (e.g. polyhydroxyalkanoates and poly-3-hydroxybutyrate) or synthesized from bio-derived monomers (e.g. polylactic acid (PLA)) fall into this category.

Petrochemical-based BDPs such as aliphatic polyesters (e.g. polyglycolic acid, polybutylene succinate and polycaprolactone (PCL)), aromatic copolyesters (e.g. polybutylene succinate terephthalate) and poly(vinyl alcohol) are produced by synthesis from monomers derived from petrochemical refining, which possess certain degrees of inherent biodegradability **[20]**. This classification differentiates between renewable (bio-based) and non-renewable (petrochemical-based) resources, but it should be noted that many commercial BDP formulations combine materials from both classes to reduce cost and/or enhance performance.

1.3 Biodegradability of Polymers

The American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO) define degradable plastics as those which undergo a significant change in chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties, as measured by standard methods. Biodegradable plastics undergo degradation from the action of naturally occurring microorganisms such as bacteria, fungi, and algae. Plastics may also be designated as photodegradable, oxidatively degradable, hydrolytically degradable, or those which may be composted. Between October 1990 and June 1992, confusion as to the true definition of "biodegradable" led to lawsuits regarding misleading and deceitful environmental advertising **[21]**. Thus, it became evident to the ASTM and ISO that common test methods and protocols for degradable plastics were needed.

There are three primary classes of polymer materials which material scientists are currently focusing on. These polymer materials are usually referred to in the general class of plastics by consumers and industry. Their design is often that of a composite, where a polymer matrix (plastic material) forms a dominant phase around a filler material. The filler is present in order to increase mechanical properties, and decrease material costs.

Conventional plastics are resistant to biodegradation, as the surfaces in contact with the soil in which they are disposed are characteristically smooth **[22]**. Microorganisms within the soil are unable to consume a portion of the plastic, which would, in turn, cause a more rapid breakdown of the supporting matrix. This group of materials usually has an impenetrable petroleum based matrix,

which is reinforced with carbon or glass fibers. The second class of polymer materials under consideration is partially degradable. They are designed with the goal of more rapid degradation than that of conventional synthetic plastics. Production of this class of materials typically includes surrounding naturally produced fibers with a conventional (petroleum based) matrix. When disposed of, microorganisms are able to consume the natural macromolecules within the plastic matrix. This leaves a weakened material, with rough, open edges. Further degradation may then occur. The final class of polymer materials is currently attracting a great deal of attention from researchers and industry. These plastics are designed to be completely biodegradable. The polymer matrix is derived from natural sources (such as starch or microbially grown polymers), and the fiber reinforcements are produced from common crops such as flax or hemp.

Microorganisms are able to consume these materials in their entirety, eventually leaving carbon dioxide and water as by-products. Materials must meet specific criteria set out by the ASTM and ISO in order to be classified as biodegradable. In general, the likelihood of microbial attack on a material is dependent on the structure of the polymer. When examining polymer materials from a scientific standpoint, there are certain ingredients that must be present in order for biodegradation to occur. Most importantly, the active microorganisms (fungi, bacteria, actinomycetes, etc.) must be present in the disposal site. The organism type determines the appropriate degradation temperature, which usually falls between 20 to 60°C. The disposal site must be in the presence of oxygen, moisture, and mineral nutrients, while the site pH must be neutral or slightly acidic (5 to 8).

Biodegradation of materials occurs in various steps **[22]**. Initially, the digestible macromolecules, which join to form a chain, experience a direct enzymatic scission. This is followed by metabolism of the split portions, leading to a progressive enzymatic dissimilation of the macromolecule from the chain ends. Oxidative cleavage of the macromolecules may occur instead, leading to metabolization of the fragments. Either way, eventually the chain fragments become short enough to be converted by microorganisms **[23]**.

Biodegradable polymers (those derived from plant sources) begin their lifecycle as renewable resources, usually in the form of starch or cellulose. As reported by Lorcks (1998), innovative polymer research and development leads to large scale production by plastic converters. The biopolymers are formed into the specific end products and used by a consumer. Ideally, the biopolymer will be disposed in a bio waste collection, and later composted. This process will ultimately leave behind carbon dioxide and water, which are environmentally friendly byproducts.

1.4 Applications for Biodegradable Polymers

Research and development is only a portion of the work that is done in order to introduce the use of biodegradable polymer materials. The design of such materials usually begins with a conceptual

application. It may be expected to replace an existing material, or to complement one. Sectors where applications for biopolymers have introduced include (but are not limited to) medicine, packaging, agriculture, and the automotive industry. Many materials that have been developed and commercialized are applied in more than one of these categories.

Biopolymers that may be employed in packaging continue to receive more attention than those designated for any other application. All levels of government, particularly in China **[24]** and Germany **[25]**, are endorsing the widespread application of biodegradable packaging materials in order to reduce the volume of inert materials currently being disposed of in landfills, occupying scarce available space. It is estimated that 41% of plastics are used in packaging, and that almost half of that volume is used to package food products.

BASF, a world leader in the chemical and plastic industry, is working on further development of biodegradable plastics based upon polyester and starch **[26]**. Ecoflex is a fully biodegradable plastic material that was introduced to consumers by BASF in 2001. The material is resistant to water and grease, making it appropriate for use as a hygienic disposable wrapping, fit to decompose in normal composting systems. Consequently, Ecoflex has found a number of applications as a packaging wrap.

Environmental Polymers (Woolston, Warrington, UK) has also developed a biodegradable plastic material. Known as Depart, the polyvinyl alcohol product is designed for extrusion, injection molding, and blow molding. Depart features user-controlled solubility in water, which is determined by the formulation employed. Dissolution occurs at a preset temperature, allowing the use of Depart in a variety of applications. Examples include hospital laundry bags which are "washed away" allowing sanitary laundering of soiled laundry, as well as applications as disposable food service items, agricultural products, and catheter bags **[27]**.

The renewable and biodegradable characteristics of biopolymers are what render them appealing for innovative uses in packaging. The end use of such products varies widely. For example, biodegradable plastic films may be employed as garbage bags, disposable cutlery and plates, food packaging, and shipping materials. Guan and Hanna **[28]** documented how biodegradable loose-fill packaging materials may be developed from renewable biopolymers such as starch. The starch material is treated by an acetylation process, chemical treatments, and post-extrusion steaming. Mechanical properties of the material are adequate, and true biodegradability is achieved.

The biopolymer materials suited for packaging are often used in agricultural products. Ecoflex, in particular, sees use in both areas. Young plants which are particularly susceptible to frost may be covered with a thin Ecoflex film. At the end of the growing season, the film can be worked back into the soil, where it will be broken down by the appropriate microorganisms. Li et al. **[29]**

concluded that the use of a clear plastic mulch cover immediately following seeding increases the yield of spring wheat if used for less than 40 days. Therefore, plastic films that begin to degrade in average soil conditions after approximately one month are ideal candidates as crop mulches.

Agricultural applications for biopolymers are not limited to film covers. Containers such as biodegradable plant pots and disposable composting containers and bags are areas of interest **[30]**. The pots are seeded directly into the soil, and breakdown as the plant begins to grow. Fertilizer and chemical storage bags which are biodegradable are also applications that material scientists have examined. From an agricultural standpoint, biopolymers which are compostable are important, as they may supplement the current nutrient cycle in the soils where the remnants are added.

The medical world is constantly changing, and consequently the materials employed by it also see recurrent adjustments. The biopolymers used in medical applications must be compatible with the tissue they are found in, and may or may not be expected to break down after a given time period. Mukhopadhyay **[31]** reported that researchers working in tissue engineering are attempting to develop organs from polymeric materials, which are fit for transplantation into humans. The plastics would require injections with growth factors in order to encourage cell and blood vessel growth in the new organ. Work completed in this area includes the development of biopolymers with adhesion sites that act as cell hosts in giving shapes that mimic different organs.

Not all biopolymer applications in the field of medicine are as involved as artificial organs. The umbrella classification of bioactive materials includes all biopolymers used for medical applications. One example is artificial bone material which adheres and integrates onto bone in the human body. The most commonly employed substance in this area is called ‘bioglass’ **[32]**. Another application for biopolymers is in controlled release delivery of medications. The bioactive material releases medication at a rate determined by its enzymatic degradation **[33].** PLA materials were developed for medical devices such as resorbable screws, sutures, and pins. These materials reduce the risk of tissue reactions to the devices, shorten recovery times, and decrease the number of doctor visits needed by patients.

The automotive sector is responding to societal and governmental demands for environmental responsibility. Bio-based cars are lighter, making them a more economical choice for consumers, as fuel costs are reduced. Natural fibres are substituted for glass fibres as reinforcement materials in plastic parts of automobiles and commercial vehicles **[34]**. An additional advantage of using biodegradable polymer materials is that waste products may be composted. Natural fibres (from flax or hemp) are usually applied in formed interior parts. The components do not need load bearing capacities, but dimensional stability is important.

There are a number of novel applications for biopolymers, which do not fit into any of the previous categories. One such example is the use of biopolymer systems to modify food textures. For example, biopolymer starch (gelatin-based) fat replacers possess fat-like characteristics of smooth, short plastic textures that remain highly viscous after melting.

Research continues into high pressure being used to manipulate biopolymers into food products. The eventual goal is improved physical characteristics such as foaming, gelling, and water- or fat-binding abilities **[35]**. Biopolymer materials are currently incorporated into adhesives, paints, engine lubricants, and construction materials **[36]**.

1.5 Methods of Biodegradation

Just as important as the way in which a material is formed is the way in which it is degraded. A general statement regarding the breakdown of polymer materials is that it may occur by microbial action, photodegradation, or chemical degradation. All three methods are classified under biodegradation, as the end products are stable and found in nature.

Many biopolymers are designed to be discarded in landfills, composts, or soil. The materials will be broken down, provided that the required microorganisms are present. Normal soil bacteria and water are generally all that is required, adding to the appeal of microbially reduced plastics. Polymers which are based on naturally grown materials (such as starch or flax fiber) are susceptible to degradation by microorganisms. The material may or may not decompose more rapidly under aerobic conditions, depending on the formulation used, and the microorganisms required.

In the case of materials where starch is used as an additive to a conventional plastic matrix, the polymer in contact with the soil and/or water is attacked by the microbes. The microbes digest the starch, leaving behind a porous, sponge-like structure with a high interfacial area, and low structural strength. When the starch component has been depleted, the polymer matrix begins to be degraded by an enzymatic attack. Each reaction results in the scission of a molecule, slowly reducing the weight of the matrix until the entire material has been digested.

Another approach to microbial degradation of biopolymers involves growing microorganisms for the specific purpose of digesting polymer materials. This is a more intensive process that ultimately costs more, and circumvents the use of renewable resources as biopolymer feedstocks. The microorganisms under consideration are designed to target and breakdown petroleum based plastics **[37]**. Although this method reduces the volume of waste, it does not aid in the preservation of non-renewable resources.

Photodegradable polymers undergo degradation from the action of sunlight (ASTM 883-96). In many cases, polymers are attacked photochemically, and broken down to small pieces. Further

microbial degradation must then occur for true biodegradation to be achieved. Polyolefins (a type of petroleum-based conventional plastic) are the polymers found to be most susceptible to photodegradation. Proposed approaches for further developing photodegradable biopolymers includes incorporating additives that accelerate photochemical reactions (e.g. benzophenone), modifying the composition of the polymers to include more UV absorbing groups (e.g. carbonyl), and synthesizing new polymers with light sensitive groups **[37]**. An application for biopolymers which experience both microbial and photodegradation is in the use of disposable mulches and crop frost covers.

Some biodegradable polymer materials experience a rapid dissolution when exposed to particular (chemically based) aqueous solutions. As mentioned earlier, Environmental Polymer's product Depart is soluble in hot water. Once the polymer dissolves, the remaining solution consists of polyvinyl alcohol and glycerol. Similar to many photodegradable plastics, full biodegradation of the aqueous solution occurs later, through microbial digestion. The appropriate microorganisms are conveniently found in wastewater treatment plants **[38]**. Procter & Gamble has developed a product similar to Depart, named Nodax PBHB. Nodax is alkaline digestible, meaning that exposure to a solution with a high pH causes a rapid structural breakdown of the material **[39]**. Biopolymer materials which disintegrate upon exposure to aqueous solutions are desirable for the disposal and transport of biohazards and medical wastes. Industrial "washing machines" are designed to dissolve and wash away the aqueous solutions for further microbial digestion.

1.6 Standards for Biodegradable Plastics

The development of standard tests to measure the rate of biodegradation of polymers is necessary in order to ensure that residues from plastic packaging do not create a long-term pollution problem in the environment. However, the standards that have so far been published on the biodegradation, and particularly the composting, of synthetic polymers if applied to nature's lignocellulosic waste products would exclude straw, leaves and wood from the category of biodegradable materials.

In essence unrealistically short times are required in these Standards for conversion of the material to carbon dioxide. For example European Standard 13432 for the industrial composting of packaging polymers stipulates that they must be substantially (>90%) converted to carbon dioxide and biomass in an aqueous biotic environment within six months **[40]**. This is to simulate the behavior of pure cellulose, which, ironically is rarely found as such in nature.

Polyethylene, PF resins, lignin, humic acid and tannic acid, oxo-biodegrade relatively slowly but are all ultimately converted to carbon dioxide and water. Humus is a complex mixture of polyphenolic compounds and the slower the mineralisation occurs, the more beneficial is the resulting organic matter to the productivity of the soil. Full scale evaluation of partially-

biodegraded oxo-biodegradable polyethylene films has demonstrated that these materials have no adverse effect on soil fertility.

There are thus important ecological implications of the existing CEN, ISO and ASTM standards, since polymers that mineralise rapidly are not beneficial to the soil and by releasing CO_2 rapidly to the environment they contribute to the "greenhouse effect."

Biodegradation of plastics within a composting unit is an important phenomenon because it will affect the decomposition of other materials enclosed by the plastic and the resulting quality and appearance of the composted material. This procedure has been developed to permit the determination of the rate and degree of aerobic biodegradability of plastic products when placed in controlled composting process. The percentage of biodegradability is obtained by determining the percentage of carbon in the test substance that is converted to CO_2 during the duration of the test. This percentage of biodegradability will not include the amount of carbon converted from the test substance that is converted to cell biomass and that is not, in turn, metabolised to CO_2 during the course of test.

The main objective(s) of this work was to analyze the extent of biodegradation of the given samples of HDPE-PLLA blends following the standard ASTM D5338 (2003).

CHAPTER: 2

LITERATURE REVIEW

Extensive work has been done to make a polymer biodegradable or partially biodegradable and then studies have been done to assess the degree of biodegradation achievable. Blending with biodegradable polymer like PLLA, PLA; pre-treatment; composting; and microbial activity are some of the ways carried out to achieve it.

2.1 National Status

Balasubramanian et al. **[41]** stated that mechanical and surface properties are considered important in governing the physical strength of polymers. A commercially available oxo-biodegradable polymer additive, which has induced surface and mechanical property changes during photo-oxidation in low-density polyethylene (LDPE) films, has been studied. LDPE films containing the oxo-biodegradable additive were irradiated with ultraviolet (UV)-B lamps at 30±1°C for an extended time period. The changes manifested on the polymer surface and in the mechanical properties were studied with respect to surface wettability, surface morphology using scanning electron microscope, surface topology by atomic force microscopy, functional groups by Fourier transformed infrared spectroscopy, absorbance spectra by UV-visible spectroscopy and elongation at break and tensile strength through mechanical testing. The increase in the wettability and surface-free energy of the irradiated samples was attributed to the formation of hydrophilic groups on the polymer surface by photo-oxidation, which occurs by the exposure of PE to UV irradiation in the presence of air. The degree of reduction in the mechanical strength and surface property modifications in our study are appreciable through the use of an oxo-biodegradable additive added to LDPE film samples.

Roy et al. **[42]** worked on the degradation of abiotically aged low density polyethylene (LDPE) films containing trace quantities of a representative pro-oxidant (cobalt stearate) in the presence of well defined enriched microbial strains namely, *Bacillus pumilus*, *Bacillus halodenitrificans* and *Bacillus cereus* in Basal salt medium. The films were initially subjected to an abiotic treatment comprising UV-B irradiation, and subsequently inoculated with the bacterial strains. The degradation in the polymeric chain was monitored by changes in the mechanical, morphological, structural and thermal properties. The abiotic treatment led to the formation of extractable oxygenated compounds as well as unoxidised low molecular weight hydrocarbons, which was confirmed by GC–MS studies. These were utilized by the bacterial consortium in the subsequent biotic phase and led to a mass loss of the polymer (8.4 ± 1.37%), which was also accompanied by an increase in the bacterial count. A decrease in the surface tension of the cell free medium was observed, which indicates that the bacterial consortium produced extracellular surface

active molecules in order to enhance the bioavailability of the polymeric fixed carbon. The spectroscopic investigations reveal that the bacteria preferentially consume the oxygenated products leading to a decrease in the Carbonyl Index (CI), which in turn leads to an increase in the initial decomposition temperature as observed in the TGA traces. The morphological investigations reveal a biofilm formation on the surface, which was found to be scattered in certain regions and not uniform on the polymeric surface.

Singh et al. **[43]** have also started working in these areas. Melt blending of linear low density polyethylene (LLDPE) and polylactide (PLLA) was performed in an extrusion mixer with post extrusion blown film attachment with and without compatibilizer- grafted low density polyethylene maleic anhydride. Varying degrees of property modifications were achieved by blending these polymers. Many of these blends are immiscible or only partially miscible and need compatibilizers to increase their compatibility. The authors developed polymeric blends having optimum performance properties based on poly(L-lactic acid) using linear low density polyethylene (LLDPE) that are partially degaradable under some specific environmental conditions and investigated the effect of PLLA composition & compatibilizer content on the degradation properties of blends.

Chandra & Rustgi **[44]**, worked on Biodegradation of maleated linear low-density polyethylene and starch blends. In order to obtain a cost-effective biodegradable plastic, starch-filled polyethylene (PE) is still the best alternative. Starch and PE blend is incompatible at the molecular level and often leads to poor performance. In order to overcome this drawback, either PE or starch should be modified. The aim of this study was to modify linear low-density polyethylene (LLDPE) and blend it with starch. Maleic anhydride (MA) was grafted onto LLDPE in xylene using peroxides as initiator. Corn starch in varying concentrations (between 10% and 60%) was blended with MA-g-LLDPE in a torque rheometer. The same blend compositions of nonfunctional LLDPE with the starch were prepared for comparative studies. The torque and totalized torque generated during blending are reported as a function of starch content. Torque decreased with increasing starch content for the compositions from 10% to 50% and increased for 60% starch content. Work energy decreased for all the compositions of blends except for 60% starch content. Tensile strength and modulus increased and percentage elongation decreased as the starch content increased in the blends. Water absorption of the blends increased with an increase in starch content. The biodegradability of MA-g-LLDPE/starch blends have been studied in two biotic environments: (1) soil environment over a period of 6 months; (2) mixed fungi inoculum (*Aspergillus niger, Penicillium funiculosum, Chaetomium globosum, Gliocladium virens* and *Pullularia pullulans**)*** for 28 days. The samples containing more than 30% starch content supported heavy fungus growth. Blends exposed to a soil environment degraded more than in fungi alone. Any changes in the

various properties of the MA-*g*-LLDPE/starch before and after degradation were monitored using FTIR spectroscopy, weight loss, a scanning electron microscope (SEM) for surface morphology, a differential scanning calorimeter (DSC) for crystallinity and a thermogravimetric analyzer (TGA) for rapid determination of starch content. Percentage crystallinity decreased as the starch content increased and biodegradation resulted in an increase of crystallinity in MA-g-LLDPE/starch blends.

Chatterjee et al. **[45]**, worked on enzyme-mediated biodegradation of heat treated commercial polyethylene by *Staphylococcal* species. According to their work, extruded low-density polyethylene (LDPE) films commonly available in the market as 20-micron thick carrier bags were autoclaved, overlaid on nutrient agar plates and inoculated with BP/SU1 strain of *Staphylococcus epidermis*. The nutrient agar plate showed growth of the organism within two to three days. The polymer film supporting the growth of the organism showed pore formation as recorded by SEM analysis. The growth of BP/SU1 is supported by the presence of shredded LDPE as its only carbon source in inorganic salt minimal nutrient medium. The organism survives even after three months of inoculation and this is accompanied by gradual breakdown of the size of the shredded plastic as seen by light scattering. The cell-free supernatant of the organism, grown with the help of shredded plastic shows the presence of the over expressed proteins with approximate molecular weight of about 55 kDa and 35 kDa, through SDS-PAGE analysis.

2.2 International Status

Wasserbauer et al. **[46]** worked on biodegradation of polyethylene foils by bacterial and liver homogenates. According to them, the evaluation of structural changes of single linear and bifurcated polyethylene foils exposed to bacterial and liver homogenates was carried out by infrared spectrography, along with observations of changes of mechanical properties. Cell homogenates were fractionated by centrifugation and by coagulating the microsomal fraction using Ca^{2+} ions. Stimulation as well as inhibition of the presumed enzyme system were studied in bacterial cultures and liver homogenates of experiment animals. Results suggest that oxidation structures in polyethylene, after exposure to these cell homogenates, are caused by the monooxygenase hydroxylation system of the bacterial or liver cells.

Nowak et al. **[47]** also worked on polymer degradation by modifying it. The degree of biodegradation of low-density polyethylene (LDPE) films modified with Bionolle polyester in different soils under laboratory conditions was evaluated. Films were incubated in soils from waste coal, a forest and an extinct volcano crater. Prior to degradation studies, soils underwent chemical and microbiological analysis. Film weight loss and mechanical properties, as well as the surface of the polymeric samples determined via scanning electron microscopy, were evaluated after 75, 150 and 225 days of biodegradation. Important chemical changes in the polymeric chains were detected

by Fourier Transform Infrared Spectroscopy (FTIR). Fungal and bacterial species that were able to grow on the film surfaces were monitored in order to see whether the films were easily colonised by autochthonous microorganisms (i.e., typical to each soil). Identification of microorganisms was based on their cellular fatty acid methyl ester (FAME) profiles. Biodegradation of modified polyethylene films in soils led to significant changes (i.e., elongation at brake of 98%) in their mechanical properties that were caused by biochemical modifications of both polyester and polyethylene. Compared to waste coal soil, films underwent rapid biodegradation in soils that were rich in organic matter. Bacteria belonging to the genus, *Bacillus*, and the fungi, *Gliocladium viride*, *Aspergillus awamori* and *Mortierella subtilissima,* were easily able to colonise both polyethylene and polyethylene modified with Bionolle.

Yam **[48]** tested the biodegradability PBSA. They tried to accelerate the biodegradation of synthetic polymers, applied modification of LDPE with PBSA. Since then we are investigating mechanisms of biodegradation of LDPE/PBSA compositions under different environmental conditions. The purpose of this study was to examine the synergistic or antagonistic effects on the oxidation, hydrolysis and biodegradation of a commercial LDPE films filled with PBSA copolyester. Investigations were conducted by first exposing polymeric films to the abiotic oxidation (action of photo- and/or thermal degradation), followed by abiotic hydrolysis under mild conditions, and subsequently to microbial biodegradation. Several techniques were employed to elucidate the chemical and physical polymers structure. Changes in chemical structure of polymeric films caused by various types of degradation were interpreted on the basis of IR spectra analysis. The scanning electron microscope (SEM) was used to examine these polymers morphologically (surface topography); the excellent resolution provided by the SEM makes it one of the best tools for this purpose.

Khabbaz **[49]** carried out studies to select a polyethylene-degrading microorganism and to study the factors affecting its biodegrading activity. A thermophilic bacterium *Brevibaccillus borstelensis* strain 707 (isolated from soil) utilized branched low-density polyethylene as the sole carbon source and degraded it. Incubation of polyethylene with *B. borstelensis* (30 days, 50 ºC) reduced its gravimetric and molecular weights by 11% and 30% respectively. *Brevibaccillus borstelensis* also degraded polyethylene in the presence of mannitol. Biodegradation of U.V photo-oxidized polyethylene increased with increasing irradiation time. FTIR analysis of photo-oxidized polyethylene revealed a reduction in carbonyl groups after incubation with the bacteria. This study demonstrated that polyethylene is considered to be inert and can be biodegraded if the right microbial strain is isolated. Enrichment culture methods were effective for isolating a thermophilic bacterium capable of utilizing polyethylene as the sole carbon and energy source. Maximal biodegradation was obtained in combination with photo-oxidation, which showed that carbonyl

residues formed by photo-oxidation play a role in biodegradation. *Brevibaccillus borstelensis* also degraded the CH_2 backbone of non-irradiated polyethylene.

Sivan et al. **[50]** worked on a two-step enrichment procedure led to the isolation of a strain of *Rhodococcus ruber* (C208) that utilized polyethylene films as sole carbon source. In liquid culture, C208 formed a biofilm on the polyethylene surface and degraded up to 8% (gravimetrically) of the polyolefin within 30 days of incubation. The bacterial adhesion to hydrocarbon assay and the salt aggregation test both showed that the cell-surface hydrophobicity of C208 was higher than that of three other isolates which were obtained from the same consortium but were less efficient than C208 in the degradation of polyethylene. Mineral oil, but not nonionic surfactants, enhanced the colonization of polyethylene and increased biodegradation by about 50%. Fluorescein diacetate (FDA) hydrolysis and protein content analysis were used to test the viability and biomass density of the C208 biofilm on the polyethylene, respectively. Both FDA activity and protein content of the biofilm in a medium containing mineral oil peaked 48–72 h after inoculation and then decreased sharply. This finding apparently reflected rapid utilization of the mineral oil adhering to the polyethylene. The remaining biofilm population continued to proliferate moderately and presumably played a major role in biodegradation of the polyethylene. Fourier transform infrared spectra of UVphotooxidized polyethylene incubated with C208 indicated that biodegradation was initiated by utilization of the carbonyl residues formed in the photooxidized polyethylene.

Chang et al. **[51]** worked on synthesis and biodegradation of aliphatic polyester. An aliphatic polyester, poly(hexalene adipate) (PHA) and an aliphatic copolyester, poly(hexalene adipate succinate) (PHAS) were synthesized by direct condensation of corresponding binary acid and binary alcohol in the presence of a catalyst, p-toluene sulfonic acid. The biodegradation of these polyesters were studied in the laboratory by enzyme attack and outdoor soil burial. The results show that these polyesters have good biodegradability and the copolyester PHAS, even displayed a better biodegradability than the polyester PHA. In the presence of *Penicillium chrysogenum* the weight loss reached 18.3% for the PHAS (film thickness 1.0 mm) and 9.1% for the PHA (film thickness 1.0 mm) after 28 days. Outdoor soil burial tests indicate that these polyesters also have good biodegradability in natural conditions. The weight loss reached 14.2% for PHAS (film thickness 0.1 mm) and 6.7% for PHA (film thickness 0.1mm) after burying in soil for 36 days.

Albertsson et al. **[52]**, worked on mechanism of polyethylene degradation. LDPE films have been exposed to abiotic and biotic environments. The films were UV irradiated for periods of 0, 7, 14, 26 and 42 days before being mixed with water and soil. Degraded LDPE films were examined by infra-red spectroscopy. The carbonyl peak increased with time in the abiotic environment and the oxidative degradation reported in their earlier works was confirmed. In the presence of a biotic atmosphere, however, this peak decreased. At the same time there was an increase in double bonds

which was related to weight loss. An explanation of this behavior is presented as a proposed mechanism for the biodegradation of polyethylene. This mechanism is compared, on the one hand, with abiotic photo-oxidation, Norrish type I and H degradation, and, on the other, with the biotic paraffin degradation. Abiotic, as well as biotic, ester formation mechanisms are also presented. An ESR spectrum confirms the presence of radicals on the polyethylene samples. At the beginning of the degradation, the main agents seem to be UV light and/or oxidizing agents. When carbonyl groups have been produced, these are attacked by microorganisms which degrade the shorter segments of polyethylene chains and form carbon dioxide and water as end products. There is a synergistic effect between photooxidative degradation and biodegradation.The biodegradation of polyethylene can be compared with the biodegradation of paraffin.

Abrusci et al. **[53]** worked on biodegradation of photo-degraded mulching films based on polyethylenes and stearates of calcium and iron as pro-oxidant additives. They stated that polyethylene film materials persist in the environment for a long time. Several bacterial species have been isolated from films buried in soil located in Murcia, Spain. Bacterial strains were characterized with a combination of culture-dependent methods and sequencing of part of the 16S ribosomal RNA gene (rDNA) after amplification by polymerase chain reaction (PCR). Three bacterial species common in soil were found attached to the polymer and identified as *Bacillus. cereus, B. megaterium,* and *B. subtilis*. These microorganisms, as well as *Brevibacillus borstelensis,* were tested for biodegradation susceptibility at 30 and 45 °C on highly photo-degraded polyethylene films (500 h under irradiation of Xe-Lamp-solar filter) that contained calcium and iron stearates as pro-oxidant additives. Biofilm formation developed on the photo-degraded materials after one week of bacterial treatment. Biodegradation of the polyethylene films was studied by chemiluminescence, ATR–FTIR, and GC-product analysis and the data confirm a more efficient biodegradation on the bioassays carried out at higher temperature. The CL emissions due to decomposition of oxidation species take place at lower temperatures; the decrease of carbonyl index and the disappearance of photogenerated low-molecular products with biodegradation were more efficient on the biodegraded films at 45 °C. Also, mineralization was evaluated by carbon dioxide measurements using an indirect impedance technique. Biodegradation by *B. borstelensis* at 30 °C was slow and in the range of 0.7–1.2% of mineralization after 90 days of bacterial bioassay. At 45 °C biodegradation was more efficient and in particular in the more photo-degraded films containing Ca and Fe stearates where mineralization extents reached values of 11.5% with *B. borstelensis* and 7–10% with the mixture of *Bacillus* (MIX).

Koutny et al. **[54]** worked on Biodegradation of polyethylene films with pro-oxidant additives. They have stated that pro-oxidant additives represent a promising solution to the problem of the environment contamination with polyethylene film litter. Pro-oxidants accelerate photo- and

thermo-oxidation and consequent polymer chain cleavage rendering the product apparently more susceptible to biodegradation. The question not fully resolved remains the biodegradation itself, its mechanism and especially the factors influencing the time-frame in which it can occur. The presented review is aimed to provide comprehensible information for both microbiologists and polymer scientists, who need to participate in the research leading to an understanding of the microorganism action on the oxidized polyethylene and to design of new materials.

Koutny, et al. **[55]** also worked on acquired biodegradability of polyethylenes containing pro-oxidant additives. According to this work, biodegrability of high density polyethylene film (HDPE) and low density polyethylene film (LDPE) both containing a balance of antioxidants and pro-oxidants was studied with defined microbial strains particularly with *Rhodococcus rhodochrous* and *Nocardia asteroides* in mineral medium. After an abiotic pre-treatment consisting of photo-oxidation and thermo-oxidation corresponding to about 3 years of outdoor weathering the samples were inoculated, incubated up to 200 days and during the period their metabolic activities were followed by measuring adenosine triphosphate content. Simultaneously the cultures were also monitored by optical microscopy and FTIR spectroscopy. The first initial phase of fast growth caused by the presence of low molecular extractable compounds was followed by a long period of stabilized metabolic activity suggesting that microorganisms continued to gain energy from the substrate but evidently at a much slower rate. Complementary analysis performed at the end of incubation revealed that during the experiment time biodegradation processes probably affected surface layer of materials only.

Zahra et al. **[56]** worked on biodegradation of LDPE by isolated fungi in solid waste medium. This study was evaluated in a controlled solid waste medium. The fungi, including *Aspergillus fumigatus, Aspergillus terreus* and *Fusarium solani*, were isolated from samples taken from an aerobic aged municipal landfill in Tehran. These fungi could degrade LDPE via the formation of a biofilm in a submerged medium. In the sterilized solid waste medium, LPDE films were buried for 100 days in a 1-L flask containing 400 g sterile solid waste raw materials at 28 °C. Each fungus was added to a separate flask. The moisture content and pH of the media were maintained at the optimal levels for each fungus. Photo-oxidation (25 days under UV-irradiation) was used as a pre-treatment of the LDPE samples. The progress of the process was monitored by measurement of total organic carbon (TOC), pH, temperature and moisture. The results obtained from monitoring the process using isolated fungi under sterile conditions indicate that these fungi are able to grow in solid waste medium. The results of FT-IR and SEM analyses show that *A. terreus* and *A. fumigatus*, despite the availability of other organic carbon of materials, could utilize LDPE as carbon source. While there has been much research in the field of LDPE biodegradation under solid conditions, this is the first report of degradation of LDPE by *A. fumigatus*.

CHAPTER: 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Blended Films: Test samples (blended films) PB1, PB2, PB3, PB4, and PB5 were obtained from the Department of Chemical Engineering (ChED). These ratio of HDPE/PLLA in these blends was 100/0, 95/5, 90/10, 80/20 and 75/25 respectively and the values of their tensile strengths were also provided. The sample names (codes), their composition and tensile strengths are given in Table 3.1.

Table 3.1: Composition and tensile strengths of different blend samples

Sr. No.	Sample code	Composition (wt%)		Tensile strength (MPa)
		HDPE	PLLA	
1	PB1	100	0	45.30
2	PB2	95	5	26.65
3	PB3	90	10	22.10
4	PB4	80	20	15.10
5	PB5	75	25	10.55

Based on the tensile strength, the blend PB4 was considered optimum for packaging applications as it meets the minimum requirement of tensile strength which is essential for packaging films (11.7 MPa).

3.1.2 Chemicals: 97% pure barium hydroxide [$Ba(OH)_2.8H_2O$], hydrochloric acid (HCl) with 35% purity, and phenolphthalein indicator were purchased from SD Fine Chemicals, Bombay, India.

3.1.3 Compost: The mature compost (municipal solid waste) was obtained from a compost plant, New Delhi Municipal Council, Okhla, New Delhi, India. The compost inoculum was free from larger inert materials (glass, stones, metals, etc.) as much as possible. These items were removed manually also to produce a homogenous compost inoculum. The compost was found to have the total solids (%TS) = 78%, volatile solids at 550°C (%VS) = 21%; pH = 7.6; C/N ratio = 18.3. It was used for providing activated microbes for the biodegradation of the polymer blends.

3.1.4 Biodegradability Testing Apparatus: The apparatus was designed and fabricated according to D 5338 by the Department of Chemical Engineering. The apparatus is capable to provide the composting environment to the polymer films through the bioreactors placed inside an incubator. The CO_2 free air was supplied to each of the bioreactor (composting vessels) at a constant rate of 60 ml/min. The incubator also provides an optimum temperature (37°C) to the bioreactors. A series

of three absorbing vessels for each of the bioreactor were placed to absorb the carbon dioxide which was supposed to be evolved from the reaction of carbon source and air.

3.2 Methodology

3.2.1 ASTM D5338:

This test method determines the degree and rate of aerobic biodegradation of plastic materials on exposure to a controlled-composting environment under laboratory conditions. The test substances are exposed to inoculums present in compost obtained from municipal solid waste. The aerobic composting takes place in an environment having temperature, aeration and humidity closely monitored and controlled. This test method is designed to yield a percentage of conversion of carbon in the sample to carbon dioxide. The rate of biodegradation is monitored as well. This test method is equivalent to IS0 14852. The percentage of biodegradability is obtained by determining the percentage of carbon in the test substance that is converted to CO_2 during the duration of the test. This percentage of biodegradability will not include the amount of carbon converted from the test substance that is converted to cell biomass and that is not, in turn, metabolised to CO_2 during the course of test.

3.2.2 Biodegradability Test

The evolution of carbon dioxide or methane from a substrate represents a direct parameter for mineralisation. Therefore, gas evolution tests can be important tools in the determination of biodegradability of polymeric materials. A number of well known test methods have been standardised for aerobic biodegradation, such as the (modified) Sturm test and the laboratory controlled composting test, as well as for anaerobic biodegradation, such as the anaerobic sludge test and the anaerobic digestion test. Although the principles of these test methods are the same, they may differ in medium composition, inoculum, the way substrates are introduced, and in the technique for measuring gas evolution. Most aerobic standard tests apply continuous aeration; the exit stream of air can be directly analysed continuously using a carbon dioxide monitor (usually infrared detectors) or titrimetrically after sorption in dilute alkali. The cumulative amount of carbon dioxide generated, expressed as a percentage of the theoretically expected value for total conversion to CO_2, is a measure for the extent of mineralisation achieved. The biodegradation of the blends was calculated for a period of 96 hrs and CO_2 evolved was measured by titration with hydrochloric acid.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Determination of carbon dioxide evolved by the test sample (theoretically) by elemental analysis:

Molecular formula of **HDPE**: $(CH_2{=}CH_2)_n$

Molecular weight of HDPE used = 28000 grams/mole

$$n = \frac{28000}{28} = 1000\ units$$

As 1 mole (unit) of HDPE contains 24 grams of carbon, therefore, 1000 units contain 24000 grams of carbon

Hence, 1 mole = 24000 grams of carbon

For 200 grams sample, $number\ of\ moles = \frac{200}{28000}$ = 0.007

Grams of carbon present in 200 grams sample = $0.007 * 24000$ = 171.36 grams.

Now,

Molecular formula of **PLLA**: $(C_3H_4O_2)_n$

Molecular weight of PLLA used = 9000 grams/mole

$$n = \frac{9000}{56} = 160.71\ units$$

1 mole (unit) of PLLA contains 36 grams of carbon, therefore, 160.71 units contains 5760.12 grams of Carbon

Hence, 1 mole = 5760.12 grams of carbon

For 200 grams sample, $number\ of\ moles = \frac{200}{9000} = 0.022$

Grams of carbon present in 200 grams sample = 0.002 * 5760.12 = 127.99 grams.

According to the above calculations, the amount of carbon present in each HDPE/PLLA blended films (2 grams approx. by weight) was calculated. And, the theoretical values of the CO_2 evolved were also calculated for each sample as per the following formula:

$$amount\ of\ CO_2 = \frac{amount\ of\ carbon\ present * 44}{12}$$

The values of carbon content in the samples and the theoretical amount of CO_2 evolved from the respective sample are summarized in Table 4.1:

Table 4.1: Amount of carbon and CO_2 evolved (theoretically) from blend samples

Sr. No.	Blend Name	Carbon content (in grams) in 2 gm of sample (film)	Theoretical CO_2 evolved (mg/L)
1.	PB1	1.71	6270
2.	PB2	1.67	6120
3.	PB3	1.65	6050
4.	PB4	1.61	5900
5.	PB5	1.59	5830

4.2 Determination of carbon dioxide evolved by the test sample (experimentally)

Determination of the amount of CO_2 produced by the film samples was obtained by calculating the difference between that of the test substance and the blank (not containing the sample). The titration was performed with 0.05 N HCl. The reaction(s) involved and the formulae used in the calculations are as follows:

$$Ba(OH)_2 + CO_2 \longrightarrow BaCO_3 + H_2O$$

The $BaCO_3$ formed is insoluble and precipitates. The amount of $Ba(OH)_2$ remaining in solution by end-point titration with HCl using phenolpthalein as an indicator according to the following equation was determined:

$$Ba(OH)_2 + 2\ HCI \longrightarrow BaCl_2 + 2\ H_2O$$

Formulae (as per ASTM D5338):

$$Number\ of\ moles\ of\ CO_2 = Moles\ of\ Ba(OH)_2 - \frac{moles\ of\ HCl}{2} \quad \text{..... (i)}$$

$$Normality = \frac{eq\ wt}{vol\ (in\ L)} \quad \text{..... (ii)}$$

$$Amount\ of\ CO_2\ evolved = moles\ of\ CO_2\ obtained * 44 \quad \text{..... (iii)}$$

$$\%\ biodegradability = \frac{mean\ carbon\ (test) - mean\ carbon\ (blank)}{carbon\ present\ in\ sample} \quad \text{..... (iv)}$$

The experimental analysis includes titration of the $Ba(OH)_2$ solution containing absorbed CO_2 evolved due to the above mentioned reactions (biodegradation of the polymer films by microorganisms present in the compost). The amount of CO_2 evolved and hence the extent of biodegradation of the samples was calculated. Table 4.2 tabulates the titration results and the amount of CO_2 produced and table 4.3 depicts the % biodegradability by each sample.

Table 4.2: Titration values and the amount of CO_2 produced by the samples

Time interval	Flask*	Amount of HCl used for blank (titration reading in mL)	CO_2 evolved (mg/L)	Amount of HCl used for sample (titration reading in mL)					CO_2 evolved** (mg/L)				
				PB1	PB2	PB3	PB4	PB5	PB1	PB2	PB3	PB4	PB5
12 hours	Flask 1 Flask 2	1.7 2.4	1460 1430	1.5 1.9	1.1 1.6	0.9 1.5	0.4 0.9	0.28 0.76	1578 1426	1758 1512	1822 1735	2072 1816	2291 1892
24 hours	Flask 1 Flask 2	1.7 2.1	1460 1440	1.5 1.8	1.1 1.4	0.9 1.3	0.4 0.7	0.28 0.5	1578 1446	1758 1578	1822 1777	2072 1891	2291 1927
48 hours	Flask 1 Flask 2	1.7 1.9	1460 1451	1.5 1.6	1.1 1.3	0.9 1.1	0.4 0.6	0.28 0.4	1578 1462	1758 1645	1822 1808	2072 1980	2291 2025
96 hours	Flask 1 Flask 2	1.7 1.7	1460 1460	1.5 1.5	1.1 1.1	0.9 0.9	0.4 0.4	0.28 0.28	1578 1513	1758 1695	1822 1819	2072 2019	2291 2218

*Two flasks were used (in series) to absorb the CO_2; when the first flask get saturated, the second flask start absorbing the CO_2
**Sample calculation is shown on the next page

Table 4.3: Percent biodegradation of each sample

Time interval	% Biodegradation of sample				
	PB1	PB2	PB3	PB4	PB5
12 hours	1.82	6.21	11.02	16.92	22.18
24 hours	1.98	7.12	11.55	18.02	22.61
48 hours	2.06	8.04	11.88	19.34	24.10
96 hours	2.73	8.71	11.92	19.85	27.26

Calculation for Amount of CO_2 evolved:

For 1.7 ml HCl

$$Normality = \frac{Eq\ wt}{Vol\ (in\ L)}$$

$\Rightarrow$ 0.02 = $\frac{Eq\ wt}{0.0017}$

Therefore, eq wt of HCl = 0.02 x 0.0017 = 3.4 x 10^{-5}

For HCl, eq wt = molecular wt (as the valency of HCl = 1)

So, moles of HCl = 3.4 x 10^{-5}

Now, as per eq (i),

$$Number\ of\ moles\ of\ CO_2 = Moles\ of\ Ba(OH)_2 - \frac{moles\ of\ HCl}{2}$$

$$Moles\ of\ Ba(OH)_2 = \frac{Mass\ of\ Ba(OH)_2\ used}{Molecular\ wt} = \frac{10.78}{315.47} = 0.0341$$

Hence, $Moles\ of\ CO_2 = 0.0341 - \frac{3.4*10^{-5}}{2} = 0.034$

As per eq (ii),

$$Amount\ of\ CO_2\ evolved = moles\ of\ CO_2\ obtained * 44$$

= 0.0340*44= 1.460 grams (per L)

= 1460 mg/L

All the other calculations are done in the similar manner and are shown in Table 4.3. The biodegradation of sample PB1 (containing 100% HDPE) is 2.73% only after 96 hours, which mean that the bacteria present in the compost was able to degrade HDPE film, but to a little extent only. As the amount of PLLA increased in the blend, it is more susceptible to biodegradation, e.g. the blends PB2, PB3, PB4 showed 8.71%, 11.92%, 19.85% biodegradation respectively (after 96 hours of exposure to composting environment). Since the blend PB5 contained the maximum amount of PLLA (25%), it was (bio)degraded maximum, i.e. 27.26%. Fig. 4.1 shows graphically, the biodegradation (in %) of different blends (film samples) at 12 hrs, 24 hrs, 48 hrs and 96 hrs.

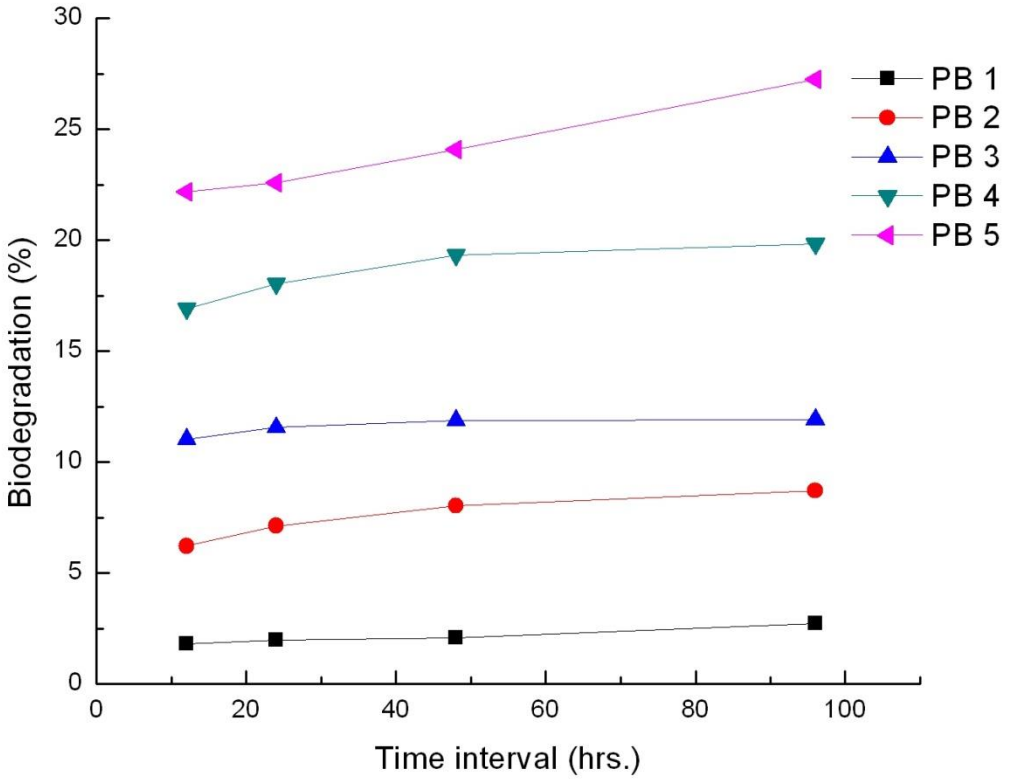

Figure 4.1: % Biodegradation of the given samples with time

CHAPTER: 5

CONCLUSIONS AND FUTURE PROSPECTS

5.1 Conclusions

Different blends of HDPE-PLLA were tested for their extent of biodegradation in composting environment as per ASTM D 5338 (2003) standard. The samples were developed and provided by the Department of Chemical Engineering. The Biodegradability Testing Apparatus (as per the mentioned standard) is also developed by the Department (under the leadership of Dr. H. Bhunia) and was used for the purpose. Six bioreactors (containing one 'blank' and five blended film samples of HDPE/PLLA ratio 100/0, 95/5, 90/10, 80/20 and 75/25 respectively) were used for determining aerobic biodegradation of the given plastic films (prepared from the blends of HDPE/PLLA) under controlled composting conditions. The zero air (CO_2 free air) was supplied to the bioreactors through rotameters (placed one for each of the bioreactors). The CO_2 evolved from each of the bioreactors was absorbed in $Ba(OH)_2$ solution contained in two flasks placed in series. The amount of CO_2 evolved due to the reaction of carbon and air (at the time intervals of 12 hr, 24 hr, 48 hr, and 96 hrs) was calculated by using phenophthelein indicator and titration against HCl solution (following the procedure and the formulae mentioned in the ASTM standard). The blend PB5 (HDPE/PLLA = 75/25) showed the maximum biodegradation, which is due to the highest content of the biodegradable polymer PLLA (25%) in it. The sample PB1 (HDPE/PLLA = 100/0) showed the minimum biodegradation. However the maximum biodegradation was noticed for the blend PB5, but it is not recommended to be used in packaging applications as the given values of the mechanical properties of this is below the minimum required ones. Therefore, the blend PB4 (HDPE/PLLA = 80/20) is proposed to be used in packaging for these two reasons – first, it is a biodegradable blend (% biodegradation in 96 hrs = 19.85%) and second, it has the optimum mechanical properties.

5.2 Future Prospects

This research work may be extended for the latest techniques of making the packaging polymers (bio)degradable, viz. pre-treatment through acid etching, thermal degradation, irradiation etc. as these methods makes the polymer films more susceptible to microbial attack. Secondly, pro-oxidants, e.g. metallic strearates (cobalt stearate, manganese stearate and iron stearate) can be added in the polymers, which are required in trace amounts to make the polymers degradable in presence of sunlight, microorganisms present in soil etc.

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