Chapter -I INTRODUCTION, OBJECT AND SCOPE OF THE STUDY

1.1 INHERENT PROPERTIES OF POLYMERS:

Polymers have become inevitable materials in our daily life, quality and comfort. This is due to the versatile qualities of polymer with respect to their strength, lightness, durability, protection and low cost. Plastics are used in almost all industries and have virtually replaced glass, paper and wood in the packaging and building industry. The other bulk polymer consuming industries are consumer goods, electrical/electronics, automobile agriculture, medical, pharmaceutical, aeronautical and space application and others. (H. F. Mark et al 1987, R. E. Kirk et al 1984, J.E. Potts, 1984)

Synthetic polymers were originally developed for their durability and resistance to all forms of degradation, including biodegradation. Some of these virtues of polymer have now become liabilities. It would be highly beneficial from the environmental stand point, if these films were biodegradable, decomposing almost completely under the attack of microorganism over a period of say few months or even they can break into fragments so that they do not become harmful to the environment. (Abraham J. Domb, et al. 1997, G.F. Moore, et al. 1999)

All polymers degrade in one way or other and hence all polymers can be considered degradable. But in practice if a polymer does not degrade within human life time it is usually considered non-degradable. Today the market of polyolefin microfilm like LDPE, HDPE and PP used in production of packaging carry bags is very wide. Unmodified poly olefins are resistant to destruction by biological agents. When these polymers are compounded with additives or plasticizers, the resultant polymer is affected by microorganism in various degrees. (Brandrup J, et al 1966).
1.2 POLYMER AND ENVIRONMENT:
Use of long-lasting polymers for short-lived applications is not entirely justified. Most of today's plastics and synthetic polymers are produced from petrochemicals. Conventional plastics accumulate in the environment. They are improperly disposed. Hence plastic materials are a significant source of environmental pollution, potentially harming wildlife on land and water. In seas, for example, plastic rubbish -from ropes and nets to the plastic bands from beer packs- chokes and entangles marine mammals. Plastics have also a costly impact on waste management, (Venkateswaran, 1995) and municipalities are becoming aware of the significant savings that are accrued in collection of 'wet' organic wastes in so-called 'biobins' to be composted. For these reasons, reaching the conditions for replacement of non-degradable polymers by degradable plastics is of major interest both to decision-makers and the plastic industry. (Bhide, A. D. et al 1983, 1984, Bhoyar R. V., et al 1996, Brown K. A et al 1994)

1.2.1 ENVIRONMENTAL ISSUES

Plastic shopping bags have advantages and disadvantages when compared to alternatives such as paper bags. All disposable bags are problematic from an energy use and disposal perspective.

Advantages

The durability, strength, low cost, water and chemicals resistance, welding properties, lesser energy and heavy chemicals requirements in manufacture, fewer atmosphere emissions and light weight are advantages of plastic bags. Many studies comparing plastic versus paper for shopping bags show that plastic bags have less net environmental effect than paper bags, requiring less energy to produce, transport and recycle; however these studies also note that recycling rates for plastic are significantly lower than for paper. Plastic bags can
be incinerated in appropriate facilities for waste-to-energy. Plastic bags are stable and benign in sanitary landfills. Plastic carrier bags can be reused as trash bags or bin bags.

Disadvantages

There are four main concerns with plastic shopping bags:

0 Plastic bag littering and associated indiscriminate waste disposal and consumer behavior.
0 Resource consumption issues, including reduction, reuse and recycling.
0 Plastic degradability issues relating to littering and resource use.

The following disadvantages were also identified:

0 Plastic bags are made of petrochemicals, a nonrenewable resource.
0 Plastic bags are flimsy and often do not stand up as well as paper or cloth.
0 When disposed of improperly, they are unsightly and represent a hazard to wildlife.
0 Conventional plastic bags are not readily biodegradable under any normal circumstance.
0 Plastic bags can cause unsupervised infants to suffocate. (Susan E.M. Selke, 2004, John Scheirs 1998)

1.2.2 WORLDWIDE ATTEMPTS (Wikipedia, the free encyclopedia, Stewart Smith 2004).
**Australia**

In Australia shoppers are encouraged to buy green bags costing few dollars, but can be reused many times. Locally, the town of Coles Bay has banned plastic shopping bags in April, 2003.

**Bangladesh**

Plastic shopping bags are banned in Bangladesh.

**Canada**

Plastic bags are included in curbside collection services in many areas of Canada. The report described the program as very successful, but gave no recycling rates.

**China**

In China the shoppers charge for plastic bags from 2004 so as to reduce waste.

**Denmark**

In Denmark, plastic bags are taxed in 1994 so as to promote the use of reusable bags.

**France**

The main mass of retailers forces customers to buy reusable plastic or non-woven bags. Nonfood related retailers (like Cloth) tend to prefer paper bags. In Paris, a ban on plastic bags will take effect in late 2007; a nationwide ban is scheduled to take effect on January 1, 2010.

**Germany**

German supermarkets charge between 5 and 25 cents per single-use bag, depending on the type of bag. Most shops also offer cloth bags or
sturdier, woven plastic bags for about €1, encouraging shoppers to re-use them. Many high-street retail shops provide bags free of charge.

Hong Kong
Hong Kong prohibits films below a specified size. There are also recovery facilities for plastic bags provided within supermarkets.

India
In August 2000, the manufacture and use of plastic shopping bags was banned in Mumbai. The northern state of Himachal Pradesh has implemented a total ban on plastic bags' production, storage, use, sale and distribution. Penalties are severe (include up to seven years in jail or a fine of up to 100,000 Rupees).
In the state of Tamil Nadu, a Bill to ban non-recyclable plastic from being sold, stored, transported and used was introduced to the state government for approval. The pollution control board of the same state is also educating the public on the dangers of improper disposal and the advantages of alternatives, using bus advertisements, exhibitions and media campaigns. In Panaji, Goa, a community campaign involves donating old newspapers and magazines by individuals to local charitable organizations. These newspapers are cut into paper-bags of various sizes and sold to volunteering shops or pharmacies to reduce the use of plastic bags. Income generated from these bags is in turn helping the charity organizations to buy the much needed provisions and medicines.

Ireland
The Republic of Ireland introduced a 15 cent levy on every plastic shopping bag. This led to a 95% reduction in use and increased use of reusable bags. Many retailers in Ireland supply (untaxed) paper bags, or do not supply bags at all. Most supermarkets continue to supply
plastic bags, subject to the tax. The charge is increased to 22 cents from July 1, 2007.

Italy

In 1989 Italy introduced a tax on plastic bags which was about 5 times the manufacturing cost of the bag.

Japan

In Japan, all stores to street vendors, provides free plastic bag for the purchase. There are some supermarkets which charge for plastic bags, this is by no means the norm. Many supermarkets may give extra points on using own bag.

New Zealand

In recent years cloth bags have been promoted and sold by some supermarkets as an alternative to plastic bags. Various communities declare itself shopping bag free area. In early 2007 the nation aims to introduce a shopping bag levy similar to Ireland’s.

Rwanda

In Rwanda, banning of plastics less than 100 microns and import bans have been applied stringently.

Singapore

The government of Singapore is launching a campaign to discourage the use of plastic bags.

South Africa

In South Africa the minimum legal thickness of the film is 30 micrometers so as to increase the cost, reusability, and recyclability of the film. The South African government collects a 3cents per shopping bag environmental levy on all shopping bags.
Taiwan

Plastic shopping bags are banned in Taiwan.

Turkey

The government has launched a feasibility study into the movement towards environ bags however this is not due till late 2008.

United Kingdom

The UK encourages some large retailers to reward customers who bring their own bags or who reuse or recycle existing bags.

United States

The United States has banned the common plastic shopping bags in 2007, all large supermarkets are required, by law, to take back and recycle plastic shopping bags. Plastic shopping bags are banned in at least 30 villages and towns in Alaska, including the towns of Emmonak, Galena, and Kotlik. Some of the retailers impose their own charge for plastic shopping bags in the US.

Zanzibar

The Island of Zanzibar has banned the import and use of plastic shopping bags in November, 2006.

1.3 APPLICATIONS OF BIOPOLYMERS:

High cost of biodegradable plastics limits the markets of conventional commodity polymers. Cost competitive biodegradable plastics can expand their market. (Kitch, 2001). With the development of various biodegradable plastics with differing structures, properties and degradation behaviors, a range of potentially suitable application areas
are emerging. Some of these emerging application areas are outlined below. (M. Kolybabal, et al 2003)

1.3.1. AGRICULTURAL MULCH FILM

Agricultural mulch films cover to inhibit weed growth and retain soil moisture. These films are made from biodegradable plastics to eliminate the need for mechanical removal, because mulch films can be ploughed into the soil. These films also prevent the loss of topsoil humus that can be removed along with the waste film. The films also enrich the soil with additional carbon. (Kitch, 2001).

1.3.2. SHOPPING BAGS

Plastic bags and other packaging films are currently not widely accepted in the recycling system. Biodegradable plastics present a potential alternative to these materials in some applications. (W. Carothers et al 2003).

1.3.3. FOOD WASTE FILM AND BAGS

PE/PP based plastic films with corn starch are used in fresh food wrapping and plastic wrap in catering industries. The biodegradable film can be advantageous in these areas. Such bags would take 8-10 weeks to fully degrade in a commercial composting operation. (Kitch, 2001)

1.3.4. CONSUMER PACKAGING MATERIALS

A wide range of plastic consumer packaging materials are not currently mechanically recycled, and may therefore be suited to the use of biodegradable plastics. Photodegradable plastic six pack beverage ring holder require 6-8 weeks of sunlight to degrade and will not degrade if buried. Other applications include bread bags, bait bags,

1.3.5. LANDFILL COVER FILM


1.3.6. LAUNDRY BAGS FOR HOSPITALS

Plastic film wrapping dissolves when placed in hot water. Dirty laundries are hygienically collected in closed plastic laundry bags. These are then simply loaded into the laundry without the sheets and clothes having to be handled again, thereby eliminating possible infection risks to the laundry workers. In hot water within the washing machine, the bags dissolve without harming the fabrics. The bedding and clothing are washed and ready for drying and ironing without a trace of the plastic bags. (J. Kaiser 2001.)

1.3.7. AGRICULTURAL AND HORTICULTURAL APPLICATIONS

Soluble bags can be used in the agriculture and horticulture industry for the collection of garden waste and other compostable materials. The bags can be loaded into the composting system with some added water, break down quickly, leaving no trace of the plastic material. (D. Platt, 2006).

1.3.8. OTHER APPLICATIONS

Other potential applications for the range of biodegradable plastics include: (Nanavaty, K P.1997).

1. Recyclable containers
2. Bait bags
3. Fishing line and nets
4. Silage wrap
5. Body bags and coffin liners
6. Nappy backing sheet
7. Various sanitary product applications
8. Cling wrap.

1.4 NEED FOR BIODEGRADATION:
Considerable environmental benefits can be derived from the use of biodegradable plastics compared to conventional plastics. Compost derived in part from biodegradable plastics increases the soil organic content. Also the water and nutrients are retained. The chemical inputs and plant diseases are suppressed. (P. Shin et al, 1997). Biodegradable shopping and waste bags disposed in a landfill can increase the rate of organic waste degradation in landfills. Methane harvesting potential is also enhanced. The landfill space usage is decreased. Biodegradable landfill covers can extend landfill life considerably. Energy required to synthesize and manufacture biodegradable plastics is much lower for most biodegradable plastics than for non-biodegradable plastics. Biodegradable plastics also offer important environmental benefits through the use of renewable energy resources and reduced greenhouse gas emissions. (Nolan-ITU 2002)

1.5 TERMINOLOGY:
Many polymers that are claimed to be ‘biodegradable’ are in fact ‘bioerodable’, ‘hydrobiodegradable’ or ‘photo-biodegradable’. These different polymer classes all come under the broader category of ‘environmentally degradable polymers’. (C. Bastioli, 2005)

Various classes of biodegradable plastics, considered in terms of the degradation mechanism are:
⊙Biodegradable
⊙Compostable
⊙Hydro-biodegradable
⊙Photo-biodegradable
11

1.5.1. BIODEGRADABLE
Biodegradation is degradation caused by biological activity, particularly by enzyme action leading to significant changes in the materials chemical structure. In essence, biodegradable plastics should break down cleanly, in a defined time period, to simple molecules found in the environment such as carbon dioxide and water. (Chandra, R. and R. Rustgi. 1998)

1.5.2. COMPOSTABLE
Compostable biodegradable plastics must be demonstrated to biodegrade and disintegrate in a compost system during the composting process (typically around 12 weeks at temperatures over 50°C). (Degli Innocenti, F., 1999)

1.5.3. HYDRO-BIODEGRADABLE
Hydro-biodegradable polymers are broken down in a two-step process - an initial hydrolysis followed by further biodegradation. (J. Scheirs, 1996, S. Takigami, Konjac mannan 2000).

1.5.4. PHOTO-BIODEGRADABLE
Photo-biodegradable polymers are broken down in a two-step process - an initial photo-degradation stage, followed by further biodegradation. (H. Tsuji and K Suzuyoshi 2002)

1.5.5. BIO-ERODABLE
Many polymers are are ‘bioerodable’. They degrade without the action of micro-organisms. This is also known as abiotic disintegration, and include processes such as dissolution in water, ‘oxidative
embrittlement' (heat ageing) or 'photolytic embrittlement' (UV ageing). (Jain, S. C. and Garg, K.K. 1997).

1.5.6. DEGRADABLE POLYMERS
A material is called degradable if it undergoes degradation to a specific extent within a given time measured by specific Standard Test methods. (G. Scott 1991.)

1.5.7. DEGRADATION
It is an irreversible process leading to a significant change of the structure of a material, typically characterized by a loss of properties (e.g. integrity, molecular weight, structure or mechanical strength) and/or fragmentation. (Fernandes E. G. et al 2001, 2002.)

1.5.8. DISINTEGRATION
Disintegration means the falling apart into very small fragments of packaging or packaging material caused by degradation mechanisms. (Sanon, C. G.1986).

1.5.9. ELIMINATION
It is the excretion and metabolism of polymer and erosion product from mammals. (Sharma V. K. et al 1996).

1.5.10. EROSION
It is the mass loss of a polymer matrix which can be due to the loss of monomers, oligomers or even pieces of non degraded polymers. Erosion can be the result of biological, chemical or physical effect. (Shivapullaiah P.V 1977).

1.6 TYPES OF DEGRADATION:
Polymer degradation is broadly of two types: (H. R. Dennis, et al 2001)

1.6.1 Chain degradation: Here the degradation starts from the chain ends resulting in successive release of monomer units. It is reverse of chain propagation hence can be called de polymerization.

1.6.2 Random degradation: It occurs at any random point along the polymer chain. It is reverse of poly condensation process.
Here the polymer degrades to lower molecular weight fragments and practically no monomers are released.

1.7 MODES OF POLYMER DEGRADATION:
Degradation usually involves the chemical modification of polymer by its environment. Degradation of (Jakubowica I. 2003) polymer may be brought about by:

1.7.1 THERMAL DEGRADATION

1.7.2 MECHANICAL DEGRADATION
Stretching, grinding, milling and any type of polymer shearing process produce free radicals as a result of main chain fracture. Upon warming; these radicals attack the polymer matrix and lead to further scission reaction through radical rearrangement reactions. In the melt, it is difficult to separate the combined degradative effects of torque, time and temperature. (Daniel I. M. et al 1983, Daniels A.U. et al 1990).

1.7.3 DEGRADATION BY IONIZING RADIATION
The interaction of high energy radiation with polymers generates free radicals and produce defected products. Aliphatic polymers are damaged largely by post irradiation thermal oxidation. (Schimmel, K, et.al, 2004).

1.7.4 METAL CATALYZED DEGRADATION
Polymers contain metallic compounds, as impurities or deliberately incorporated additives induce both photo and thermal stability problems. (Han F., et al 1998).

1.7.5 OXIDATIVE DEGRADATION
Oxygen is present in the amorphous domains of all polymers, crystallites of some polymers and in fast quenched polyolefin. The oxidative chain reaction is initiated by any process capable of generating free radicals. (Chiellini E. Corti A. Swift G. 2003)
### 1.7.6 SOLAR DEGRADATION

Photo catalytic decomposition of organic dyes in aqueous solution has been carried out with nano size TiO$_2$. Solar degradation of aqueous wastes are carried out by outdoor exposure to sun on rotating plastic disc fitted with TiO$_2$ coated plastic sheet. (Anseth KS, et al 1997)

### 1.7.7 HYDROLYTIC DEGRADATION

Hydrolysis of the polymer backbone requires water and can be considered a bimolecular reaction. (J. Buchert, M. et al 1993).

### 1.7.8 ULTRASONIC WAVE AND HIGH ENERGY RADIATION DEGRADATION

Polymers are subjected to Ultrasonic waves, \(uv\) and \(\gamma\) radiation during polymer processing to reduce the bacterial contamination. Radiation effects occur at random, throughout a polymer. (Z. Cheng, et al 2004)

### 1.7.9 PHOTO DEGRADATION

Photo degradation occurs when polymers are exposed to sunlight during their outdoor service. Pigments protect against or sensitize photo degradation. (NIIR board, 2006).

### 1.7.10 CHEMICAL DEGRADATION

It occurs by introducing hydrolysable or oxidative functional group into the polymer backbone. The polymer chains become labile to an aqueous environment and thus, chemical degradation initiates polymer erosion. (James W. Garthe, et al 2002).

### 1.7.11 BIO DEGRADATION

It implies the degradation that is mediated by a biological system. It is a mass loss of monomers, oligomers. Chemical reactions describing biodegradation of a hydrocarbon polymer in aerobic (Ishigaki, T. et. al. 2004) and anaerobic environment can be expressed as:

**AEROBIC ENVIRONMENT:**

\[
\text{Polymer} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Biomass} + \text{Residue}
\]

**ANAEROBIC ENVIRONMENT:**

\[
\text{Polymer} \rightarrow \text{CO}_2/\text{CH}_4 + \text{H}_2\text{O} + \text{Biomass} + \text{Residue}
\]
1.8 FACTORS AFFECTING DEGRADATION:

Synthetic polymers are inherently resistant to biological attack. But susceptibility to biodegradation varies and is affected by:

1.8.1 ADDITIVES

Various compounding ingredients may have nutritive value for microorganisms and hence may invite microbial attack. Most of the plasticizers, lubricants, thickening agents, starch and cellulose fillers are susceptible to microbial attack. (R. Gatcher and Muller, 1985)

1.8.2 PLASTICIZERS

Plasticizer tends to force the chain apart, giving them greater freedom of movement and also reducing van der Waals' forces between the chains. All plasticizers are affected by fungal or bacterial attacks. Susceptibility of microbial attack increases as the plasticizer level increases. (Ullmann's Encyclopaedia, Vol. A 20, 1992).

1.8.3 THE TYPE OF CHEMICAL BOND

Various chemically degradable polymer bonds are: polycyanoacrylates, polyanhydrides, polyketals, polyorthoesers, polyacetals, poly(2-hydroxy-esters), poly(E-caprolactone), polyphosphazenes, polyB-Hydroxyesters, polyamino carbonates, polypeptides, polycarbonates, polyphosphate esters. (Alcock HR 1999).

1.8.4 WATER UPTAKE

The hydrolysis of the polymer backbone requires water. Degradation rates increase when the hydrophilic component contents are increased. (Danjaji, I.D., et al 2002).

1.8.5 CRYSTALLINITY AND MOLECULAR WEIGHT

Crystalline polymers degrade slower than amorphous polymers. High molecular weight leads to slower degradation. (Holmes, P. A. Vol. 2 1988).
1.8.6 PH


1.8.7 COPOLYMER COMPOSITION


1.8.8 ENZYMATIC DEGRADATION

Biodegradable polymers can be hydrolyzed passively or actively via enzymatic catalysis. (William DF, Mort E 1977)

1.9 CHARACTERISTICS OF AN IDEAL BIODEGRADABLE POLYMER:

The ideal characteristics of a biodegradable polymer should be:

◊ It should meet the overall needs of the application with additional technical and potential environmental benefits.
◊ It should reduce labor or energy required to manage solids (e.g. composting facilities).
◊ It should reduce the environmental and social impact of other conventional products.
◊ It should reduce pollution in waterways due to high BOD concentrations resulting from the breakdown of starch-based biodegradable plastic.
◊ It should reduce migration of plastic degradation by-products such as residual pigments, catalyst residues and isocyanate via run-off and leachate from landfills and composting facilities to groundwater and surface water bodies. (Datta M. 1997).
◊ It should reduce trauma and death of marine species resulting from only partial or slow degradation of biodegradable plastic products in marine environments.
◊ It should reduce the incidence of littering due to the belief that biodegradable plastics will disappear quickly.
It should reduce soil and crop degradation resulting from the use of compost that may have unacceptably high organic and or metal contaminants derived from biodegradable plastic residuals, additives and modifiers such as coupling agents, plasticizers, fillers, catalysts, dyes and pigments.

Disintegration must occur in a reasonable time frame (e.g., 3 months or 6 months)

They must not leave behind any toxic residues.

It must be able to be formed into film.

It must have adequate tensile strength and elongation.

It must have adequate puncture resistance.

It must have adequate tear resistance (should not have too splits.)

It must possess properties that resemble low-density polyethylene (LDPE) or high density polyethylene (HDPE) in overall physical properties and rheological characteristics.

Degradable plastics for bags are required to degrade rapidly at the end of their useful life and their mechanical properties should remain unchanged during use.

It is essential that the polymer retain its useful properties during fabrication procedures, e.g., blending, palletizing, extrusion, blown or cast film fabrication.

The film/bag must have a reasonable storage and reuse life.

The customer expects to have functional bags that serve a useful purpose under a variety of circumstances. It is only at the end of the service life that the polymer must degrade in the disposal environment. (Nolan-ITU September 2003, 2004).

1.10 OBJECTIVES AND SCOPE OF STUDY:

Today there is as tremendous rise in the use of polymers in each and every field of product application. The polymers have reported to be
easily available, readily processed in almost any shape and color of our dream. This is available in addition to good strength and durability.

In the present context of modernization readily use and throw articles are in great demand. This can be easily fulfilled by polymer material. But their easy disposal has become difficult. Though naturally degradable polymers are available, their use is restricted up to drugs, surgical implants, sutures, agricultural chemicals etc. because of their lower mechanical, chemical, electrical, environmental properties.

Out of all polymer products, the problem of disposal of packaging film material has become acute because today most of the consumers products are packed in carry bags. The plastic carry bag has replaced the use of cloth, jute etc. bags. After certain period of usage this carry bags litter around and cause environmental problem. To overcome this problem:

◊ To reduce the use of polymer films. This will result in consumption of scarcely available material i.e. wood, minerals, metals, crops etc.

◊ To manufacture films having thickness greater than 20 microns. This will result in consumption of more material i.e. greater cost and more material to be disposed.

◊ Develop a fully degradable polymer having all the properties comparable with that of the conventional polymer. Researchers are working hard in this area.

◊ At the time of invention of polymeric material the primary concerns were about preventing or retarding the attack of bacteria, fungi, rodents, insects, and other animals on polymer. Hence various factors affecting the degradability of polymer were identified and remedial measures to overcome those factors were implemented.

◊ Today the same factors affecting the degradability are studied to measure the extent of degradability, the duration of degradability and their effect on the properties of polymers is studied.
1.10.1 SCOPE:
◊ To study various mechanisms of polymer degradation.
◊ To study various factors affecting polymer degradation.
◊ To study the extent of degradation.
◊ To study the duration of degradation.
◊ To study the effect on the property of polymer.
◊ To study the commercial viability of the biodegradable polymer.

1.10.2 OBJECTIVES:
◊ To identify the most economical mechanism of degradation.
◊ To identify the most prominent factor affecting the degradation.
◊ To develop the polymer showing shortest duration of degradation.
◊ To develop the polymer showing highest extent of degradation.
◊ To develop the polymer showing lowest reduction in property.
◊ To identify the specie of microorganism that is most susceptible to biodegradation.
◊ To assess the plant toxicity of the biodegradable polymer developed.
◊ To assess the fertility of the soil after land fill.
◊ To carry out cost analysis of the biodegradable polymer developed.
◊ Assess the commercial viability of the biodegradable polymer developed.