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REVIEW ARTICLE

Biodegradable Polymers: An Ecofriendly Approach In Newer Millenium.

Parth N. Patel, Khushboo G. Parmar, Alpesh N Nakum, Mitul N Patel, Palak R Patel, Vanita R Patel, Dr. Dhrubo Jyoti Sen*

Shri Sarvajanik Pharmacy College, Gujarat Technological University, Arvind Baug, Mehsana-384001, Gujarat, India.

ABSTRACT

Biodegradation or biotic degradation or biotic decomposition is the chemical dissolution of materials by bacteria or other biological means. The term is often used in relation to ecology, waste management, biomedicine and the natural environment (bioremediation) and is now commonly associated with environmentally friendly products that are capable of decomposing back into natural elements. Organic material can be degraded aerobically with oxygen, or anaerobically, without oxygen. A term related to biodegradation is biomineralisation, in which organic matter is converted into minerals. Biosurfactant, an extracellular surfactant secreted by microorganisms, enhances the biodegradation process. Biodegradable matter is generally organic material such as plant and animal matter and other substances originating from living organisms, or artificial materials that are similar enough to plant and animal matter to be put to use by microorganisms. Some microorganisms have a naturally occurring, microbial catabolic diversity to degrade, transform or accumulate a huge range of compounds including hydrocarbons (e.g. oil), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pharmaceutical substances, radionuclides and metals. Major methodological breakthroughs in microbial biodegradation have enabled detailed genomic, metagenomic, proteomic, bioinformatic and other high-throughput analyses of environmentally relevant microorganisms providing unprecedented insights into key biodegradative pathways and the ability of microorganisms to adapt to changing environmental conditions. Products that contain biodegradable matter and non-biodegradable matter are often marketed as biodegradable.

KEYWORDS: biodegradation, biosurfactant, polyaromatic hydrocarbons, polyethylene, polypropylene and polystyrene polychlorinated biphenyls, hydro-biodegradable plastics, oxo-biodegradable plastics, polyhydroxyalkanoates, polyhydroxybutyrate-valerate, polylactic acid, polycaprolactone, polyvinyl alcohol, polyamides, polyethylene terephthalate, polyhydroxyalkanoates, poly-3-hydroxybutyrate, polyhydroxyvalerate, polyhydroxyhexanoate, polybutylene succinate, polycaprolactone, polyanhydrides, polyvinyl alcohol, starch derivatives, cellulose esters, nitrocellulose, celluloid

INTRODUCTION

"Biodegradable" product has the ability to break down, safely, reliably, and relatively quickly, by biological means, into raw materials of nature and disappear into nature.

METHODS OF MEASURING BIODEGRADATION:

In nature, different materials biodegrade at different rates. To be able to work effectively, most microorganisms that assist the biodegradation need light, water and oxygen. Temperature is also an important factor in determining the rate of biodegradation. This is because microorganisms tend to reproduce faster in warmer conditions. Many products that are biodegradable in soil – such as tree trimmings, food wastes and paper – will not biodegrade when placed in landfills, because the artificial landfill environment lacks the light, water and bacterial activity required for the decay process to begin. Biodegradation can be measured in a number of ways. Scientists often use respirometry tests for aerobic microbes. First one places a solid waste sample in a container with microorganisms and soil and then aerate the mixture. Over the course of several days, microorganisms digest the sample bit by bit and produce carbon dioxide – the resulting amount of CO2 serves as an indicator of degradation. Biodegradation can also be measured by anaerobic microbes and the amount of methane or alloy that they are able to produce. In formal scientific literature, the process is termed bio-remediation.

BIODEGRADABLE PLASTICS:

There are two main types of biodegradable plastics in the market: Hydro-Biodegradable Plastics (HBP) and Oxo-Biodegradable Plastics (OBP). Both will first undergo chemical sodium carbon dioxide degradation by hydrolysis and oxidation respectively. This results in their physical disintegration and a drastic reduction in their molecular weight. These smaller, lower molecular weight fragments

*Corresponding author: Dr. Dhrubo Jyoti Sen / Email: dhrubosen69@yahoo.com

are then amenable to biodegradation. OBPs are made by adding a small proportion of compounds of specific transition metals (iron, manganese, cobalt and nickel are commonly used) into the normal production of polyolefins such as polyethylene (PE), polypropylene (PP) and polystyrene (PS). The additives act as catalysts to speed up the normal oxidative degradation, increasing the overall process by up to several orders of magnitude (factors of 10)

Approximated time for compounds to Biodegrade Plastics

Product	Time to Biodegrade	Product	Time to Biodegrade
Vegetables	5 days-1 month	Plastic coated milk carton	5 years
Orange peels	6 months	Leather shoes	24-40 years
General paper	2-5 months	Nylon fabric	30-40 years
Paper towel	2-4 weeks	Tin cans	50-100 years
Cardboard box	2 months	Aluminium cans	80-100 years
Tree leaves	1 year	Glass bottles	1 million years
Wool socks	1-5 years	Plastic bags	500 years-forever

Table-1: Time period for biodegradation of compounds

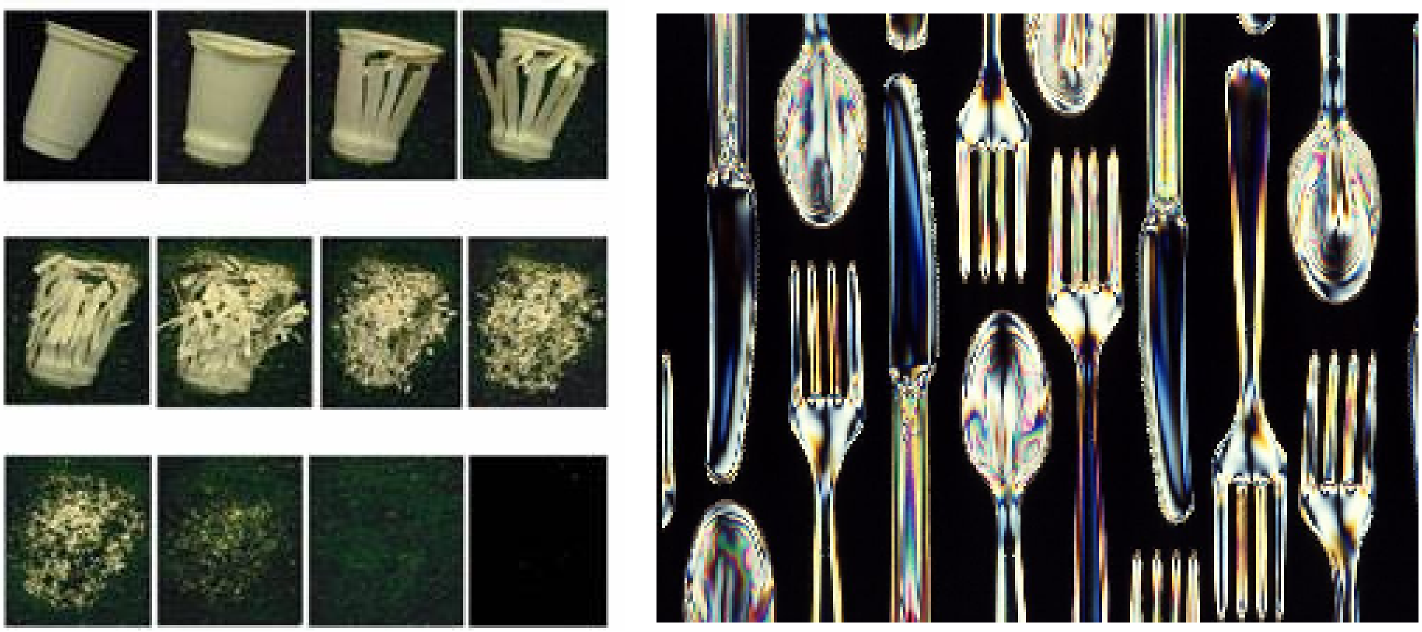


Figure-1: Biodegradable polymers (Ref: 1, 2)

The products of the catalyzed oxidative degradation of the polyolefins are precisely the same as for conventional polyolefins because, other than a small amount of additive present, the plastics are conventional polyolefins. Many commercially useful hydrocarbons (e.g., cooking oils, polyolefins and many other plastics) contain small amounts of additives called antioxidants that prevent oxidative degradation during storage and use. Antioxidants function by 'deactivating' the free radicals that cause degradation. Lifetime (shelf life + use life) is controlled by antioxidant level and the rate of degradation after disposal is controlled by the amount and nature of the catalyst. Since there are no existing corresponding standards that can be used directly in reference to plastics that enter the environment in other ways other than compost - i.e. as terrestrial or marine litter or in landfills, OBP technology is often attacked by the HBP industry as unable to live up to the standards (which are actually the standards for composting). It has to be understood that composting and biodegradation are not identical. OBP can however be tested according to ASTM D6954, and (as from 1.1.2010) UAE 5009:2009.

HBPs tend to degrade and biodegrade somewhat more quickly than OBP, but they have to be collected and put into an industrial composting unit. The end result is the same - both are converted to carbon dioxide (CO_2), water (H_2O) and biomass. OBP are generally less expensive, possess better physical properties and can be made with current plastics processing equipment. However, HBP emits methane in anaerobic conditions, but OBP does not. Polyesters play a predominant role in hydro-biodegradable plastics due to their potentially hydrolysable ester bonds. HBP can be made from agricultural resources such as corn, wheat, sugar cane, or fossil (petroleum-based) resources, or blend of the two. Some of the commonly-used polymers include PHA (polyhydroxyalkanoates), PHBV (polyhydroxybutyrate-valerate), PLA (polylactic acid), PCL (polycaprolactone), PVA (polyvinyl alcohol), PET (polyethylene terephthalate), etc. It would be misleading to call these "renewable" because the agricultural production process burns significant amounts of hydrocarbons and emits significant amounts of CO_2. OBPs (like normal plastics) are made from a by-product of oil or natural gas, which would be produced whether or not the by-product was used to make plastic. HBP technology claims to be biodegradable by meeting the ASTM D6400-04 and EN 13432 Standards. However, these two commonly quoted standards are related to the performance of plastics in a commercially managed compost environment. They are not biodegradation standards. Both were developed for hydro-biodegradable polymers where the mechanism including biodegradation is based on reaction with water and state that in order for a production to be compostable, the following criteria need to be met:

1.Disintegration, the ability to fragment into non-distinguishable pieces after screening and safely support bio-assimilation and microbial growth;

2.Inherent biodegradation, conversion of carbon to carbon dioxide to the level of 60% and 90% over a period of 180 days for ASTM D6400-04 and EN 13432 respectively; there is therefore little or no carbon left for the benefit of the soil, but the CO_2 emitted to atmosphere contributes to climate-change.

3.Safety, that there is no evidence of any eco-toxicity in finished compost and soils can support plant growth; and

4.Toxicity, that heavy metal concentrations are less than 50% regulated values in soil amendments.

Biodegradable technology:

In 1973 it was proved for first time that polyester degrades when disposed in bioactive material such as soil. As a result, polyesters are water resistant and can be melted and shaped into sheets, bottles, and other products, making certain plastics now available as a biodegradable product. Following, Polyhydroxylalkanoates (PHAs) were produced directly from renewable resources by microbes. They are approximately 95% cellular bacteria and can be manipulated by genetic strategies. The composition and biodegradability of PHAs can be regulated by blending it with other natural polymers. In the 1980's the company ICI Zenecca commercialized PHAs under the name Biopol. It was used for the production of shampoo bottles and other cosmetic products. Consumer response was unusual. Consumers were willing to pay more for this product because it was natural and biodegradable, which had not occurred before. Now biodegradable technology is a highly developed market with applications in product packaging, production and medicine. Biodegradable technology is concerned with the manufacturing science of biodegradable materials. It imposes science based mechanisms of plant genetics into the processes of today.1

Figure-2: Biodegradable technology (Ref: 3, 4)

Scientists and manufacturing corporations can help impact climate change by developing a use of plant genetics that would mimic some present technologies. By looking to plants, such as biodegradable material harvested through photosynthesis, waste and toxins can be minimized. Oxo-biodegradable technology, which has further developed biodegradable plastics, also emerged. By creating products with very large polymer molecules of plastics, which contain only carbon and hydrogen, with oxygen in the air, the product is capable of decomposing anywhere from a week to one to two years.The chemical degradation process involves the reaction of very large polymer molecules of plastics, which contain only carbon and hydrogen, with oxygen in the air. This reaction occurs even without prodegradant additives but at a very slow rate. That is why conventional plastics, when discarded, persist for a long time in the environment. With this reaction, formulations catalyze and accelerate the biodegradation process. Biodegradable technology is especially utilized by the bio-medical community. Biodegradable polymers are classified into three groups: medical, ecological, and dual application, while in terms of origin they are divided into two groups: natural and synthetic. The Clean Technology Group is exploiting the use of supercritical carbon dioxide, which under high pressure at room temperature is a solvent that can use biodegradable plastics to make polymer drug coatings. The polymer (meaning a material composed of molecules with repeating structural units that form a long chain) is used to encapsulate a drug prior to injection in the body and is based on lactic acid, a compound normally produced in the body, and is thus able to be excreted naturally. The coating is designed for controlled release over a period of time, reducing the number of injections required and maximizing the therapeutic benefit.

Professor Steve Howdle states that biodegradable polymers are particularly attractive for use in drug delivery, as once introduced into the body they require no retrieval or further manipulation and are degraded into soluble, non-toxic by-products. Different polymers degrade at different rates within the body and therefore polymer selection can be tailored to achieve desired release rates.

Other biomedical applications include the use of biodegradable, elastic shape-memory polymers. Biodegradable implant materials can now be used for minimally invasive surgical procedures through degradable thermoplastic polymers. These polymers are now able to change their shape with increase of temperature, causing shape memory capabilities as well as easily degradable sutures. As a result, implants can now fit through small incisions, doctors can easily perform complex deformations, and sutures and other material aides can naturally biodegrade after a completed surgery.

HISTORY OF THE TERM BIODEGRADABLE:

The first known use of the word in biological text was in 1961 when employed to describe the breakdown of material into the base components of carbon, hydrogen, and oxygen by microorganisms. Now biodegradable is commonly associated with environmentally friendly products that are part of the earth’s innate cycle and capable of decomposing back into natural elements.

Biodegradable plastics are plastics that will decompose in natural aerobic (composting) and anaerobic (landfill) environments. Biodegradation of plastics can be achieved by enabling microorganisms in the environment to metabolize the molecular structure of plastic films to produce an inert humus-like material that is less harmful to the environment. They may be composed of either bioplastics, which are plastics whose components are derived from renewable raw materials, or petroleum-based plastics which utilize an additive. The use of bio-active compounds compounded with swelling agents ensures that, when combined with heat and moisture, they expand the plastic's molecular structure and allow the bio-active compounds to metabolize and neutralize the plastic.

Biodegradable plastics typically are produced in two forms: injection molded (solid, 3D shapes), typically in the form of disposable food service items, and films, typically organic fruit packaging and collection bags for leaves and grass trimmings, and agricultural mulch.2

SCIENTIFIC DEFINITIONS OF BIODEGRADABLE PLASTIC:

Now-a-days a biodegradable plastic would typically be defined as one in which degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi and algae. There are ranges of standards for biodegradable plastics. The requirements vary from 60 to 90% decomposition of the material within 60 to 180 days of being placed in a standard environment - this may be either a composting situation or a landfill. In the United States, the Federal Trade Commission is the authoritative body for biodegradable standards. ASTM International defines appropriate testing methods to test for biodegradable plastic, both anaerobically and aerobically as well as in marine environments. The specific subcommittee responsibility for overseeing these standards falls on the Committee D20.96 on Environmentally Degradable Plastics and Biobased Products. The current ASTM standards are defined as standard specifications and standard test methods. Standard specifications create a pass or fail scenario whereas standard test methods identify the specific testing parameters for facilitating specific time frames and toxicity of biodegradable tests on plastics. Currently, there are three such ASTM standard specifications which mostly address biodegradable plastics in composting type environments, the ASTM D6400-04 Standard Specification for Compostable Plastics, ASTM D6868 - 03 Standard Specification for Biodegradable Plastics Used as Coatings on Paper and Other Compostable Substrates, and the ASTM D7081 - 05 Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment. The most accurate standard test method for anaerobic environments is the ASTM D5511 - 02 Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions. Another standard test method for testing in anaerobic environments is the ASTM D5526 - 94(2002) Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials under Accelerated Landfill Conditions, this test has proven extremely difficult to perform. Both of these tests are used for the ISO DIS 15985 on determining anaerobic biodegradation of plastic materials.

1. While aromatic polyesters are almost totally resistant to microbial attack, most aliphatic polyesters are biodegradable due to their potentially hydrolysable ester bonds:

2. Naturally Produced: Polyhydroxyalkanoates (PHAs) like the poly-3-hydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and polyhydroxyhexanoate (PHH)

3. Renewable Resource: Polylactic acid (PLA)

4. Synthetic: Polybutylene succinate (PBS), polycaprolactone (PCL)

5. Polyvinyl alcohol

6. Most of the starch derivatives

7. Cellulose esters like cellulose acetate and nitrocellulose and their derivatives (celluloid).

Figure-3: Biodegradable plastic (Ref: 5)

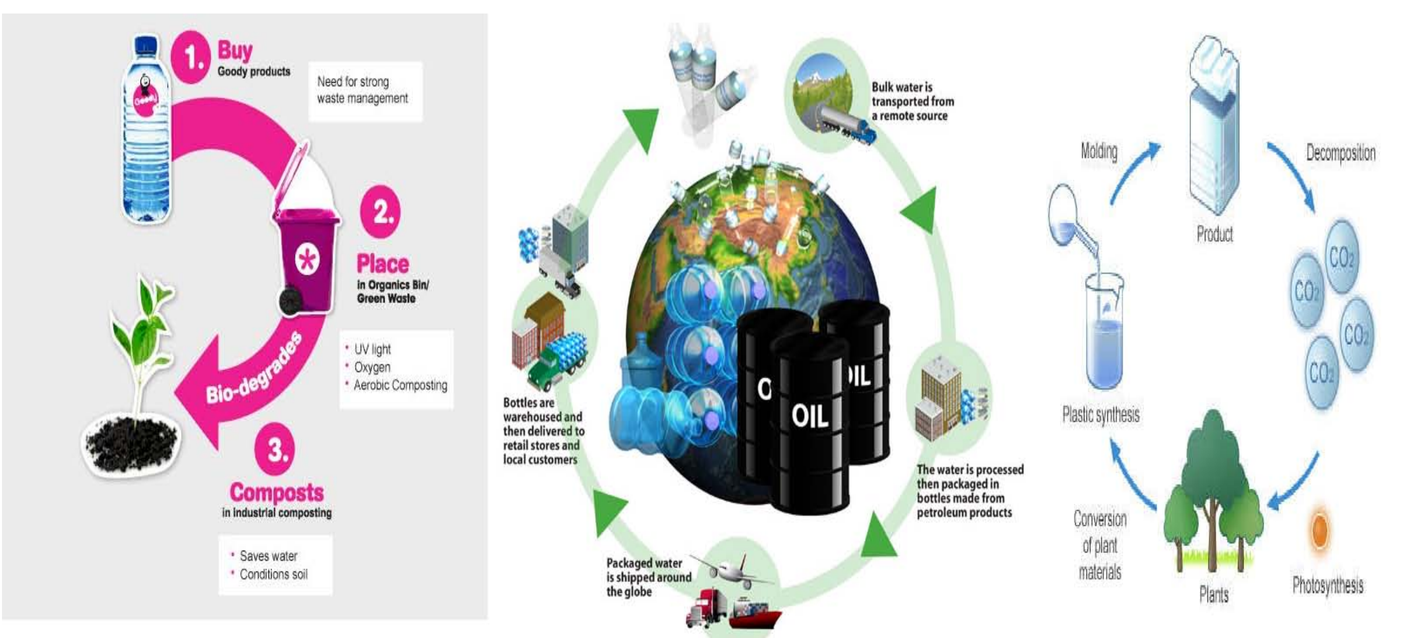


Figure-4: Cycle of biodegradation (Ref: 6)

ENVIRONMENTAL BENEFITS OF BIODEGRADABLE PLASTICS DEPEND UPON PROPER DISPOSAL:

There are several identifiable environmental benefits that may potentially be derived from the use of biodegradable plastics compared to conventional petroleum-based plastics.

These are: Compost derived in part from biodegradable plastics increases the soil organic content as well as water and nutrient retention, while reducing chemical inputs and suppressing plant disease.

Biodegradable shopping and waste bags disposed of to landfill may increase the rate of organic waste degradation in landfills while enhancing methane harvesting potential and decreasing landfill space usage. Biodegradable landfill covers may also considerably extend landfill life. The energy required to synthesize and manufacture biodegradable plastics is generally much lower for most biodegradable plastics than for non-biodegradable plastics. The exception is PHA biopolymers which consume similar energy inputs to polyethylenes. New feedstock for PHA should lower the energy required for their production. Biodegradable plastics are not a panacea, however. Some critics claim that a potential environmental disadvantage of certified biodegradable plastics is that the carbon that is locked up in them is released into the atmosphere as a greenhouse gas. However, biodegradable plastics from natural materials, such as vegetable crop derivatives or animal products, sequester CO2 during the phase when they're growing, only to release CO2 when they're decomposing, so there is no net gain in carbon dioxide emissions. However, certified biodegradable plastics require a specific environment of moisture and oxygen to biodegrade, conditions found in professionally managed composting facilities. There is much debate about the total carbon, fossil fuel and water usage in processing biodegradable plastics from natural materials and whether they are a negative impact to human food supply. Traditional plastics made from non-renewable fossil fuels lock up much of the carbon in the plastic as opposed to being utilized in the processing of the plastic. The carbon is permanently trapped inside the plastic lattice, and is rarely recycled. There is concern that another greenhouse gas, methane, might be released when any biodegradable material, including truly biodegradable plastics, degrades in an anaerobic (landfill) environment. Methane production from landfills is rarely captured or burned, but rather enter the atmosphere, where it is a potent greenhouse gas. Most landfills today capture the methane biogas for use in clean inexpensive energy. Of course, incinerating non-biodegradable plastics will release carbon dioxide as well. Disposing of biodegradable plastics made from natural materials in anaerobic (landfill) environments will result in the plastic lasting for hundred of years. It is also possible that bacteria will eventually develop the ability to degrade plastics. This has already happened with nylon: two types of nylon eating bacteria, Flavobacteria and Pseudomonas, were found in 1975 to possess enzymes (nylonase) capable of breaking down nylon. While not a solution, it is likely that bacteria will evolve the ability to use other synthetic plastics as well. In 2008, a 16-year-old boy reportedly isolated two plastic-consuming bacteria. The latter possibility was in fact the subject of a cautionary novel by Kit Pedler and Gerry Davis, the creators of the Cybermen, re-using the plot of the first episode of their Doomwatch series. The novel, Mutant 59: The Plastic Eater, written in 1971, is the story of what could happen if a bacterium were to evolve—or be artificially cultured—to eat plastics, and be let loose in a major city.3

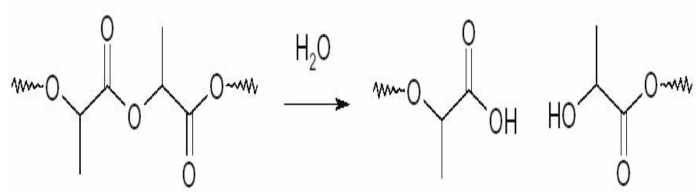
MECHANISMS:

DEGRADATION MECHANISMS.

Materials such as a polyhydroxyalkanoate (PHA) biopolymer are completely compostable in an industrial compost facility. Polylactic acid (PLA) is another 100% compostable biopolymer which can fully degrade above 60°C in an industrial composting facility. Fully biodegradable plastics are more expensive, partly because they are not widely enough produced to achieve large economies of scale.

1.Enzymatic degradation

2.Hydrolysis (depend on main chain structure: anhydride > ester)



3.Homogenous degradation

4.Heterogenous degradation

ADVANTAGES & DISADVANTAGES:

Biodegradable plastics are a new generation of polymers emerging in the market. Biodegradable plastics have an expanding range of potential applications, and are driven by the growing use of plastics in packaging and the perception that biodegradable plastics are 'environmentally friendly', their use is predicted to increase. However, issues are also emerging regarding the use of biodegradable plastics and their potential impacts on the environment and effects on established recycling systems and technologies. There is an extensive range of potential applications. Some of these include: Film including over wrap, shopping bags, waste and bin liner bags, composting bags, mulch film, silage wrap, landfill covers, packaging - incl.O2 & H2O barriers, bait bags and cling wrap, flushable sanitary products, sheet and non woven packaging, bottles, planter boxes and fishing nets, food service cups, cutlery, trays, and straws.

A. MULCH FILM FROM BIODEGRADABLE PLASTICS

This kind of mulch film can be useful for farmers. Mulch films are laid over the ground around crops, to control weed growth and retain moisture. Normally, farmers use polyethylene black plastic that is pulled up after harvest and trucked away to a landfill (taking with it topsoil humus that sticks to it). However, field trials using the biodegradable mulch film on tomato and chilly crops have shown it performs just as well as polyethylene film but can simply be ploughed into the ground after harvest. It's easier, cheaper and it enriches the soil with carbon.

B. PLANTABLE POTS

Another biodegradable plastic product is a plant pot produced by injection moulding. Gardeners and farmers can place potted plants directly into the ground, and forget them. The pots will break down to carbon dioxide and water, eliminating double handling and recycling of conventional plastic containers.

C. DIFFERENT POLYMER BLENDS FOR DIFFERENT PRODUCTS

Depending on the application, scientists can alter polymer mixtures to enhance the properties of the final product. For example, an almost pure starch product will dissolve upon contact with water and then biodegrade rapidly. By blending quantities of other biodegradable plastics into the starch, scientists can make a waterproof product that degrades within 4 weeks after it has been buried in the soil or composted. Under proper conditions biodegradable plastics can degrade to the point where microorganisms can metabolise them. Degradation of oil-based biodegradable plastics may release previously stored carbon as carbon dioxide. Starch-based bioplastics produced from sustainable farming methods can be almost carbon neutral but could have a damaging effect on soil, water usage and quality, and result in higher food prices. There are concerns over "Oxo Biodegradable (OBD)" plastic bags. These are plastic bags which contain tiny amounts of metals such as cobalt, iron or manganese. They degrade in the presence of sunlight and oxygen, but there are concerns about the metals leftover and the time it takes for the plastics to degrade in certain circumstances. Microbial consumption of polymers are available through addition of hydrophilic type additives onto the surface of the polymer chains. These types of additives are readily available and are used worldwide. The advantages of using these types of materials are heat stability, methane capturing and product performance.

Figure-5: Domestic biodegradable items (Ref: 7)

DEGRADATION SCHEMES:

1. Surface erosion (poly(ortho)esters and polyanhydrides)
2. Sample is eroded from the surface
3. Mass loss is faster than the ingress of water into the bulk
4. Bulk degradation (PLA,PGA,PLGA, PCL)
5. Degradation takes place throughout the whole of the sample
6. Ingress of water is faster than the rate of degradation

Environmental concerns; benefits:

Over 200 million tons of plastic are manufactured annually around the world, according to the Society of Plastics Engineers. Of those 200 million tons, 26 million are manufactured in the United States. The EPA reported in 2003 that only 5.8% of those 26 million tons of plastic waste are recycled, although this is increasing rapidly. Much of the reason for disappointing plastics recycling goals is that conventional plastics are often commingled with organic wastes (food scraps, wet paper, and liquids), making it difficult and impractical to recycle the underlying polymer without expensive cleaning and sanitizing procedures. On the other hand, composting of these mixed organics (food scraps, yard trimmings, and wet, non-recyclable paper) is a potential strategy for recovering large quantities of waste and dramatically increases community recycling goals. Food scraps and wet, non-recyclable paper comprises 50 million tons of municipal solid waste.

Biodegradable plastics can replace the non-degradable plastics in these waste streams, making municipal composting a significant tool to divert large amounts of otherwise nonrecoverable waste from landfills. If even a small amount of conventional plastics were to be commingling with organic materials, the entire batch of organic waste is "contaminated" with small bits of plastic that spoil prime-quality compost humus. Composters, therefore, will not accept mixed organic waste streams unless they are completely devoid of nondegradable plastics. So, because of a relatively small quantity of nondegradable plastics, a significant waste disposal strategy is stalled. However, proponents of biodegradable plastics argue that these materials offer a solution to this problem. Certified biodegradable plastics combine the utility of plastics (lightweight, resistance, relative low cost) with the ability to completely and fully biodegrade in a compost facility. Rather than worrying about recycling a relatively small quantity of commingled plastics, these proponents argue that certified biodegradable plastics can be readily commingled with other organic wastes, thereby enabling composting of a much larger position of nonrecoverable solid waste. Commercial composting for all mixed organics then becomes commercially viable and economically sustainable. More municipalities can divert significant quantities of waste from overburdened landfills since the entire waste stream is now biodegradable and therefore easier to process. The use of biodegradable plastics, therefore, is seen as an enabler for the complete recovery of large quantities of municipal sold waste (via aerobic composting) that were are heretofore unrecoverable by other means except land filling or incineration.4

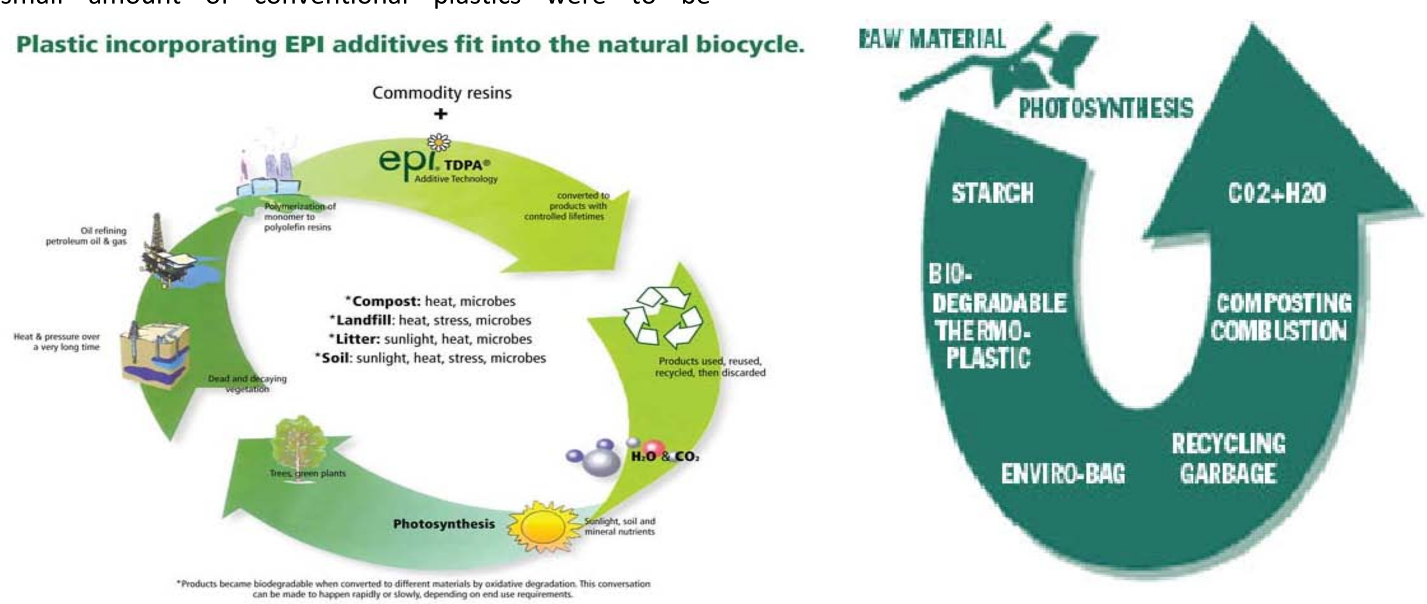


Figure-6: Ecofriendly biodegradation (Ref: 8)

CONFUSION OVER PROPER DEFINITION OF TERMS:

Until recently there were few legal standards regarding marketing claims surrounding the use of the term 'biodegradable'. In 2007, the state of California passed regulation banning companies from claiming their products are biodegradable without proper scientific certification from a third-party laboratory. The Federal Court of Australia declared on March 30, 2009 that a director of a company that manufactured 'biodegradable' disposable diapers (who also approved the company's advertising) had been knowingly making false and misleading claims about biodegradability. In June 2009, the Federal Trade Commission charged two companies with making unsupported marketing claims.

ENERGY COSTS FOR PRODUCTION:

Various researchers have undertaken extensive life cycle assessments of biodegradable polymers to determine whether these materials are more energy efficient than polymers made by conventional fossil fuel-based means. Research done by Gerngross, et al. estimates that the fossil fuel energy required to produce a kilogram of polyhydroxyalkanoate (PHA) is 50.4 MJ/kg, which coincides with another estimate by Akiyama, et al. who estimate a value between 50-59 MJ/kg. This information does not take into account the feedstock energy, which can be obtained from non-fossil fuel based methods. Polylactide (PLA) was estimated to have a fossil fuel energy cost of 54-56.7 from two sources, but recent developments in the commercial production of PLA by NatureWorks has eliminated some dependence fossil fuel based energy by supplanting it with wind power and biomass-driven strategies. They report making a kilogram of PLA with only 27.2 MJ of fossil fuel-based energy and anticipate that this number will drop to 16.6 MJ/kg in their next generation plants. In contrast, polypropylene and high density polyethylene require 85.9 and 73.7 MJ/kg respectively, but these values include the embedded energy of the feedstock because it is based on fossil fuel. Gerngross reports a 2.65 total fossil fuel energy equivalent (FFE) required to produce a single kilogram of PHA, while polypropylene only requires 2.2 kg FFE. Gerngross assesses that the decision to proceed forward with any biodegradable polymer alternative will need to take into account the priorities of society with regard to energy, environment, and economic cost. Furthermore, it is important to realize the youth of alternative technologies. Technology to produce PHA, for instance, is still in development today, and energy consumption can be further reduced by eliminating the fermentation step, or by utilizing food waste as feedstock. The use of alternative crops other than corn, such as sugar cane from Brazil, are expected to lower energy requirements- manufacturing of PHAs by fermentation in Brazil enjoys a favorable energy consumption scheme where bagasse is used as source of renewable energy. Many biodegradable polymers that come from renewable resources (i.e., starch-based, PHA, PLA) also compete with food production, as the primary feedstock is currently corn. For the US to meet its current output of plastics production with BPs, it would require 1.62 square meters per kilogram produced. While this space requirement could be feasible, it is always important to consider how much impact this large scale production could have on food prices and the opportunity cost of using land in this fashion versus alternatives.

EXAMPLES OF BIODEGRADABLE PLASTICS:

Bioplastics or organic plastics are a form of plastics derived from renewable biomass sources, such as vegetable fats and oils, corn starch, pea starch, or microbiota, rather than fossil-fuel plastics which are derived from petroleum. Some, but not all, bioplastics are designed to biodegrade.

APPLICATIONS:

Biodegradable bioplastics are used for disposable items, such as packaging and catering items (crockery, cutlery, pots, bowls and straws). Biodegradable bioplastics are also often used for organic waste bags, where they can be composted together with the food or green waste. Some trays and containers for fruit, vegetables, eggs and meat, bottles for soft drinks and dairy products and blister foils for fruit and vegetables are manufactured from bioplastics. Nondisposable applications include mobile phone casings, carpet fibres, and car interiors, fuel line and plastic pipe applications, and new electroactive bioplastics are being developed that can be used to carry electrical current. In these areas, the goal is not biodegradability, but to create items from sustainable resources.

A. Compostable plastic: A plastic that undergoes biological degradation during the composting process (up to 2-3 months in a windrow) to yield carbon dioxide, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues.

B. Biodegradable plastic: A degradable plastic in which the degradation must result from the action of naturally occurring microorganisms over a period of time (up to 2-3 years in a landfill).

C. Degradable plastic: An oil-based plastic containing a chemical additive that undergoes significant change in its chemical structure causing it to break down into smaller particles. The degradation process is triggered only when material is exposed to specific environmental conditions (such as UV, heat and moisture). Residues are not food matter for microorganisms and are not biodegradable or compostable.

The range of degradable plastics now available includes:

• Starch-based products including thermoplastic starch, starch and synthetic aliphatic polyesters
• Naturally produced polyesters.
• Renewable resource polyesters such as PLA.
• Synthetic aliphatic polyesters.
• Aliphatic-aromatic (AAC) co polyesters.
• Hydro-biodegradable polyester such as modified PET.
• Water soluble polymer such as polyvinyl alcohol and ethylene vinyl alcohol.
• Photo-degradable plastics.
• Controlled degradation additive master batches

PLASTIC TYPES:

CELLULOSE-BASED PLASTICS

Packaging blister made from cellulose acetate, a bioplastic Cellulose bioplastics are mainly the cellulose esters, (including cellulose acetate and nitrocellulose) and their derivatives, including celluloid.

Starch-based plastics:

Constituting about 50 percent of the bioplastics market, thermoplastic starch, such as Plastarch Material, currently represents the most important and widely used bioplastic. Pure starch possesses the characteristic of being able to absorb humidity, and is thus being used for the production of drug capsules in the pharmaceutical sector. Flexibiliser and plasticiser such as sorbitol and glycerine are added so the starch can also be processed thermo-plastically. By varying the amounts of these additives, the characteristic of the material can be tailored to specific needs (alsocalled"thermoplasticalstarch"). Simple starch plastic can be made at home shown by this method.[5]

Figure-7: Disposable bioplastics for daily use (Ref: 9)

ALIPHATIC POLYESTERS:

POLYLACTIC ACID (PLA) PLASTICS

Polylactic acid (PLA) is a transparent plastic produced from cane sugar or glucose. It not only resembles conventional petrochemical mass plastics (like PE or PP) in its characteristics, but it can also be processed easily on standard equipment that already exists for the production of conventional plastics. PLA and PLA blends generally come in the form of granulates with various properties, and are used in the plastic processing industry for the production of foil, moulds, cups and bottles.

POLY-3-HYDROXYBUTYRATE (PHB)

The biopolymer poly-3-hydroxybutyrate (PHB) is a polyester produced by certain bacteria processing glucose or starch. Its characteristics are similar to those of the petroplastic polypropylene. The South American sugar industry, for example, has decided to expand PHB production to an industrial scale. PHB is distinguished primarily by its physical characteristics. It produces transparent film at a melting point higher than 130°C, and is biodegradable without residue.

POLYAMIDE 11 (PA 11)

PA 11 is a biopolymer derived from natural oil. It is also known under the tradename Rilsan B, commercialized by Arkema. PA 11 belongs to the technical polymers family and is not biodegradable. Its properties are similar to those of PA 12, although emissions of greenhouse gases and consumption of nonrenewable resources are reduced during its production. Its thermal resistance is also superior to that of PA 12. It is used in high-performance applications like automotive fuel lines, pneumatic airbrake tubing, electrical cable antitermite sheathing, flexible oil and gas pipes, control fluid umbilicals, sports shoes, electronic device components, and catheters.

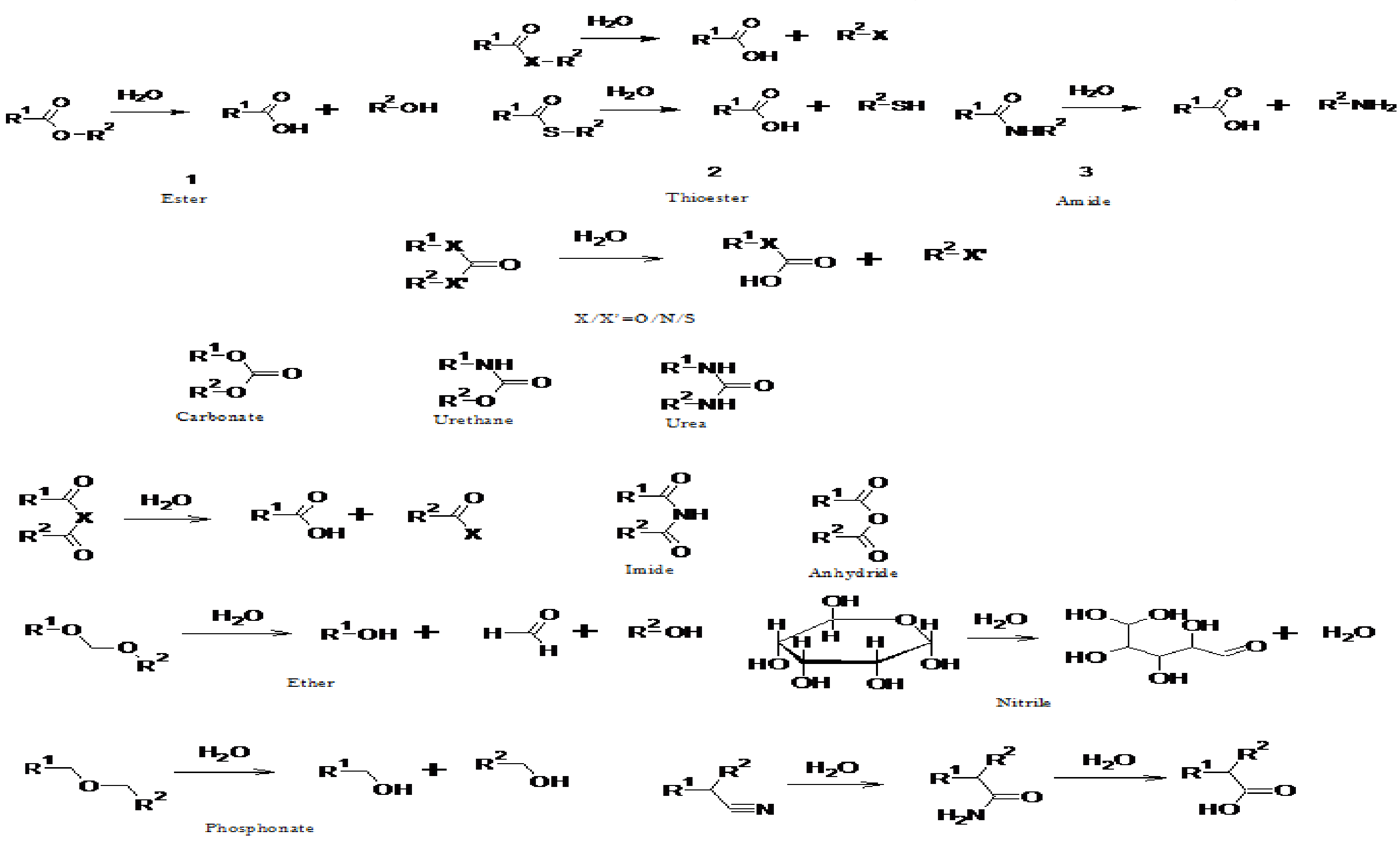
BIO-DERIVED POLYETHYLENE:

The basic building block (monomer) of polyethylene is ethylene. This is just one small chemical step from ethanol, which can be produced by fermentation of agricultural feedstocks such as sugar cane or corn. Bio-derived polyethylene is chemically and physically identical to traditional polyethylene – it does not biodegrade but can be recycled. It can also considerably reduce greenhouse gas emissions. Brazilian chemicals group Braskem claims that using its route from sugar cane ethanol to produce one tonne of polyethylene captures (removes from the environment) 2.5 tonnes of carbon dioxide while the traditional petrochemical route results in emissions of close to 3.5 tonnes. Braskem plans to introduce commercial quantities of its first bio-derived high density polyethylene, used in a packaging such as bottles and tubs, in 2010 and has developed a technology to produce bio-derived butene, required to make the linear low density polethylene types used in film production.

GENETICALLY MODIFIED BIOPLASTICS:

Genetic modification (GM) is also a challenge for the bioplastics industry. None of the currently available bioplastics – which can be considered first generation products – require the use of GM crops, although GM corn is the standard feedstock. Looking further ahead, some of the second generation bioplastics manufacturing technologies under development employ the "plant factory" model, using genetically modified crops or genetically modified bacteria to optimise efficiency.

BIODEGRADABLE POLYMERS: CARBONYL BOND TO: O/N/S (ESTER/THIOESTER/AMIDE)



Flowchart of bioconversion of chemicals (Ref: 5, 6)

BIODEGRADABLE POLYMERS USED FOR MEDICAL APPLICATIONS:

1. NATURAL POLYMERS:

- Collagen
- Chitosan
- Gelatin
- Hyaluronan

2. SYNTHETIC POLYMERS:

- PLA, PGA, PLGA, PCL, Polyorthoesters
- Poly (dioxanone)
- Poly (anhydrides)
- Poly (trimethylene carbonate)

3. DEGRADATION CAN BE DIVIDED INTO 4 STEPS:

- Water sorption
- Reduction of mechanical properties (modulus & strength)
- Reduction of molar mass
- Weight loss

4. FACTORS INFLUENCE THE DEGRADATION BEHAVIOR:

- Chemical Structure and Chemical Composition
- Distribution of Repeat Units in Multimers
- Molecular Weight
- Polydispersity

5. PRESENCE OF LOW Mw COMPOUNDS (MONOMER, OLIGOMERS, SOLVENTS, PLASTICIZERS, ETC)

- Presence of Ionic Groups
- Presence of Chain Defects
- Presence of Unexpected Units
- Configurational Structure

6. MORPHOLOGY (CRYSTALLINITY, PRESENCE OF MICROSTRUCTURE, ORIENTATION AND RESIDUE STRESS

- Processing methods & Conditions & Method of Sterilization
- Storage History
- Physiochemical Factors (shape, size)
- Mechanism of Hydrolysis (enzymes vs water)

ENVIRONMENTAL IMPACT:

The production and use of bioplastics is generally regarded as a more sustainable activity when compared with plastic production from petroleum (petroplastic), because it relies less on fossil fuel as a carbon source and also introduces fewer, net-new greenhouse emissions if it biodegrades. They significantly reduce hazardous waste caused by oil-derived plastics, which remain solid for hundreds of years, and open a new era in packing technology and industry. However, manufacturing of bioplastic materials is often still reliant upon petroleum as an energy and materials source. This comes in the form of energy required to power farm machinery and irrigate growing crops, to produce fertilisers and pesticides, to transport crops and crop products to processing plants, to process raw materials, and ultimately to produce the bioplastic, although renewable energy can be used to obtain petroleum independence. Italian bioplastic manufacturer Novamont states in its own environmental audit that producing one kilogram of its starch-based product uses 500g of petroleum and consumes almost 80% of the energy required to produce a traditional polyethylene polymer. Environmental data from NatureWorks, the only commercial manufacturer of PLA (polylactic acid) bioplastic, says that making its plastic material delivers a fossil fuel saving of between 25 and 68 per cent compared with polyethylene, in part due to its purchasing of renewable energy certificates for its manufacturing plant.6

A detailed study examining the process of manufacturing a number of common packaging items in several traditional plastics and polylactic acid carried out by Franklin Associates and published by the Athena Institute shows the bioplastic to be less environmentally damaging for some products, but more environmentally damaging for others. This study however does not consider the end-of-life of the products, thus ignores the possible methane emissions that can occur in landfill due to biodegradable plastics. While production of most bioplastics results in reduced carbon dioxide emissions compared to traditional alternatives, there are some real concerns that the creation of a global bioeconomy could contribute to an accelerated rate of deforestation if not managed effectively. There are associated concerns over the impact on water supply and soil erosion.

BIOPLASTICS AND BIODEGRADATION:

The terminology used in the bioplastics sector is sometimes misleading. Most in the industry use the term bioplastic to mean a plastic produced from a biological source. One of the oldest plastics, cellulose film, is made from wood cellulose. All (bio- and petroleum-based) plastics are technically biodegradable, meaning they can be degraded by microbes under suitable conditions. However many degrade at such slow rates as to be considered non-biodegradable. Some petrochemical-based plastics are considered biodegradable, and may be used as an additive to improve the performance of many commercial bioplastics. Non-biodegradable bioplastics are referred to as durable. The degree of biodegradation varies with temperature, polymer stability, and available oxygen content. Consequently, most bioplastics will only degrade in the tightly controlled conditions of industrial composting units. In compost piles or simply in the soil/water, most bioplastics will not degrade (e.g. PH), starch-based bioplastics will, however. An internationally agreed standard, EN13432, defines how quickly and to what extent a plastic must be degraded under commercial composting conditions for it to be called biodegradable. However, it is designed only for the aggressive conditions of commercial composting units. There is no standard applicable to home composting conditions.

The term "biodegradable plastic" has also been used by producers of specially modified petrochemical-based plastics which appear to biodegrade. Biodegradable plastic bag manufacturers that have misrepresented their product's biodegradability may now face legal action in the US state of California for the misleading use of the terms biodegradable or compostable. Traditional plastics such as polyethylene are degraded by ultra-violet (UV) light and oxygen. To prevent this process manufacturers add stabilising chemicals. However with the addition of a degradation initiator to the plastic, it is possible to achieve a controlled UV/oxidation disintegration process. This type of plastic may be referred to as degradable plastic or oxy-degradable plastic or photodegradable plastic because the process is not initiated by microbial action. While some degradable plastics manufacturers argue that degraded plastic residue will be attacked by microbes, these degradable materials do not meet the requirements of the EN13432 commercial composting standard.

The bioplastics industry has widely criticized oxo-biodegradable plastics, which the industry association says do not meet its requirements. Oxo-biodegradable plastics - known as "oxos" - are conventional petroleum-based products with some additives that initiate degradation. The ASTM standard used by oxo producers is just a guideline. It requires only 60% biodegradation, P-Life is an oxo plastic claiming biodegradability in soil at a temperature of 23 degrees Celsius reaches 66% after 545 days. Dr Baltus of the National Innovation Agency has said that there is no proven evidence that bio-organisms are really able to consume and biodegrade oxo plastics.

RECYCLING:

There are also concerns that bioplastics will damage existing recycling projects. Packaging such as HDPE milk bottles and PET water and soft drinks bottles is easily identified and hence setting up a recycling infrastructure has been quite successful in many parts of the world, although only 27% of all plastics actually get recycled. The rest are in landfills and oceans. However, plastics like PET do not mix with PLA, yielding unusable recycled PET if consumers fail to distinguish the two in their sorting. The problem could be overcome by ensuring distinctive bottle types or by investing in suitable sorting technology. However, the first route is unreliable, and the second costly.

MARKET:

- Tea bags made of polylactide (PLA), (peppermint tea)
- Prism pencil sharpener made from cellulose acetate biograde.

Because of the fragmentation in the market and ambiguous definitions it is difficult to describe the total market size for bioplastics, but estimates put global production capacity at 327,000 tonnes. In contrast, global consumption of all flexible packaging is estimated at around 12.3 million tonnes.

COPA (Committee of Agricultural Organisation in the European Union) and COGEGA (General Committee for the Agricultural Cooperation in the European Union) have made an assessment of the potential of bioplastics in different sectors of the European economy:

Items	Tonnes/year
Catering products	450,000
Organic waste bags	100,000
Biodegradable mulch foils	130,000
Biodegradable foils for diapers	80,000
Diapers, 100% biodegradable	240,000
Foil packaging	400,000
Vegetable packaging	400,000
Tyre components	200,000
Total	2,000,000

Table-2: Industrial production of biodegradable items

Biodegradable bags are bags made from materials that are able to decompose under specified conditions of light, moisture, and oxygen. Every year approximately 500 billion to 1 trillion plastic bags are used worldwide. Often composting conditions or exposure to sun, moisture, and oxygen are needed: degradation is slow in landfills. Many stores and companies are beginning to use different types of biodegradable bags to comply with perceived environmental benefits. In the years 2000 to 2008, worldwide consumption of biodegradable plastics based on starch, sugar, and cellulose - so far the three most important raw materials - has increased by 600 %. The NNFCC predicted global annual capacity would grow more than six-fold to 2.1 million tonnes by 2013. BCC Research forecasts the global market for biodegradable polymers to grow at a compound average growth rate of more than 17 percent through 2012. Even so, bioplastics will encompass a small niche of the overall plastic market, which is forecast to reach 500 billion pounds (220 million tonnes) globally by 2010.7

COST:

With the exception of cellulose, most bioplastic technology is relatively new and is currently not cost competitive with (petroplastics). Bioplastics do not yet reach the fossil fuel parity on fossil fuel-derived energy for their manufacturing, reducing the cost advantage over petroleum-based plastic. However, in certain, special applications bioplastics are already unbeatable because pure material costs form only a part of the entire product costs. For example, medical implants made of PLA, which dissolve in the body, save patients a second operation. Compostable mulch films for agriculture, already often produced from starch polymers, do not have to be collected after use and can be left on the fields.

Research and development:

1. In the early 1950s, Amylomaize (>50% amylose content corn) was successfully bred and commercial bioplastics applications started to be explored.

2. In 2004, NEC developed a flame retardant plastic, polylactic acid, without using toxic chemicals such as halogens and phosphorus compounds.

3. In 2005, Fujitsu became one of the first technology companies to make personal computer cases from bioplastics, which are featured in their FMV-BIBLO NB80K line.

4. In 2007 Braskem of Brazil announced it had developed a route to manufacture high density polyethylene (HDPE) using ethylene derived from sugar cane.

5. In 2008, a University of Warwick team created a soap-free emulsion polymerization process which makes colloid particles of polymer dispersed in water, and in a one step process adds nanometre sized silica-based particles to the mix. The newly developed technology might be most applicable to multi-layered biodegradable packaging, which could gain more robustness and water barrier characteristics through the addition of a nano-particle coating.

TESTING PROCEDURES:

1.BIODEGRADABILITY - EN 13432, ASTM D6400

The EN 13432 industrial standard is arguably the most international in scope and compliance with this standard is required to claim that a product is compostable in the European marketplace. In summary, it requires biodegradation of 90% of the materials in a lab within 180 days. The ASTM 6400 standard is the regulatory framework for the United States and sets a less stringent threshold of 60% biodegradation within 180 days, again within commercial composting conditions. Many starch based plastics, PLA based plastics and certain aliphatic-aromatic co-polyester compounds such as succinates and adipates, have obtained these certificates. Additivated plastics sold as photodegradable or Oxo Biodegradable do not comply with these standards in their current form.

2. BIOBASED - ASTM D6866

The ASTM D6866 method has been developed to certify the biologically derived content of bioplastics. Cosmic rays colliding with the atmosphere mean that some of the carbon is the radioactive isotope carbon-14. CO2 from the atmosphere is used by plants in photosynthesis, so new plant material will contain both carbon-14 and carbon-12. Under the right conditions, and over geological timescales, the remains of living organisms can be transformed into fossil fuels. After ~100,000 years all the carbon-14 present in the original organic material will have undergone radioactive decay leaving only carbon-12. A product made from biomass will have a relatively high level of carbon-14, while a product made from petrochemicals will have no carbon-14.The percentage of renewable carbon in a material (solid or liquid) can be measured with an accelerator mass spectrometer. There is an important difference between biodegradability and biobased content. A bioplastic such as high density polyethylene (HDPE) can be 100% biobased (i.e. contain 100% renewable carbon), yet be non-biodegradable. These bioplastics such HDPE play nonetheless an important role in greenhouse gas abatement, particularly when they are combusted for energy production. The biobased component of these bioplastics is considered carbon-neutral since their origin is from biomass.

3. ANAEROBIC - ASTM D5511-02 AND ASTM D5526

The ASTM D5511-02 and ASTM D5526 are testing methods that comply with international standards such as the ISO DIS 15985.

DEGRADATION OR BIODEGRADATION:

A material that simply breaks up into smaller and tiny portions is no longer regarded as being biodegradable. Naturally occurring polymers include: polysaccharides e.g., starch from potatoes and corn, their derivatives, cellulose from marine crustaceans; proteins such as gelatin (collagen), casein (from milk), keratin (from silk and wool) and zein (from corn); polyesters such as poly hydroxyl alkanoates formed by bacteria as food storage; lignin; shellac and natural rubber polylactic acid, jute, flux, silk, cotton can fall into the category of natural polymers where the monomer is produced by fermentation. While there are a number of biodegradable synthetic resins, including: polyalkylene esters, polylactic acid polyamide esters, polyvinyl esters, polyvinyl acetate, polyvinyl alcohol, polyanhydrides. The materials mentioned here are those that exhibit degradation promoted by micro-organisms. This has often been coupled to a chemical or mechanical degradation step.8

THERE ARE FIVE DIFFERENT KINDS OF DEGRADABLE PLASTIC:

- Biodegradable,
- Compostable,
- Hydro-biodegradable,
- Photo-degradable
- Bioerodable.

Plastic bags can be made "Oxo-degradable" by being manufactured from a normal plastic polymer (i.e. polyethylene) with an additive which causes fragmentation of the polymer (polyethylene) due to oxidation of metal additives (often cobalt). Other degradable technology utilizes organic additives to polyethylene which allows it to fragment into little pieces (but note that unless the small pieces are themselves completely biodegradable this does not constitute true biodegredation).Template:Cite ref The trade association for the Oxo-biodegradable plastics industry is the Oxo-biodegradable Plastics Association (www.biodeg.org), which will certify products tested according to ASTM D6954 or (as from 1st Jan 2010) UAE 5009:2009 The trade associations for the compostable plastics industry are the Biodegradable Products Institute (BPI), "European Bioplastics," and SPIBioplastics Council. Plastics are certified as biodegradable under composting conditions in the United States if they comply with ASTM D6400, and in Europe EN13432. Standards appropriate to compostable plastics are not appropriate for oxo-degradable plastics, and vice-versa.

COMPANIES:

Different companies use different kinds of biodegradable bags. Many stores use biodegradable bags. Multinational baking giant Grupo Bimbo SAB de CV of Mexico City claims to have been the first to make "Oxo Biodegradable metalized polypropylene snack bag". In addition to that, a company named "Doo Bandits" has created biodegradable bags used for picking up dog waste. The Supermarket Chain Aldi Süd in Germany offers biodegradable Ecovio bags. Ecoflex bags are flexible, tear-resistant, waterproof, and suitable for printing. It gives the bags renewable raw material, making them biodegradable. All of these examples show where companies have claimed biodegradable products without qualification of how long, conditions required, end state results, or weither the residue contains harmful by products as outlined in the pass/fail ASTM D6400 standard. In most cases, without clarification that these products require composting conditions to achieve endstate, the products will be placed in traditional landfills and there will be no environmental benefits and no improvement in degradation of the

PRODUCT:

MATERIALS:

Most bags are mostly manufactured from plastic made from corn-based materials, like Polylactic acid (PHA). Biodegradable plastic bags require more plastic per bag, because the material is not as strong. Many bags are also made from paper, organic materials, or polycaprolactone. "The public looks at biodegradable as something magical," even though the term is mostly meaningless, according to Ramani Narayan, a chemical engineer at Michigan State University in East Lansing, and science consultant to the Biodegradable Plastics Institute. "This is the most used and abused and misused word in our dictionary right now. Simply calling something biodegradable and not defining in what environment it is going to be biodegradable and in what time period it is going to degrade is very misleading and deceptive." In the Great Pacific Garbage Patch, biodegradable plastics break up into small pieces that can more easily enter the food chain by being consumed."

RECYCLING:

In- plant scrap can often be recycled but post-consumer sorting and recycling is difficult. Many biodegradable polymers have the potential to contaminate the recycling of other more common polymers. Degradable bags need to be kept separate from the normal recycling stream. SPI Resin identification code 7 is applicable.

MARKETING QUALIFICATION AND LEGAL ISSUES:

Since many of these plastics require access to sunlight, oxygen, or lengthy periods of time to achieve degradation or biodegradation the Federal Trade Commission's, GUIDES FOR THE USE OF ENVIRONMENTAL MARKETING CLAIMS, commonly called the "green guide" require proper marking of these products to show their performance limits.

THE FTC PROVIDES AN EXAMPLE:

Example: A trash bag is marketed as "degradable," with no qualification or other disclosure. The marketer relies on soil burial tests to show that the product will decompose in the presence of water and oxygen. The trash bags are customarily disposed of in incineration facilities or at sanitary landfills that are managed in a way that inhibits degradation by minimizing moisture and oxygen. Degradation will be irrelevant for those trash bags that are incinerated and, for those disposed of in landfills; the marketer does not possess adequate substantiation that the bags will degrade in a reasonably short period of time in a landfill. The claim is therefore deceptive. Since there are no pass fail tests for "biodegradable" plastic bags manufactures must print on the product the environmental requirements for biodegradation to take place, time frame and end results in order to be within US Trade Requirements. In 2007, the State of California essentially made the term "biodegradable bags" illegal unless such terms are "substantiated by competent and reliable evidence to prevent deceiving or misleading consumers about environmental impact of degradable, compostable, and biodegradable plastic bags, food service ware, and packaging."Legal Considerations of Marketing Claims. In 2010, an Australian manufacturer of plastic bags (who made unsubstantiated or unqualified claims about biodegradability) was fined by that country's equivalent of the FTC.9

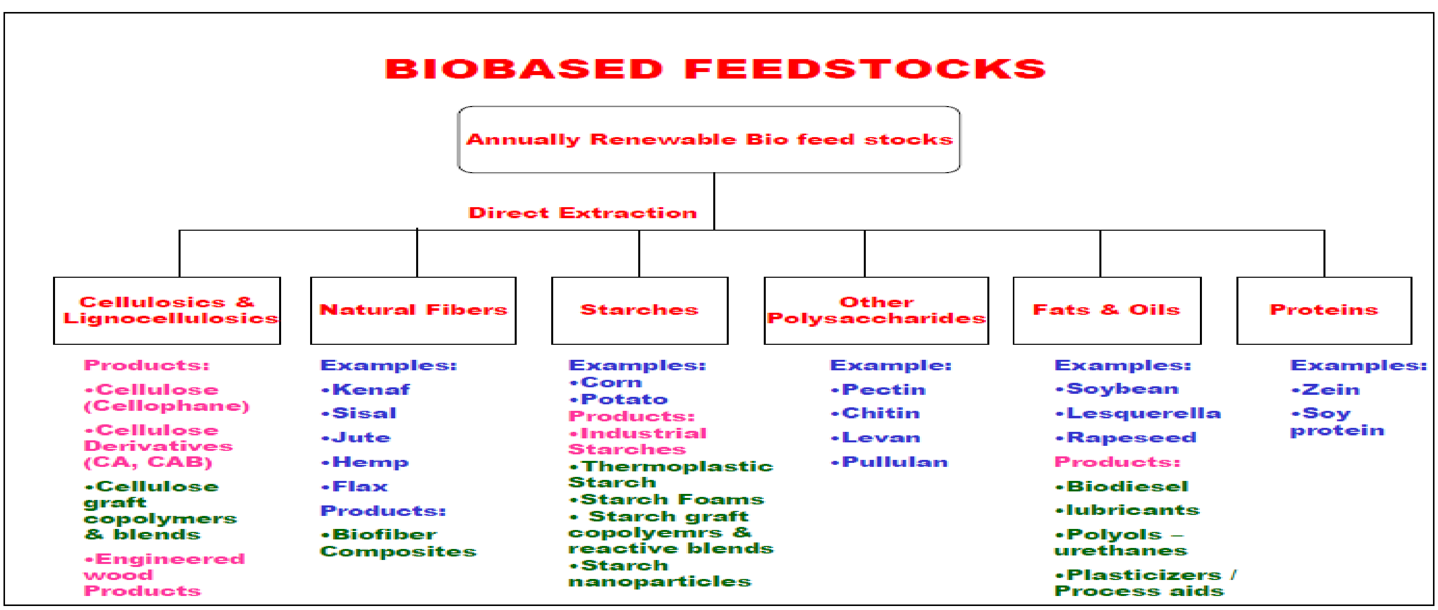
FACTORS THAT ACCELERATE POLYMER DEGRADATION:

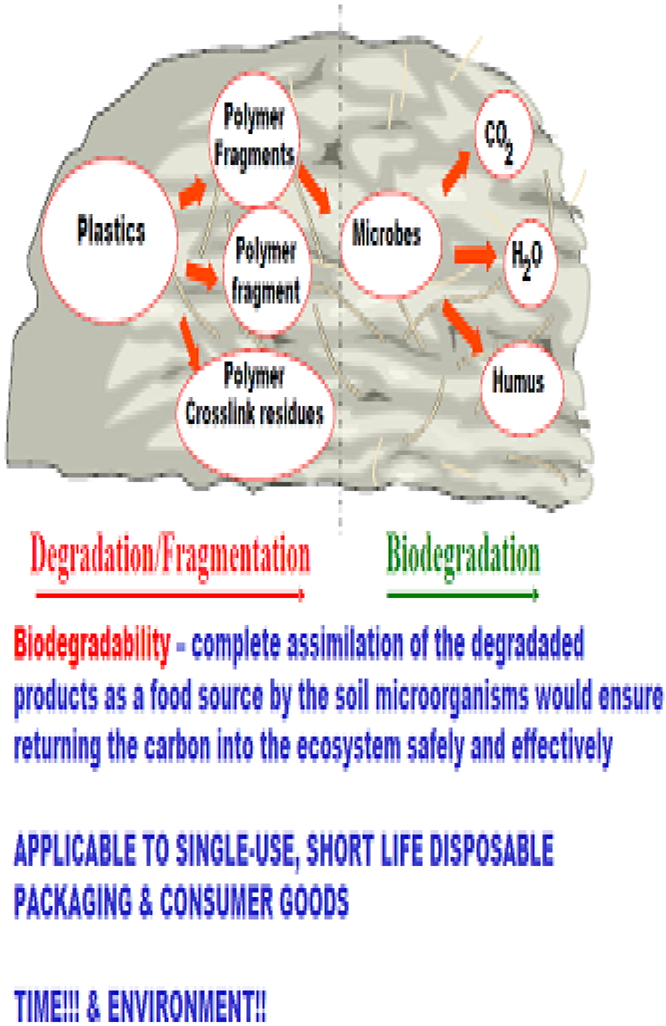
- More hydrophilic backbone
- More hydrophilic endgroups
- More reactive hydrolytic groups in the backbone
- Less crystallinity
- More porosity
- Smaller device size

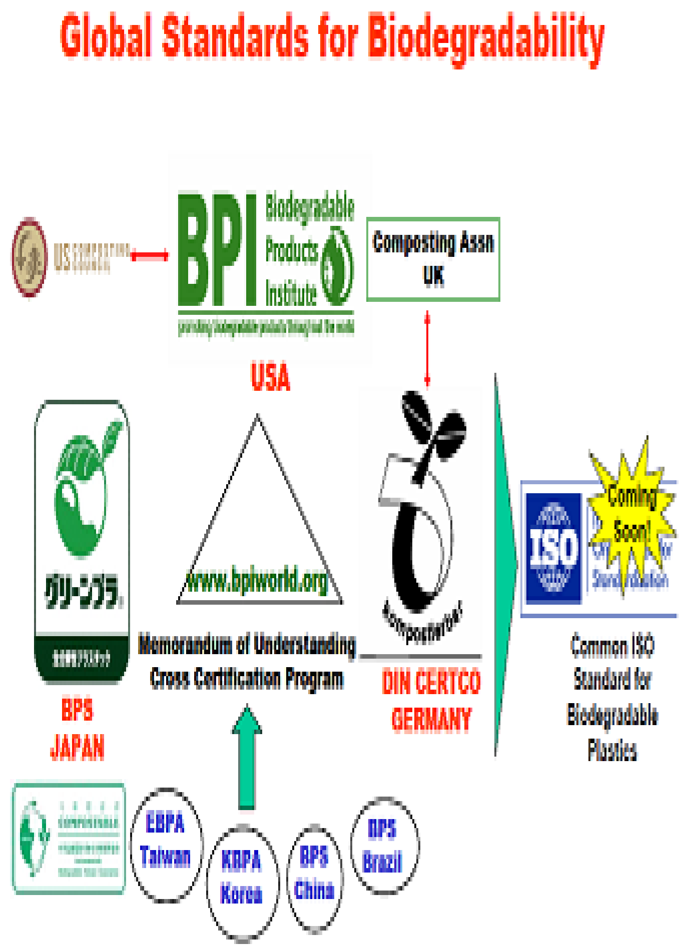
METHODS OF STUDYING POLYMER DEGRADATION:

1. Morphological changes (swelling, deformation, bubbling, disappearance)
2. Weight lose
3. Thermal behavior changes
4. Differential Scanning Calorimetry (DSC)
5. Molecular weight changes
6. Diluted solution Viscosity
7. Size exclusion chromatography (SEC)
8. Gel Permeation Chromatography (GPC)
9. MALDI Mass Spectroscopy
10. Change in chemistry
11. Infra-Red Spectroscopy
12. NMR Spectroscopy
13. TOF-SIMS

CONCLUSION







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