CHAPTER 2

THEORETICAL CONSIDERATION AND LITERATURE REVIEW

Polyethylene

The basic structure of polyethylene(PE) is the chain--$(CH_2\text{-}CH_2)_n$--. In commercial polyethylene, "n" may be between about 400 and above 50,000; alkyl substituents, called short-chain branches, are usually present on the chain back-bones. Polyethylene is perhaps the most important class of polymers in industry at the present time, the homopolymer is widely used as an inexpensive molding resin or film. The copolymers with other olefins or monomers are versatile plastics or elastomers with excellent improved properties.

Polyethylenes are divided into the following groups:

High pressure, low density polyethylene (LDPE), includes polymers made by free-radical polymerizations: homopolymers with densities 0.915-0.930 g/cm^3, containing alkyl substituents with 2-8 carbon atoms (most often 4) with long branches, formed during synthesis.

Linear low and medium density polyethylene (LLDPE) includes only α-olefin copolymers of densities 0.915-0.940 g/cm^3, usually containing 1-butene, 1-hexene, or 1-octene. Most of these products are made with Ziegler-type catalysts.

High density polyethylene (HDPE) includes polymers made with Phillips or Ziegler-type catalysts: homolymer of densities 0.960-0.970 g/cm^3, including so called high molecular weight polyethylene (HMW-PE), and α-olefin copolymers of densities 0.940-0.958 g/cm^3.

Ultra high molecular weight polyethylenes are special polymers with a molecular weight nearly ten times that of the HMW-PE products; they are essentially unbranched and require special and fabrication techniques.

1. Production

The polymerization of ethylene can be released by radical initiators at high pressure as well as by organometallic coordination catalysts. The polymerization can be carried out either in solution or in bulk. For pressures above 100 MPa, ethylene itself acts as a solvent. Both low and high molecular weight polymers can be synthesized by either organometallic coordination or high pressure radical polymerization. The structure of the polyethylene differs with the two methods. Radical initiators give more or less branched polymer chains whereas organometallic coordination catalysts synthesize linear molecules.

The reaction of polymerization is :

$$nC_2H_4 \longrightarrow 1/n\ (C_2H_4)_n \qquad \Delta H = -22 \text{ kcal/mol} \tag{2.1}$$

The reaction is an exothermic reaction from which 850 calories are released for each gram of ethylene.

2. Properties

Polyethylene was introduced initially as a special purpose dielectric material of particular value for high frequency insulation. With increasing availability the polymer subsequently began to be used for chemical plant and to a small extent, for water piping. The present position of polyethylene as a general purpose thermoplastic material is due to the characteristics of polyethylene, which lead to its widespread use, may be summarized as follows: low cost, easy processability, excellent electrical insulation and chemical resistance, toughness and flexibility even at low temperatures, reasonable clarity of the films, free from odor and toxicity, and sufficiently low water vapor permeability for many packaging.

The limitations of polyethylene are the susceptibility of low molecular weight grades to environmental stress cracking, the low softening point, the susceptibility to oxidation (however polyethylene is better in this respect than many other polymers), the opacity of the material in bulk, the wax-like appearance, the poor scratch resistance, the lack of rigidity (a limitation in some applications but a virtue in others), the low tensile strength and the high gas permeability. For many purposes these limitations are not serious whilst in other cases the correct choice of polymer, additives processing conditions and after treatment can help considerably (Brandup, 1975).

Starch

Starch is one of the most abundant plant materials in the world. It is a carbohydrate, a very large group of compounds containing carbon, hydrogen, and oxygen. The latter two elements are essentially in the same retail as they exist in water, two atoms of hydrogen to one of oxygen, hence the name carbohydrates, or hydrates of carbon. Carbohydrates are classified as monosaccharides, disaccharides, trisaccharides, and polysaccharides. Polysaccharides, very numerous, do not have the sweet taste of the other carbohydrates, are insoluble, and are of high molecular complexity. On hydrolysis, a polysaccharide molecule yields many molecules of monosaccharide sugars. Starch, cellulose and glycogin are polysaccharides.

Starch is a solid material with a density of approximately 1.5 g/ml. The granular themselves vary considerably in shape (from spheres to rods) and size (from a diameter of 1 to 1000 μm). For cassava starch, the size of the granules ranged from 5 to 35 μm. The largest are usually 25 to 35 μm and the smallest are 5 to 15 μm.

1. Chemistry of Starch

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 as an empirical formula of $C_6H_{10}O_5$, placing in the class of carbohydrate. It is a condensation polymer of glucose. The glucose units in the starch are present as anhydroglucose units being formed as if a molecule of water is removed during a step polymerization. The linkage of one glucose to another through the C-1 oxygen is normally known as a glucoside bond. The glucoside linkage is an acetal, stable under alkaline conditions and hydrolyzable under acid conditions. The hydroxyl groups can react to form ethers and can be oxidized to aldehyde, ketone, and carboxyl groups (Brautechet, 1953).

2. Molecular Structure

Most starch consists of a mixture of two polysaccharide types: amylose, an essentially linear polymer; and amylopectin, a highly branched polymer. The relative amounts of these starch fractions in particular starch are the major factor in determining the properties of that starch.

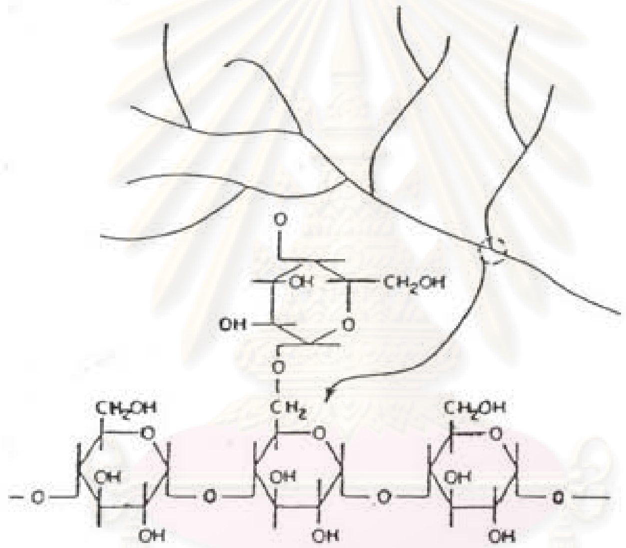

Figure 2.1 Branch structure of amylopectin and chemical configuration at the branch point.

Amylose, a linear polymer, consists of a chain of glucose units connected to each other by 1-4 linkages. The glucose units are in the "*alpha-D-glucopyranose*" form. This means that the glucose is arranged in the form of a six-membered ring in such a way that the hydroxyl group on carbon atom 1 is on the same side of the ring as the hydroxyl group on carbon atom 2.

Starch molecules have a multitude of hydroxyl groups, which impart hydrophilic, or water loving, properties to the starch. In the addition to their affinity for water, these hydroxyl groups also trend to attract each other, forming hydrogen bonds. Since amylose is a linear polymer containing hydroxyl groups, its shows special properties when sufficient interchain hydrogen bonds are formed, the individual amylose molecules are associated to form molecular aggregates with reduced hydration capacity and lower solubility.

Amylopectin has a highly branched structure consisting of short linear amylose chains connected to each other by alpha-1,6-linkages (Figure 2.1). The amylopectin is easily dispersed in water because of the association of the outer chains of the amylopectin (Banks and Greenwood, 1975).

Definitions of Degradation Terms

Several attempts have been made in the recent years to define terms such as "degradation" or "biodegradation" within the context of environmental applications. This has proved to be surprisingly difficult; while several sets of such definitions are available, they tend to be less general than might be expected from a chemical standpoint. It is useful to review these definitions, some reached by a consensus process, proposed during the last few years.

Degradation is a change in the chemical structure of a plastic, involving a deleterious change in properties.

Degradable plastics - the plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which is reasonably accelerated as compared to a control, and which leads to fragmentation or disintegration of the plastics.

Biodegradable plastics - those degradable plastics where primary mechanism of degradation is through the action of microorganisms such as bacteria, fungi algae, yeast.

Photodegradable plastics - those degradable plastics where the primary mechanism of degradation is through the action of sunlight.

Biodegradation - The capability of being chemically transformed by the action of biological enzymes or microorganisms into products which they are capable of further biodegradation.

Photodegradation - The absorption of high energy radiation in the ultraviolet portion of the (light) spectrum, which activates the (plastics) electrons to higher activity and causes oxidation, cleavage and other degradative reactions.

The term "degradation" is used in a fairly broad sense in polymer chemistry to mean chemical changes brought about by factors such as light, heat, water, ultrasound, or oxidative reactions. Most of these are typically related natural environments, but others, such as ultrasound or high electric fields, are man-made environments. The changes in properties of the polymer, which accompany the degradation process may or may not be desirable, depending on the application considered. In most cases, such as the yellowing of poly(vinyl chloride) siding, or the loss of extensibility in rubber products, all resulting from exposure to sunlight, the change is undesirable and tends to reduce the service life of the material.

The term "biodegradation" indicates a degradation process brought about by living organisms. Biodegradation resulting from environmental exposure, however, generally involves the action of microorganisms, usually resulting in a reduction in degree of polymerization and degradation of the polymer to simple organic molecule. An important example of biologically-mediated disintegration of polymers is the biodeterioration of a blend of synthetic nonbiodegradable polymer and a biodegradable additive. The additive itself may or may not be polymeric; phthalate plasticizers in poly(vinyl chloride), blend of poly-(caprolactone) with polyolefins, or blends of starch with polyethylene are examples of such systems. In each case, on exposure to a biotic environment, the biodegradable component is able to biodegrade preferentially, yielding, at least in theory, a void-filled matrix of the nonbiodegradable polymer which is mechanically weak and amenable to deterioration. In these systems the synthetic polymer component is not biodegraded but disintegrated as a result of biological activity.

Under field exposure, environmental disintegration proceeds via several concurrent mechanisms such as photodegradation, biodegradation, hydrolysis, and thermooxidation. However, it is often possible to identify a single predominant mechanism which brings about the disintegration. These are particularly true in the case of enhanced degradable polymers where the polymer, the compound, or both, has been chemically designed to accelerate the disintegration process. Even with compositions such as polyethylene-starch blends containing metal compound pro-oxidants, concurrent photooxidation and biodeterioration proceed at different rates. Under exposure to sunlight, even in a biotic environment, the material will predominantly show enhanced photodegradation, while in the absence of light under similar conditions, enhanced biodeterioration might be obtained. It is clear that the various technical working definitions from the general definition are based on chemical interpretation of the terms (Technical Report, 1992).

Starch-Containing Plastic

One commercial product based on this material is Ecostar, sold by St. Lawrence Starch Company. For this product, regular corn starch is treated with a silane coupling agent to make it compatible with hydrophobic polymer, and dried to less than 10% of its normal 10-12% water content. It is then mixed with an unsaturated fat or fatty acid autooxidant to form a masterbatch which is added to a commodity polymer such as polyethylene. The polymer can then be processed by conventional methods, including film blowing, blow molding or injection molding, with the limitations that the temperature must be kept below 230^{o}C to avoid decomposition of the starch, and exposure of the masterbatch to air must be minimized to avoid water absorption. Direct addition of the starch and autooxidant without the masterbatch step can also be used; as this requires some specialized equipment, it is only practical for large volumes.

Degradation of the polymer proceeds by two mechanisms . While the starch is consumed by microorganisms, the autooxidant interacts with transition metal complexes present in soil or in water to produce peroxides, which attack the synthetic polymer chains. This oxidation is enhanced by weakening of the polymer matrix and increased surface area caused by consumption of the starch component. Final degradation of the fragmented polymer backbone relies on microorganisms. Apart from material composition, the rate of degradation depends on factors such as temperature, pH, moisture level, the presence and types of microorganisms and metal salts, product surface area, and thickness (Hocking, 1992).

Constraints on Decay of Starch-Plastic Blends

1. Limitations to Bacterial Colonization

Amylase and cellulose production is a widespread character among the anaerobic bacteria, and their growth and activity would be expected when aerobic bacteria and fungi fail. Several factors may limit bacterial attack on polymer blends. First, bacteria in soil and water are firmly attached to the solid phase of terrestrial and aquatic ecosystems and facile movement from an attachment site to adjacent film is not readily done. Fungi were major colonizers of plant debris buried in soil and primary agents for decay of above ground cellulosic materials. Since plant debris and plastics are mainly water insoluble, it is likely that the same microbial group to whit, the fungi-should be the primary colonizer of insoluble plastics, whether the plastics are buried in soil or remain above ground (Boddy, 1983). Second, Imam and Gould (1989) found that bacteria they tested did not attach readily to starch-plastic films. Since the attachment of cells to insoluble substrates precedes substrate decay, in most cases the failure to attach would limit potential attack. The results obtained by Imam and Gould are not typical, since numerous investigators have reported rapid bonding of microorganisms ranging from bacteria to algae to plastic surfaces. Third, bacteria tend to be relatively poor colonizers of pores. Hattori (1981) showed that when pore diameters were in the range of 100 to 200 µm, about 35% of all pores were not colonized and few pores were heavily colonized. Internal pore diameters of films have ranged between 5-25 µm. In general, smaller pores should present a greater impediment to bacterial invasion and therefore one would expect a higher percentage of vacant piled in polysaccharide-plastic blends than Hattori observed. kohlmeyer (1980) indicated that aerobic marine bacteria attacked cellophane films mainly from the surface and that cellulose diffusion into the films did not occur readily. He (1969) had previously reported that bacterial attack on wood in the deep sea was seen only on the wood surface even though wood is a naturally porous material. Fourth, most soil bacteria produce exopolysaccharides that would clog pores even when successful invasion occurred. Clogging would greatly reduce the degradation potential of the colonizing organism by limiting diffusion of nutrients enzymes and degradation products within the pore.

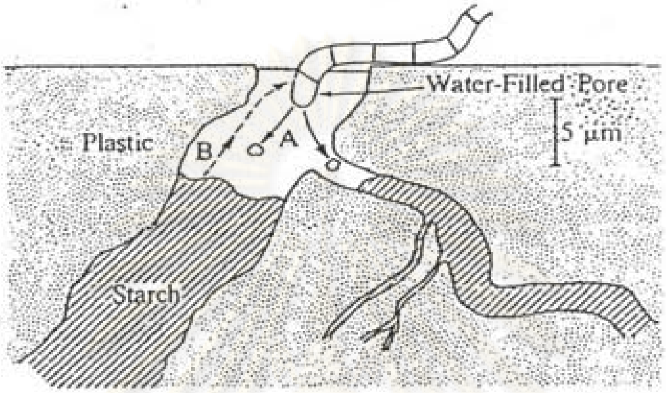

Figure 2.2 Mechanism for microbial decay of microbial decay of starch-plastic blends.
A: Diffusion of amylase to starch
B: Diffusion of digestion products to fungus

2. Principal Mechanism for Starch Degradation

For the reasons stated above deep intrusion of degrading microbes into starch-plastic films is demonstrably and theoretically improbable. Since starch removal does occur when the films are buried in soil, the primary mechanism must be microbial production of amylase in or near a pore, diffusion of the enzyme into pores and diffusion of soluble digestion products back to the surface where they are metabolized (Figure 2.1). This mechanism would be the only choice within the pore diameter is too small to admit a microbial cell (i.e., at diameters < 0.5 µm). An alternative mechanism could be diffusion of a water-soluble starch to the film surface, at which point degradation would occur. None of the materials losses of starch even when soaked in water for extended periods with microbial inhibitors present. Therefore, diffusion of amylase to the substrate rather than diffusion of the substrate to the film surface is the more likely mechanism.

The scheme proposed above requires microbial colonization of the material and excludes degradation by amylases and cellulases that are present in soils (Pancholy and Rice, 1973), but are not newly synthesized or associated with microbial cells. Active polysaccharide hydrolases are found in nearly all soils, but these enzymes are primarily bound to soil organic matter or mineral components; attachment is firm enough to severely limit migration of the enzymes from surrounding soil to the film.

3. <u>Critical Film Properties that Affect Degradation Rate</u>

A common feature to both intrusive and non-intrusive mechanisms of attack is that decay can be initiated only from the surface, a conclusion from which three correlaries can be derived: [1] The decay rate ultimately depends on the percentage of surface area consisting of degradable material; [2] Among materials of the same composition, the number of vulnerable sites per unit area depends on the dimensions of the degradable component, and [3] decay will not occur if the dimensions of the degradable component are so small that neither microbial intrusion nor amylase diffusion into the material can take place.

Dimensions of pore may have a more subtle effect on decay rate depending on component dimensions and production method of the manufactured material. Since flux is dependent on diffusional path area, the smaller pores can be an impediment to movement of solutes from the interior to the surface of the films. Figure 2.2 illustrates two films in which the laminate units are the same thickness, but differ in length.

When the starch is removed from the surface inward, channels are created through which amylase would diffuse inward and digestion products outward (B, D, Figure 2.2). In the degraded material (D), there are a few sites where constrictions occur (arrows), and these sites would control enzyme and product flux through the entire channel. In contrast, the degraded material (B) does not have the severe constrictions in channels. Therefore, material A would likely be more repulsely degraded than material C, even though the percentage composition of A and C is identical. In such cases, the decay rate is not governed by the average pore size, but by the minimum porous than the surface and smaller surface pores would further hinder product release from the film interior. Bottlenecks (arrow, Figure 2.2) may also have a localized effect on concentrations on the "upstream" side of the path, there may be some compensation for the smaller path dimensions and the influence of path restrictions can be reduced. It should be evident from such considerations that predicting the decay rate of these materials requires more than information about the volumetric composition of blends.

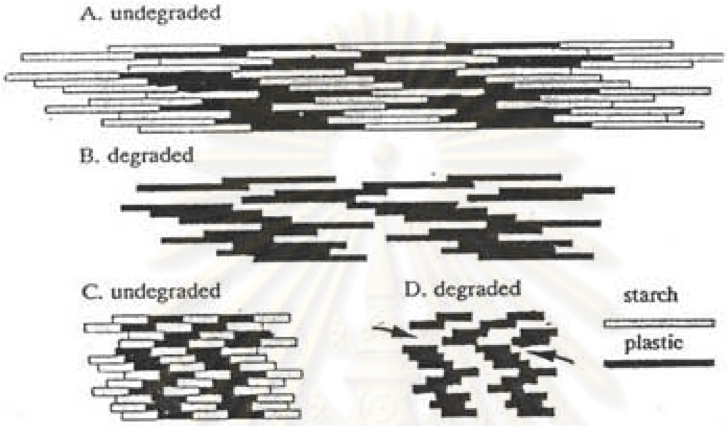

Figure 2.3 Influence of submit size on diffusion paths in starch-plastic laminates containing equal volumes of starch and plastic (not to scale). A and C: intact film; B and D: after starch removal. Arrows indicate on the constrictions that would control diffusion processes.

4. Effect of Plastic Additives on Biodegradability

The physical properties, durability and ease of processing of plastics can be improved by additives and processing aids. There are several potential impacts of these compounds on the utility and degradability of plastic-polysaccharide blends. The majority of commonly used additives are metal salts or low molecular weight alkanes, aromatics and their derivatives. Many of the organics in this group are biodegradable, but are sufficiently toxic to inhibit microbial growth in culture at concentrations in the parts per thousand range. There compounds are weak inhibitors compared to antibiotics that are effective at parts per million concentrations and inhibition of microbial activity is an inadvertent secondary effect, not the primary reason for their inclusion in plastics. If there compounds migrate to the plastic surface during processing or are deliberately applied to the surface (lubricants, for example), concentrations may be high enough to prevent microbial growth on the material and thereby retard degradation of an otherwise biodegradable material. Where inhibitors are deliberately added to minimize marine fouling, the best control is achieved with additives that diffuse to the plastic surface and then dissipate into the surrounding water. An inhibitory surface concentration is maintained by continuos diffusion, but biocontrol is eventually lost upon exhaustion of the inhibitor (Bowden and Taylor, 1980). If one applies this concept to polysaccharide-plastic blends, then one would expect temporary inhibition of decay if the additive migrates, but there should be less effect if the additive has a high affinity for the plastic. Where inhibition does occur, microbial degradation would be delayed, but not prevented. There in virtually no published work in the partitioning of additives between the plastic and polysaccharide components in prepared blends and this area appears to be a critical deficiency in our ability to predict degradability based on material composition. It seems likely that judicious use of additives will be a simple means of controlling the life span of products. For example, starch loss from LDPE-cornstarch films is complete within 120 days of soil contact when starch connectivity exists, but this rate of loss is too rapid when the films are used as agricultural mulches with a desired residence time of 180 to 300 days. In this case, use of an inhibitory but diffusible additive would increase the useful life of the film but would not have a long-term effect on film stability.

Several additives are known microbial inhibitors, cannot readily migrate from the films and avoiding these compounds is recommended. For example, Otey *et al.* reported that carbon black inhibited biodegradation of starch-plastic blends (Otey, Westhoff, Doane, 1980), which indicates that use of carbon black or solvents added with it is not compatible with a biodegradable technology. Sparingly-soluble cadmium and lead salts are likely to inhibit degradation of starch-plastic blends since they have been shown to be solubilized by soil bacteria (Cole, 1979) and to inhibit starch degradation in soil (Michel, 1990).

Application

In order to understand some of the areas of application for degradable plastics, it is useful to examine the current end users for plastics in general, and to follow the way in which they end up in the waste stream. This helps to illustrate the most suitable end uses for degradable plastics and areas in which they could be used to substitute for conventional plastics.

The current world wide demand for plastics is in excess of 100 million tones per year. The rapid growth in consumption of plastics in recent years has led to concerns from consumers, environmentalists and indeed the plastics industry regarding the effective management of post-consumer waste and the greater use of (and dependence on) fossil fuels.

The emphasis now is on minimizing the unnecessary use of plastics and on developing methods of recovery and recycling. Alongside and compatible with these, much work is being carried out into different methods of reducing the environmental impact of plastics. One way of doing this could be by the use of degradable plastics.

1. Agricultural and Horticultural Applications

Plastic mulch films improve the rate of growth of plants by conserving moisture, reducing weed infestation and increasing soil temperatures. Thin black polyethylene film has been used in this application for many years but this can cause damage to certain crops because of excessive heat build-up. This can lead to restricted root growth and scorching at the stem and on outer leaves. Consequently, there is a need for spray irrigation using these types of film.

A further problem is the high cost of disposal of the plastic after use. Mulch films are generally used over wide areas, making collection difficult and expensive, and the recovered film requires cleaning if it is to be recycled. The result is that the recycling of agricultural plastics of this type is generally not visible, on both economic and technical grounds.

These problems led to the development of degradable mulch films, which offer significant advantages: there are no additional costs for recovery and disposal of the plastic, the temperature under the surface of such products is 6-7 °C lower than that of black PE film resulting in improved root development, and water requirements are reduced, i.e. there is no need for spray irrigation, an important point in areas of limited water supply.

The plastic photodegrade, resulting in the formation of small fragments of polymer film which are ploughed into the soil after harvest of the crop. It is claimed that these small fragments are then subject to biodegradation and this have no effect on subsequent crops.

Successful mulch films must be stable in storage, must have different exposure times for different crops (i.e. be timed to degrade when the crop has grown), must not affect soil preparation for the next crop, and must not release any harmful substances during their use.

2. Packing

The packing industry represents a potentially large area of application for degradable plastics, with the growing concerns over litter and solid waste. The majority of plastics packaging waste is not easy to recover, particularly in the case of food and drink packaging, where the material is often contaminated. Although there are a number of schemes in place for the recovery of plastic bottles, it is often uneconomic to collect food packaging waste, making this a prime target area for degradable packaging. Almost any instance where plastics are used in a disposable manner is being considered as a market for degradable plastics. Examples include retail and refuse bags, PS foam, bottles, blister, pack for tablets, razor blades, etc.

One of the main packaging applications for degradable plastics, particularly starch-based degradable polyethylene, is the production of refuse bags used for the management of compostable waste. In Europe alone about 65 million tones per year of household and garden waste could be treated in this way, making a significant contribution to waste management. However, the marginally higher cost of these and similar types of one-trip packaging, together with the slow development of composting schemes, has meant that they have achieved only limited success up to now

A resent study has shown that around 75% of litter on beaches along the 45,000 km Mediterranean coastline comprises plastics with metals, glass and wood accounting for the rest. The increased use of degradable plastics in packaging applications could help prevent some of these problems and forthcoming legislation on disposal of waste at sea will possibly encourage the development of their use in other marine applications such as ropes, fishing nets and lines and buoys (Technical Report, 1992).

Literature Review

Goheen, S.M. and Wool, R.P. (1991) investigated the degradation of LLDPE-corn starch blended in soil over a period of 8 months. Both weight loss and FTIR data show that high-percentage starch binary blends (52 and 67%) exhibit an extensive removal of the starch during the first 40 days, whereas lower percentage starch blend (< 30% by mass) exhibit a slower and probably incomplete removal of starch weight loss data support spectroscopic data showing similar gross features. The matrixes show evidence of swelling, an increase in surface area, and removal of low molecular weight components. The content of organic matter in the soil appears to make little difference in the degradation of the blends after 1 month.

Chiquet, A. and Glane, V. (1990) studied thermoplastic α- olefins, selected from the group consisting of PE and ethylene copolymers, contains a biodegradable substance having one or several double bonds from fatty acids and derivatives, a transition metal compound of $FeOH(sterate)_2$ as an iron compound which is soluble in the composition as an initiator and promoter of further degradation. The change in tensile strength and elongation at break at different temperatures, under composting conditions and under UV condition which was measured for each composition demonstrated a markedly improved degradation capacity when exposing to the mentioned condition promoting decomposition.

Sung, W. and Nikolov, L.Z. (1992) investigated the degradation of two different starch-PE films containing about 5% (wt %) corn starch. The major difference between the two films was the presence/absence of a prooxidant additive in the formulation. The accelerated starch biodegradation of the film examined by using a buffered *Bacillus sp.*α amylase solution whereas oxidative degradation of the PE was hastened by incubating the starch-PE film in a forced-air oven at 70^{o}C. The progress of degradation was followed by monitoring physical and chemical changes of the sample by using tensile and elongation testing, high-temperature GPC, FTIR and SEM. The result showed that the presence of a prooxidant additive was essential of initiating the PE degradation, which then led to much higher levels of starch removal from films. The films without a prooxidant containing, lost their physical properties after 20 days of heat treatment. The rapid disintegrating of plastic in the environment was probably due to synergistic actions of oxidative degradation of the polymer and starch biodegradation enhanced by mechanical force.

Byungtae, L., Anthony, L.P., Alfred, F., and Theodore, B.B. (1991) described a pore culture system for evaluating the biodegradable of degradation plastic films containing prooxidant and 6% starch. The lignocellulose degrading micro-organisms used were the *Phanerochaete* and *Streptomyces* species. The biodegradability was evaluated by weight distribution. Chemical degradation of the plastic was initiated by a 70^{o}C heat pretreatment or a 365 nm. UV irradiation pretreatment of the film. The result demonstrated that there is strong evidence to support reduction in plastic integrity caused by microbial; biodegradation of plastics. Furthermore, use of a pure culture system permits the distinction between chemical and biological degradation of these materials by providing the necessary controls. The pure culture demonstrates that lignin-degrading microorganisms can actually degrade the oxidizes PE component as indicated by molecular weight reductions.

Strantz, A.A., and Zottola, E.A. (1992) investigated the stability of corn starch-containing polyethylene films to starch-degrading enzymes. Processes have been developed to incorporate corn starch into plastics with the intent of increasing the rate of plastic biodegradation. The effect of starch-degrading enzymes on food-grade PE film that contained 6% corn starch (CSPE) was examined. Controled polyethylene film with no added starch, CSPE, and laboratory grade soluble starch were treated with α-amylase or amyloglucosidase. Samples are removed periodically and were subjected to the Nelwon-Somogyi method for the determination of reducing sugar content. Treatment with α-amylase and β-amylase released over 30% of the soluble starch as glucose, while less than 1% of the starch in CSPE was released. Amyloglucosidase activity released up to 50% of the soluble starch as reducing sugar. However, less than 4% of the CSPE starch was liberated. Image analysis of iodine-stained films showed that enzymatic treatment did not remove surface granules. These results indicated that breakdown of CSPE by starch degrading enzymes was limited.

Vincent, T. and Boen, L. (1993) examined the film of polyethylene and starch-polyethylene composite in sea water on flow-through seatables in the laboratory. The deterioration of these films following exposure was measured by determining changes in tensile properties, weight loss, starch loss, and carbonyl content of the sheet plastic films. Differences in the rate of deterioration of starch-polyethylene composite and controlled LDPE and LLDPE films were measured for films weathered in sea water and the strawline of a marsh. However, the composite starch-polyethylene film deteriorated more rapidly in both the strawline of a marsh and submerged in sea water as compares to a corresponding LDPE control film weathered under similar conditions. Deterioration of starch-polyethylene and controlled films in the strawline was rapid and primarily initiated by photodegradation. Sample which was weathered in sea water experienced cool water temperatures, moderate biological activity, and reduced quantities of solar radiation, each factor contributing to the lower observed rate of deterioration.

Roque, L.E, Zivko, L.N., Wei, S., Jay-lin, J., and Robert J. G. (1991) investigated the properties of LLDPE with native and modifies (octenyl succinate) corn starch films. The optimum conditions for continuous compounding were 205^{o}C and 20 rpm resulted in bubble-free cast films containing up to 15% NCS and up to 20% SOS. Physical properties of LLDPE containing starch octenyl succinate (SOS) were compared to the cast films that contained native corn starch (NCS). The addition of either starch to LLDPE decreased the tensile strength and elongation and increased the water absorption. In all cases, SOS/LLDPE cast films, the biodegradation rate of starch for SOS-containing films was lower than the rate observed for NCS-containing films.

Peanasky, J.S., Long, J.M. and Wool, R.P. (1991) investigated the accessibility of starch blends by computer simulation, percolation theory, and acid hydrolysis experiments. The object of this work was to model the bilateral invasion of microbes on polyethylene-starch blends as a function of starch concentration (*p*), and thickness of the material. It was found that computer simulations in three dimensions were in agreement with both percolation theory and the acid digestion experiments. In computer simulation the accessibility is highly dependent on the percolation threshold concentration (p_C) , which is 31.17%. Similarly, the accessibility of starch is highly dependent on an apparent percolation threshold near 30% by volume, an approximately 40% by weight of starch. At $p < p_C$, a small amount of starch is removed from the surfaces only, but at $p > p_C$ connected pathways existing throughout the bulk of the material facilitate large amounts of starch extraction. The sharpness of the transition at p_C increased with the ratio of sample thickness to starch particle size. The results of this work have application to conduction and reacting system where one component is dispersed in a matrix of the other.

Nakatsuka,S., and Andrady, A.L. (1992) examined thermogravimetric analysis as a technique for rapid determination of starch content in LDPE/starch blend films. At least in the range of 0-12% by weight starch, the thermogravimetric weight loss in a selected temperature range correlated well with the starch content that was determined by a conventional extraction/ spectrophotometric technique. The method might be also applicable to moderately deteriorated starch-polyethylene films as well. The method was used to estimate the residual starch content of LDPE/starch films, containing approximately 6.0% starch, exposed under several biotic exposure conditions. Generally 87-88% of the initial starch content was present in the films after different types of environmental exposures. The main limitation of the method is that it did not yield good data for samples exposed for longer periods of time. This might be due to interference by low-molecular weight oxidation products of polyethylene (formed rapidly due to the presence of metal compound catalysts), which volatilized in the temperature range where starch degraded. Biomass infiltrating the polymer matrix may also complicate the analysis in the case of heavily biodegraded samples.

Griffin, G.L.S. (1988) studied a degradable polymer composition comprised a blend of a normally stable, chemically saturated polymer, such as polyethylene, a less stable chemically unsaturated polymer or copolymer, such as a styrene/ butadiene block copolymer, or natural rubber, an antioxidant active over a limited period and a latent prooxidant, such as an organic salt of a transition metal, e.g. cobalt naphthenate. The presence of the antioxidant also with the prooxidant give rise to a period of induction before a sharp loss of physical strength occurs, whereby the period id induction can be exploited as the effective working life of the polymer composition. The polymer composition preferably also includes filler particles of a directly biologically sensitive material such as natural starch, a derivative of natural starch or a natural cellulose product of melting point higher than the processing temperature of the host polymer composition, whereby, the biological breakdown, in natural environments or in the especially biologically active surroundings of compositing urban garbage, of the molecular fragments created by the onset of oxidative scission of the molecular chains of the chemically saturated polymer is accelerated by the presence of said filler particles.