CHAPTER 2

THEORETICAL CONSIDERATION AND
LITERATURE REVIEW

2.1 Gamma Rays

Gamma rays are high-energy photons and as such carry no charge or mass. X-rays and gamma rays are of the same property except for their source. X-rays are the result of an extranuclear process, i.e., the energy released when an electron falls into an unfilled orbital of an atom. Gamma rays are the result of nuclear processes; they are released in the fission process and also in the decay process of radioactive isotopes.

When electromagnetic radiation passes through matter its intensity decrease, primarily as a result of scattering and energy absorption by some of the irradiated molecules. Three major processes are operative.

a) Photoelectric Process

In the photoelectric process, a photon is completely absorbed in a collision with an orbital electron and the electron is ejected from the atom. This can happen whenever the energy of the photon is greater than the binding energy of the electron. The difference between the electron binding energy and the photon energy is carried away by the electron.

The photoelectric effect is greatest for radiation of low energy and for materials of a high atomic number.

b) Compton Process

The Compton process is the result of an elastic collision between a photon and an orbital electron in which part of the photon energy is transferred to the electron. The electron causes further ionization and excitation, while the photon is scattered with reduced energy.

The Compton scattering process is often the principal effect for γ-rays in radiation chemistry: for example, it is the only important process occurring when Co^{60} γ-rays (1.17 and 1.33 MeV) interact with water or other substances of low atomic numbers.

c) Pair Production

If a photon has an energy greater than twice that equivalents to the rest mass of an electron, then the pair-production process can occur. Since the rest mass of an electron is 0.51 MeV, the minimum energy for a pair production is 1.02 MeV. In this process, the photon interacts with a nucleus and disappears with the production of two particles, a positive and a negative electron . The energy of photon in excess of the minimum 1.02 MeV appears primarily as kinetic energy of the pair of particles.

The positron so formed usually is annihilated by an electron. When this occurs, two annihilation protons occur, traveling in opposite directions and carrying one-half of the energy, that is 1.02/2 MeV, or 0.51 MeV [2].

2.2 Starch

Starch is a reserve carbohydrate found principally in the seeds, roots, tubers, fruits, and sometimes in the pith of plants. It occurs as very small water-insoluble granules, usually associated with proteins, fats, and inorganic salts. The granules vary in shape and size ranging from about 1 to 1000 μm in diameter depending on the sources. For cassava starch, the size of the granules ranges from 5 to 35 μm. The largest sizes are usually 25 to 35 μm and the smallest ones are 5 to 15 μm.

2.2.1 Chemistry of Starch

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 as an empirical formular of $C_6H_{10}O_5$, placing it in the class of carbohydrate. It is a condensation polymer of glucose. The glucose units in the starch are present as anhydroglucose units (AGU), the linkage between the glucose 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.

2.2.2 Molecular Structure

Most starches consist 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 major factor in determining the properties of that starch.

a) Amylose

The linear polymer consists of a chain of glucose units connected to each other by 1-4 linkages. These glucose units are in the "α-D-glucopyranose" (see Figure 2.1). The amylose polymer fraction of starch will show a distribution of molecular sizes, and the average decree of polymerization (D.P.) will vary with plant variety from which the starch is obtained. Depending upon the type of starch, the D.P. will range from about 250 to 4000 AGU per amylose molecule, corresponding to a molecular weight of approximately 40,000 to 650,000. Most starches such as regular corn, wheat, and potato contain approximately 28% amylose. For cassava starch, the amylose content is about 16.5-22.2%.

Starch molecules have a multitude of hydroxyl groups impart hydrophilic to starch. In addition to their affinity for water, these hydroxyl groups also tend to attract each other, forming hydrogen bonds. The linear amylose molecules can readily align themselves next to each other and form interchain hydrogen bonds through the hydroxyl groups. When sufficient interchain hydrogen bonds are formed, the individual amylose molecules are associated to form molecular aggregates with reduced hydration capacity and hence, lower solubility.
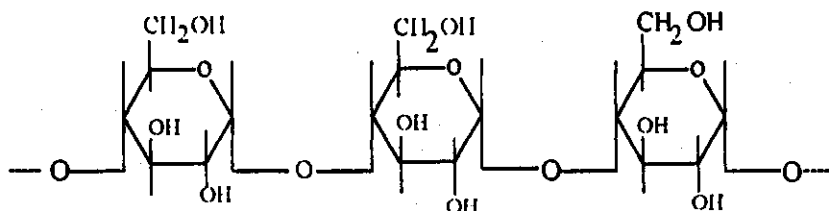
Figure 2.1 Chemical structure of amylose chain

b) Amylopectin

Amylopectin has a highly branched structure consisting of short linear amylose chains with a D.P. ranging from 12 to 50 AGU and an average chain length of about 20 AGU, connected to each other by alpha-1,6-linkage [3].
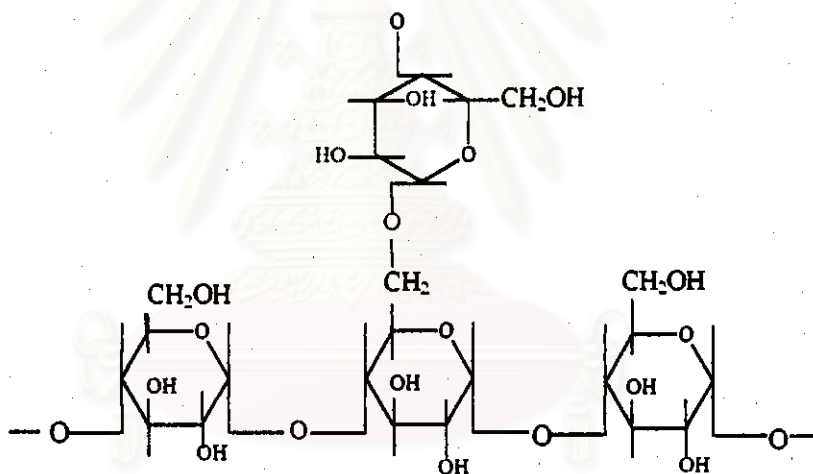

Figure 2.2 Branched structure of amylopectin

2.3 Free Radical Graft Copolymerization of Starch by Radiation Methods

A graft copolymer consists of a polymeric backbone with covalently linked polymeric side chains. In principle, both the backbone and side chains could be homopolymer or copolymers. Graft copolymers are of great interest in the field of absorbency in a number of aspects. Grafting can be carried out in such a way that the properties of the side chain can be added to those of the substrate polymer without greatly changing the latter.

In free radical-initiated graft copolymerization, a free radical produced on starch reacts with a monomer to form a grafted copolymer. One of the free radical initiation methods of starch is irradiation with ionizing radiation.

2.3.1 The Different Methods of Radiation Grafting

As indicated above, the irradiation of organic macromolecules leads predominantly to the formation of the free radicals. If the irradiation is carried out in air, an effective free radical scavenger, peroxides and hydroperoxides are formed within the polymer. If, however, the polymeric substrate is highly crystalline and in particular if the irradiation is carried out at low temperatures in the complete absence of air, the free radicals can be trapped in the system and can remain "active" for a considerable time. The free radicals, peroxides, and hydroperoxides formed or trapped in polymeric substrates upon irradiation can be used quite conveniently to initiate block and graft copolymerizations. Experimentally then, radiation synthesis of graft and block copolymers can be accomplished by the following methods.
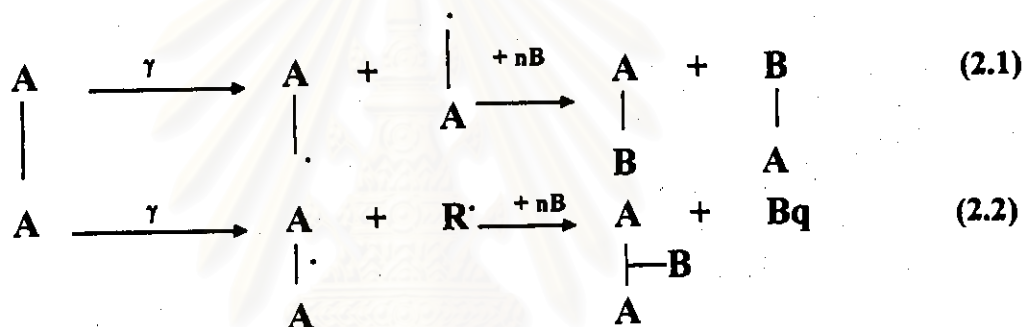
2.3.1.1 The Direct Grafting Method.

In its simplest form, the direct grafting method involves the irradiation of a polymeric substrate in the presence of a monomer and in the absence of oxygen. Graft copolymerization of monomer to the polymer is then initiated through the free radicals generated in the latter.

A number of important factors must be considered, however, before applying the direct radiation method to a given polymer-monomer system. Ionizing radiation as such is unselective. One must therefore consider not only the effect of radiation on the polymeric substrate but also the effect on the monomer, the solvent, or any other substrate present in the system.

The radiation sensitivity of a substrate is measured in terms of its G_r value or free radical yield which is the number of free radicals formed per 100 eV energy absorbed per gram. The highest grafting yields will occur for polymer-monomer combinations in which the free radical yield of the polymer is much greater than for the monomer. It also follows that the grafting yield will increase with the lower monomer

concentration. The free radical yield of a monomer can be directly derived from the kinetics of its radiation polymerization and from experiments with free radical scavengers.

Together with the radiation sensitivity of the polymer-monomer combination, one must also consider the effect of the radiation on the actual polymeric substrate. In general, polymers either degrade or crosslink under irradiation. If the polymer degrades, then irradiation in the presence of a monomer will lead predominantly to block-type copolymers (eq. 2.1); if the polymer crosslinks, graft structures will result (eq. 2.2). This may be represented schematically as follows:

$$
\begin{array}{c}
A \\
| \\
A
\end{array}
\xrightarrow{\ \gamma\ }
\begin{array}{c}
A \\
| \\
\overset{\cdot}{|}
\end{array}
+
\begin{array}{c}
| \\
A
\end{array}
\xrightarrow[\ A\ ]{\ +nB\ }
\begin{array}{c}
A \\
| \\
B
\end{array}
+
\begin{array}{c}
B \\
| \\
A
\end{array}
\qquad (2.1)
$$

$$
A \xrightarrow{\ \gamma\ }
\begin{array}{c}
A \\
| \cdot \\
A
\end{array}
+ \ R^{\cdot}
\xrightarrow{\ +nB\ }
\begin{array}{c}
A \\
\vdash\!\!-B \\
A
\end{array}
+ \ Bq
\qquad (2.2)
$$

Here A------ . and A-------A represent polymeric free radicals derived from A_p, $R^{\cdot}$ represents a low molecular weight radical or hydrogen atom and B represents a monomer atom.

The dose and dose-rate of irradiation are important factors in any radiation grafting system. In the direct method, the total dose determines the number of grafting sites while the dose-rate determines the length of the grafted branches. The length of the branches is also controlled by other factors, such as the presence of chain transfer agent, the concentration of monomers, the reaction temperature, the viscosity of the reacting medium, diffusion phenomenon, etc.

Diffusion of the monomer into the polymer plays an important role in the direct radiation method as it is by this means that the monomer reaches the active sites within the polymer. It would be expected that the rate of graft polymerization

would be directly proportional to the radiation dose-rate. In some cases, however, the diffusion of monomer can not satisfy the increased rate of initiation within the polymer.

It will be appreciated that in the direct radiation method a certain amount of homopolymer will always be formed, because of the effect of radiation on the monomer and as a normal consequence of the grafting reaction (eq. 2.2). Contamination of the grafted product with homopolymer can be quite inconvenient, as most polymers are incompatible and due to a segregative tendency, the presence of physically mixed polymer impurity can yield a product with poor physical, optical, and electrical properties. The direct radiation method is, on the other hand, by far the most efficient technique since it involves rapid utilization of the accessible backbone polymer radicals as soon as they are formed.

2.3.1.2 Preirradiation Method.

In principle, the preirradiation method should not yield homopolymer because the monomer is never directly exposed to radiation. In some cases, however, there is evidenced that irradiation in air leads to the formation of hydroperoxides on the polymer backbone. The hydroperoxides on heating, decompose to give hydroxyl radicals which can initiate the homopolymerization of the added monomer.

2.3.2 Kinetic Features of Radiation Grafting.

Kinetic feature of the direct radiation technique, if one assumes that the graft polymerization occurs by a radical chain process then the overall reaction scheme can be divided into three main steps: initiation, propagation, and termination [4]. This may be represented as follows:
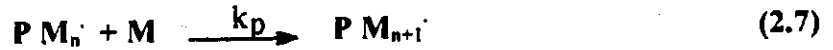
Initiation:

$$P \xrightarrow{k} P \cdot \qquad (2.3)$$

$$r = k I \qquad (2.4)$$

Propagation of initial radical:

$$P \cdot + M \xrightarrow{k_i} P M \cdot \qquad (2.5)$$

$$r_i = k_i [P^.] [M] \tag{2.6}$$

Propagation:

$$P M_n^. + M \xrightarrow{k_p} P M_{n+1}^. \tag{2.7}$$

$$r_p = k_p [P M_n^.] [M] \tag{2.8}$$

Termination by two growing radicals:

$$P M_m^. + P M_n^. \xrightarrow{k_t} P M_{m+n} \text{ or } P M_{m+1} + P M_{n-1} \tag{2.9}$$
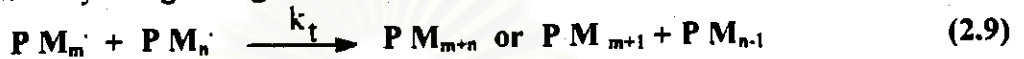
$$r_t = 2k_t [P M^.]^2 \tag{2.10}$$

If one makes the normal assumption that the length of the polymer chains is long, then reaction 2.5 can be neglected with respect to reaction 2.7, and one obtains the following relation for the rate of graft polymerization:

$$r_p = k_p [PM_n^.] [M] \tag{2.11}$$

Introducing the conventional steady-state assumption that the rate of change in the radical concentration is small compared to its rates of formation and disappearance, then:

$$k_i [P^.] [M] = 2k_t [P M_n^.]^2 \tag{2.12}$$

i.e.,

$$r_i = 2k_t [P M_n^.]^2 \tag{2.13}$$

then

$$[P M_n^.] = (r_i / 2k_t)^{1/2} \tag{2.14}$$

On combining eqs. 2.11 and 2.14 one obtains the rate of graft polymerization as the following:

$$r_p = k_p [M] (r_i / 2k_t)^{1/2} \tag{2.15}$$

where

I = intensity of radiation.

P = backbone polymer.

$P^.$ = polymer radical.

$P M_{m+1}$, $P M_{n-1}$ or $P M_{m+n}$ = graft copolymer.

M = grafting monomer

r = rate of initiation of polymer radicals.

r_i = rate of initiation of graft reaction.

r_p , r_t = rate of propagation and termination, respectively.

k = rate constant for initiation of polymer radicals.

k_i = rate constant for initiation of graft reaction.

k_p , k_t = propagation and termination rate constant, respectively.

2.3.3 Radiation-Induced Crosslinking and Degradation

The high energy ionizing radiation interacts with materials to produce ionization and excitation. The resulting species can further react to give free radicals. Polymer radicals are formed by the irradiation of polymer.

$$P^* \longrightarrow R_1{}^{\cdot} + R_2{}^{\cdot} \quad \text{(main chain scission)} \qquad (2.16)$$
$$R_3{}^{\cdot} + H^{\cdot} \quad \text{(side chain scission)} \qquad (2.17)$$

The reaction (2.16) leads to degradation of polymer. The polymer radicals thus formed are so active that react with each other or monomers.

$$R_3{}^{\cdot} + R_3{}^{\cdot} \longrightarrow R\text{-}R \qquad (2.18)$$
$$R_3{}^{\cdot} + M \longrightarrow RM^{\cdot} \qquad (2.19)$$

The reaction (2.18) is known as crosslinking of polymer by recombination of the polymer radicals. The reaction (2.19) is the initiation step of graft polymerization, which occurs when monomers interact with polymer radicals. Monomer radicals can initiate polymerization when monomer is irradiated.

$$M \longrightarrow M^{\cdot} \qquad (2.20)$$
$$M^{\cdot} + nM \longrightarrow M_{n+1}{}^{\cdot} \text{ (polymer)} \qquad (2.21)$$

When exposed to very high dose of radiation all polymers loose their valuable properties and either harden and become brittle, or else soften and are eventually converted into sticky liquids. The chemical changes underlying these

physical modifications are limited to a few basic reactions: gas evolution, changes in unsaturation, crosslinking and degradation. In most polymers crosslinking and degradation occur simultaneously, two different types of behavior are depending on whether the rate of crosslinking is greater than that the rate of main chain scission or vise versa. Many polymers which crosslink under irradiation in vacuo will degrade when irradiated in oxygen (oxidative degradation). The behavior observed depends on two factors, the type of polymer and the presence of oxygen. Thus, for irradiation in vacuo it is possible to divide polymers into two groups, crosslinking polymer such as polyethylene, poly(vinyl chloride), polystyrene, polyacrylates, polyacrylamide, poly (vinyl alcohol), and natural rubber and degradation polymers such as polytetrafluoroethylene, polybutylene, polymethacrylates, poly(vinylidene chloride), polymethacrylamide and cellars.

Crosslinking is the commercially most important area of radiation chemistry of polymers. The advantages of radiation crosslinking are as follows: rapid, easiness of control and cost effective. The main chemical issue related to the radiation crosslinking is that of enhancing the crosslinking and reducing the oxidative degradation during irradiation. Usually polyfunctional monomers such 1,6-hexanediol diacrylate and trimethylolpropane triacrylate are used to enhance the crosslinking. For the reduction of the oxidative degradation the high dose rate irradiation is effective. This is one of reasons to use electron beams for crosslinking.

Irradiation of polytetrafluoroethylene which belongs to the radiation degradation polymers causes such as embrittlement that it can be crushed down to a medium particle size by grinders. The obtained fine powders are widely used as dry lubricants. Thus the degraded polymers by radiation contribute to recycling of used polymers. The radiation degradation technique will be useful for material and chemical recycling.

2.4 Terminology and Definition

Before proceeding to the experimental part, several technical terms need to be clarified for the better understanding of readers.

Percent Add-on

It is refereed to as the weight percent of the synthetic polymer in the graft copolymer and is determined as follows:

$$\%\text{add-on} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of the grafted copolymer}} \qquad (2.22)$$

It is calculated by the acid hydrolysis method. The grafted polymers are separated from the starch backbone by heating the graft copolymer under reflux in dilute acid solution.

Grafting Efficiency

It is a term often used to describe graft polymerization reactions and is defined as the percentage of the total synthetic polymer formed that has been grafted to starch. High grafting efficiencies are desirable since a polymerization of the low grafting efficiency would afford mainly a physical mixture of starch and homopolymer. It can be calculated as follows:

$$\%\text{grafting efficiency} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of homopolymer} + \text{weight of polymer grafted}} \qquad (2.23)$$

Percent Conversion

It is used to describe the degree of converting a monomer, which undergoes graft copolymerization and homopolymerization. It can be evaluated by the following expression:

$$\%\text{conversion} = \frac{\text{weight of polymer formed} \times 100}{\text{weight of monomer charged}} \qquad (2.24)$$

Grafting Ratio

It is a term used to describe a graft copolymerization which is defined as the percentage ratio between the polymer grafted starch and can be calculated by the following expression:

$$\%\text{grafting ratio} = \frac{\text{weight of polymer grafted} \times 100}{\text{weight of starch}} \qquad (2.25)$$

2.5 Polystyrene

Polystyrene is a clear solid with the glass transition temperature (T_g) of about 100°C. Most types of polystyrene used commercially are prepared by the free-radical addition polymerization of styrene monomer, sometimes in the presence of a peroxide initiator. The chains contain an average of 750 to 1300 monomer units, typically about 1000. However, in all cases, the chains vary in length, so that there is a distribution of molecular sizes.

2.5.1 General-purpose grades (GPPS) of polystyrene contain no rubber, but may contain small amounts of a plasticizer or other additives. They have excellent clarity, but relatively poor impact strength. Five groups are operative.

a) High-heat resins have the highest molecular weight, with $\overline{M}w$ of about 300,000 and $\overline{M}n$ of about 130,000. They have better toughness than easy-flow grades, but lower processing rates, because of the high melt viscosity. They are used for various food-packaging applications.

b) Easy-flow resins have the lowest molecular weight ($\overline{M}w$ of about 220,000 and $\overline{M}n$ of about 75,000), and contain 3-4% of added mineral oil to give easy molding. These resins are used for injection molding of thin-walled parts, such as disposable medical ware and dinnerware, toys, and packaging.

c) Medium-flow resins contain less mineral oil (1-2%) and have intermediate property. They are used for injection-mold tumblers, medical wares, and toys.

d) Food-contact specialty resins are almost identical to high-heat resins, except for somewhat lower residual volatile materials, typically less than 400 parts per million, in order to reduce effects on taste and odor.

e) Fast-cycle resins contain no mineral oil, but have a controlled molecular weight and molecular weight distribution to give a good balance between melt flow rate and toughness, while maintaining a relatively high heat-deflection temperature.

2.5.2 Rubber-modified grades contain about 4-14% of rubber, medium-impact grades exhibit Izod impact strengths of 32 to 75 J/m. High-impact grades (sometimes called HIPS) have impact strengths of 80 to 128 J/m. Superimpact polystyrene have impact strengths of 133 to 320 J/m [5].

2.6 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 [6].

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

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 sunlight.

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

Photodegradation-The absorption of high energy radiation in the ultraviolet portion of the electromagnetic 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 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 molecules. An important example of biologically-mediated disintegration of polymer 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 polycaprolactone 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 polyethylene-starch blends containing metal compound pro-oxidant, 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.

2.7 Starch-Containing Plastic

One commercial product based on starch containing plastics 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 water content (10-12%). It is then mixed with 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°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 changed 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.

2.8 Literature Review

Fanta, et al. [7] prepared corn starch-g-polystyrene by a grafting copolymerization reaction of styrene onto starch backbone via gamma rays initiation method. Copolymers were characterized in terms of the percent add-on, the molecular weight, and the molecular distribution. In a typical polymerization, 4 g each of starch and styrene were blended with 1 cm^3 water and 1.5 cm^3 of an organic solvent. They found that, the highest %add-on (43%) and the highest conversion of styrene to grafted polymer (76%) were obtained when the organic solvent was omitted and water alone was used. When water was also omitted, polymerization of styrene was negligible.

Henderson, and Rudin [8] prepared starch-g-polystyrene by simutaneous ^{60}Co irradiation of mixtures of wheat starch and styrene at room temperature. They found that, the extent of conversion of monomer to polymer was increased drastically with increasing water content up to a level of about 26 wt% on starch. Methanol had approximately the same effect as water at equivalent concentrations but ethanol was clearly less effective as a promoter of homopolymerization and graft copolymerization. Drying the starch reduced the conversion to polymer with all promoters but caused the greatest deterioration in the ability of ethanol to promote polymerization. Water and methanol are better radical scavengers and polymerization promoters because they can better disrupt hydrogen bonds and permeate the starch structure.

Henderson, and Rudin [9] prepared wheat starch-g-polystyrene and starch-g-poly (methyl acrylate) by gamma radiation and chemical initiation, respectively. The respective percent add-on values were 46 and 45; 68% of the polystyrene formed was grafted to starch, and the corresponding proportion of poly(methyl acrylate) was 41%. The molecular weight distributions of the homopolymer and graft portions were

characterized, and extrusion conditions were established for production of ribbon samples of starch-g-PS and starch-g-PMA. Both copolymer types were considerably weakened by soaking in water, and this effect was more immediate and drastic for starch-g-poly(methyl acrylate). Both graft copolymers regained their original tensile strengths on drying, but the poly(methyl acrylate) specimens did not recover their original unswollen dimensions and retained high breaking elongation characteristic of soaked specimens.

Garnett, and Jankiewicz [10] reported that the inclusion of mineral acid in a solution of styrene in methanol subjected to ^{60}Co γ- irradiation markedly enhanced the yield of monomer grafted to cellulose. It is found that the presence of acid in a monomer solution such as styrene in 1,4-dioxan leads to an enhancement in the homopolymer yield of styrene, and, for the first time, it has been shown that acid also effects the number-average molecular weight ($\overline{M}n$) of this homopolymer. One explanation for the observed effects due to acid inclusion in the G(H) yields are enhanced, leading ultimately to much higher radical concentrations in the reaction solution. Sources of this enhancement may include the interaction between added protons and solvated electrons or the overcoming of the effect of radical scavenging impurities in solvents. Higher radical concentrations must directly increase the rate of initiation and of termination of polymerization.

Ang, et al. [11] reported that additives can increase the yield in the radiation grafting of monomers to polymers. The use of polyfunctional monomers as additives (≈ 1% v/v) are shown to enhance significantly the copolymerization yields of styrene in methanol to films of polyethylene and polypropylene under certain radiation conditions. It is found that the presence of polyfunctional monomers in the grafting solution does not lead to a uniform enhancement in grafting. Instead, increased yields of copolymer are only observed at specific monomer concentrations.

Ang, et al. [12] found that sulfuric acid (0.2 M) and divinylbenzene (DVB) give the expected enhancement in grafting, especially at the Trommsdorff peak, when each additive is included separately in the grafting solution. Significantly, when acid and DVB are combined as additives in the same copolymerization solution, a synergistic

effect is observed such that the grafting yield is significantly increased above the values obtained for each additive individually. Moreover, this enhancement is observed at all monomer concentrations studied and is particularly evident at the Trommsdorff peak which occurs at 50% styrene in methanol.

Garnett, Jankiewicz, and Long [13] reported the original mechanism of the acid effect, the enhancement due to this additive was attributed essentially to two predominant factors, namely the radiolytic yield of hydrogen atoms and also the extent to which grafting polystyrene was solubilized in the bulk solution. In the former mechanism, it was proposed that inclusion of acid resulted in higher $G(H^{\cdot})$ yields from thermalized electron capture reactions, leading to the creation of more grafting sites by hydrogen atom abstraction reactions. Although this proton model is consistent with the known increase in yield of hydrogen atoms from irradiated methanol upon the addition of acid. A new group of additives, namely certain inorganic salts, have been found to enhance radiation grafting yields in a manner similar to that previously observed with mineral acids.

Garnett, Jankiewicz, and Long [14] found that lithium perchlorate in the monomer solution leads to enhancement in photografting at all styrene concentrations studied. Lithium perchlorate is also more efficient than acid in increasing copolymerization yields under the experimental conditions used. The number-average molecular weight ($\overline{Mn}$) of the copolymers from both acid and lithium perchlorate samples are similar and consistently higher than for the copolymers without additive. When low-density polyethylene film is used instead of cellulose as backbone polymer, an analogous lithium perchlorate enhanced grafting of styrene in methanol is observed. At the lower styrene concentrations, lithium perchlorate is more efficient than acid as an additive in increasing grafting yields with polyethylene, a result consistent with the previous cellulose data.

Dworjanyn, Garnett, and Jankiewicz [15] reported the scope of UV and ionizing radiation grafting techniques for the immobilization of bioactive materials. This involves copolymerization of a monomer containing an appropriate functional group to a backbone polymer, then attachment of the reagent by subsequent chemical reactions.

Novel additives which lower the total radiation dose in grafting were discovered and their value in immobilization processes assessed. A theory for this additive effect in grafting is proposed. Methods for speeding up these radiation processes for immobilization involving sensitized UV and electron beam (EB) curing reactions are considered.

Dworjanyn, and Garnett [16] reported that the enhancement effect of urea in the photografting of styrene in methanol to polypropylene film at 30% monomer concentration. When TMPTA is included in the grafting solution, an extremely large increase in photografting yield is observed at all monomer concentrations studied. The grafting enhancement in particularly effective in the monomer concentrations corresponding to the Trommsdorff peak (30-40%). Urea and TMPTA independently increase photografting yields when present as additives. Inclusion of both additives in the same monomer solution leads to a synergistic effect in grafting analogous to that previously observed with mineral acid and the PMFs.

Garnett, Jankiewicz, and Sangster [17] reported that the enhancement of radiation grafting or photografting yields found in the presence of either acid or neutral salt has been attributed to a "salting out" of monomer from the solution into the grafting region within the polymer substrate. Measurements using a swelling/leaching technique and tritium labelled styrene, have shown that the rate of transfer and the equilibrium distribution are dependent on the polarities of the monomer, substrate and solvent as well as the concentrations of ionic solute and monomer. Molecular weight studied and the effect of other additives confirmed the proposed mechanism. A number of other additives exhibited specific radiolytic chemical effects. These usually reduced the grafting yield.

El-Assy [18] reported that the effect of mineral and organic acids on the radiation-induced graft polymerization of styrene onto low-density polyethylene films. Effects of different solvents and dose rate of irradiation on the grafting yield were also investigated. The influence of irradiation time and monomer concentration in the presence and absence of acid on the initial rate and grafting yield was studied. The dependence of the grafting rate on monomer concentration was found to be of the

order 1.34 (in absence of acid), 0.61(in presence of HCl), and 1.25 (in presence of oxalic acid). Such acid enhancement of the radiation grafting process is of practical importance from an economical point of view.

Peanasky, Long, and Wool [19] reported the accessibility of starch in polyethylene starch blends was investigated by computer simulation, percolation theory, and acid hydrolysis experiments. The object of this work was to model the bilateral invasion of microbes in 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 or 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 increase with the ratio of sample thickness to starch particle size. The result of this work have applications to conduction and reacting systems where one component is dispersed in a matrix of the other.

Goheen, and Wool [20] reported that binary polymer films containing different percentages of corn starch and low-density polyethylene (LDPE) were exposed to soils over a period of 8 months and monitored for starch removal and chemical changes of the matrix using FTIR spectroscopy. A standard curve using the area of the C-O stretch band and an empirical second-degree polynomial to fit the data made it possible to calculate starch concentration over a wide range (0-46% by mass). Starch removal was found to proceed rapidly during the first 40 days and to near completion in very high starch blends (52% and 67% by weight). Starch removal was slower, consisting of mostly surface removal in 29% starch blends. Weight loss data supported spectroscopic data showing similar gross features. Weight loss and spectroscopic data were consistent with percolation theory and suggested that starch removal continues past 240 days. Degradation rates in different soils containing different amounts of organic matter were approximately the same after a period of a few weeks. IR analysis

did not show significant chemical changes in the polyethylene matrix after 240 days. However, the matrix did show evidence of swelling, an increase in surface area, and removal of low molecular weight components.

Johnson, Pometto, and Nikolov [21] reported that the degradation performance of 11 types of commercially produced degradation starch-polyethylene plastic compost bags was evaluated in municipal yard waste compost sites. Chemical and photodegradation properties of each material were evaluated. Materials from St. Lawrence Starch Co. Ltd. And Fully Compounded Plastics photodegraded faster than did materials from Archer Daniels Midland Co., whereas all materials containing transition metals demonstrated rapid thermal oxidative degradation in 70°C-oven (dry) and high-temperature, high-humidity (steam chamber) treatments. Degradation was followed by measuring the change in polyethylene molecular weight distribution via high-temperature gel permeation chromatography. Our initial 8-month study indicated that materials recovered from the interior of the compost row demonstrated very little degradation, whereas materials recovered from the exterior degraded well. In the second-year study, however, degradation was observed in several plastic materials recovered from the interior of the compost row by month 5 at the Carroll site and almost every material by month 12 at the Grinnell site. The plastic bags collected from each community followed a similar degradation pattern. To our knowledge, this is the first scientific study demonstrating significant polyethylene degradation by these materials in a compost environment.

Albertsson, Barenstedt, and Karlsson [22] reported that degradation of LDPE films containing a biodegradable starch filler and a prooxidant formulation was performed in aqueous media inoculated with bacteria or fungi at ambient temperatures for 1 year. The samples were characterized with the aim of elucidating the mechanisms that occur during the first stages and that are responsible for initiating the degradation of the LDPE matrix. Two interactive mechanisms were observed: The basal salt medium (water containing trace elements) triggered autoxidation of the prooxidant through decomposition of trace hydroperoxides, which, in synergistic combination with biodegradation of the starch, eventually initiated autoxidation of the LDPE matrix as monitored by chemiluminescence (CL), differential scanning calorimetry (DSC), and

confocal scanning laser microscopy (CSLM). The length of the induction period was dependent on the sample thickness and on the activity of the microbiological system. Up to 48% of the starch was consumed during the first year as revealed by polarized-light microscopy.

Kiatkamjornwong, et al. [23] prepared the degradation polyethylene films containing 0-20% w/w of cassava starch, 0-2% w/w of soya oil and 0-0.1% w/w of ferric stearate. The oxidative degradation of the films was measured by outdoor weathering testing in comparison with indoor testing, and soil burial testing for six months. It was found that the iron stearate starch-PE films lost their physical properties after two months of outdoor exposure. The starch containing PE films by a soil burial test took a longer time to degrade. Biodegradation of the films was determined by measurement of the populations of *Aspergillus niger* and *Penicillium pinophilum* fungi. It showed that the latter had a much higher population, indicating that it effectively promoted biodegradation of the starch-filled PE film in the presence of soya oil and iron stearate.