CHAPTER II
LITERATURE SURVEY

In recent years an increased interest in polymers which are friendly for the environment can be observed. This is due to the fact that the rapid rise of polymer consumption became a real menace for the environment. In order to obtain cost-effective degradable plastics, the introduction of biodegradable polymers such as starch into synthetic polymers is good alternative.

2.1 Compatibility of Polyethylene/Starch Blends

However, the addition of granular starch to PE leads to a reduction in mechanical properties because of totally different polar character of both components. In contrast with hydrophobic PE, starch is a hydrophilic polymer due to the presence of hydroxyl groups in starch molecules. As a result of this immisciblility, the maximum amount of starch in the blends usually should not exceed 10% by weight. The granular starch lead to stress concentration points in the blends that resulting in low tensile strengths and elongations at break (Bikiaris, 1997).

There are several methods to enhance the compatibility between two immiscible polymers, including chemical modification of hydroxyl groups of the starch with a hydrophobic compound, and introduction of reactive functional groups into synthetic polymers. An alternative approach is the use

of a compatibilizer that h as functional groups capable of reacting with both the starch and the PE.

2.1.1 Modification of Starch Hydroxyls

The objective of the modification of starch is to make hydroxyl groups of starch more hydrophobic in order to more compatibilize with polymer matrix.

Bong *et al.* (1997) modified starch by the use of isocyanate as a linkage material between starch hydroxyl and hydrophobic alcohol such as cholresterol and studied the properties of HDPE/modified starch blends. They found that HDPE-blown film containning the modified starch showed a higher tensile strength and elongation than correspondent HDPE containning the native starch.

Another modification is esterification of starch hydroxyl with fatty acid chloride. Aburto *et al.* (1996) prepared starch octanoates (OCST) by esterification of native starch with octanoyl chloride then mixed with LDPE at various proportions. The LDPE/OCST blends showed better mechanical properties higher elongation at break higher thermal stability and lower water absorption compared to LDPE/plasticized starch blends.

Thiebaud *et al.* (1997) studied the properties of fatty-acid esters of starch, OCST and dodecanoates (DOST), and their blends with low density polyethylene. OCST and DOST were prepared by esterification of native corn starch with fatty acid chlorides. The ester group was found to act like an interanal plasticizer, with an increase in the a number and size of fatty acyl chain grafted onto starch. LDPE/DOST blends showed better thermal stability and higher elongation, but lower tensile strength and water absorption than LDPE/OCST blends.

Akaranta *et al.* (1997) modified Cassava Mesocarp carbohydrate by esterification with acetic anhydride and used it as fillers in LDPE. They

found that the tensile strength decreased with an increase in the amount of the filler incorporated. The modification of carbohydrate made it hydrophobic and therefore more compatible with LDPE.

2.1.2 Modification of Polyethylene

The modification of synthetic polymer by graft copolymerization of reactive group, anhydride, onto the polymer backbone is another approach to improve interfacial adhesion. Anhydride group such as maleic anhydride can be incorporated quickly into polymer to be graft copolymer. Then the reaction between cyclic anhydride graft copolymer and starch leads to better mechanical properties due to better interfacial adhesion.

Chandra *et al.* (1997) modified LLDPE by producing MA-g-LLDPE and blended it with starch. Maleic anhydride (MA) was grafted onto LLDPE in xylene using dicumyl peroxide (DCP) as an initiator. The degree of grafting in the grafted LLDPE was found to be 1.7 MA per 100 PE. They reported that the torque during mixing of MA-g-LLDPE/starch blends is higher than the torque of LLDPE/starch blends due to possible reaction for reactive blending of MA-g-LLDPE and starch. For the mechanical properties of MA-g-LLDPE in the presence of starch. it was found that an increase in starch leads to an increase in tensile strength and modulus of the blends. It is because of better interfacial adhesion resulting from the reaction between starch and MA-g-LLDPE.

2.1.3 Using Compatibilizers

An alternative approach to bring about more compatibility in starch and synthetic polymer is blending starch with polymers containing polar functional groups that can interact with starch which is called compatibilizer. Compatiblizers, for example, EAA, PE-g-MA and EVA, contain groups

capable of hydrogen bonding with starch hydroxyl and hydrophobic parts to compatibilize with polymer matrix.

Otey *et al.* (1984) studied starch-based PE films using poly (ethylene-*co*-acrylic acid) (EAA) as a compatibilizer and found that the content of starch can be increased without effecting the physical properties of the films. Shogren *et al.* (1992, 1993) who studied on the polymer compatibility of starch-EAA-PE blends reported that starch can interact with EAA via the formation of V-type inclusion complexes and hydrogen bonds. PE appeared to be immiscible with the starch-EAA complex. Blends that still have acceptable mechanical properties could be produced.

Prinos *et al.* (1998) observed that poly(ethylene-*co*-vinyl acetate) (EVA) could be used as a compatibilizer by the formation of V-type starch complexes like in the case of EAA. They found that LDPE/PLST blends exhibit better mechanical properties than the blends with granular starch.The mechanical properties of the blends, especially elongation at break were satisfactory even for blends containing high amounts of starch up to 20-30 %.

Recently, it was found that the blends containing polyethylene-*graft*-maleic anhydride (PE-*g*-MA) as a compatibilizer could retain satisfactory mechanical properties in comparison with uncompatibilized blends, apparently due to the reaction of anhydride groups with hydroxyl groups of starch. As the amount of anhydride groups in the copolymer increase a finer dispersion of PLST in the LDPE matrix and higher mechanical properties of the blends are achieved (Bikiaris, 1998).

2.2   Oxidative Degradation of Polyethylene

The reaction of hydrocarbon compounds with molecular oxygen is called autoxidation because it is normally auto-accelerating (Grassie, 1988).

The oxidation mechanisms were developed by many researchers to explain the thermooxidation. The numerous reactions took place involving the initiation reaction generation free radicals, the propagation reaction yielding oxidation products and the termination reactions.

The polymer may undergo many radical reaction. In PE, chain scission and chain branching occur simultaneously as competitive reaction (Hinsken,1991). The possible form of the reaction sequence is shown in Scheme 2.1.
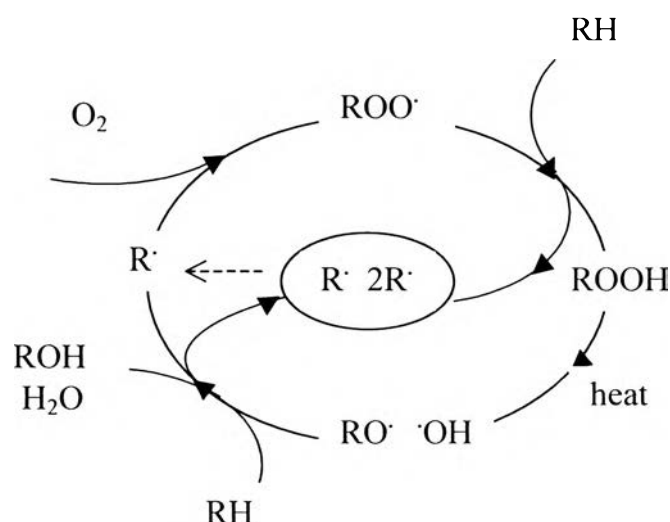
Scheme 2.1 Cycle of polyethylene thermooxidation (Hinsken, 1991).

Guqumus *et al.* (1990) assumed that primary radicals (R˙) were formed through the combination actions of heat and mechanical stress or though catalyst residues. The fixation of an oxygen molecule is generally reaction especially at the excess oxygen condition. Alkyl radicals (R˙) transformed to be peroxy radicals (ROO˙). The next step is rate determination It is involve the breaking of carbon-hydrogen bond which have high activation energy step yielding hydroperoxide.

Hydroperoxide species (ROOH) have been suggested by Lacoste (1991) that they are unstable to both heat exposure and ultraviolet light. They will decompose immediately to form the alkoxy radical (RO·) and hydroxyl radical (·OH). The decomposition of hydroperoxide is efficiently catalyzed by the presence of transition metal ions such as cobalt, iron and manganese as in this reaction.

$$2ROOH \xrightarrow{\text{Me}^{n+/(n+1)+}} ROO· + RO· + H_2O$$
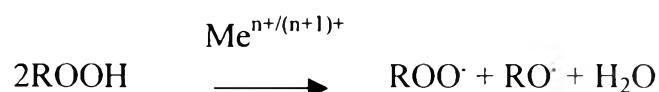
The hydroxyl radicals may further reacted by abstraction of hydrogen radical from polymer backbone. The alkoxy radicals were expected to undergo some β-scission which caused backbone scission and generated carbonyl compounds as in this reaction (Grassie, 1988).

$$\text{---}CH_2CHCH_2\text{---} \xrightarrow{\beta\text{-scission}} \text{---}CH_2CH{=}O + ·CH_2\text{---}$$

Hinsken *et al.* (1991) reported that the addition of vinyl groups (-CH=CH₂) led to an increase in the molecular weigh due to chain branching as in the reaction below.

$$2R· + \text{-}CH{=}CH_2 \longrightarrow \begin{array}{c} R \\ | \\ \text{-}CH\text{-}CH_2 \\ | \\ R \end{array}$$
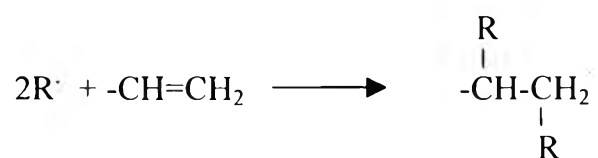
Another possible way to explain crosslinking is the destruction of 2 radicals in chain termination (Guqumus, 1990). Large amounts of radicals formed during thermooxidation increases the possibilities for chain elongation reaction as in this reaction.

$$2R· \longrightarrow R\text{-}R$$
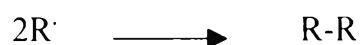
Karlsson *et al.* (1999) detected chemical changes of environmentally degradable LDPE films exposed to thermo-oxidation by using solid phase micro extraction (SPME) techinque and gas chromatography mass spectroscopy (GC-MS) to identify volatile and semivolatile degradation products. They reported that the major degradation products of LDPE were homologous series of carboxylic acids, ketones, hydrocarbons and lactone. Carboxylic acids, benzoic acid and hydrocarbon were the most abundant components that could be identified. 4-oxopentanoic acid, 5-oxohexanoic acid and benzoic acid were identified only in PE containing prooxidant system, SBS and manganese stearate. Because they were degradation product of styrene part in SBS.

The work of Karlsson also reported the morphological changes during thermo-oxidation that LDPE samples containing prooxidant system showed the greatest susceptibility to thermal oxidation since the prooxidant system is responsible for initiation the autooxidation of LDPE matrix. This behavior can be confirmed by a large increase in carbonyl index and the drop in molecular weight determined by size exclusion chromatography (SEC) analysis. Thermolanalysis implied that chain scission was the predominant reaction and preferential scission at tertiary carbon atom occurred which reduced chain branching leading to an increase in the crystalline melting point.

2.3 Degradation of Starch-Base Plastic

The degradation of the blends is also attractive because there is no use if the developed products have high strength but not degradable. Degradation mode depends on application of products but generally are multi-action mode. Photooxidation is important in outdoor product and thermooxidation is

dominant in composting. Many researchers try to explain the behavior of degradation to reach to successful degradable polymer.

Lawton (1996) studied on the effect of starch type on the properties of starch containing PVA films. He found that the starch type did not make a difference in the properties of the films but the films containing high amylose cornstarch was more stable over time than films made with other starches.

Nikolov and Wei (1992) studied the effect of prooxidant additives on oxidative degradation and effect of starch on biodegradation of starch filled PE films. The amount of starch hydrolyzed by α-amylase was directly related to physical properties of the films. The levels of starch degradation ranged between 10 to 50 wt% of initial starch depending on the extent of the PE degradation. The films containing a prooxidant lost their physical properties after 20 days of heat treatment at 70°C but the films without a prooxidant did not change. This work showed that the presence of a prooxidant was essential for initiating the PE degradation leading to much higher levels of starch removal. The disintegration of plastic in the environment probably was due to synergistic actions of oxidative degradation of the PE and starch biodegradation by mechanical forces.

Albertsson *et al.* (1993) studied biodegradation of LDPE-starch composites by using liquid scintillation counting (LSC) of evolved $^{14}CO_2$. LSC not only is measurement of the metabolic activity of biological system but can also be used to detecting degradation of synthetic polymer containing labeled ^{14}C within polymeric chain. They found that induction time before degradation starts reduced by preheating. Preheated starch-filled LDPE biodegrades to about 2.5% during 1 year while the corresponding pure LDPE biodegrade about 0.1%.

Piyush *et al.* (1995) characterized the initial degradation mechanism of starch filled LDPE. They reported that α-amylase acted on the surface starch to cause cracks, holes and erosion which increase the surface area. The

blends become brittle when it underwent thermal oxidation. The prooxidant system, oleate and iron, enhanced the rate of thermal oxidation by 15-20%. An increase in the carbonyl index shown that chain scission reaction was occurred in polymer chain.

The results from Karlsson *et al.* (1997) were appeared in a same trend with previous works. They analyzed the mode of action of cornstarch and a prooxidant system, SBS and manganese sterarate as a system creating a degradable LDPE. The blends were subject to thermooxidation at 65 and 95° C. The degradation rates were discussed based on the molecular weight changes measured by SEC. They reported that LDPE with prooxidant and cornstarch (MB) is more susceptible to thermal degradation than pure LDPE and LDPE with only cornstarch. The samples aged at 95°C shown an immediate reduction in MW.

Krishna-sastry *et al.* (1998) studied on the degradation of PE-starch blend films in accelerated and environmental weathering. Vegetable oil from sunflower was used as a compatibilizer. They found that the PE films containing vegetable oil were more susceptible to the degradative treatments than pure films and the PE films containing starch. It can be explained that vegetable oil not only acted as a plasticizer to improve the film quality but also acted as a prooxidant to accelerate degradation of the film due to unsaturated functionality which is a good trigger for proliferation of free radicals.

The susceptibility of starch-filled polyethylene to oxygen in air and water was analyzed and compared by Hakkarianen *et al.* (1997). They demonstrated that LDPE containing starch and prooxidant was the most susceptible material to degradation in both environments. The degradation at 80°C was faster in air than in water since the prooxidant leached out of during the aging. LDPE-starch was more stable than pure LDPE towards thermal aging in water. The lower oxygen concentration in water increased the

probability for molecular enlargement reactions compared to the degradation in air.

The sturcture and properties of degradable LDPE-plasticized starch blends were studied by Zuchowska *et al.* (1998). Potato starch was plasticized by glycerol and blended with LDPE. They concluded that in the initial stage of degradation with microorganisms the most important factor is the continuity of starch phase. An increase in starch content improved the accessibility of the polymer matrix. A susceptibility to degradation during soil or fungus aging not only of the starch phase but also the polymer phase was observed.

Panayiotou *et al.* (1997) examined the effect of EAA and plasticized starch (PLST) upon the thermooxidative degradation of LDPE. This measurement indicated that EAA added as a compatibilizer accelerated LDPE thermooxidation whereas PLST inhibited it. The prooxidative behavior of EAA must be the ease of hydrogen abstraction during oxidation. On the other hand. the antioxidant effect is due to the presence of various leftovers.

They expanded their work to examined the effect of methyl methacrylate butadiene styrene copolymer (MBS) on the thermooxidation of LDPE/PLST blends. EAA was used as a compatibilizer and cobalt stearate as a prooxidant. It was found that the oxidation rate increased with increasing amount of MBS in the blends due to the presence of unsaturated part of butadiene in MBS which unstable during incubation. The blends with higher amount of PLST shown a higher rate of biodegradation by burial in soil.