# CHAPTER II

# LITERATURE SURVEY

Inert synthetic polymers can have enhanced degradability by introducing prodegradant additives into the matrix. These additives provide the plastic materials with different types of potential degradation mechanisms that can be triggered upon environmental exposure.

Harnden *et al.* (1990) patented an environmentally degradable polyethylene. This polymeric composition could be degraded by either thermal oxidation, photo-oxidation or a combination thereof. The composition comprised a blend of polyethylene, e.g. low density polyethylene, and 0.05 - 0.5 weight percent of cerium (III) stearate which promotes thermal oxidation and photo-oxidation. This composition is especially useful for degradable food wrap, packaging material and agricultural mulch film.

Weiland and David (1994) studied the thermal oxidation of polyethylene film containing transition metal catalysts (cobalt acetylacetonate, cobalt stearate and manganese stearate) in three different types of composts. It was shown that the degradation was very slow in composts compared to the degradation of the same films placed in an oven at the same temperature (60 - 70°C). There are two main reasons for this: the low partial pressure of $O_2$ in the wet compost and the leaching out (or deactivation without leaching out) of the catalyst.

The use of starch as a filler in plastics has been of interest for the past 30 years, but especially since the mid-1970s when polymer starch blends with acceptable physical properties were started to be developed. Two major approaches to the addition of starch to polyethylene (PE) have emerged. The first one uses gelatinized starch as a biodegradable filler in the compositions. The second approach utilizes native or modified granular starch as fillers in formulated degradable products.

## 2.1    The Use of Gelatinized Starch as a Filler

Starch granules that have been ruptured in aqueous media such as water, glycerol, and poly(ethylene-co-vinyl alcohol) are said to be gelatinized.

Otey *et al.* (1979) developed a process for incorporating gelatinized starch into a copolymer of ethylene and acrylic acid (EAA) or a combination of EAA and polyethylene. Addition of ammonia increased the compatibility between the starch and EAA and therefore improved the properties of the film. Films produced by this technology yielded a uniform distribution of starch particles throughout the polymer matrix. These films typically contain 30 - 60% starch by weight. The degree of transparency, resistance to UV radiation, flexibility and tensile strength all decreased with an increase in the proportion of starch used.

## 2.2    The Use of Granular Starch as a Filler

Griffin has invented formulations based on granular starch. In his early patents (1977), he developed a process for introducing biodegradability property into synthetic commodity polymers by adding granular corn starch.

Low-density polyethylene (LDPE) was known to be hydrophobic. In order to make starch compatible with LDPE, modification of either the starch or the polymer was necessary. Corn starch was treated with a silane coupling agent to provide the necessary compatibility with hydrocarbon polymers. The presence of starch did not have any detrimental effect on the quality of the material but produced a textured product with enhanced printing properties. The degradation of LDPE film was accelerated by the absorption of unsaturated lipids such as corn oil.

Ecostar International (formerly a part of St. Lawrence Co. Ltd.) produces masterbatches containing a modified granular starch and an unsaturated fatty acid or a fatty acid derivative (i.e. vegetable oils) as "autooxidant" to promote oxidative degradation of the polyolefin according to the early patents of Griffin.

In his later patents (1988,1991,1993) Griffin also invented a system that comprised a blend of a normally stable and chemically saturated polymer (such as polyethylene), a less stable and chemically unsaturated polymer or copolymer (such as a styrene/butadiene block copolymer, or natural rubber) and an organic salt of a transition metal (such as cobalt naphthenate) to give materials with improved physical properties and which can be degraded by a variety of mechanisms such as photo-degradation and biodegradation.

Archer Daniels Midland Co. (ADM) produces a masterbatch containing native granular starch, an unsaturated polymer as "autooxidant", and trace amounts of a transition metal (Fe, Cu, Mn) salt to catalyze the oxidative degradation of the polyolefin according to later patents by Griffin.

Gonsalves *et al.* (1989) conducted research on PE/starch composites blended in a Haake Buchler System 40 torque rheometer at 190°C. A metal catalyst and an autooxidant were included to promote chemical degradation. These blends were then compression molded into sheets after which tensile bars were cut from the sheets and placed in a marine environment for 3

months. The starch/PE samples with 15% starch loading showed a 2% increase in weight after being exposed to the marine environment. At the same time, the tensile strength decreased by 6%. From GPC data, the molecular weight of the blend had lowered and there was a decrease in the $M_w/M_n$ ratio. The surface of these samples revealed a migration of large starch granules onto the surface. The DSC peak exotherm moved to a lower temperature, probably due to a lowering of the molecular weight and/or to change in crystallinity.

Iannotti *et al.* (1990) studied the effect of prooxidant on starch removal from starch-PE blends that contained from 3 to 6 wt% starch using Fourier Transform Infrared (FTIR) Spectroscopy. The plastic films exposed to soil, refuse, and anaerobic environment lost between 25 and 30 wt% of their original starch content after 24 weeks of exposure and the film samples containing a prooxidant lost significantly more starch than those containing only starch.

Albertsson *et al.* (1991) studied the degradation of LDPE films containing a biodegradable starch filler, a prooxidant formulation (SBS and manganese stearate) and a thermal stabilizer. Thermal ageing was carried out in an air environment at 100°C and 60°C and UV ageing in a weatherometer. The LDPE containing corn starch as the sole additive was found not to be degraded, suggesting that the prooxidant formulation was responsible for the observed degradation.

Sung and Nikolov (1992) studied the degradation of starch-polyethylene films containing prooxidant additives in the formulations. The accelerated starch biodegradation of the PE film was hastened by including a buffered *bacillus* sp. $\alpha$-amylase solution whereas oxidative degradation of LDPE was hastened by incubating the starch-LDPE films in a forced-air oven at 70°C. The workers found that the films without a prooxidant additive did not change significantly during the heat treatment. The increased starch

hydrolysis in starch-PE films have been attributed to the oxidative degradation of PE. The levels of starch degradation ranged between 10 and 50 wt% of initial starch, depending on the extent of polyethylene degradation.

Ndon *et al.* (1992) tested four commercially produced starch-based polyethylene materials containing prooxidants under both aerobic and anaerobic conditions to measure their biodegradability. It was found that degradation rates and total percentage of carbon conversion were higher under aerobic tests as compared to tests under anaerobic conditions. Overall carbon conversion in starch-based plastics was less than that of pure starch. Surface analysis of the plastics indicated removal of some starch granules from the polyethylene matrix. Significant changes did not occur in the average molecular weights of the plastics determined by HT-GPC which indicated no degradation of the polyethylene matrix.

Albertsson and Karlsson (1993) attempted to increase the rate of biodegradation of the LDPE matrix in starch-filled LDPE materials by heating. Preheated $^{14}$C-labeled LDPE-films containing 15 wt% corn starch and a prooxidant were incubated in aqueous solution with fungi at ambient temperature. They found that the inbuilt induction time before autooxidation commenced could be shortened by using an initial preheating period. Preheated samples biodegraded about five times faster than nonpreheated samples.

Greizerstein *et al.* (1993) studied the degradation of commercially available leaf bags made of polyethylene compounded with ECOSTAR PLUS (a starch-based additive) after exposure to a passive composting environment. Half of the bags were buried inside and half on the surface of the compost pile. The tensile properties, FTIR, UV-VIS spectra, DSC and light microscopy determinations were performed on the exposed samples. It was found that for samples exposed to daylight, photo-oxidation had a marked effect on the degradation of the "surface" bags while the degradation of buried bags may

possibly have involved other processes. Temperature and humidity were higher in the buried bag environment and thus made a stronger contribution to thermal oxidation.

Barr-Kumarakulasinghe (1993) developed a model to describe the degradation of starch-polyethylene composite films containing metal prooxidants, using percentage elongation as the indicator of degradation. An equation derived from a kinetic model for the change of peroxy radicals with degradation, developed by Guryanova *et al.*, was adapted to describe the variation of percentage elongation with time and the variation in carbonyl concentrations. The model appeared capable of describing physical and chemical properties of polyethylene film during the thermal oxidative degradation process. The model may be further improved by taking into account of the varying prooxidant concentrations. Half-life calculations using this model facilitated a description of the degradation processes of polyethylene film.

Albersson *et al.* (1994) studied the degradation of LDPE films containing a biodegradable starch filler and a prooxidant formulation in aqueous media inoculated with bacteria or fungi at ambient temperatures for 1 year. They tried to clarify the mechanisms that occur during the initial stages of degradation and which are responsible for initiating the degradation of the LDPE matrix. Interactive mechanisms were observed. The basal salt medium (water containing trace elements) triggered autoxidation of the prooxidant through decomposition of trace hydroperoxides, which, in combination with the biodegradation of the starch, eventually initiated autoxidation of the LDPE matrix. The length of the induction period was dependent on the sample thickness and on the activity of the microbiological system.