

CHAPTER II

LITERATURE REVIEW

2.1 Starch as a Filler in Polymer Blends

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.

Griffin *et al.* (1973) introduced the idea of increasing degradability to otherwise inert polymers by incorporating a cheap biodegradable additive. Granular corn starch in its natural form was mixed with LDPE and it was found that the degradation of PE/starch composite films containing 6-10% of starch in a compost environment was accelerated by the absorption of unsaturated lipids. Peroxides were generated and consequently, autoxidation was enhanced. Thus, a purely chemical effect of the biotic surroundings, even with no enzymatic actions, could enhance the degradative autoxidation of the polymers.

Maddever *et al.* (1987) reported work carried out with Ecostar, a starch-based LDPE master batch manufactured by St. Lawrence of Canada. The research findings showed that the effect of starch on polyethylene/starch film properties was similar to that found from the addition of other fillers such as CaCO₃ at similar levels. When starch contents were varied from 0 to 9%, the tear strength increased in the machine direction. The yield strength remained constant within a narrow range while the break strength decreased in both the machine and transverse directions. The ultimate elongation was reduced and the impact strength dropped sharply at 9% loading level.

Griffin *et al.* (1988) formulated a LDPE material combining several potential degradative effects. LDPE mixed with corn starch, a prooxidant formulation consisting of an unsaturated polymer, a transition metal salt, and a

thermal stabilizer, gave a material which could degrade by several mechanisms such as photooxidation and biodegradation. The starch granules were biodegraded while sunlight and oxygen triggered autoxidation of the chemically unstable prooxidant, generating free radicals which could then attack the molecular structure of the LDPE.

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 autoxidant were added to promote chemical degradation. These blends were then compression molded into sheets and placed in a marine environment for three months. Tests conducted included observation of changes in morphology and thermal properties. The PE/starch samples containing 15% starch showed a 2% increase in weight after exposure to the marine environment. At the same time, the tensile strength decreased by 6% of unplaced in marine environment sample. From GPC data, the molecular weight of the blend was lowered and there was a decrease in M_w/M_n ratio. The surface of the 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.

Nikolov *et al.* (1992) studied on the degradation of two different starch/LLDPE 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 films was investigated by using a buffered *Bacillus* sp. α -amylase solution whereas oxidative degradation of the polyethylene was hastened by incubating the PE/starch films in a forced-air oven at 70°C. The films without a prooxidant additive did not change significantly during the heat treatment. The films containing a prooxidant lost their physical properties after 20 days of heat treatment. The amount of starch hydrolyzed by α -amylase was directly related to the physical properties of the PE films. The levels of starch degradation

ranged between 10 and 50 wt% of initial starch, depending on the extent of the PE degradation.

Yoon *et al.* (1993) studied the effect of native starch on the physical properties of native starch-based polyethylene films. They found that a sharp decline in physical properties of the films occurred at starch loading of more than 10%.

Willett *et al.* (1994) studied the mechanical properties of composites of granular starch and low density polyethylene (LDPE) as functions of starch volume fraction, granule size, and presence of compatibilizer. Results were interpreted in terms of theories developed to describe the elongation, tensile strength and modulus of starch-filled composites. The elongation and tensile strength decreased with increasing starch volume fraction in agreement with theoretical predictions, although the proportionality constants were lower than prediction. The composite modulus increased with increasing starch volume fraction. The addition of ethylene-co-acrylic acid copolymer (EAA) as a compatibilizer had no effect on elongation and tensile strength, but significantly increased the composite modulus. Composites with potato starch, which have larger particle sizes than corn starch, had lower tensile strength and moduli than corresponding corn starch/LDPE composites; particle size had no effect on elongation.

Bong *et al.* (1995) found that the addition of starch to the HDPE film resulted in decreasing of crystallinities in the HDPE film.

2.2 Modified Starch in Polymer Blends

For improving the properties of polyethylene/starch composites, many researchers attempted to modify starch.

Swanson *et al.* (1988) found that tensile strength and elongation of EAA/LDPE composite films were improved by using the modified starch and introducing hydroxypropyl or acetyl groups in starch.

Nikolov *et al.* (1991) reported that LDPE/modified starch composite films improved the tensile strength and elongation in comparison with the LDPE/native starch composite films, but the enzyme degradation rate of the modified starch-filled cast film was lower than the rate of the native starch-filled film.

Kang *et al.* (1996) reported that modified starch could be used to improve the mechanical properties of starch-filled polyethylene films by introducing a cholesterol moiety as a hydrophobic material. The HDPE films with different starch compositions were prepared with addition of either native starch or modified starch to compare their physical properties. The addition of either native starch or modified starch resulted in decreased crystallinity in all the different composite films containing starch. The modified starch-filled blown films showed higher dispersion and adhesion of filler than native starch-filled films. Accordingly, the tensile strength and elongation at break of modified starch/HDPE compounds were improved in almost all cases.

Thiebaud *et al.* (1997) studied the properties of fatty acid esters of starch and their blends with LDPE. Starch octanoates and dodecanoates were prepared by esterification of native potato starch with fatty acid chlorides. The ester group was found to act like an internal plasticizer. These starch esters were then mixed with LDPE in various proportions in a Haake Rheomixer. Torque and melt temperature were recorded. Water and moisture absorption, thermal and mechanical properties were investigated as a function of blend composition. The starch octanoates/LDPE blends showed better thermal stability and higher elongation, but lower tensile strength and water absorption than the starch dodecanoates/LDPE blends. It was also found that esterified starch could be used for preparing of blends with LDPE for packaging use and containing up to 15-20 wt% of starch. This amount is higher than the amount of the unmodified starch (6-9wt%) which can be incorporated in industrial LDPE/starch blends with satisfactory mechanical properties.

2.3 Using of Compatibilizers in Polyethylene/Starch Blends

To increase the incorporated amount of starch, the compatibilizers can be used.

Otey *et al.* (1979) discovered that compounds of ethylene-acrylic acid copolymer (EAA) and starch could be formed into films that were flexible, water-resistant, heat stable and biodegradable. Then they developed a process for incorporating starch into a copolymer of ethylene and acrylic acid (EAA) or a combination of EAA and polyethylene. Either casting, simple extruding, or milling the starch-EAA compositions were used to produce films. The processes were relatively slow and expensive in comparison with the more conventional extrusion blowing technique. 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 contained 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. In 1987, they prepared blend films incorporating starch in a polyethylene matrix and found that the content of starch in starch-based films could be increased without affecting the physical properties of the films by adding urea and polyol to the starch-EAA system.

Shogren *et al.* (1992) studied about compatibility of starch/EAA/LDPE blends and found that part of the polar portion of EAA interacted with starch while part of the hydrocarbon portion interacted with LDPE. From this reason, the starch/EAA/LDPE blends had good compatibility.

Prinos *et al.* (1998) reported that ethylene-vinyl acetate copolymer could be used as a compatibilizer for LDPE/starch blends. The advantage of using this copolymer was that when it was used in high concentration, the elongation of the blends was superior even to that of LDPE. This means that

higher amounts of starch can be used for blend preparation with satisfactory mechanical properties.

Bikiaris *et al.* (1998) reported that LDPE/starch blends containing high amounts of starch, which still retained high extension in tensile strength of LDPE, could be prepared by using the polyethylene-graft-maleic anhydride copolymer (PE-g-MA) as a compatibilizer. It was found that the blends compatibilized with PE-g-MA containing 0.8 mol% of anhydride groups had the same tensile strength as that of pure LDPE.