1993

Evaluation for food packaging potential and environmental compatibility of novel degradable starch-polyethylene plastics

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Iowa State University, 1993

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Evaluation for food packaging potential and environmental compatibility of novel degradable starch-polyethylene plastics

by

Meera Kim

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Department: Food Science and Human Nutrition
Major: Food Science and Technology

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa

1993

To my father, Jongman Kim
and
my mother, Jungja Chung

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ABSTRACT

Linear low-density polyethylene films were prepared that contained native corn starch (7, 14, or 28%), low- or high-molecular weight oxidized-polyethylene (15%) and a pro-oxidant mixture (manganese 55 ppm and vegetable oil). Each plastic blend was first mixed in a twin-screw extruder at 195°C, pelletized, then cast into films using a single-screw extruder at 205°C. Oxidized-polyethylene addition to starch-polyethylene films did not impair transparency and thickness of the films, and relatively small reductions in film mechanical properties were observed.

Thermal and photodegradation properties of each film were evaluated by 70°C forced-air oven treatment (20 days), by high-temperature high-humidity treatment in a steam chamber (20 days), and by exposure to ultraviolet light (365 nm) (4 weeks). Changes were determined in the mechanical properties, carbonyl index and molecular weight distribution of the films. The addition of oxidized-polyethylene, especially high-molecular weight oxidized-polyethylene, and up to 14% starch to the films, significantly increased the rate of thermal and photodegradation.

Biodegradability was determined by using a pure-culture assay with ligninolytic *Streptomyces badius* 252, *S. setonii* 75Vi2, and *S. viridosporus* T7A and by using an extracellular-enzyme assay prepared from *S. setonii* 75Vi2

culture concentrate. The results from the pure-culture assay were inconclusive because of biomass accumulation on the film surface which inhibited chemical and biological degradation of the films. The extracellular-enzyme assay illustrated biodegradation for all 14 and 28% starch-polyethylene films, which suggests that the starch-polyethylene films could degrade in a biologically active compost environment.

The food packaging potential of each film was evaluated. The films were stable in paraffin oil and alkali but were not stable in strong acids. Starch in the films did not impair the heat sealing property. Water vapor transmission of the films increased with increasing starch content, whereas oxygen permeability was not affected by the addition of oxidized-polyethylene nor starch. Starch in the films did not accelerate microbial growth in wrapped ground beef and most films showed relatively inert mechanical properties after use. Consequently, degradable films containing 7 to 14% starch, oxidized-polyethylene and pro-oxidant illustrated good degradability and food packaging potential.

GENERAL INTRODUCTION

The use of plastics has been increasing since 1950's. Plastics have the advantages of being inert to microorganisms and chemicals, being a good barrier to gases and moisture, and exhibiting elasticity, transparency and low density. However, extensive utilization of plastics has led to concern for environmental pollution due to plastics resistance to degradation. Landfills are the dominant disposal sites for waste plastics, and the waste management problem generated by plastics in landfills has prompted the development of degradable plastics.

Degradable plastics contain materials that enhance photo-, bio-, or chemical-degradation processes. Photodegradable plastics are degraded by ultraviolet and visible light coming from the sun and intense terrestrial source (66). Photodegradable plastics have been prepared by incorporating carbonyl groups into the polymer chains (39, 40), or copolymerizing carbon monoxide and polymer (48). The rate of photodegradation obviously depends on weather and seasons (26, 68, 72). Another type of degradable plastic contains biodegradable fillers (i.e. starch in polyolefin). Chemically degradable plastics contain additives that accelerate oxidative and hydrolytic reactions (56). Although degradable plastics have been the subject of much research, more studies are needed to evaluate degradation mechanisms and to develop new

kinds of degradable plastics.

The research reported in this dissertation concerns the evaluation of the degradability of polyethylene containing starch, pro-oxidant and oxidized-polyethylene and an assessment of the potential of these plastics as food packaging materials.

Explanation of Dissertation Format

This dissertation is composed of three papers which will be submitted to scholarly journals. The first manuscript describes the preparation of the starch-polyethylene degradable plastics and characterization of their thermal and photodegradation. The second manuscript deals with the biodegradation of these plastics. The third manuscript evaluates the food packaging potential of these materials. Following the third paper is the summary and conclusion. References cited in the general introduction, literature review and summary and conclusion are listed in the bibliography. Each paper and reference section is presented in the format of the American Society for Microbiology.

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LITERATURE REVIEW

Degradable Plastics

Concept and necessity of degradable plastics

According to an analysis for municipal solid waste (MSW) in 1984 performed by the U.S. Environmental Protection Agency (EPA), total discarded plastics were estimated to be 9.6 million tons per year. Of the MSW 95% was placed in landfills and 5% was incinerated. Nearly 30% consisted of nonbiodegradable inorganics and plastics (48). In 1988, 80% of MSW was placed in landfills, 10% was incinerated and 10% was recycled (78). In spite of the efforts to increase recycling or incinerating ratios, landfills continue to be the dominant destination for solid waste despite the rapidly decreasing capacity of landfills.

Actually, there are some difficulties in incinerating and recycling used plastics. Incineration reduces the volume of discarded plastic and converts waste to energy. However, problems arise from dioxins, acid gases, heavy metals, and polynuclear aromatic hydrocarbons. The carbon dioxide generated may add to the problem of global warming. On the other hand, for plastic recycling, waste plastics must be collected, sorted into polymer types and then washed. These steps require a lot of time and labor. Furthermore, laminated

packaging materials used for many food wrappers are composed of a variety of resins, and it is almost impossible to separate such plastics into recyclable categories. Recycled products prepared from a mixture of different polymer types have poor properties. Therefore, degradable plastics may be a viable alternative to alleviating the environmental pollution associated with waste plastics.

Degradable plastics are materials which degrade faster than conventional plastics when exposed to various environmental conditions (66). These plastics can be degraded by light, living organisms, oxygen, and heat, and reduced in size by the mechanical effects of wind and rain etc. Eleven states in the U.S. requires the use of photodegradable six-pack ring connectors for canned beverage. The federal government requires the compliance with the International Convention *Annex V* for the Prevention of Pollution from ships, which regulates the disposal of trash at sea.

Studies evaluating the performance of degradable plastics are critically needed. Currently, degradable plastics are used in garbage bags, grocery bags, and mulch films. Additional studies are required to determine the degradation mechanism in the laboratory and under natural conditions, and to develop new kinds of degradable plastics designed to degrade in specific environments.

Degradation of conventional synthetic polymers

Conventional synthetic polymers are considered to be resistant to microbial attack (recalcitrant) because their high molecular weights (MWs) and hydrophobic character inhibit enzymatic activity. Many organisms metabolize carbon-chain polymers in the range C_{12}-C_{40} by the conversion of the terminal carbons to carboxyl groups, but degradation slows and/or stops with increasing chain lengths (49).

Polyethylene chains often consist of more than 1,000 ethylene units and in addition are branched, which increases their resistance to microbial attack (49). The chain ends of low MW materials are accessible by microorganisms. Polyethylene above a MW of several thousands, however, crystallizes in folded chain in which chain ends are unlikely to be found near the surface and hence accessible to oxidation.

Polyesters, polyamides, polyurethanes, and polyethers are relatively susceptible to enzymatic attack compared with carbon-chain polymers such as polyethylene (8). These hetero-chain polymers have linkages such as C-O and C-N. The chains containing such hydrolyzable groups in the backbone can be attacked randomly to reduce the MW more efficiently than the oxidation of chain ends. This reduction in MW of the polymers is expected to enhance biodegradability. The biodegradation of polymers generally is attributed to enzymes. Hydrolases found in soil and water microorganisms cleave esters and

amides and break down high MW polymers in order to transport them into their cells. Therefore, polymers must have chemical groups that are susceptible to enzymatic attack to be degraded by this mechanism. The biodegradation of alkanes usually occurs by terminal hydroxylation to the primary alcohol and further oxidation to the carboxylic acid (8). In polyethylene, there are no points of attack except at terminal carbon.

Polyethylene degradation has been elucidated in several studies. Corbin (23) studied biodegradation using ^{14}C-[labeled]-polyethylene. He reported the carbon dioxide evolution rate from polyethylene in soils was only about 2% per year. Albertsson et al. (3) evaluated the biodegradation of ^{14}C-[labeled]-high-density-linear-polyethylene by *Fusarium redolens* under aerated conditions over two years. The liberated $^{14}CO_2$ quantity corresponded to 0.56% of the polyethylene by weight. Albertsson (2) also determined biodegradation of ^{14}C-[labeled]-polyethylene to $^{14}CO_2$ by some soil fungi. The net yield of $^{14}CO_2$ evolution was 0.5% in two years. Albertsson and Banhidi (4) found that the output of respiratory $^{14}CO_2$ dropped when low MW components of high-density polyethylene were eliminated by extraction with cyclohexane after 2 year aerated cultivation with *Fusarium redolens*. This suggests that short-chain oligomers were the primary material utilized. From these studies Albertsson et al. (6) proposed that three stages were involved in polyethylene degradation under aerated cultivation over a 10 years period. In the first stage, the polymer

changes rapidly until some kind of equilibrium with the environment is achieved. Carbon dioxide evolution, rapid oxygen uptake and mechanical property changes are observed during the first stage. The second stage is characterized by a parabolic decline in oxygen uptake and carbon dioxide evolution and slow changes of mechanical properties and MW. The changes in mechanical properties are not necessarily synchronous with the decrease in MW. In the final stage, rapid deterioration of structure, loss of all mechanical properties and the nearly complete mineralization can be observed.

Categories of degradable plastics

Degradable plastics can be generally classified into biodegradable, photodegradable, and chemically degradable plastics. These mechanisms may operate in a synergistic, concerted, or consecutive manner depending on the environmental conditions and the resin.

Photodegradable plastics

Photodegradation occurs when the primary mechanism of degradation of polymeric materials is by the action of ultraviolet (UV) and visible light from the sun or some intense terrestrial source (66). The technology for preparing photodegradable plastics can be divided into two categories.

One category can be defined as copolymer technology. The pure

polymer, which is not susceptible to photodegradation, is modified by introducing carbonyl groups, which absorb UV energy in the range of 270 to 360 nm. UV energy can break the chain at such carbonyls and render the polymer brittle. Ketone copolymers made by copolymerization of ketone molecules with polymer chain were developed by Guillett (39, 40). This copolymer undergoes a Norrish I type reaction (Figure 1), which is temperature dependent.

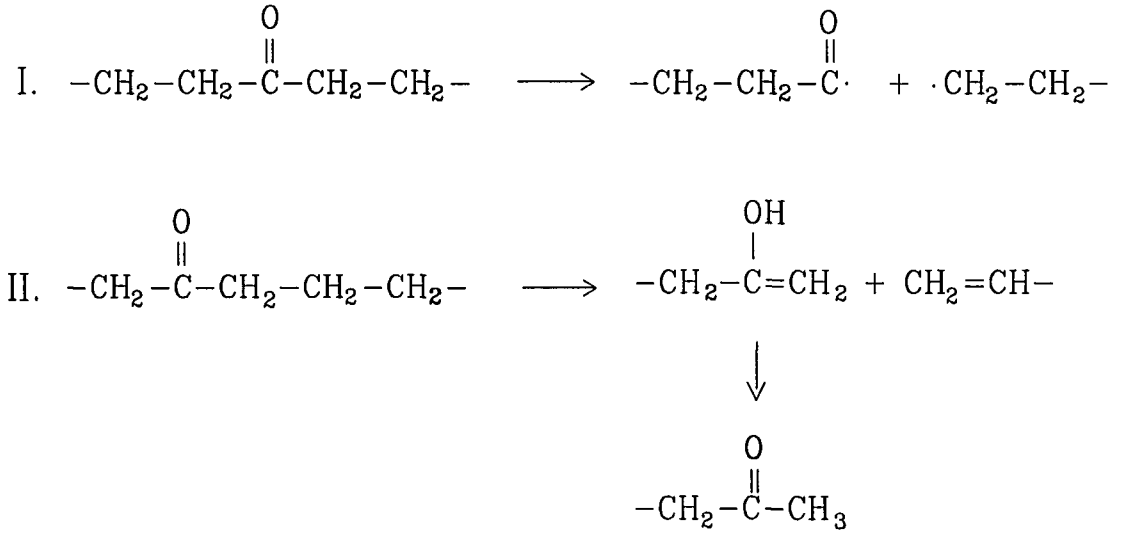

Figure 1. Norrish I and II reactions

Radicals formed from a Norrish I reaction can generate further oxidative reactions, cross-linking and depolymerization during the later stages of the UV degradation of polyethylene (72). The degradation commences without an induction period (68). The technology has been developed commercially, and it is basis of the Ecolyte masterbatch technology (EcoPlastics, Willowdate, Ontario, Canada). This masterbatch provides a concentrated form of the ketone copolymer to be mixed with a larger quantity of unmodified resin. The treated material is used for trash bags, grocery bags and agricultural mulch film in Europe. Use of the masterbatch adds 8 to 10% to the cost of the film (48).

Another method of incorporating carbonyl groups is copolymerizing carbon monoxide and polyethylene to form an ethylene-carbon monoxide polymer (E/CO). The level of carbon monoxide incorporated is typically less than 2% (48). The carbonyl molecules incorporated in E/CO absorb UV light, and this causes the molecule chain to break into smaller parts. According to Brubaker's patent (68, 72), copolymers of ethylene and carbon monoxide are sensitive to light, and subsequently photolysis occurs, predominantly by the Norrish II type reaction that involves the cleavage of aliphatic ketones in light. A Norrish II reaction is independent of temperature (Figure 1).

Degradation of polymer begins immediately on exposure to UV light without an apparent induction period. Therefore UV stabilizers are added for product stability prior to disposal. In the later stages of UV exposure the vinyl

double bonds appear to become involved in macromolecular enlargement, producing a copolymer which is not biodegraded (68). Carbon monoxide-containing resins are produced by several plastic resin manufacturers such as Dow Chemical (Midland, MI), DuPont Co. (Wilmington, DE) and Union Carbide Corporation (Danbury, CT). This copolymer is currently used for degradable six-pack yokes in the U.S. E/CO beverage rings begin to be degraded at exponentially increasing rates after six hours of exposure to light, and they are brittle enough to disintegrate when handled within a week (50).

Another category of photodegradable plastics contains additives to accelerate photodegradation. During polymer processing, thermal oxidation can occur in the presence of oxygen generating hydroperoxides. These products interfere with the manufacture of plastics because of the MW changes in the polymer (20). Therefore, antioxidants are commonly added to the plastic resin to scavenge oxygen and prevent thermal oxidative degradation during processing. Some antioxidants act to stabilize polyolefins at high concentration, but then act to catalyze photodegradation at low concentration. They are usually transition metal salts of stearates, dithiocarbonates and acetoacetonates.

The photodegradation mechanisms of plastics that contain additives are not well understood, but alkoxy radicals seem to lead chain scission, yielding aldehydes and ketones, which are prone to further free radical formation and

subsequent oxidation (31). Plastigone by Ideamasters, Inc. (Miami, FL) is a material of this kind offered for agricultural mulch film in Israel (50). Poly-grade masterbatch is provided by Ampacet Corporation (Mt. Vernon. NY) for Bespac trash bags in the U.S. The dual additive system composed of a photo-activator such as benzothiozol or benzophenone plus transition-metal-salts pro-oxidant such as zirconium stearate or nickel acetate is another example (44). These photodegradable plastics with additives can become biodegradable when their MWs are lowered by photodegradation, whereas carbonyl modified plastics cannot.

A variety of factors influence the rate of photodegradation, for example, geographical location, seasons, weather, direct versus indirect sun light, and artificial lights (26, 68, 72). Statz et al. (72) reported that increased CO content accelerated the rate of degradation, and resins were degraded more rapidly in the summer than in winter. The success of photodegradable plastics lies in the control of degradation rate in different environmental conditions. Scott and Gilead (68) developed a photo-biodegradation process and antioxidant-photoactivator system, which provides a predictable induction period for storage and normal package use under controlled conditions. Copolymer technology has an advantage in food applications due to their non-toxicity, but carbonyl-modified plastics will not degrade in landfill. On the other hand, additive systems may promote polymer chain scission, generating low

MW fractions, which might be utilized by microorganisms. Moreover, degradation can proceed in the absence of UV radiation only after a threshold of free radical formation is reached. Polymers containing metal salt could continue oxidative degradation through a chain reaction. However, in food-contact applications those additives must be nontoxic and not migrate out of the polymer.

Biodegradable plastics

Biodegradation is the breakdown of materials by the action of living organisms. Bacteria, fungi and actinomycetes are important for plastic degradation, although larger organisms can play a part (45, 66). Plastics may be degraded by microorganisms with a biophysical effect in which cell growth causes mechanical damage. Likewise there can be biochemical effects in which substances from the microorganisms can degrade polymers. Finally, direct enzymatic action is possible, in which enzymes produced from the microorganisms attack components of the plastic (54).

Microorganisms require proper temperature, pH, and O_2 for growth. Heterotrophic bacteria need preformed organic carbon substrates as their energy sources. All natural polymers, such as cellulose or collagen are biodegradable, resulting in complete loss of integrity and dissolution of the original substrate.

Biodegradable plastics can be divided into two classes. One class includes polymers containing a biodegradable filler. In this instance only a small portion of the material is readily biodegradable. The second class is truly biodegradable and includes poly(3-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-3-hydroxyvalerate) (PHBV), polycaprolactone (PCL) and polylactides.

PHB and PHBV are thermoplastic polyesters that are produced by bacteria in industrial fermentations (70). The polymers are subject to enzymatic attack directly. *Alcaligenes eutrophus* produces polymers from various carbon sources such as glucose, fructose, molasses, or simple alcohols. Ammonia, minerals, and trace elements are also required in the process. The polymer is soluble in water, a trait which is useful in the manufacturing process when the polymer is separated from the bacterium. These material are more suitable for special applications such as those in the medical field. They have a high cost and complex processing requirements.

PCL is a highly crystalline, thermoplastic linear polyester prepared by ring opening polymerization of ϵ-caprolactone (66). The repeating unit consists of a straight chain of five methylene units with a terminal ester unit. The polymer has a sharp melting point of 60°C and physical properties similar to polyethylene. PCL could be incorporated into synthetic backbone polymers such as ethylene and styrene (69).

Polylactides are made by polymerization of free lactic acid or by catalytic ring-opening polymerization of lactide, a dilactone of lactic acid (52). Lactic acid or lactide could be copolymerized with caprolactone to provide various properties.

Another class of biodegradable plastics is a polymer containing a biodegradable filler. This polymer is degraded by two interactive mechanisms (33). Degradable filler such as starch is attacked by microorganisms. Biodegradation of the starch results in increasing the surface area of polymers. Degradation of the main polymer is stimulated by the addition of pro-oxidants (also called prodegradants). This second mechanism for degradation is caused by the formation of peroxides in the presence of oxygen, a process that may be aided by pro-oxidants found in the environment or added to the polymer. These peroxides begin breaking the polymer chain, weakening the material, reducing the chain length, and thus producing a MW level that can be metabolized by microorganisms. The ultimate products of degradation by microorganisms are carbon dioxide and water. The rate of degradation depends on several factors such as moisture, oxygen tension, type of microorganisms, temperature, pH, availability of metal salts and surface area. Therefore, plastics containing starch degrade through both chemical degradation and biodegradation.

Two different technologies are used for the preparation of starch-filled plastics. Griffin (35-38) developed a process for incorporating granular starch

particles into plastic films. Films produced with this method can have up to 30% starch by weight. Otey (59-63) incorporated gelatinized starch into plastics to yield a uniform distribution of starch molecules into the plastic films. The films produced by the later technology typically contain 20-50% starch by weight. These two methods will be described in more detail in the section of preparation of starch-filled polyethylene plastics.

Chemically degradable plastics

Chemically degradable plastics are degraded by chemical reactions. Additives are incorporated into plastics to accelerate oxidative and/or hydrolytic degradation of the polymer (56). The proposed mechanism of chemical oxidative degradation consists of initiation, propagation and termination step (57). Initiation:

$$RH \longrightarrow R\cdot + H\cdot$$

Propagation:

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$R\cdot + ROOH \longrightarrow RH + ROO\cdot$$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

Termination:

$$R^{\cdot} + R^{\cdot} \longrightarrow R\text{-}R$$

$$R^{\cdot} + ROO^{\cdot} \longrightarrow ROOR$$

$$ROO^{\cdot} + ROO^{\cdot} \longrightarrow ROOR + O_2$$

Preparation of starch-filled plastics

Starch is an abundant, low cost and completely biodegradable natural polymer. For many years, up to the early 70s, petroleum was readily available at low costs. Since that time, the price of petroleum has increased 5- to 10-fold. Moreover, increasing concern about environmental pollution generated by synthetic polymers has stimulated intense interest in the development of less expensive and more degradable polymers. One approach has been the development of degradable starch-polyethylene films containing pro-oxidants.

Griffin (35) developed a process for incorporating starch into blown low-density polyethylene films. Among potential biodegradable fillers, only dry and raw starch among potential biodegradable fillers satisfied the requirements for adequate thermal stability and minimum interference with melt-flow properties and disturbance of product quality. He found that rice, wheat, potato, corn, and tapioca starches were blended readily into low-density polyethylene, and blends of small and large particle starch could give maximum starch loading.

Griffin (38) used 15-30% native starches, either directly or blended with lubricants such as ethyl oleate, calcium stearate, iso-octyloleate and paraffin wax, into the polymer.

Starch is inherently water sensitive. When starch is dried, it becomes rigid and brittle from the high degree of molecular branching and hydrogen bonding. The embrittlement imparted to starch-polyethylene plastics by starch can be overcome to various degrees by adding plasticizers and other materials. Otey et al. (59) prepared cast films from aqueous dispersions of starch (gelatinized starch), poly(vinyl alcohol), glycerol, surfactant, and formaldehyde. These cast films showed inferior wet strength, but cast films coated with polyvinyl chloride or poly(vinylidine chloride) and acrylonitrile copolymer had improved wet strength. Otey et al. (60, 61, 63) prepared the films by blending starch with poly(ethylene-co-acrylic acid). They introduced gelatinized starch up to 50% into blown films. Water was added to make a slurry consisting of starch, poly(ethylene-co-acrylic acid) (EAA), and ammonium hydroxide. Alkali was added to solubilize the EAA, and the slurry was heated at 90-100°C for 45 min. The mixture was extruded repeatedly to reduce the moisture content to 5-10% before blowing. This film was clearer than the film made by dry blending and similar to the appearance of conventional films.

Plastics containing starch usually have shown mechanical properties inferior to polyethylene without starch because of the weak interaction between

hydrophilic starch and hydrophobic polyethylene. This problem led to the modification of starch by making hydrophilic starch's surface hydrophobic. Griffin (36, 37) proposed a process for making low-density polyethylene blown films containing modified starches to improve the film property. Autoxidants such as unsaturated fatty acid salts of manganese or iron were added to the polyethylene, so that both chemical degradation and biodegradation could occur. A low moisture level in the starch was important because bubbles formed in the blowing films containing 9% starch with 2% moisture. Additionally, starch with low moisture content could be processed in polymer melts typically above 160°C (54). Swanson et al. (77) evaluated the effects of modified starches on plastic film. The mixture of low-density polyethylene and EAA polymers filled with hydroxypropyl or acetyl derivatives of starch showed greater elongation and tensile strength than film containing underivatized starch. Evangelista et al. (28) prepared low-density polyethylene with corn starch modified with octenyl succinate groups. The cast films containing such modified starch had higher tensile strength and elongation than films with native corn starch when processed under optimum conditions of 205°C and 20 rpm. These modified, starch-filled polyethylenes, however, exhibited reduced access to amylases compared with native corn starch (76).

Studies for determining degradability of polymers

Photodegradability

Photodegradation mechanism can be thought of as a two stage process (67). In the first stage, exposure to UV light leads to embrittlement of the plastic. Next, the mechanical action of wind and rain makes the plastic into small fragments. Subsequent to photodegradation a slower biodegradation of the low MW fragments generated *via* photodegradation occurs.

Studies for photodegradability can be performed by either outdoor or indoor exposure. The photodegradability of plastics exposed to light for a constant period have been evaluated by various tests such as fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and high-temperature gel-permeation chromatography (HT-GPC).

Albertsson et al. (7) examined the susceptibility of degradable polyethylene to thermal and photo-oxidation. The low-density polyethylene films containing starch, pro-oxidant and thermal stabilizer were subjected to accelerated thermal aging in an air environment at 60°C and 100°C and to UV aging. Films found to be degradable were susceptible to thermal and photo-oxidation, whereas films containing only corn starch were not degraded.

Omichi et al. (58) evaluated photodegradable polyethylene film containing radiation-modified atactic polypropylene as a photo-sensitiser. The film was used indoors (greenhouse) and outdoors as a protective cover (plastic mulch) for seedbeds of strawberry for half-a-year. The tensile strength and percent elongation of the film used indoors were maintained at 70-80% of the initial values, whereas those used outdoors continuously decreased to 50% and 30%, respectively. The increase in infra-red (IR) absorption at 1720 cm^{-1} was closely related with the decrease in elongation. Weight loss and IR absorption showed that the oxidized film was biodegradable when exposed to bacteria found in soil around petroleum wells.

Barish (18) examined differential shrinkage between skin and core in the sunlight degradation of polypropylene textile fibers. He found that surface cracks formed perpendicular to the fibers axis, while the core remaining undamaged in the initial stages of degradation. With further irradiation the skin and core separated and eventually the skin was eroded away.

Giesse and De Paoli (32) quantified the relationship between depth of light penetration and the formation of oxidation products in low-density polyethylene under UV-irradiation. The concentration of oxidation products was higher in the bulk of the films than on the exposed surface at the beginning of the reaction, but the concentration of oxidation products on the surface increased as exposure time continued.

Johnson et al. (46) correlated the presence of iron with polyethylene to photodegradation patterns for 11 compositions of starch-polyethylene films by measuring mechanical properties and MW distribution.

Biodegradability

Although there are no uniform methods for determining the biodegradability of plastics, several methods have been used routinely. Tests for biodegradability of polymers can be classified broadly into laboratory and field tests.

Laboratory tests

ASTM G 21-90 (16) Plastic test specimens (50 X 50 mm or 50 mm dia.) are placed on a solid agar growth medium that is deficient only in carbon. The medium and specimens are inoculated with a suspension of the test microorganisms and incubated for three weeks at the appropriate temperature. Microbial growth is dependent on the utilization of the specimen as a source of carbon. Mixtures of *Aspergillus niger*, *Aspergillus flavus*, *Chaetomium globosum* and *Penicillium funiculosum* typically are used. After various exposure times, samples are examined for evidence of fungal growth on the plastic surface. The method can be used with plastic specimens in the form of molded plaques, blown film, or granulated material.

ASTM G 22-76 (17) This test is similar to ASTM G 21-70 except that a bacterium such as *Pseudomonas aeruginosa* is employed instead of fungi. Generally, fungi are preferred to bacteria because of their greater activity on complex macromolecules, and their insensitivity to additives or impurities in the sample. Therefore, it is necessary to be certain that the polymer sample is free from solvents or toxic additives prior to testing. A positive test is interpreted that the polymer itself serves as a carbon source. Negative results indicate that the organisms evaluated can not assimilate the carbon in the sample.

Clear zone method (29, 66) For this test a water-immiscible polymer is suspended in a nutrient-agar medium and poured into Petri dishes. The dilute suspension is hazy. After inoculation and incubation, colonies of cells are observed. If a clear zone occurs in the medium surrounding a colony, the polymer in the zone is considered to be broken down into fragments that are soluble or metabolized. A positive result is usually due to the excretion of extracellular enzymes by the microorganisms.

Quantitative Petri dish method (29) For this test a polymer is deposited as a continuous layer on the bottom of a Petri dish, residual solvent is removed by drying in a vacuum oven and the sample weight is determined. A nutrient agar mixture is poured over the polymer. The plate is inoculated and incubated. The agar culture is washed away and the plastic residue is dried in a

vacuum oven and reweighed to determine the weight lost. Other properties, such as tensile strength and viscosity of the polymer, can also be measured.

Radiocarbon-14 tracer method (8, 66) The ultimate products of biodegradation of synthetic organic polymers by microorganisms are carbon dioxide and water. When the polymer is the sole carbon source, the measurement of carbon dioxide evolved correlates to polymer mineralization. The use of ^{14}C-[labeled]-polymers permits the distinction of carbon dioxide produced from metabolism of the polymer and that generated by other carbon sources in soil or in a lab culture. However, this method requires the preparation of ^{14}C-[labeled]-polymers, which can be difficult and expensive.

Measurement of oxygen consumption (8) Aerobic oxidation of polymers by microorganisms requires oxygen. Therefore, polymer degradation can be quantified by measuring oxygen uptake if polymer is the only oxidizable substrate. This method is useful only with readily degradable polymers.

Cell mass or biomass method (8, 66) This is a variation of the ASTM methods which utilize microorganisms but it is more quantitative. Polymer which is the sole carbon and energy source is placed in a mineral medium. Increase of cell numbers signals degradation of the polymer. This method is not useful for biologically recalcitrant polymers such as polyethylene.

Pure-culture method (51, 64) Chemically disinfected films are transferred into sterile culture medium and inoculated with test microorganisms.

After incubation for specific period, films are dried, and changes in weight, mechanical properties, MW distribution or spectra are measured to determine biodegradability.

Extracellular-enzyme method (65) Test microorganisms are cultured in large volumes, and extracellular-enzyme is separated from the cell mass and concentrated. Chemically disinfected films are treated with extracellular-enzyme concentrates for specific period. Films are dried, and changes of mechanical properties, MW distribution and spectra are measured to determine biodegradability.

Indoor soil burial method (8, 66) Plastics are buried in indoor soil under controlled conditions. Samples are taken at specific intervals, carefully washed, vacuum dried and weighed. Indoor soil burial tests permit control over the microbial population, but inoculation of soil with specific test organisms usually is not successful due to competition from soil strains. Reinoculation after soil sterilization could be used, but symbiotic relationships between various native strains would be lost.

Field tests

Outdoor soil burial method (8, 22, 66) This test is the same as indoor soil burial method except that it is located outdoors. Outdoor soil burial test tends to lack reproducibility because of climate factors and lack of control

of the microbial population in soil.

Composting (46, 74) Composting is defined as the accelerated degradation of heterogeneous organic matter by a mixed microbial population in a moist, warm and aerobic environment (55). The compost bioreactor can be inoculated with special hydrocarbon degraders to speed up the degradation of hydrocarbon-based plastic (74). Composting performance can be monitored by measuring changes in the organic content and other manifestations of decomposition. In organic content measurement, volatile solids test (percent of dry solid lost by ignition at 550°C), total organic carbon (TOC), carbon to nitrogen ratio, chemical oxygen demand (COD), and biochemical oxygen demand (BOD) are frequently used (30). Manifestations of decomposition involve the measurement of heat generation, temperature elevation, oxygen consumption and carbon dioxide production (53, 75).

Colin (21) determined the deterioration of polyolefin, poly(ethylene-terephthalate) and polyamide under soil burial condition for 32 months by measuring changes in percent elongation, IR spectroscopy, luminescence spectroscopy and SEM. The biodegradation increased in the following order: polyester, polypropylene < low- and high-density polyethylene < nylon-66.

Ennis and Kramer (27) measured the biodegradability of nylons and related polyamides by determining the carbon dioxide evolved through microbial metabolism. They found polyethylene introduced with ester groups showed

enhanced biodegradability compared to polyethylene itself.

Cornell et al. (24) measured the biodegradability of photooxidized polyalkylenes. The films after exposure to UV radiation of various intensities and oligomer fractions separated from the high MW polymer were challenged microbiologically. The oligomer fractions supported microbial growth, but the high MW polymers gave minimal or no growth. They concluded that oligomers supported growth if separated from the polymer matrix and that photooxidative degradation of polyolefins does not *per se* induce progressive attack by microorganisms.

Albertsson et al. (5) studied the mechanism of biodegradation for polyethylene. The films were UV irradiated and exposed to abiotic and biotic environments. In a biotic environment, double bond formation and weight loss increased. They found a synergistic effect between photooxidative degradation and biodegradation.

Johnson et al. (46) evaluated the degradation of 11 types of commercially produced starch-polyethylene compost bags in municipal yardwaste compost sites in Iowa. Bags differed in starch content (5-9%) and pro-oxidant additives. Each compost site was seeded with test strips (200 to 800 each type) that were taped together. The strips were recovered periodically over an 8- to 12-month period. Degradation was followed by measuring change in polyethylene MW distribution *via* HT-GPC. Their 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 after five months, and almost every material degraded by 12-months. Significant reductions in polyethylene were detected for several materials.

Chemical degradability

Studies of chemical degradability usually are performed by thermal treatments of the polymers. After exposure to heat for a specific period, changes in mechanical properties, MW distribution and functional groups are measured and/or oxidation products are determined.

Spore and Bethea (71) studied oxidative degradation of polyethylene at 75 to 200°C in atmosphere containing 0-100% of oxygen. They identified 24 degradation products using gas chromatography. The concentration of the degradable products increased proportionally with the oxygen concentration and temperature.

Johnson et al. (46) determined changes in mechanical properties and polyethylene MW distribution for 11 compositions of starch-polyethylene films in 70°C dry heat (oven) and high-temperature high-humidity (steam chamber) treatments. Different chemical degradation patterns were observed depending

on the pro-oxidant blend present in the films.

Adams (1) analyzed the nonvolatile oxidation products of polypropylene obtained through thermal treatment at 70°C. They found γ-lactones, which are indicators of the importance of an intramolecular compound formation.

Holmstrom and Sorvik (43) evaluated thermooxidative degradation of low-density polyethylene, high-density polyethylene and tetratetracontane heated at temperature between 120 and 180°C, using gel chromatography, viscometry, IR spectroscopy, DSC and gravimetric measurements. At temperature below 150°C MW increases were observed after long exposure time, but at 180°C such increases occurred immediately. The increase in MW was attributed to peroxide curing, which becomes increasingly important above 150°C. Ester formation occurred at both temperatures.

Food Packaging

Use of plastics as food packaging material

Plastic packaging materials are among the newest materials used by the food industry. Plastics accounted for 26.5% of all food packaging materials in 1991, compared with 13.2% in 1981 (19). Plastics often are preferred over metal, wood, paper and glass because of their unique characteristics: inertness to many chemicals and microorganisms, toughness, transparency, elasticity,

impermeability by many gases and moisture, ability to be coextruded, and design capabilities not available with other packaging materials.

The use of degradable plastics has been required in areas with ecological and environmental concerns. In 1985, 13,200 million pounds of plastics were used as food packaging materials and 22,580 million pounds of plastics are expected to be used in 2000 (19). Degradable plastic use in food packaging can help solve some plastic pollution problems. Therefore, studies describing the performance and acceptability of degradable plastics as food packaging material are needed.

Requirements and functions of food packaging

There are some general requirements for food packaging. The primary container, which is in direct contact with foods, must be nontoxic and compatible with the food, causing no color or flavor change, or other undesirable chemical reactions. Food packaging also should provide protection against microorganisms, insects, rodents or dirt. Lack of moisture transfer is a requirement for some food packaging materials. Dried foods cannot absorb moisture from the atmosphere, and moist foods cannot lose their moisture. Foods also have gas and odor protection requirements. When controlled gas atmosphere storage is applied to increase food storage stability, gas protection property of the packaging material is very important. Food packaging should be

resistant to damage from impact or other physical stresses. Transparency of packaging materials also is desirable because consumers often want to see the food product that they are purchasing. Conversely, food packaging should protect food's deterioration from light. Tamper resistance is required to protect consumers. The ability to reseal containers (e.g. coffee) may retard food product staling. Light weight packaging material provides enormous cost savings in transportation.

Properties of polyethylene

Satisfaction with the performance of plastic packaging material depends on the characteristics of the resins. Thermoplastic resins consist of long, linear or slightly branched molecules that are not cross-linked (25). These plastics repeatedly soften and melt at high temperatures and harden again at low temperature. Six main types of thermoplastics are used in packaging: polyethylene, polypropylene, polyvinylchloride, polyethylene terephthalate, polystyrene, and acrylonitrile-butadiene-styrene. Thermoset resins are long molecules, that form cross-linkages, and become irreversibly changed upon heating. Such materials do not soften on heating. There are three thermosets used in packaging. Phenol-formaldehyde and urea-formaldehyde are used mainly for bottle closures, while glass-reinforced polyesters are used for large containers. Elastomers are long and linear molecules with limited cross-linking

that are soft, have high elongation, and recover from large deformations rapidly (42). Natural rubber, polyisoprene, polychloroprene, polysulfide and silicones are elastomers. Like thermoset resins, it cannot be resoftened after polymerization occurs.

Polyethylene is prepared by the polymerization of ethylene gas obtained as a by-product of the coal and oil industries. Polyethylene accounts for half of all plastic packaging materials (19). Polyethylene has the characteristics of being easily processed, being an excellent electrical insulater, being chemically inert to many reagents, being tough and flexible even at low temperatures, having clarity of thin films, being free from odors, being non-toxic, exhibiting low water permeability, and being inexpensive low cost. These characteristics have led to polyethylene's widespread use. The molecular formula of polyethylene is $(CH_2)_n$ and the carbon atoms in such macromolecule are arranged in a zig-zag fashion, although the chains are referred to as linear. Polymerization under high pressure (1000-3000 atm) produces a macromolecule with branching. Branched chains prevent close packing of polymer chains, which lowers the overall degree of crystallinity and produces a low-density material (0.915-0.940 g/cm^3). This low-density polyethylene is flexible, tough, translucent and resistant to most chemicals below 60°C. It is a good barrier to water vapor, but less so for other gases, such as oxygen. Over the years many methods have been developed to produce polyethylene with short chain

branches, so-called linear low-density polyethylene. Linear low-density polyethylene has higher impact strength, tensile strength and extensibility than low-density polyethylene. High-density polyethylene is prepared under low temperature (50-75°C) and low pressure (10 atm). Its density is 0.945-0.965 g/cm^3. High-density polyethylene is stiffer, harder, less transparent than low-density polyethylene. High-density polyethylene exhibits better resistance to oil and water vapor. It is used in bags, bottles and tubs.

Tests for food packaging materials

Molecular weight distribution

All synthetic polymers have a distribution of MWs due to random polymerization. To obtain information about the MW distribution, it is necessary to separate the molecular species in a sample by a fractionation process, and to determine the amounts and MWs of all the fractions. From these data, the distribution of MWs can be calculated. ASTM (American Society for Testing and Materials) provides standard methods for determining the MW average and MW distribution by HT-GPC (13, 14).

HT-GPC separation is an essential part of any study of MW distribution. The separation in HT-GPC is based on separation by molecular size. Chromatographic processes refer to those operations in which the solute is

transferred between stationary and mobile phases. Both phases in gel permeation chromatography (GPC) are liquid as in liquid-liquid chromatography, but the two phases in GPC are the same liquid, unlike liquid-liquid chromatography in which two liquid phases are immiscible. In GPC the phases are differentiated only in that the stationary phase is that part of the solvent inside the porous gel-particles, while the mobile phase is outside. The transfer of solute between the two phases takes place by diffusion, resulting from a difference in concentration of solute between the two liquid phases. Separation of polymers is achieved on the basis of the molecule size and the ability of the molecules of various sizes to penetrate the pore structure of the gel. Gels used in gel filtration such as cross-linked dextrans are soft and compressible, while GPC gels are typically hard and incompressible, which permits the use of the gels under high pressures. The original gels used in GPC consisted of polystyrene cross-linked with divinyl benzene. Porous glass can also be used in place of cross-linked polystyrenes.

The number-average molecular weight ($\overline{M_n}$) is the simple counting average in which the mass of the sample is divided by the number of molecules (20).

$$\overline{M_n} = \frac{w}{N} = \frac{\sum N_i M_i}{\sum N_i}$$

N is the sum over the number of all molecules, N_i is the molecule numbers of the $_i$ th kind, and M_i is the MW of the $_i$ th kind.

The weight-average molecular weight ($\overline{M_w}$) is defined as follows:

$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

The averages may be sensitive to presence of a small fraction of material in an extreme range of MW (20). $\overline{M_n}$ is highly sensitive to the presence of a small number fraction of low MW species regarded, i.e. oligomers. $\overline{M_w}$ is similarly sensitive to small amounts by weight of high MW polymer. Because of their accessibility, the ratio of $\overline{M_w}$ to $\overline{M_n}$, so-called polydispersity, is often used. It is used as an indication of the range of MWs in a polymer.

Mechanical properties

Testing standards are established by the American Society for Testing and Materials (ASTM). Mechanical properties are evaluated by compression tests, tension tests and shear tests. Tensile characteristics by tension test are the most widely reported mechanical properties of any material.

Tensile strength (11) is a measure of the resistance of a material to stresses pulling in opposite directions (34).

$$\text{Tensile strength} = \frac{\text{load (kg)}}{\text{cross-sectional area (mm}^2\text{)}}$$

As an indication of the resistance of a material to continuous stress, for instance, a screw cap on a bottle and heavy-duty bags, the tensile strength is a good criterion.

Elongation is the distance that a specimen stretches when pulled in tension (34).

$$\text{Percent elongation} = \frac{\text{ultimate length-original length (mm)}}{\text{original length (mm)}} \times 100$$

For rigid materials, the stretch is short. Materials that can be stretched at least twice their original length are known as elastomers.

Physical properties

Water vapor transmission (15) is a measure of the gain or loss of water through a film (41). This property is important for the packaging of foods which should not lose their moisture or absorb the moisture from their surroundings.

Gas permeability (12) is a measure of gas transmission rate through a film. The rate decreases almost proportionately to film thickness. The permeation rates for gases are independent of pressure, but temperature can be an important factor. Combination of gases act independently and penetrate the plastic as though they were alone (41).

Chemical resistance (9) is a measure of the resistance against various

chemicals such as acids, alkalies and oils. The effect of chemicals varies with each plastic. Some substances cause plastics to swell and soften, or become sticky on the surface. Such substances can result in less strength and stress cracking. Stiffening of plastics may result from extraction of plasticizer by contact with various substances.

Heat resistance (10) is a measure of the resistance of plastics to exposure to various temperatures and periods. It can be determined by measuring the changes of weight or dimension of specimen. This parameter can be used to determine packaging stability during transport and storage. Changes of color or odor after thermal exposure can also provide qualitative measures of heat resistance.

Microbial tests

Synthetic polymers are resistant to microbial attack, but degradable plastics containing biodegradable fillers may be attacked by microorganisms. Therefore, for degradable plastics used in foods, microbial tests are needed to determine whether use of such plastics affects the microbial population in the food product. This kind of research has been rare. Strantz (73) evaluated the effect of cornstarch in plastic film on the bacterial survival under food storage conditions. Generally, bacterial survival was not enhanced by the presence of cornstarch, but enhanced growth of *Salmonella typhimurium*, *Aeromonas*

hydrophila and *Pseudomonas fragi* was observed under saturated relative humidity at some storage temperatures in minimal salts medium. Enhanced growth was not apparent in nutritionally complex growth medium. They concluded that cornstarch-containing polyethylene film could be successfully used to food package from a microbiological viewpoint.

Toxicity tests

Degradable plastic use as a primary food container presents an additional problem of the possible release of toxic degradation products into the food product prior to consumption. Johnson et al. (47) began to address this issue by testing for the release of water-soluble toxic compounds from different starch-polyethylene films *via* the Microtox® Toxicity Analyzer. Each plastic strip was placed in a 250-ml Erlenmeyer flask with 100 ml of ASTM type I water with or without trace-element solutions at 65°C with shaking for 20 weeks. Water samples were taken periodically and analyzed for toxicity *via* the change in light emission of *Photobacterium phosphoreum* after exposure to a toxic material. Their results illustrated no water-soluble toxic products were released during the period of most rapid polyethylene degradation. Acute, subacute and chronic toxicity studies for degraded materials are needed (25).

PAPER I. CHARACTERIZATION OF NOVEL DEGRADABLE STARCH-POLYETHYLENE PLASTICS CONTAINING OXIDIZED-POLYETHYLENE

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Characterization of Novel Degradable Starch-Polyethylene Plastics Containing Oxidized-Polyethylene[1]

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1. Journal Paper No. J- of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Project No. 0178 and 2889.

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ABSTRACT

Linear low-density polyethylene films were prepared that contained native corn starch (7, 14, or 28%), low- or high-molecular weight oxidized-polyethylene (15%) and a pro-oxidant mixture (18% POLYCLEAN II) that contains manganese and vegetable oil. For each mixture all components were first mixed at high temperatures in a twin-screw extruder, and pelletized. The pellets were cast into films using a single-screw extruder. Oxidized-polyethylene addition did not impair transparency and thickness of the films, and relatively small reductions in film mechanical properties were observed. Thermal and photodegradation properties of each film were evaluated by 70°C forced-air oven treatment (20 days), by high-temperature high-humidity treatment in a steam chamber (20 days), and by exposure to ultraviolet light (365 nm) (4 weeks). Changes were determined in the mechanical properties of the films by an Instron Universal Test Machine, in the carbonyl index by FT-IR, and in the molecular weight by high-temperature gel-permeation chromatography (HT-GPC). The addition of oxidized-polyethylene, especially, high-MW oxidized-polyethylene, and up to 14% starch to the films significantly increased the rate of thermal and photodegradation.

INTRODUCTION

Many successful plastic products have the properties of low density, toughness, transparency, elasticity, resistance to chemicals and microbial attack, the ability to control moisture and gases transfer, and recyclability. However, when plastics are used in a disposable product, their resistance to degradation becomes a disadvantage. The amount of waste plastics produced each year in the United States is 10 million tons (22) and is causing a tremendous disposal problem. Polyethylene degradation rate in landfills is estimated to be 100 to 200 years (32). To address this environmental concern degradable plastics that respond to chemical-, photo- and/or biological attack are being developed (23).

Photodegradable plastics depend on exposure to light as the primary mechanism for their degradation. Guillett (14, 15) developed a photodegradable plastic by incorporating keto groups into the polymer chains. Thus, carbon monoxide co-polymerization with ethylene produces a polymer sensitive to specific wavelengths of ultraviolet radiation (270 to 360 nm) (22). However, for these photodegradable plastics all degradation stops in the absence of light, so their degradation is affected by factors such as seasons, latitude, weather and the light wavelength to which they are exposed (8, 29).

Polyethylene also can be rendered more degradable by blending in various

additives that accelerate chemical and biological degradation (16, 18, 20, 24). The additive is usually a combination of a natural polymer, such as starch, plus vegetable oil containing pro-oxidant and transition metals such as copper, iron, and/or manganese (16). In the presence of oxygen these pro-oxidants initiate free-radical polymer degradation that produces carbonyl groups (ketone, ester, and carboxyl group) and chain scission throughout the polyethylene (16, 29). Oxidized-polyethylene also can be added to polyethylene to increase plastic degradation (19). This chemical degradation accelerates biological degradation of the polyethylene (24, 27) as well as starch degradation (31). Dry granular starch has been used as a filler in biodegradable plastics (11, 12, 13), and modified starch, gelatinized starch, and oxidized-polyethylene have been used as fillers to improve the biodegradability of plastics (12, 25, 26, 33).

In this study, cast films were prepared that contained corn starch (7, 14, and 28%), a pro-oxidant (POLYCLEAN II), oxidized-polyethylene with either a low- or high-molecular weight (MW) and polyethylene. The characteristics of these films were determined and compared to control films in which either starch, pro-oxidant or oxidized-polyethylene was omitted. The films demonstrated significantly faster thermal and photodegradation along with some reduction in mechanical strength.

MATERIALS AND METHODS

Film Preparation. Linear low-density polyethylene (Dow Chemical Co., Midland, MI), native corn starch (American Maize-Products Co., Hammond, IN), POLYCLEAN II (Archer Daniel Midland Co., Decatur, IL), and oxidized-polyethylene with high- or low-MW (Aldrich Chemical Co., Milwaukee, WI) were used as plastic components. Native corn starch was dried in a vacuum oven at 100°C to < 0.3% moisture as determined by a Karl Fisher titration (4). POLYCLEAN II contained native corn starch (40%), vegetable oil and manganese stearate (280-330 ppm Mn) in polyethylene pellets. A total of 12 different combinations of cast films were prepared (Table 1) by mixing the component in a twin-screw extruder (Model 15-02-000 extruder, C.W. Brabender, South Hackensack, New Jersey). The barrel temperatures were sequentially 185, 195, 200, and 195°C. The die temperature was 190°C, and the screw speed was 20 rpm (9). The extruded rods (dia. 0.3 cm) were air-cooled and pelletized into 0.5 cm chips. Each of the 12 mixtures were cast into films using a single-screw extruder with barrel sequential temperatures of 175, 185, 190, and 195°C, a die temperature of 200°C, and a screw speed of 15 rpm (9). The cast films were collected with a water-cooled Univex take-off system, and stored in polyethylene bags at 4°C.

Cast Film Characteristics.

(i) Determination of transition metal contents. The concentration of transition metal (Mn) in the prepared plastics was determined by atomic absorption by the procedure of Johnson et al. (21) on a Smith-Hieftje 12 instrument (Thermo Jarrel Ash Corp. Franklin, MA) using an air-acetylene flame.

(ii) Determination of starch content. Starch content of the plastics was determined chemically by using the modified phenol-sulfuric acid procedure developed by Fratzke et al. (10) and spectrophotometrically *via* fourier-transformed infrared (FT-IR) spectroscopy. FT-IR for the analysis of the starch content was performed on a Bruker (Billerica, MA) Model IR 113V Instrument controlled by Bruker IFS version 12/87 software. Each plastic film was attached to a FT-IR plate and scanned from 600 to 4000 cm^{-1}. The area of the starch absorption peak (871-1190 cm^{-1}) was divided by the area of the methylene peak (1471-1485 cm^{-1}) to eliminate variations in film thickness. FT-IR analysis provides a qualitative starch determination.

(iii) Determination of the oxidized materials. The concentration of low- or high-MW oxidized materials incorporated into each film was determined by FT-IR spectroscopy as a carbonyl index which was the ratio of the peak area from 1701 to 1732 cm^{-1} divided by the methylene peak area from 1471 to 1485 cm^{-1} (1).

(iv) Mechanical properties. The tensile strength, percent elongation and strain energy of cast films were measured using an Instron Model 4502 Universal Test Machine (Instron Corporation, Canton, MA). The each film was cut into strips (2.5 x 10.2 cm) in the same direction extruded (machine direction). The strips of film were equilibrated to 50% relative humidity for at least 40 h prior to testing (3). The thickness of each strip was measured with a hand-held caliper. Crosshead speed was 500 mm/min, and the starting gap between the jaws was 50 mm. Tensile strength, percent elongation and strain energy were calculated by using series IX Automated Materials Testing System software (Instron Corp., version 4.09).

Chemical and Photodegradation Assays. The cast films were cut into strips (2.5 x 10.2 cm) in machine direction and treated as follows:

(i) Forced-air oven treatment. Strips were placed into a forced-air oven at 70°C with both sides of strips exposed to air (23). The strips were taken out after 2, 4, 6, 8, 10, 12, 16 or 20 days and evaluated for change in weight, mechanical properties, polyethylene MW distribution, and carbonyl index.

(ii) High-temperature high-humidity (HT-HH) treatment. Strips were placed on a vinyl-coated racks and exposed to a constant flow of steam. Strips were turned every 3 to 4 days. The strips were taken out after 2, 4, 6, 8, 10, 12, 16 or 20 days (20) and evaluated as in **(i)** except for weight change.

(iii) Ultraviolet (UV) treatment. Strips were exposed to longwave UV light (365 nm) for 4 week using the procedure of Lee et al. (24). Every 3 to 4 days films were moved and turned over to insure even light exposure. Each film was evaluated as in **(i)** except for weight loss.

Procedures for Film Degradation Evaluations.

(i) Weight changes. The weight of each strip was measured to the 0.1 mg before and after 70°C heat treatment. The percent weight change was calculated.

(ii) Changes of mechanical properties and carbonyl index. Instron and FT-IR spectroscopy were employed to examine the changes in film mechanical properties and carbonyl index, respectively.

(iii) Changes in the MW distribution. High-temperature gel-permeation chromatography (HT-GPC) was performed with a Waters Model 150C Chromatograph (Waters/ Millipore Co., Milford, MA) using the method of Lee et al. (24). Three Water's columns were used in series, and each column had a functional MW range of 2,700-610,000 daltons. Each run of 16 samples included a set of polystyrene MW standards (4,016; 53,500; and 610,000 daltons). The mobile phase was 1,2,4-trichlorobenzene (Burdick & Jackson/ Bacter Inc., GC/GPC grade, Markeson, MI) at 1 ml/min. Sample volume 200 μl, and columns, injector, and refractive index detector were held at 140°C and the solvent pump was held at 50°C. Weight-average MW ($\overline{M_w}$), number-average

MW ($\overline{M_n}$) and polydispersity ($\overline{M_w}/\overline{M_n}$) were determined by using Maxima 820 computer software (Waters/millipore Co.).

Data Analysis. The data obtained from the experiments was analyzed by PC-SAS program (version 6.04) by using an analysis of variance, contrast and regression (28).

RESULTS AND DISCUSSION

Characteristics of Cast Films. Each plastic film type had a relatively uniform thickness (Table 2). The plastic films appeared colorless, white or cream color, depending on their starch levels, whereas films blended with low- or high-MW oxidized-polyethylene without starch were transparent. All plastics prepared with 18% POLYCLEAN II contained 51 to 58 ppm of manganese (Table 2). The starch contents as determined by the chemical method and FT-IR demonstrated that the films contained the starch contents close to the expected values (Table 2). Chemical method illustrated that films containing 7% and 14% starch were closer to expected starch values than films containing 28% starch. A similar pattern was showed in the FT-IR method. The 14% and 28% starch-containing films exhibited a FT-IR absorbance two, and four to six times higher than 7% films, respectively. The chemical and FT-IR analysis suggest that starch was not evenly distributed in the 28% starch-containing films. Furthermore, the incremental starch loading of 7, 14, and 28% with a constant addition of pro-oxidant resulted into an average manganese content of 57, 64 and 76 ppm with respect to polyethylene for the different films, respectively. FT-IR spectra of the initial materials confirmed the presence or absence of oxidized-polyethylene (1701 to 1732 cm^{-1}) and the increasing concentrations of starch (871-1190 cm^{-1}) (Figure 1). The carbonyl

index of the initial materials suggested that each of the film contained almost the same level of oxidized-polyethylene except for HP-0 which seemed to contain almost twice the average level (Table 3). Overall, manganese content, starch content and carbonyl index analysis confirmed that the components of the plastics were properly incorporated into the films except for 28% starch loading.

Increased levels of starch resulted in a corresponding reduction in mechanical strength. Percent elongation represents the film's ability to stretch (6). When compared with the plastics containing no starch, percent elongation decreased averaged 5% and 26% for 7% and 28% starch additions, respectively (Table 4). The addition of high- or low-MW oxidized-polyethylene did not significantly change the percent elongation except for LP-28. Film tensile strength and strain energy represent the force per unit of area required to tear the film and the work required to take the film to its breaking point, respectively (6). Significant reduction in tensile strength and strain energy values resulted from the addition of oxidized-polyethylene and/or starch to polyethylene. Nevertheless, tensile strength, percent elongation, and strain energies for HP-14 film were not significantly reduced when compared with P-14 film.

Degradation by Oven Treatment. The addition of oxidized-polyethylene, starch and pro-oxidant accelerated the thermal degradation rates for degradable

plastics. The initial weight loss in each type of plastic was probably due to starch moisture loss, which paralleled the starch levels (Figure 2). Furthermore, as starch levels increased, the rate of weight gain decreased. This was probably caused by the sequential reduction in total polyethylene with the corresponding increase in starch loadings. The only material being chemically oxidized and resulting in a weight increase was the polyethylene during 2-8 days of oven treatment. Furthermore, the overall rate of weight gain was significantly increased with the addition of oxidized-polyethylene in the presence of pro-oxidant with high-MW giving a greater effect than low-MW. On the other hand, for films containing starch but no oxidized-polyethylene (P-7, P-14 and P-28) the rate of weight change was significantly slower. The weight decrease after 8-10 days of oven treatment for films containing oxidized-polyethylene was probably due the production of volatile compounds like CO_2, formaldehyde and acetaldehyde (7, 30). Films containing no pro-oxidant (P-0, LP-0, and HP-0) demonstrated virtually no weight gain over the 20 day of the oven treatment.

Decreases in tensile strength, percent elongation and strain energy also were accelerated by the addition of pro-oxidant, oxidized-polyethylene and starch (Figure 3). The plastics containing both pro-oxidant and low- or high-MW oxidized-polyethylene degraded more rapidly, becoming brittle after 2 to 4 days of oven treatment. Films containing no pro-oxidant or starch did not

degrade except for the film containing 15% low-MW oxidized-polyethylene.

Changes in MW distribution for the various films paralleled the loss of mechanical strength with films containing oxidized-polyethylene, pro-oxidant and starch degrading the fastest (Figure 3). The data for $\overline{M_w}$ were analyzed by regression using PC-SAS to resolve the oxidative-degradation rate during the oven treatment. The degradation rates of the films containing POLYCLEAN II without oxidized-polyethylene (P-7, P-14 and P-28) followed a first order reaction ($R^2 = 0.98$). As starch levels increased, degradation rates increased and films containing high-MW oxidized-polyethylene degraded faster than those with low-MW oxidized-polyethylene. Additionally, the plastics lost their measurable mechanical properties when their $\overline{M_w}$ fell below 50,000. These results were consist with those of Holmstrom and Sorvik (17) who found that further changes in the mechanical properties and MW distributions were not observed after achieving a $\overline{M_w} < 50{,}000$ by long-term exposure at temperatures below 150°C. Furthermore, Figure 4 shows that there was a reduction in polydispersity with time, indicating a narrowing in the overall MW distribution. This reduction in polydispersity may be attributed to a continuing polyethylene chain scission.

Carbonyl indices were affected in the oven treatment by the presence of oxidized-polyethylene (Table 3). Albertsson et al. (1, 2) determined the biodegradability of polyethylene using the carbonyl index, and Benham et al. (5)

detected ketone and carboxyl groups from the oxidation of polyethylene. The wavelength range used for the carbonyl index in our study included carboxylic acid, ester, aldehyde and ketone absorption bands. The absorbance in this region markedly increased during the oven treatment of most films (Table 3). The carbonyl index was greater for films that contained oxidized-polyethylene and pro-oxidant than in those without oxidized-polyethylene.

The presence of oxidized-polyethylene and pro-oxidant produced a synergistic increase in the degradation of polyethylene during the oven treatment. The degradation rate for films containing both oxidized-polyethylene and pro-oxidant was faster than the sum of the degradation rates for the film containing oxidized-polyethylene and only pro-oxidant (Table 3). Moreover, the high-MW oxidized-polyethylene clearly had a greater affect on the thermal-oxidative degradation than low-MW oxidized-polyethylene. Additionally, it was observed that the percent elongations of all plastics reduced and $\overline{M}_w$ of most plastics except for LP-14, HP-14 and HP-28 were degraded slowly during the storage at 4°C for 18 months (Figure 5).

Degradation by HT-HH. Faster reduction of the percent elongation was observed in films containing oxidized-polyethylene and pro-oxidant (Figure 6), which was the same result obtained in the 70°C oven treatment. However, compared to the 70°C oven treatment, the degradation by HT-HH treatment was slower. The percent elongation of LP-0 did not decrease by the HT-HH

treatment, in contrast with the oven treatment. The plastics without oxidized-polyethylene (P-0, P-7, P-14, and P-28) exhibited faster reductions in the percent elongation by the HT-HH treatment than by the oven treatment.

The $\overline{M_w}$ reduction for the HT-HH treatment was also generally slower than for the 70°C oven treatment (Figure 6). Polydispersity values were generally higher in the HT-HH treated films than the 70°C oven treated films (Figure 4). This broadening in MW distribution could explain the faster decline in percent elongation and slower rate of decline of $\overline{M_w}$. This retardation of $\overline{M_w}$ decline might be due to the lower oxygen tension in the film as a result of the high humidity (20).

The carbonyl index was increased by the HT-HH treatment except for LP-0 and HP-0 (Table 3). Moreover, the starch-filled plastics generated a larger increase in the carbonyl index than the plastics without starch in the HT-HH and 70°C oven treatment. However, the carbonyl indices after the HT-HH treatment were lower than those after the 70°C oven treatment. This observation supports our hypothesis of a lower oxygen tension being present in the HT-HH treatment and resulting in a corresponding reduction in polyethylene degradation.

Photodegradation with UV. The addition of oxidized-polyethylene, pro-oxidant and starch resulted in significant differences in photodegradation as measured by the decline in percent elongation and $\overline{M_w}$ of films (Figure 7).

Changes in percent elongation did not parallel reduction in $\overline{M_w}$. Percent elongation demonstrated marginal degradation for films containing only polyethylene and/or oxidized-polyethylene whereas HT-GPC demonstrated enhanced degradation for films containing polyethylene plus oxidized-polyethylene. For starch-filled films containing pro-oxidants, high-MW oxidized-polyethylene, addition caused the greatest photodegradation as determined by $\overline{M_w}$. Increases in starch content caused a corresponding increases in the decline of percent elongation. Finally, carbonyl index data indicated that among the degradation treatments the least polyethylene oxidation occurred during photodegradation (Table 3). Films containing high-MW oxidized-polyethylene tended to show greater oxidation during photodegradation.

CONCLUSION

Addition of oxidized-polyethylene, especially high-MW oxidized-polyethylene, to starch-loaded polyethylene films significantly increased the rates of oxidative-thermal degradation and photodegradation while causing minimal effect on film color and thickness. Oxidized-polyethylene addition did not significantly improve the mechanical properties of films at the different starch loadings. Addition of 15% oxidized-polyethylene, pro-oxidant and up to 14% starch to polyethylene films could be expected to increase the rate of degradation of such plastic in natural environments.

ACKNOWLEDGEMENTS

This research was supported by the Iowa Corn Promotion Board, the Iowa State University Center for Crops Utilization Research, Iowa General Assembly, Iowa Agriculture and Home Economic Experimental Station and the Iowa Department of Natural Resources.

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Table 1. Amount of the various compounds per kilogram in the experimental plastic mixtures

Film designation	Expected starch content (%)	Native corn starch (g)	POLY-CLEAN II[a] (g)	Oxidized-polyethylene[b] (g)	Polyethylene (g)
P-0	0				1000
P-7	7		180		820
P-14	14	70	180		750
P-28	28	210	180		610
LP-0	0			150 low-MW	850
LP-7	7		180	150 low-MW	670
LP-14	14	70	180	150 low-MW	600
LP-28	28	210	180	150 low-MW	460
HP-0	0			150 high-MW	850
HP-7	7		180	150 high-MW	670
HP-14	14	70	180	150 high-MW	600
HP-28	28	210	180	150 high-MW	460

[a]POLYCLEAN II contained 280 to 330 ppm Mn and 40% starch plus vegetable oil.

[b]Acid number for low- and high-MW oxidized-polyethylene is 15 and 28 mg KOH/g, respectively.

Table 2. Thickness, manganese and starch content of the experimental films

Film designation	Thickness (mm)	Mn content (ppm)[a]	Starch content[a]	
			Chemical method (%)	FT-IR method (ratio)[b]
P-0	0.006	ND[c]	ND	0.0
LP-0	0.006	ND	ND	0.0
HP-0	0.007	ND	ND	0.0
P-7	0.075	53	6	4.9
LP-7	0.075	54	6	5.0
HP-7	0.075	56	6	4.7
P-14	0.075	58	14	12.3
LP-14	0.075	51	14	11.3
HP-14	0.075	56	14	10.2
P-28	0.080	53	31	23.3
LP-28	0.085	52	30	30.4
HP-28	0.085	59	32	27.7

[a]Each value is mean for two replicates.

[b]Ratio represents the starch absorbing peaks (871-1190 cm^{-1}) divided by the methylene absorbing peak area (1471-1485 cm^{-1}).

[c]ND is for not determined.

Table 3. Carbonyl index of the experimental films initially and after various accelerated degradation treatments[a]

Film designation	Carbonyl index[b]			
	Initial day	Oven treatment (20 days)	HT-HH treatment (20 days)	UV treatment (4 weeks)
P-0	0.00	0.00	0.00	0.00
LP-0	0.15	0.22	0.05	0.30
HP-0	0.32	0.33	0.15	0.29
P-7	0.00	1.21	0.44	0.15
LP-7	0.10	0.94	0.81	0.15
HP-7	0.13	1.06	0.74	0.93
P-14	0.01	1.90	0.74	0.13
LP-14	0.18	2.13	0.74	0.31
HP-14	0.16	3.93	0.46	0.36
P-28	0.01	0.86	0.90	0.06
LP-28	0.22	1.15	0.94	0.33
HP-28	0.17	2.34	0.55	0.43

[a]Each value is a mean for two replicates.

[b]Carbonyl index represents the ratio of the carbonyl absorbing peak area (1701 to 1732 cm^{-1}) divided by the methylene absorbing peak area (1471 to 1485 cm^{-1}).

Table 4. The initial mechanical properties of the experimental films[a]

Film designation	Tensile strength (kg/mm^2)	Percent elongation (%)	Strain energy (kg.mm)
P-0	3.22	764	1263
LP-0	2.24[bc]	758	828[bc]
HP-0	2.38[bc]	753	1026[c]
P-7	2.73	747	1270
LP-7	2.43[b]	704	984[b]
HP-7	2.14[bc]	718	878[b]
P-14	2.07	683	834
LP-14	1.67[b]	607[c]	786
HP-14	1.93	677[c]	765
P-28	1.81	633	741
LP-28	1.14[b]	477[bc]	559[b]
HP-28	1.21[b]	582[c]	531[b]

[a]Each value is a mean for 4 replicates.

[b]Values are significantly different from the same film with no oxidized-polyethylene among the plastics containing the same starch content ($P<0.05$).

[c]Values are significantly different between low- and high-MW oxidized-polyethylene plastics among the plastics containing the same starch content ($P<0.05$).

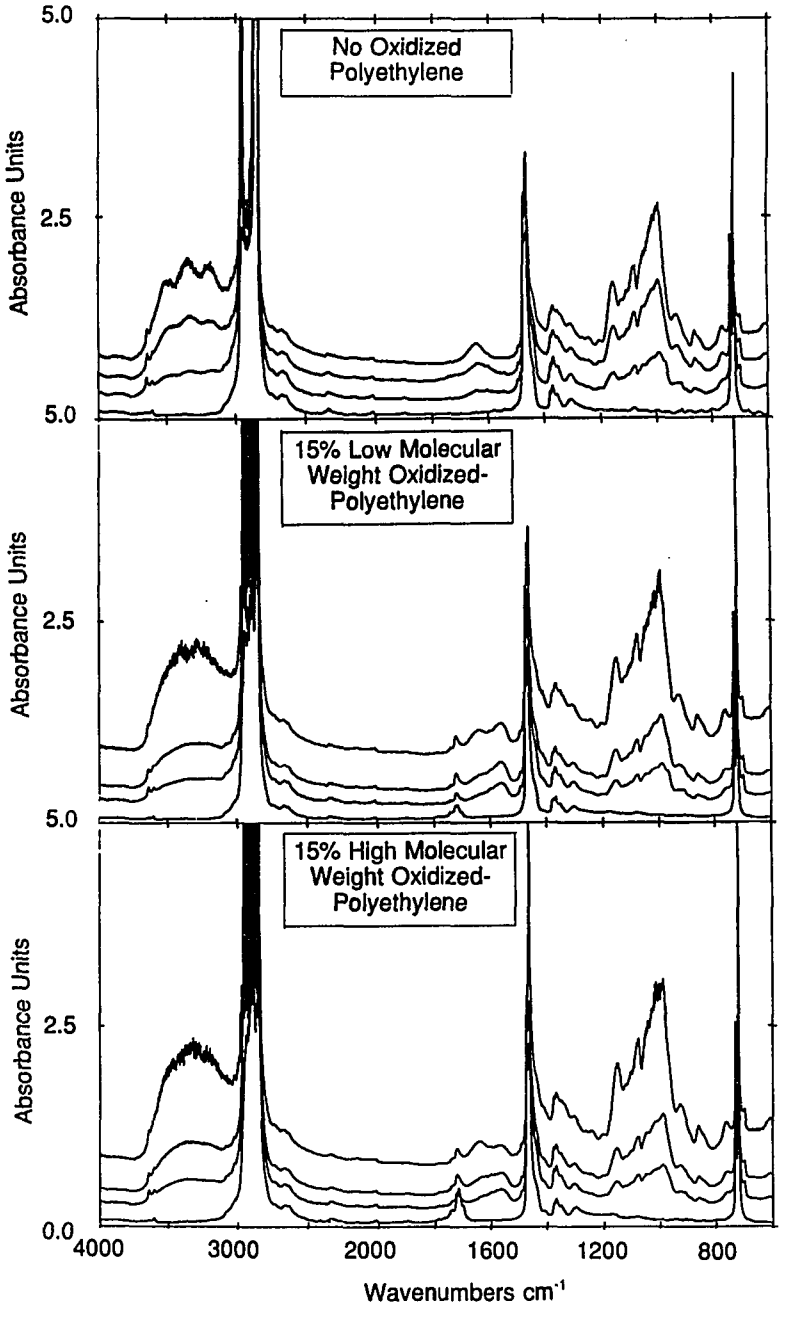

Figure 1. FT-IR spectra for films containing high- or low-MW oxidized-polyethylene. For each set of spectra the top to bottom sequence in 28%, 14%, 7%, and 0% added starch. The starch-containing films also contain POLYCLEAN II

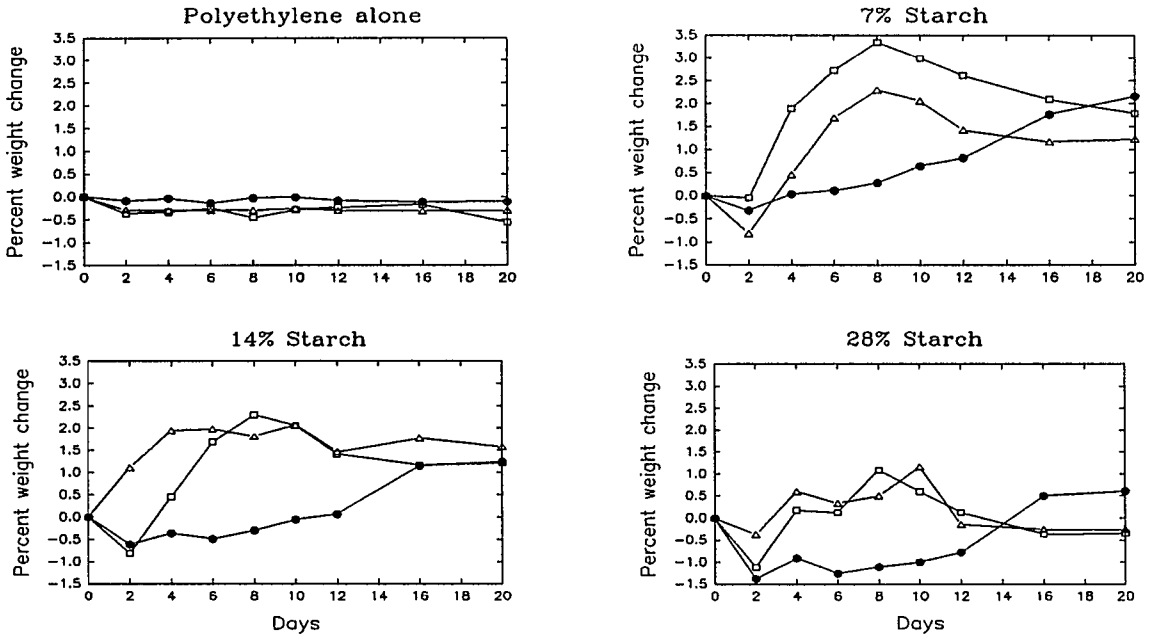

Figure 2. Percent changes in weight of films after 20 days at 70°C. Symbols: no oxidized-polyethylene (●), 15% low-MW oxidized-polyethylene (△), and 15% high-MW oxidized-polyethylene (□). Each data point represents an average of four replicates

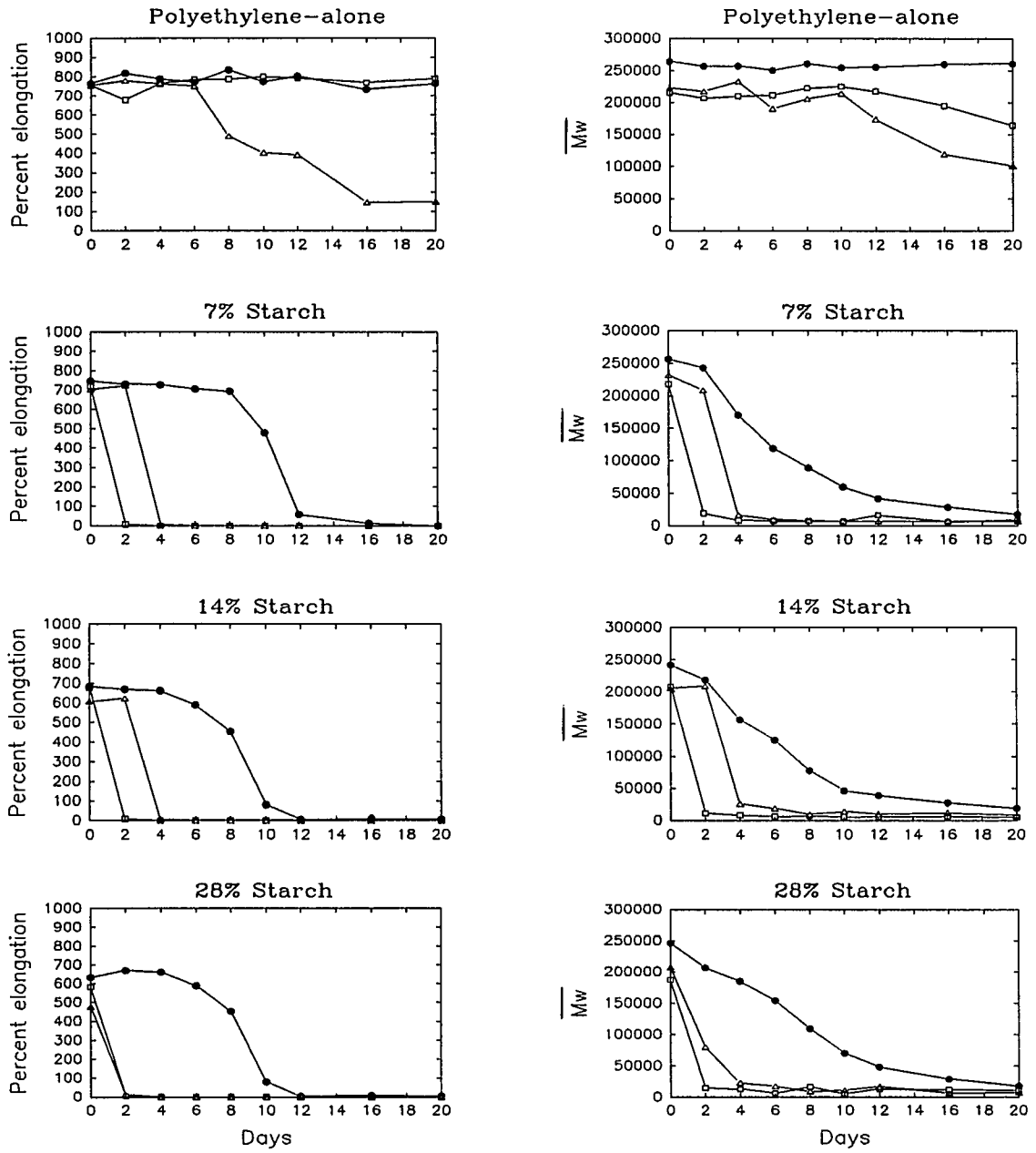

Figure 3. The percent elongation (each data point represents an average of four replicates) and $\overline{M}_w$ (each data point represents an average of two replicates) for films after 20 days at 70°C. Symbols: no oxidized-polyethylene (●), 15% low-MW oxidized-polyethylene (▵), and 15% high-MW oxidized-polyethylene (□)

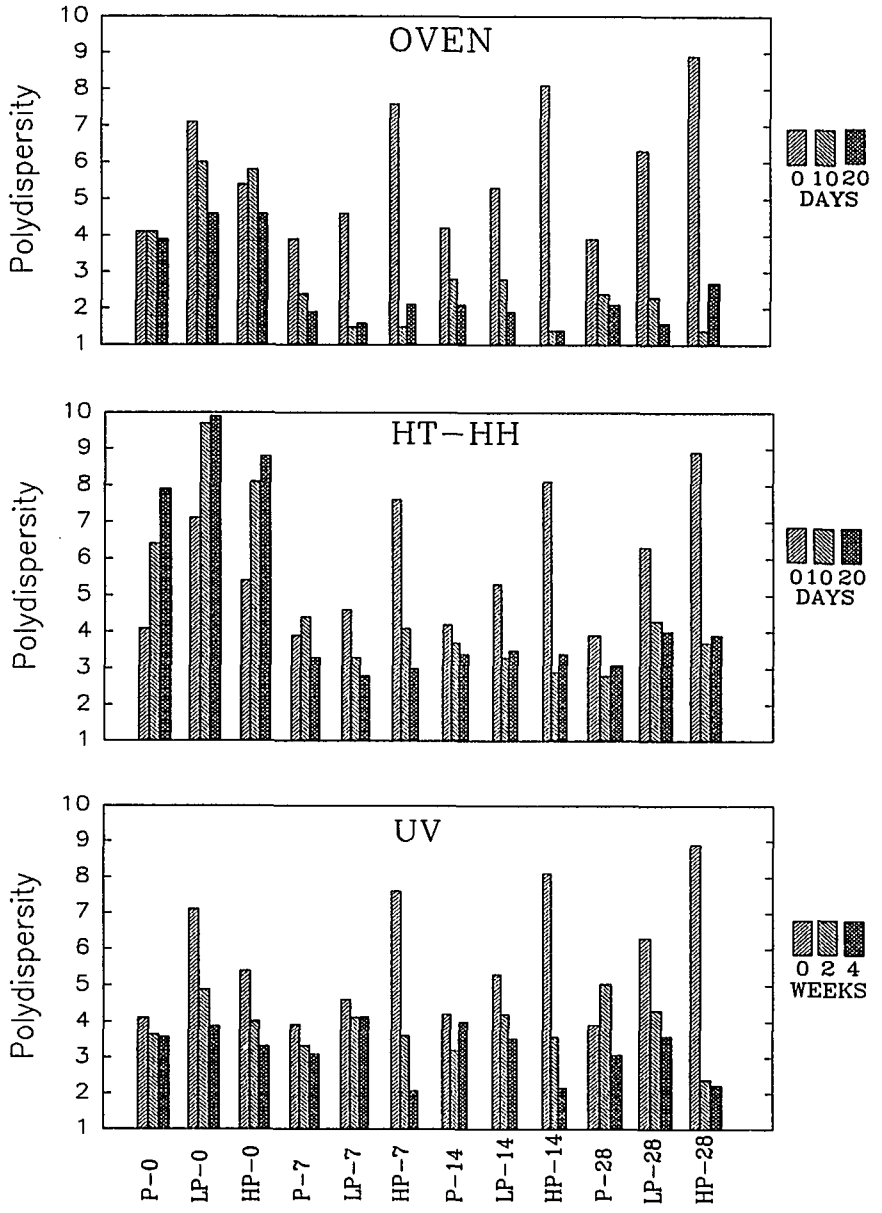

Figure 4. Polydispersity ($\overline{M}_w/\overline{M}_n$) for films exposed to a 70°C oven, HT-HH and UV. Each value is a mean for two replicates

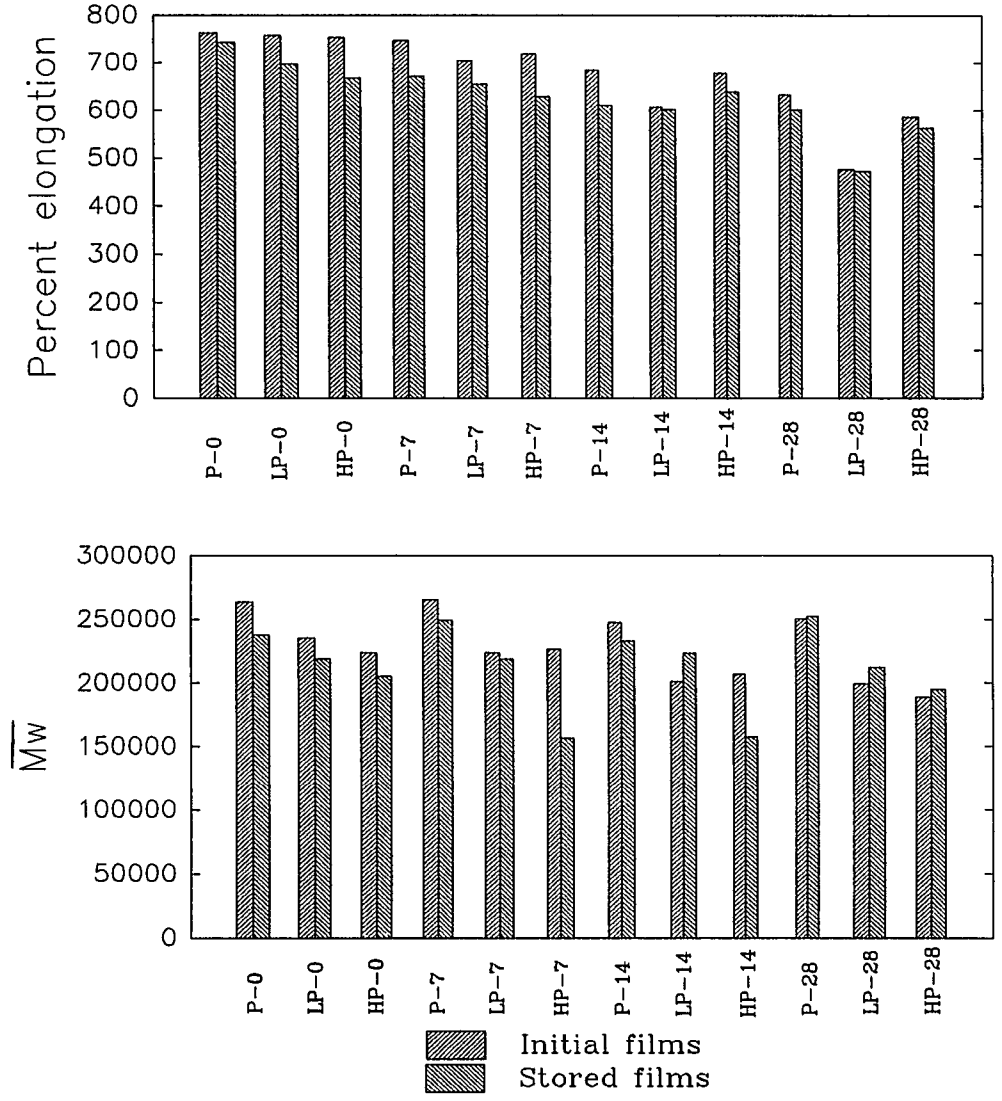

Figure 5. The percent elongation (each data point represents an average of four replicates) and $\overline{M}_w$ of the films at initial day and at storage at 4°C for 18 months

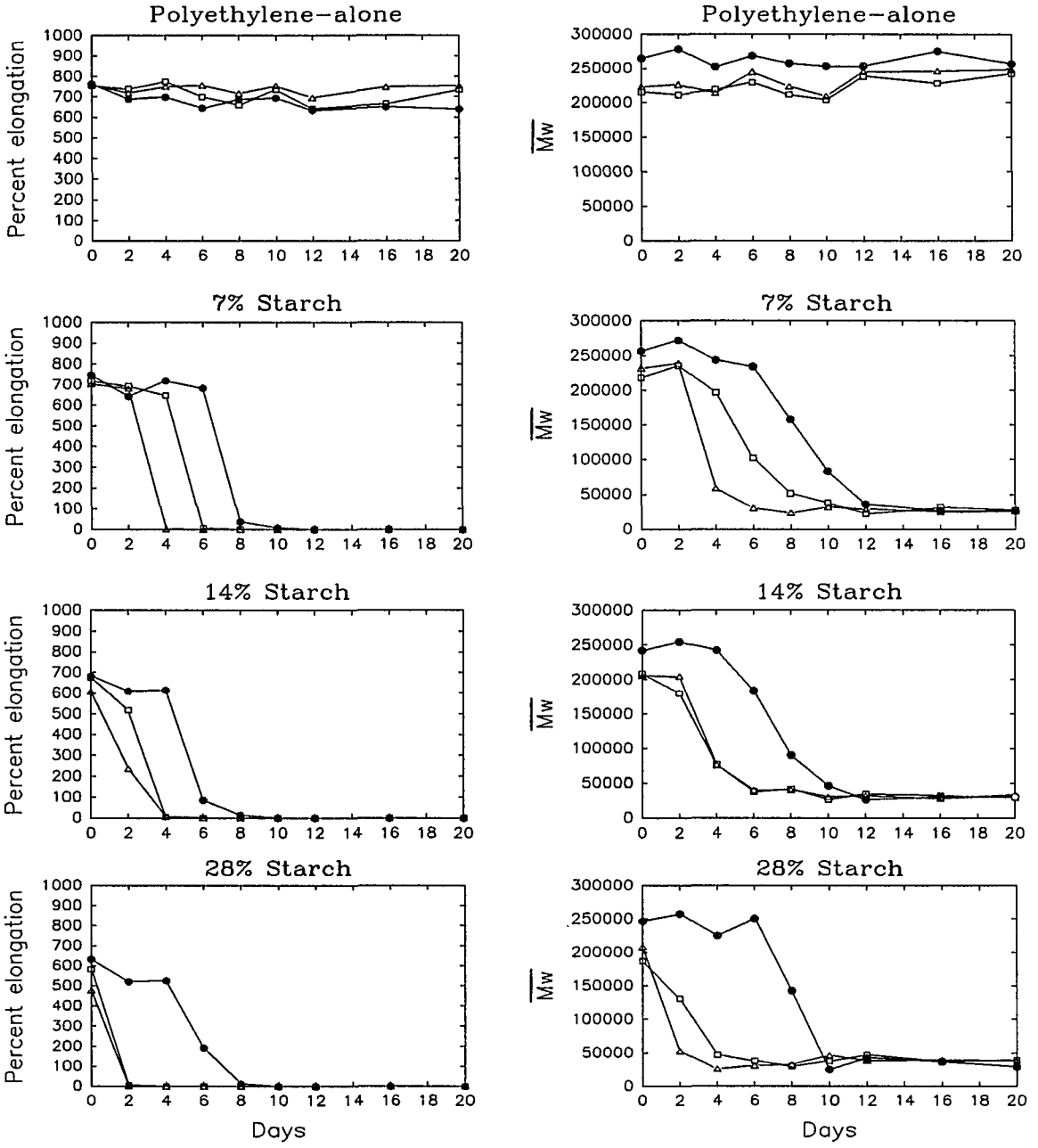

Figure 6. The percent elongation (each data point represents an average of four replicates) and $\overline{M}_w$ (each data point represents an average of two replicates) for films after 20 days of the HT-HH treatment. Symbols: no oxidized-polyethylene (●), 15% low-MW oxidized-polyethylene (▵), and 15% high-MW oxidized-polyethylene (□)

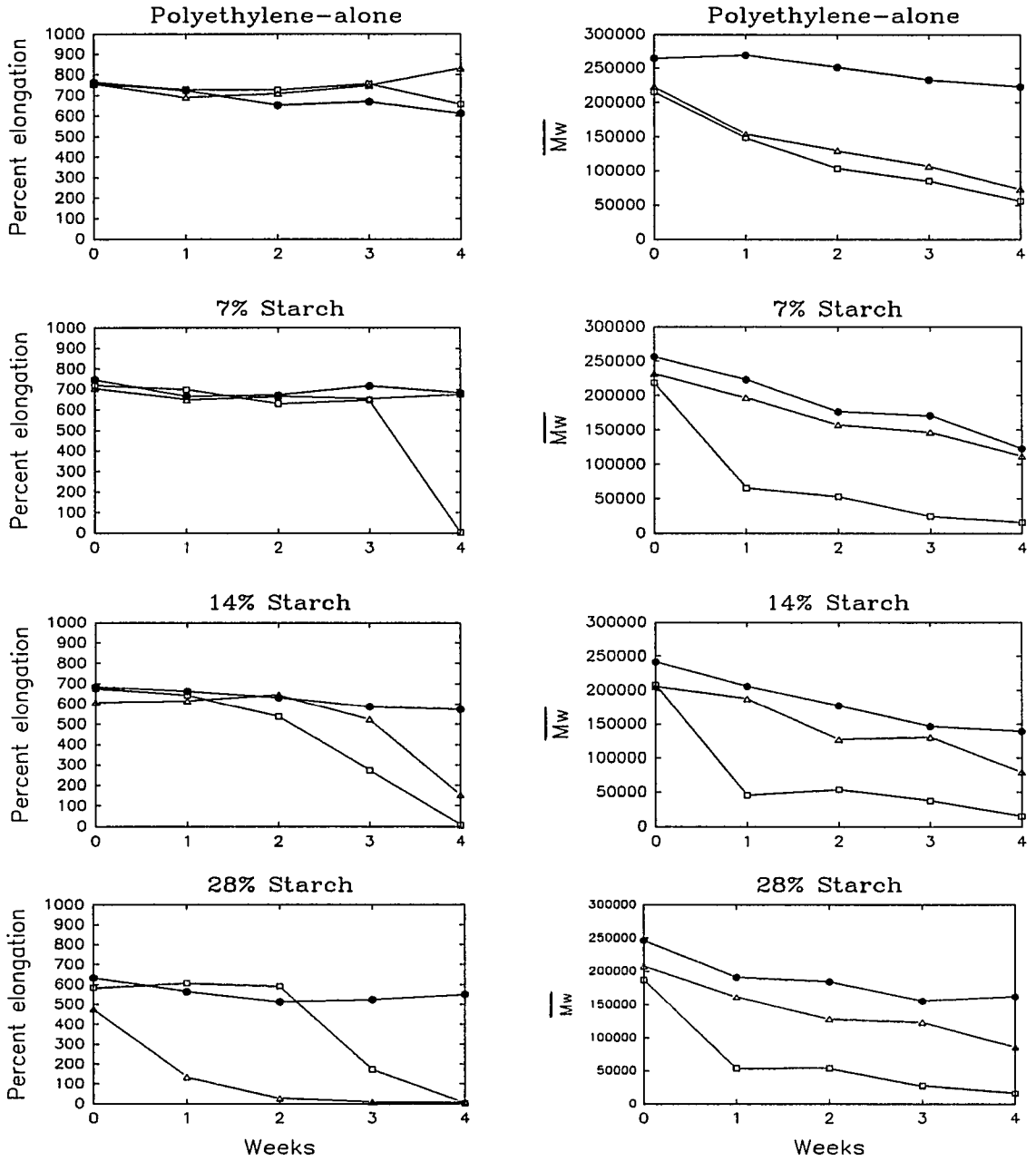

Figure 7. The percent elongation (each data point represents an average of four replicates) and $\overline{M}_w$ (each data point represents an average of four replicates) for the films after 4 weeks of the UV treatment. Symbols: no oxidized-polyethylene (●), 15% low-MW oxidized-polyethylene (△), and 15% high-MW oxidized-polyethylene (□)

PAPER II. BIODEGRADATION ASSAY OF STARCH-POLYETHYLENE PLASTICS AS DETERMINED WITH PURE-CULTURE AND EXTRACELLULAR-ENZYME

Biodegradation Assay of Starch-Polyethylene Plastics as Determined with Pure-Culture and Extracellular-Enzyme[1]

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1. Journal Paper No. J- of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Project No.

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ABSTRACT

Biodegradability of degradable starch-polyethylene films prepared and developed at Iowa State University was evaluated. The films were composed of linear low-density polyethylene, oxidized-polyethylene with low- or high-molecular weights (MWs) (15%), corn starch (0, 7, 14, 28%) and pro-oxidant (51 to 59 ppm manganese plus vegetable oil). Biodegradability was determined by a culture assay with either *Streptomyces badius* 252, *S. setonii* 75Vi2 or *S. viridosporus* T7A and by using an enzyme assay using a *S. setonii* 75Vi2 preparation. The results from the culture assays indicated that biomass accumulation on the film surface inhibited chemical and biological degradation of the films. The enzyme assay illustrated biodegradation for all the starch-polyethylene films containing 14 and 28% starch, suggesting some biodegradability.

INTRODUCTION

In the 1970's degradable plastics containing a starch filler plus pro-oxidants were developed (11, 12, 18, 19) and these materials have demonstrated accelerated rates of degradation in various laboratory and field studies (14, 17, 21, 22). Pro-oxidants play an important role in biodegradation by triggering the chemical oxidation of polyethylene, which can stimulate biodegradation (17). The addition of oxidized-polyethylene to plastics containing pro-oxidants has the potential to further accelerate chemical oxidation because of their synergistic effect with pro-oxidant (13, 16).

Various methods have been used to measure the biodegradability of plastics. In various soil studies, production of $^{14}CO_2$ from ^{14}C-[labeled]-polyethylene (1-4), and changes in polymer properties, such as tensile strength, molar mass and weight loss, have been used (6). Soil burial tests traditionally have been used to test degradation because of their similarity to landfill disposal (7, 10). Composting studies are considered the best indices of biodegradation because of their activity and reproducibility (8, 14). Johnson et al. (14) observed that starch-polyethylene materials degraded at slightly different rates in several different compost sites. However, all fields studies are considered long-term (1-10 years), and it is difficult to maintain uniform conditions over such long periods. Thus, fast, sensitive, uniform, and reproducible methods to

measure the biodegradability of plastics still need to be developed.

Recently, our laboratory demonstrated biodegradation of polyethylene in a shake-flask study with pure-culture of lignin-degrading *Streptomyces* species (17). Extracellular-enzyme concentrates from these bacteria also exhibited polyethylene biodegradation (21). A study evaluating the biodegradability of several starch-polyethylene films using this pure-culture method and an extracellular-enzyme concentrate of *Streptomyces setonii* 75Vi2 illustrated biodegradation for almost every enzyme treated film (22). These two methods gave reproducible results in 3-4 weeks.

This study reports the biodegradability of additional starch-polyethylene plastics developed at Iowa State University using various *Streptomyces* cultures and extracellular-enzymes.

MATERIALS AND METHODS

Plastic Films. Twelve starch-polyethylene films were cast that contained various concentrations of linear low-density polyethylene, starch (0, 7, 14, and 28%), oxidized-polyethylene (15% low- or high-MW), and pro-oxidant (POLYCLEAN II from Archer Daniel Midland Co., Decatur, IL) (Table 1). The processing and characteristics of these films have been described by Kim et al. (16).

Microorganism. *Streptomyces viridosporus* T7A (ATCC 39115), *Streptomyces badius* 252 (ATCC 39117), and *Streptomyces setonii* 75Vi2 (ATCC 39116) were maintained on agar slants at 4°C. *S. badius* and *S. viridosporus* degrade starch whereas *S. setonii* does not (17).

Chemical Disinfection of Films. The films were cut into strips (2.5 x 10 cm) in the direction of extrusion (machine direction) and chemically disinfected using the procedure from Pometto et al. (22). Each disinfected strip was transferred aseptically to a sterile petri dish and dried for 15 h at 45°C.

Pure-culture Assay (17). A disinfected strip was aseptically added to 100 ml culture medium containing 0.6% (w/v) yeast extract medium, inoculated with culture spores, and incubated with shaking at 125 rpm at 37°C for 4 weeks. Controls of unincubated-disinfected films (zero-control) and uninoculated-incubated films (uninoculated-control) also were prepared.

Extracellular-enzyme Assay. Extracellular-enzyme concentrate was prepared from *S. setonii* 75Vi2 according to Pometto et al. (22). A 50-liter culture of *S. setonii* 75Vi2 was prepared in 0.6% (w/v) yeast extract in a Braun U-50 fermentor (Allentown, PA) incubated at 37°C until a pH $\geq$ 8.0 was achieved. Cells were removed by centrifugation, and the supernatant was concentrated to 4-liters, using a hollow-fiber filtration unit (Amicon Corp., Danvers, MA) with a 10,000-MW cut-off. Half of the concentrated supernatant was filter sterilized, and half was autoclaved for 15 min at 121°C to inactivate the enzymes. Antibiotic solution (20 ml/L) (Penicillin/streptomycin/neomycin solution, Sigma chemical Co., St. Louis, MO) was added to the cool and sterile supernatant. A set of the twelve kinds of disinfected film strips was added aseptically to flasks containing 1 L of either active- or inactive-enzyme culture, and incubated with shaking at 125 rpm and 37°C for 3 weeks.

Film Harvest. After culture or enzyme treatments film strips were soaked in 70% ethanol for 30 min and dried at 45°C for 15 h.

Evaluation of Biodegradability.

(I) Mechanical properties. The strips were equilibrated to 50% relative humidity for at least 40 h (5), film thickness was measured with a hand-held caliper. The maximum percent elongation of the films was measured by an Instron Universal Test Machine (Model 4502, Instron Corporation, Canton, MA) using a 50 mm starting gap and crosshead speed of 500 mm/min.

(ii) Polyethylene MW distribution. The polyethylene MW distribution was determined using a Waters Model 150C (Waters/Millipore Co., Milford, MA) high-temperature gel-permeation chromatography (HT-GPC) according to Lee et al. (17). The mobile phase was 1,2,4-trichlorobenzene (Burdick & Jackson/Bacter Inc., GC/GPC grade, Markeson, MI) at 1 ml/min, and sample volume was 200 μl. Calibration was achieved with a set of polystyrene MW standards (4,016; 53,500; and 610,000 daltons). Columns, injector and refractive index detector were at 140°C, and solvent pump at 50°C. Weight-average MW ($\overline{M_w}$) and number-average MW ($\overline{M_n}$) were determined by using Maxima 820 computer software (Waters/Millipore Co.)

(iii) FT-IR spectroscopy. FT-IR analysis was performed using a Bruker Instruments (Billerica, MA) Model IR 113V controlled by Bruker IFS version 12/87 software. The area of the hydroxyl region (871-1190 cm^{-1}) was divided by the area of the methylene region (1471- 1485 cm^{-1}) to eliminate variations in film thickness.

Data Analysis. The data obtained from the experiments was analyzed by PC-SAS program (version 6.04) by using an analysis of variance and contrast (23).

RESULTS AND DISCUSSION

Pure-culture Assay.

(i) Chemical degradation. The changes in mechanical properties and MW distribution between the zero-control and uninoculated-control films in Figure 1 are measures of chemical oxidative degradation. These changes are affected by conditions such as incubation temperature, transition metal in the medium and films, pH, dissolved oxygen, and mechanical shaking. Elongations were generally lower in the uninoculated control except for LP-14, P-28, and LP-28, but none were statistically significant. Changes in $\overline{M_w}$ and $\overline{M_n}$ of the polyethylene gave no consistent pattern. This result was unexpected because accelerated degradation was observed for these films in 70°C oven and high-temperature high-humidity treatments (16).

(ii) Biological degradation. Changes from the uninoculated-control in Figure 1 after culture treatment are measures of biological degradation. Changes in mechanical properties and MW distributions in the various films did not coincide. Reductions in $\overline{M_w}$, which represent high-MW polyethylene degradation, were observed for film P-0 (*S. badius*), and films LP-0 and P-28 (*S. setonii*) with LP-0 being significantly reduced ($P<0.05$). Reductions in $\overline{M_n}$, which represent low-MW polyethylene degradation, were observed for films P-0 (*S. badius*), LP-0, LP-7 (*S. viridosporus* and *S. setonii*), HP-7 (*S. badius* and *S.*

viridosporus) with P-0 being significantly reduced ($P<0.05$).

Figure 2 shows HT-GPC chromatograms of LP-0 film (upper) and HP-14 film (lower) acted on by *S. setonii* 75Vi2. A similar peak shift to the right as in the upper chromatogram was observed in many films treated with *S. setonii* 75Vi2 (P-0, LP-0, HP-0, P-28 and HP-28) and in some films treated with *S. viridosporus* T7A (LP-0 and HP-0). This shift to the right in the chromatogram indicates a decrease of $\overline{M_w}$ caused by polyethylene breakdown. For almost every chromatogram including zero-control, uninoculated-control and inoculated film a second peak was observed at 33 to 37 min except for film HP-0 (Figure 2). $\overline{M_w}$ and $\overline{M_n}$ were calculated from data with < 30 mins of elution time to avoid biasing the data by this late peak.

In some instances treated samples seem less degraded than controls (Figure 1). This has been attributed to inhibition of chemical degradation as a result of cell mass accumulation on the films (17, 22). Such inhibition was observed for each of the film types for at least one bacterial culture, and HP-28 degradation seemed to be inhibited by all the cultures. Thus, cell mass accumulation on plastic films is not a very good index for biodegradation and actually can signal inhibition of degradation.

Extracellular-enzyme Culture.

Biodegradation determined by extracellular bacterial enzyme concentrates eliminates any possible influence from cell mass accumulation on the films.

Figure 3 shows the percent elongation and FT-IR ratio in the films treated with enzyme. LP or HP films illustrated greater percent elongation reduction than P films in 0 or 7% starch-loading films (Table 2). Film HP-14 showed the greatest reduction of percent elongation among 14% starch-containing films, and film LP-28 among 28% starch-containing films. All the 14 and 28% starch-containing films treated with active-enzyme concentrate illustrated significant reduction in percent elongation. As the starch concentration increased, the polyethylene concentration correspondingly decreased. This reduction in total polyethylene for the 14 and 28% starch films could explain the detectable changes in mechanical properties and FT-IR ratios for these films after treatment with active-enzyme. Primary alcohols are considered intermediates in the oxidation of hydrocarbons before the formation of ketone (20). *S. setonii* was used because it does not degrade starch (17). Starch degradation in these films results in a reduction in FT-IR absorbance for hydroxy groups (24). For every film except P-28 an increase in FT-IR absorbance was detected with an increase of 0.912 (Table 2). The cast films used in this study were ten times thicker (0.075 mm) than the blown films previously evaluated (0.006 mm) (14, 17, 21, 22). In thick films small changes in the polyethylene matrix possibly were more difficult to detect.

Previous studies of blown starch-polyethylene films evaluated by the two assays used in this study demonstrated better correlation of the enzyme assay

to films treated in a composting environment than the culture assay (14, 22). Therefore, the data from this study does suggest that these films will degrade in a biologically active compost environment.

ACKNOWLEDGEMENTS

This research was supported by the Iowa Corn Promotion Board, the Iowa State University Center for Crops Utilization Research, Iowa General Assembly, Iowa Agriculture and Home Economic Experimental Station and the Iowa Department of Natural Resources.

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Table 1. Compositions of the various plastic films used in the study

Film designation	% starch		Mn content (ppm)[b]	Oxidized-polyethylene[c]
	Expected	Actual[a]		
P-O	0	ND[d]	0	0%
LP-O	0	ND	0	15% low-MW
HP-O	0	ND	0	15% high-MW
P-7	7	6	53	0%
LP-7	7	6	54	15% low-MW
HP-7	7	6	56	15% high-MW
P-14	14	14	58	0%
LP-14	14	14	51	15% low-MW
HP-14	14	14	56	15% high-MW
P-28	28	31	53	0%
LP-28	28	30	52	15% low-MW
HP-28	28	32	59	15% high-MW

[a]Actual starch percentage was determined by the method of Fratzke et al. (9).

[b]The manganese content was determined by the atomic absorption method of Johnson et al. (15).

[c]Acid number for low- and high-MW oxidized-polyethylene is 15 and 28 mg KOH/g, respectively.

[d]ND, not determined.

Table 2. Difference between average values for changes in percent elongation and FT-IT absorbance between inactive- and active-enzyme treated films

% starch	Film type					
	P		LP		HP	
	Percent elongation[a]	FT-IR[b]	Percent elongation[a]	FT-IR[b]	Percent elongation[a]	FT-IR[b]
0	55.9	0.42	15.6	0.40	-5.2	0.54
7	31.3	0.58	0.9	0.19	-8.1	0.08
14	-40.6	0.60	-28.0	1.54	-68.0	0.61
28	-74.2	-3.78	-286.0	4.01	-48.3	1.06

[a] Negative values indicate reduction in percent elongation. Values are the differences between the mean of two replicates.

[b] Positive values indicate increase in the hydroxyl region of the FT-IR spectrum. Values are the differences between single replicate.

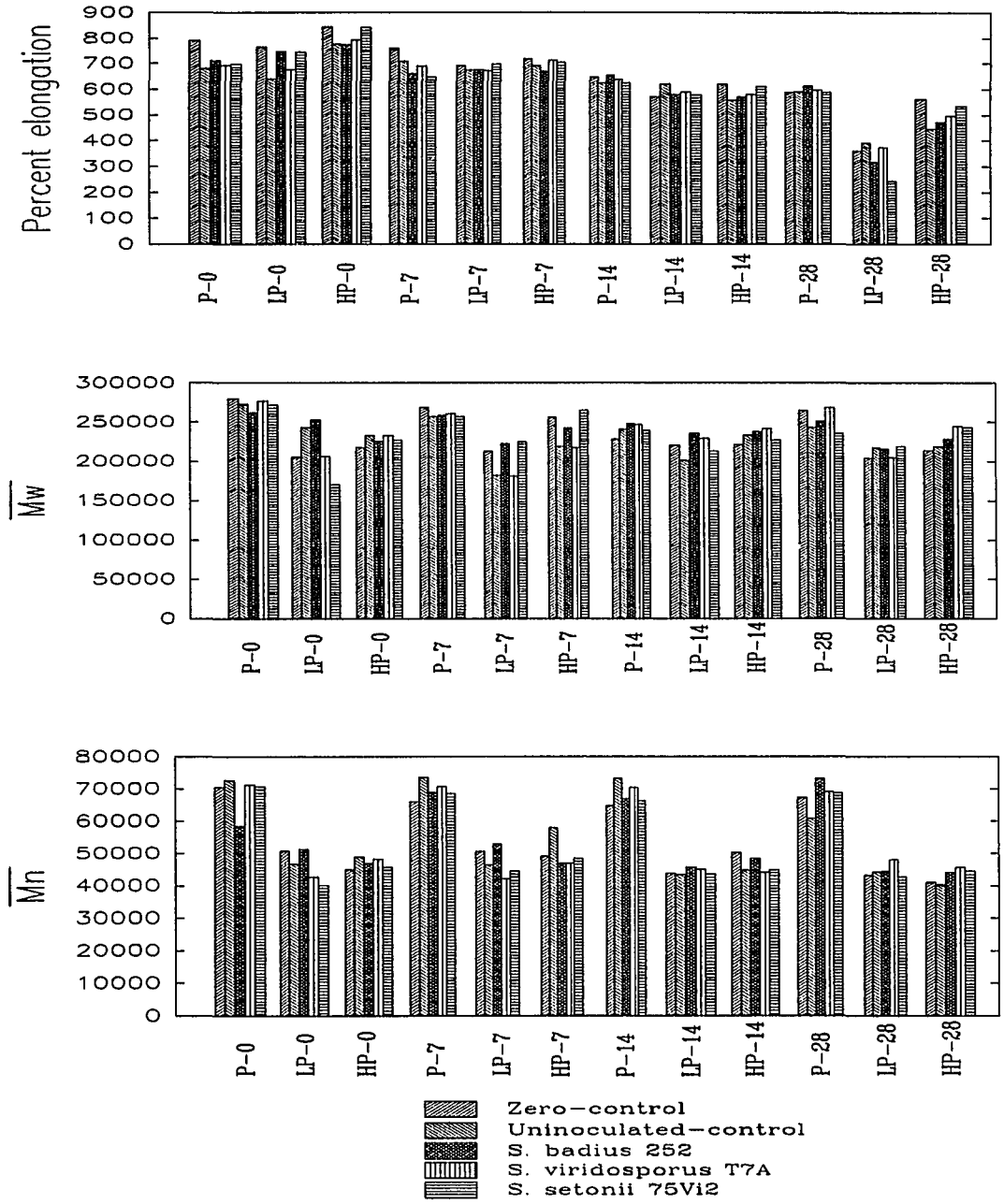

Figure 1. The percent elongation (each data point represents an average of four replicates), $\overline{M_w}$ (each data point represents an average of two replicates) and $\overline{M_n}$ (each data point represents an average of two replicates) for films by pure culture of ligninolytic *Streptomyces*

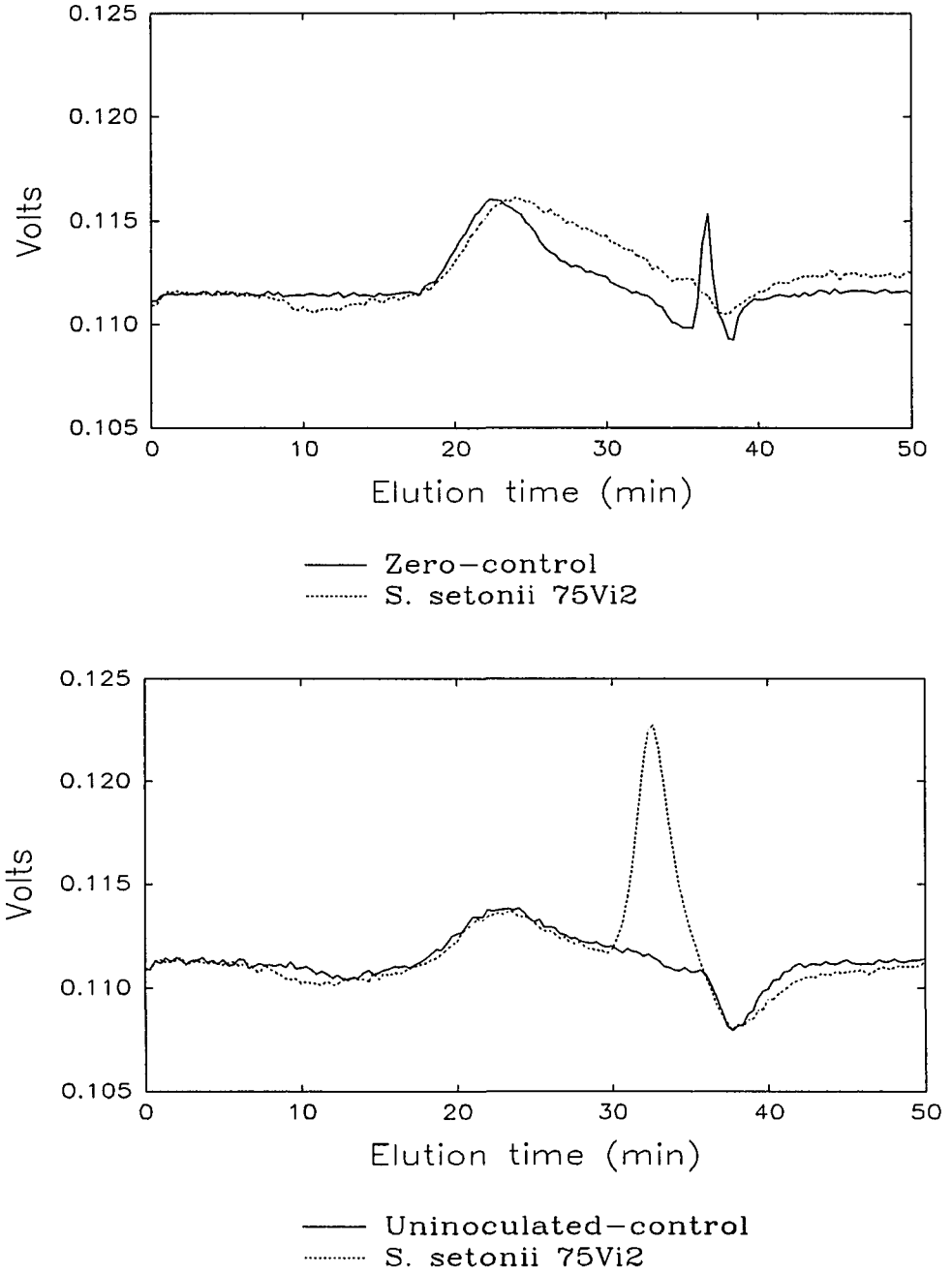

Figure 2. HT-GPC chromatograms of LP-0 (upper) and HP-14 (lower) in pure-culture assay

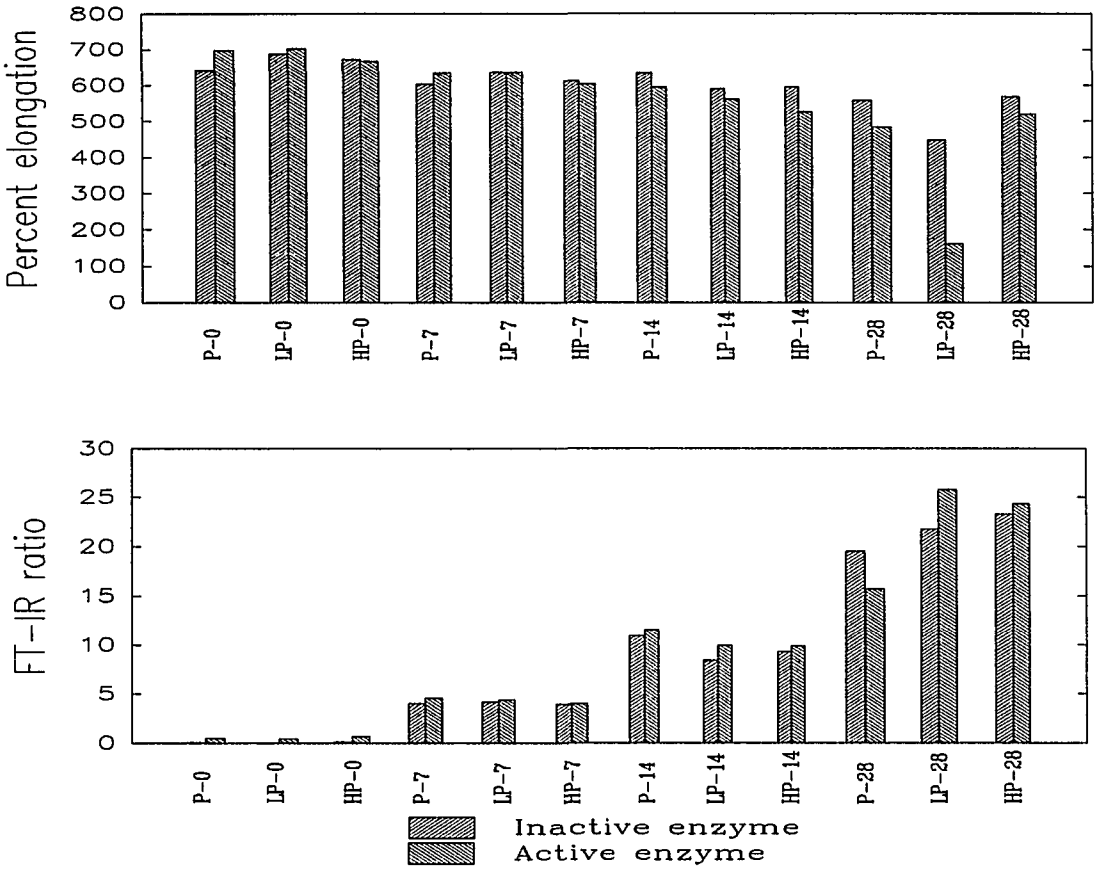

Figure 3. The percent elongation (each data point represents an average of two replicates) and FT-IR ratio (hydroxyl region of 871-1190 cm^{-1} divided by methylene region of 1471-1485 cm^{-1}) for films treated by extracellular-enzyme of *Streptomyces setonii* 75Vi2

PAPER III. FOOD PACKAGING POTENTIAL OF SOME NOVEL DEGRADABLE STARCH-POLYETHYLENE PLASTICS

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Food Packaging Potential of Some Novel Degradable Starch-Polyethylene Plastics[1]

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1. Journal Paper No. J- of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Project No.

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ABSTRACT

The food packaging potential of twelve degradable starch-polyethylene films containing corn starch (7, 14, or 28%), oxidized-polyethylene with low- or high-molecular weight (15%) and pro-oxidant (51-59 ppm manganese plus vegetable oil) was evaluated. Plastic films were evaluated by measuring physical and chemical properties and by food packaging storage studies. Mechanical properties of the films were more affected by acids (concentrated sulfuric or nitric acids) than alkali (60% sodium hydroxide) but were stable in paraffin oil. Starch in the films did not impair film heat sealing property. Water vapor transmission of the film increased with increasing starch content but was not affected by the addition of oxidized-polyethylene. Oxygen permeability was not affected by starch or oxidized-polyethylene addition. Oil oxidation, however, was stimulated with films containing pro-oxidant and high-molecular weight oxidized-polyethylene. Starch in the films did not accelerate microbial growth, and mechanical properties of most films did not reduced after use. Oxygen and water vapor permeability did not influence the microbial load of ground beef packaged in the films and stored at 10°C or frozen. These results suggest that these degradable starch-polyethylene films are acceptable as a primary food container for some food products and storage requirements.

INTRODUCTION

Food product development and package development are conducted simultaneously and interactively. In the food packaging industry plastic use has shown the most rapid growth. Plastics occupied 26.5% of all food packaging materials in 1991, compared with 13.2% in 1981 (5). Plastic offers advantages in such areas as microbial and chemical resistance, transmission of gases and moisture, toughness and flexibility, and the possibility of coextrusion. The build-up of conventional slow-degrading plastics in landfills and in the environment has prompted the development of degradable plastics. For these materials degradation is accelerated by light, living organisms, chemicals, heat and mechanical forces (11). Currently, photodegradable plastic use is required for six-pack beverage ring connectors in 11 states in the United States. Degradable plastics are also used for grocery sacks, garbage bags and mulch films. However, degradable plastics have not been approved for use as primary containers in food packaging.

Starch-polyethylene is one type of degradable plastic. To make such material commercially, starch (5-9%) and pro-oxidant (Mn, Fe, and/or Cu at 50-200 ppm plus vegetable oil) are blended with polyethylene. These additives and possible degradation during use may affect food safety and packaging properties of such degradable polyethylene materials. Therefore, several

concerns need to be addressed prior to commercial use of these materials as a primary food container. These concerns include degradation rates under various conditions, changes in mechanical property during storage, microbial growth, and release of toxic compound into the food product.

Strantz and Zottola (13) evaluated the effect of corn starch in degradable films on bacterial survival under food storage conditions. They found that bacterial survival was not generally enhanced by the presence of cornstarch in nutritionally complex growth medium, but growth of *Salmonella typhimurium*, *Aeromonas hydrophila* and *Pseudomonas fragi* was enhanced under conditions of saturated relative humidity at some storage temperatures in minimal salts medium. They concluded that cornstarch-containing polyethylene film could be successfully used for food packages as far as microbiological safety was concerned.

Johnson et al. (9) tested the release of water-soluble toxic compounds from degradable starch-polyethylene by using the Microtox® Toxicity Analyzer. They detected no water-soluble toxic compounds during the period of most rapid polyethylene degradation.

This study evaluated the food packaging potential of degradable starch-polyethylene cast films containing starch (0, 7, 14, and 28%), pro-oxidant (51-59 ppm manganese plus vegetable oil) and some with low- or high-molecular weight (MW) oxidized polyethylene (15%). The photo-, chemical-, and

biological-degradability of these materials have been illustrated previously (10, 11). The chemical resistance, water vapor transmission, oxygen permeability, and heat sealing properties of the films were determined. Finally, oil oxidation in the plastic bags and changes in microbial counts, mechanical properties of the used films and color for ground beef after storage at different temperatures were determined.

MATERIALS AND METHODS

Plastic Films. The twelve starch-polyethylene cast films prepared and evaluated by Kim et al. (10, 11) were used (Table 1). The films were composed of different levels of linear low-density polyethylene, native corn starch (0, 7, 14, 28%), low- or high-MW oxidized-polyethylene (15%) and POLYCLEAN II (18%) (Archer Daniel Midland Co., Decatur, IL). The POLYCLEAN II contained corn starch, manganese stearate and vegetable oil. These cast films were prepared by high-temperature extrusion at Iowa State University. Saran Wrap (DowBrands L.P., Indianapolis, IN) and Glad Cling Wrap (First Brands Corporation, Danbury, CT) were also used as controls.

Chemical Resistance Property. Each film was cut into strips (15.2 x 2.5 cm) in the same direction that it was extruded (machine direction). Each strip was carefully placed into a glass tube containing a specific chemical reagent. Any contact of strip with the wall of the glass tube was avoided to insure chemical contact with both sides of the film. After 7 days at room temperature, strips were removed from the reagent, washed with distilled water, wiped with tissue, and tested for mechanical properties after equilibrated to 50% relative humidity for at least 40 h prior to testing (3). The percent elongations of treated and control films were measured by using an Instron Model 4502 Universal Test Machine (Instron Corporation, Canton, MA) with

series IX Automated Materials Testing System software (Instron Corporation, version 4.09). The thickness of each strip was measured with a hand-held caliper. Crosshead speed was 500 mm/min, and the starting gap between the jaws was 50 mm. The chemicals used were 60% (w/v) sodium hydroxide, concentrated sulfuric acid (36 N), paraffin oil (saybolt viscosity 125/135, Fisher Scientific Co. Fair lawn, NJ) and concentrated nitric acid (15.8 N) (2).

Heat Sealing Property. Two strips (4 x 2.5 cm) of the same plastic films were joined *via* a heat-sealing machine (Cleveland Lathe & Machine Co., Cleveland, OH) at 120-150°C for 3-5 seconds. The strength of the heat seal was determined with the Instron Universal Test Machine using the same method used for measuring chemical resistance.

Water Vapor Transmission. A plastic bag (18 x 5 cm) was prepared by folding a 36 x 5 cm strip of each material and heat sealing the sides. Anhydrous calcium chloride (No. 8 sieve, Fisher Chemical Co., Fair Lawn, NJ), was dried at 200°C in a vacuum oven for 24 h before use. To each bag 50 g of dried anhydrous calcium chloride was added and the opening was heat sealed. The initial weight for each bag was measured to 0.1 mg, and each bag was placed into 50 or 90% relative humidity chambers at 37°C. The weight was measured every day for 3 days, and the rate of water vapor transmission was calculated (4).

Oxygen Permeability. Long heat sealed plastic bags (18 x 5 cm) were made from each film. The bags were degased and filled with nitrogen using a Fresh vac® machine, Model A300 (CVP system Inc., Downers gorve, IL). Each bag was heat sealed so as to produce two compartments. An IL 307 head space oxygen analyzer (Instrumentation Laboratory Inc., Andover, MA) was used to determine the initial oxygen concentration in one compartment and after storage at 25°C for 72 h in the second. Difference between the two oxygen concentrations was calculated.

Oil Oxidation. Safflower seed oil without added antioxidants (Sigma Chemical Co., St. Louis, MO) was placed in a nitrogen atmosphere and passed through a neutral alumina column (Sigma Chemical Co.) to remove oxidized products. Each plastic bag (5 x 5 cm) was filled with 7 ml of safflower seed oil, air in the bag was excluded, and the opening was folded and clamped. Bags were stored in the dark at 45°C for 10 days, and peroxide values were measured (1). Five gram of oil sample was mixed with 30 ml of the 3:1 acetic acid-chloroform and 0.5 ml of saturate potassium iodide solution. After starch indicator solution was added, and shaken for 1 min, the sample was titrated with 0.1 N sodium thiosulfate.

Ground Beef Storage Studies.

(i) Microbial analysis. A plastic bag (13 x 5 cm) for each material was prepared as above, and 10 g of fresh ground beef was added. Each bag

opening was folded, and clamped. One set of bags was stored at 10°C for 48 h and a second set was stored at -18°C for 4 weeks. The 10-g sample was homogenized in 90 ml of sterile 0.1% (w/v) peptone (Difco Laboratories Inc., Detroit, MI) broth with a stomacher for 3 min, serially diluted in sterile 0.1% peptone broth, and spread plated on plate-count agar (Difco Laboratories Inc.) in duplicate. Plates were incubated at 35°C for 48 h in replicates of two for each film and temperature. Standard plate counts were reported in colony forming units/g (CFU/g) of beef.

(ii) Mechanical property change of the film. Percent elongations of the bags before and after use as ground beef packages were determined by using an Instron Universal Test Machine. Each film was washed with distilled water, then wiped with tissue prior to testing. Sample preparation and testing conditions were the same as those used for chemical resistance.

(iii) Color measurement. Twenty-grams of ground beef was added to heat-sealed plastic bags (10 x 5 cm) made from the various plastics and vacuum sealed. The bags were stored at 10°C for 48 h and the surface color of the undisturbed ground beef was measured. Then the ground beef was mixed, and the total color determined. For color determinations samples were placed into sterile-clean plastic petri dishes (60 x 15 mm, Fisher Scientific Co.). A Hunter colorimeter (Hunterlab, Fairfax, VA) was used to measure the color. Measurements were made three-times for each sample with illuminant F and a

10°-standard observer, and average values were calculated.

Data Analysis. The data obtained from the experiments was analyzed by PC-SAS program (version 6.04) by using an analysis of variance, Duncan's multiple test and contrast (12).

RESULTS AND DISCUSSION

Chemical Resistance Property. All the films were relatively stable in the paraffin oil treatment and no significant reduction of percent elongation was detected (Figure 1). However, slight reductions were observed for films LP-0, P-7, and HP-14. Films were more weaken by the acid than by the alkali treatment. Sodium hydroxide treatment caused reductions in the percent elongation for all the films containing 28% starch with a statistically significant decrease for HP-28 ($P<0.05$). Reduction was also observed for films P-7 and HP-14. The concentrated sulfuric acid treatment caused the most consistent reductions in film mechanical properties. The only films exhibiting no or little change to sulfuric acid were P-0, HP-0, LP-7, and LP-28. The percent elongations of films P-14, P-28 and HP-28 were significantly reduced ($P<0.05$) by sulfuric acid treatment. Nitric acid treatment caused a reduction for films P-7 and HP-14 with significant reduction ($P<0.05$) for films P-14 and HP-28. Film sensitivity to acid treatment was attributed to starch hydrolysis. These results suggest that starch-polyethylene films can not be recommended as a packaging material for strongly acid foods.

Heat Sealing Property. Good heat sealing is essential for a food packaging material. Starch in the films did not impair heat sealing. The films without oxidized-polyethylene (P-0, P-7, P-14 and P-28) exhibited about the

same percent elongation value for the sealed film in spite of increasing starch loading (Figure 2). The films containing oxidized-polyethylene exhibited better strength after heat sealing compared to the initial films.

Water Vapor Transmission. Among films with the same starch loading no real differences in transmission were observed at 50% relative humidity (Table 2). However, films LP-0, HP-7, and HP-14 had higher transmission than other films with the same starch loading at 90% relative humidity. No real differences were observed with 28%-starch films. Starch addition significantly affected water vapor transmission ($P<0.05$), but oxidized-polyethylene addition did not. These results suggest that films with low starch-loadings will provide better vapor protection for moisture-sensitive foods. Finally, at 50 and 90% relative humidity, the water vapor transmission rate steadily increased with starch loading. There is about a doubling in rate of moisture transmission for starch-containing films at 90% relative humidity. The hygroscopic property of starch seemed to play a key role in accelerating water vapor transmission for these films.

Oxygen Permeability. The rate of oxygen permeability as determined by the oxygen analyzer was not affected significantly by starch loading or by the presence of low- and high-MW oxidized-polyethylene (Table 3). Oxygen permeability of the films also can be predicted indirectly by oil oxidation and by the color measurement of ground beef.

Oil Oxidation. The oil in the plastic bags containing high-MW oxidized-polyethylene (HP-films) was consistently more oxidized in 10 days than in the plastic bags blended with low-MW oxidized-polyethylene (LP-films) or without oxidized-polyethylene (P-films) (Table 4). These results suggest that the films containing pro-oxidant and high-MW oxidized-polyethylene may possibly catalyze the propagation of oil oxidation. Contrast analysis illustrated that peroxide values for the films containing pro-oxidant and starch were significantly different from films without pro-oxidant ($P<0.05$). Therefore, manganese, which was a component of the pro-oxidant may also affect the oil oxidation with high-MW oxidized-polyethylene producing the greatest peroxide values. Starch loadings in the films did not significantly influence peroxide values, which is consistent with the result from oxygen permeability.

Ground Beef Storage Studies.

(i) Microbial analysis. Due to the presence of starch and transition metals (Cu, Fe, or Mn) in degradable plastics there is a possibility of stimulating microbial growth in foods such as ground beef when it is in direct contact with the film (primary container). Compared to Glad Wrap and Saran Wrap only minor differences were observed for microbial counts of ground beef packaged in degradable starch-polyethylene films at both 10 and -18°C (Figure 3). None of the differences were significant ($P<0.05$). These results are consistent with those of Strantz and Zottola (13).

(ii) Mechanical property change of the film. After being used to package ground beef, the films containing 28% starch, P-7 and LP-0 showed reductions in percent elongation when compared to their controls (Figure 4). But only HP-28 at 10°C was significantly reduced ($P<0.05$). Those results indicate that mechanical properties of films with high starch-loadings could be weaken under cold storage condition.

(iii) Color measurement. Meat color usually becomes bright red and then brown during storage due to oxygenation of myoglobin to oxymyoglobin and oxidation to metmyoglobin. Therefore, oxygen permeability of the films can be predicted by measuring meat color. There was no significant difference in lightness (L) and yellow color (b) for the various films (Table 5); only red color (a) was significantly different among the samples ($P<0.05$). Films with high levels of starch loading showed better red color retention on the surface of ground beef. Gas permeability is generally regarded to have an inverse proportionate relationship to film thickness (7). Therefore, film thickness derived from increasing starch-loadings (Table 1) might be affecting oxygen permeability of the films. The color of the mixed ground beef stored in various films exhibited a similar pattern to that of the surface color, but fewer of the differences were significant (Table 6). The higher red values for the mixed ground beef than for the surface of the ground beef suggest that oxygen did not penetrate into the ground beef when wrapped in some films. Ground beef

color when packaged with Glad or Saran wrap exhibited similar lightness and yellow colors as the starch-polyethylene films (Table 7). However, Glad wrap, which is a polyethylene film, exhibited a similar red color to the starch-polyethylene films, whereas Saran wrap, which is a polyvinyl chloride film, showed a more intense red color.

CONCLUSION

These degradable starch-polyethylene films generally exhibited good chemical resistent properties against oil and alkali but not against strong acids. Water vapor transmission of the films increased with increasing starch concentrations in the films, but it was not affected by the addition of oxidized-polyethylene. Neither starch nor oxidized-polyethylene significantly affected oxygen permeability. However, oil oxidation was stimulated with films containing pro-oxidant and high-MW oxidized-polyethylene. Starch addition did not impair the heat sealing property, nor did it accelerate microbial growth in ground beef. The mechanical properties of the films used for packaging ground beef were not significantly changed after refrigerated and frozen storage. Finally, these level of oxygen and water vapor permeability did not affect microbial load in ground beef at refrigerated and frozen temperature. These results suggest that degradable starch-polyethylene films are acceptable as primary food containers for some food products.

ACKNOWLEDGEMENTS

This research was supported by the Iowa Corn Promotion Board, the Iowa State University Center for Crops Utilization Research, and Iowa Agriculture and Home Economic Experimental Station.

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Table 1. Composition and thickness of each plastic film

Film designation	% starch		Mn content (ppm)[b]	Oxidized-polyethylene[c]	Thickness (mm)
	Expected	Actual[a]			
P-O	0	ND[d]	0	0%	0.060
LP-O	0	ND	0	15% low-MW	0.060
HP-O	0	ND	0	15% high-MW	0.070
P-7	7	6	53	0%	0.075
LP-7	7	6	54	15% low-MW	0.075
HP-7	7	6	56	15% high-MW	0.075
P-14	14	14	58	0%	0.075
LP-14	14	14	51	15% low-MW	0.075
HP-14	14	14	56	15% high-MW	0.075
P-28	28	31	53	0%	0.080
LP-28	28	30	52	15% low-MW	0.085
HP-28	28	32	59	15% high-MW	0.085

[a]Actual percent starch content was determined by the chemical method of Fratzke et al. (5).

[b]The manganese content was determined by atomic absorption by the method of Johnson et al. (7).

[c]Acid number for low- and high-MW oxidized-polyethylene is 15 and 28 mg KOH/g, respectively.

[d]ND is for not determined.

Table 2. The water vapor transmission of the starch-polyethylene films at 37°C and 50% or 90% relative humidity[a]

50% relative humidity at 37°C (g/24 h.m^2)					
Film		P	LP	HP	*Average*
Starch (%)	0	1.76	2.30	1.49	*1.85*^{e}
	7	2.02	2.02	2.59	*2.21*^{d}
	14	2.92	2.48	2.58	*2.66*^{c}
	28	3.00	3.04	2.65	*2.90*^{b}
Average		*2.42*	*2.46*	*3.10*	
90% relative humidity at 37°C (g/24 h.m^2)					
Film		P	LP	HP	*Average*
Starch (%)	0	7.22	10.42	7.54	*8.39*^{h}
	7	8.17	8.83	10.22	*9.07*^{h}
	14	11.78	10.43	14.06	*12.09*^{g}
	28	16.73	16.73	16.56	*16.67*^{f}
Average		*10.97*	*11.60*	*12.09*	

[a]Each value is from a single measurement.

[b-e]Means in a column for 50% relative humidity with different superscripts are significantly different by Duncan's multiple test ($P<0.05$).

[f-h]Means in a column for 90% relative humidity with different superscripts are significantly different by Duncan's multiple test ($P<0.05$).

Table 3. Change of percent oxygen concentration in the starch-polyethylene bags after 72 h at 25°C[a]

Film		P	LP	HP	*Average*
Starch (%)	0	5.9	5.4	4.9	*5.4*
	7	4.5	4.2	4.9	*4.6*
	14	4.7	4.3	4.8	*4.6*
	28	4.2	4.1	4.2	*4.2*
Average		*4.9*	*4.5*	*4.7*	

[a]Each value is a mean for two replicates.

Table 4. Peroxide value of safflower seed oil packaged with the starch-polyethylene bags after storage at 45°C for 10 days[a]

Peroxide value (milliequivalents peroxide/1,000 g oil)					
Film		P	LP	HP	*Average*
Starch (%)	0	40	41	44	*42[d]*
	7	49	36	59	*48[e]*
	14	36	45	57	*46[e]*
	28	36	54	56	*49[e]*
Average		*40[c]*	*44[c]*	*54[b]*	

[a]Each value is a mean for two replicates. Oil not placed in a bag but exposed to atmospheric oxygen had a peroxide value of 70.

[b-c]Means in the same row with different superscripts are significantly different by Duncan's multiple test ($P<0.05$).

[d-e]Means in the same column with different superscripts are significantly different by contrast ($P<0.05$).

Table 5. Surface color of ground beef packaged with the starch-polyethylene films stored at 10°C for 48 h[a]

L (lightness)					
Film		P	LP	HP	*Average*
Starch (%)	0	36.8	36.8	39.3	*37.6*
	7	36.8	36.4	36.7	*36.6*
	14	37.2	35.3	38.3	*36.9*
	28	36.4	36.3	36.4	*36.4*
Average		*36.8*	*36.2*	*37.7*	
a (red)					
Film		P	LP	HP	*Average*
Starch (%)	0	5.3	5.8	5.2	*5.4[d]*
	7	6.0	5.1	5.4	*5.5[c]*
	14	5.8	6.6	5.3	*5.9[b]*
	28	6.1	5.6	6.0	*5.9[b]*
Average		*5.8*	*5.7*	*5.5*	
b (yellow)					
Film		P	LP	HP	*Average*
Starch (%)	0	9.1	9.0	9.4	*9.2*
	7	9.2	8.8	9.1	*9.0*
	14	9.0	8.8	9.0	*8.9*
	28	9.2	8.9	8.9	*9.0*
Average		*9.1*	*8.9*	*9.1*	

[a]Each value is a mean for 2 replicates. Starting ground beef had L, a and b value of 36.6, 10.4 and 9.4.

[b-d]Means in a column with different superscripts are significantly different by Duncan's multiple test ($P<0.05$).

Table 6. Total color of mixed ground beef packaged with the starch-polyethylene films stored at 10°C for 48 h[a]

L (lightness)					
Film		P	LP	HP	*Average*
Starch (%)	0	40.4	39.1	41.6	*40.4*
	7	40.1	40.0	39.8	*40.0*
	14	39.2	39.9	39.7	*39.6*
	28	40.5	40.3	38.5	*39.8*
Average		*40.1*	*39.8*	*39.9*	
a (red)					
Film		P	LP	HP	*Average*
Starch (%)	0	10.1	10.6	8.6	*9.8*
	7	9.9	9.0	10.3	*9.7*
	14	10.7	10.7	9.9	*10.4*
	28	9.3	9.0	9.0	*9.1*
Average		*10.0*	*9.8*	*9.5*	
b (yellow)					
Film		P	LP	HP	*Average*
Starch (%)	0	10.4	10.2	10.5	*10.4*
	7	10.1	10.3	10.4	*10.3*
	14	10.2	10.0	10.1	*10.1*
	28	10.5	9.7	9.9	*10.0*
Average		*10.3*	*10.1*	*10.2*	

[a]Each value is a mean for 2 replicates. Starting ground beef had L, a and b value of 36.6, 10.4 and 9.4.

Table 7. Color of ground beef packaged in commercial films stored at 10°C for 48 h[a]

	Glad wrap		Saran wrap	
	Surface	Mixed	Surface	Mixed
L	37.3	40.7	35.7	37.9
a	6.5	8.3	11.6	15.1
b	9.7	10.2	8.8	10.2

[a]Each value is a mean for 2 replicates. Starting ground beef had L, a and b value of 36.6, 10.4 and 9.4.

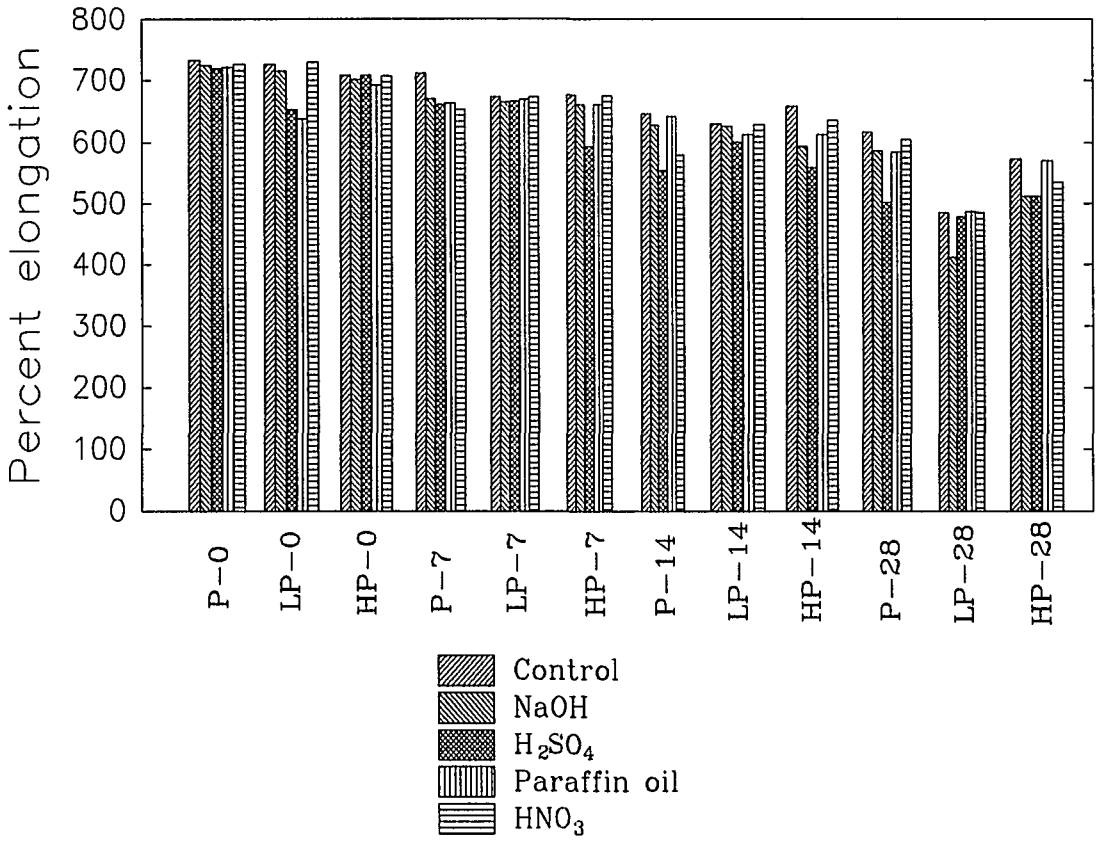

Figure 1. The percent elongation of the starch-polyethylene films by the chemical reagent treatments (each value represents an average of four replicates)

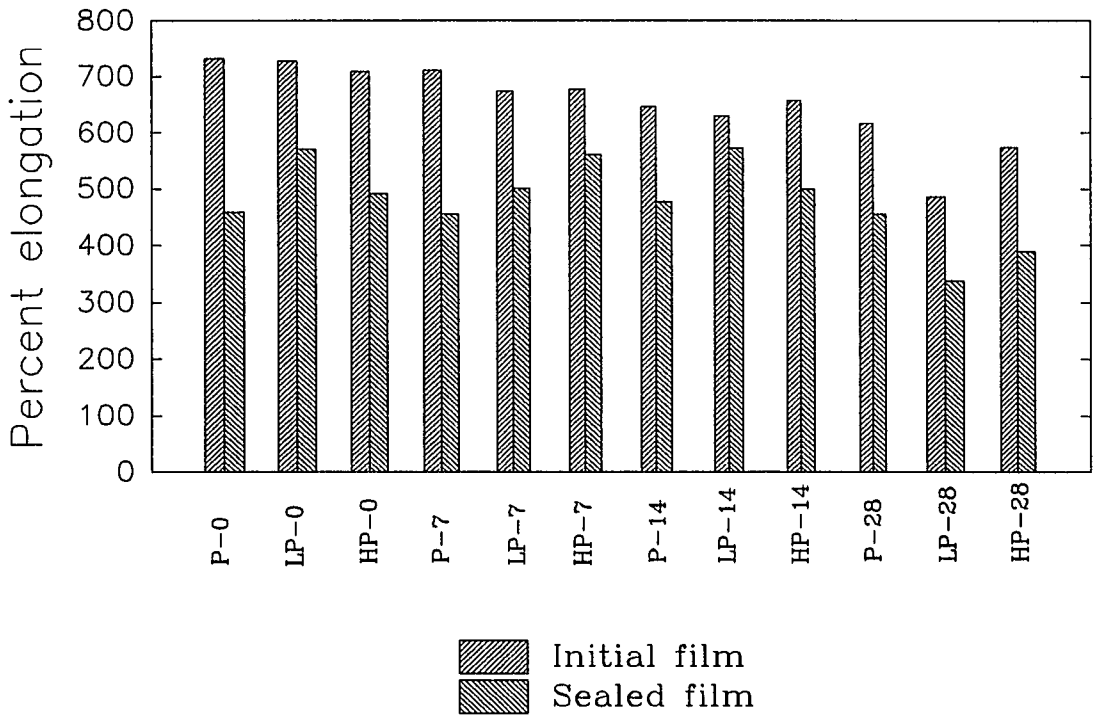

Figure 2. The percent elongation of the heat-sealed starch-polyethylene films (each value represents an average of four replicates)

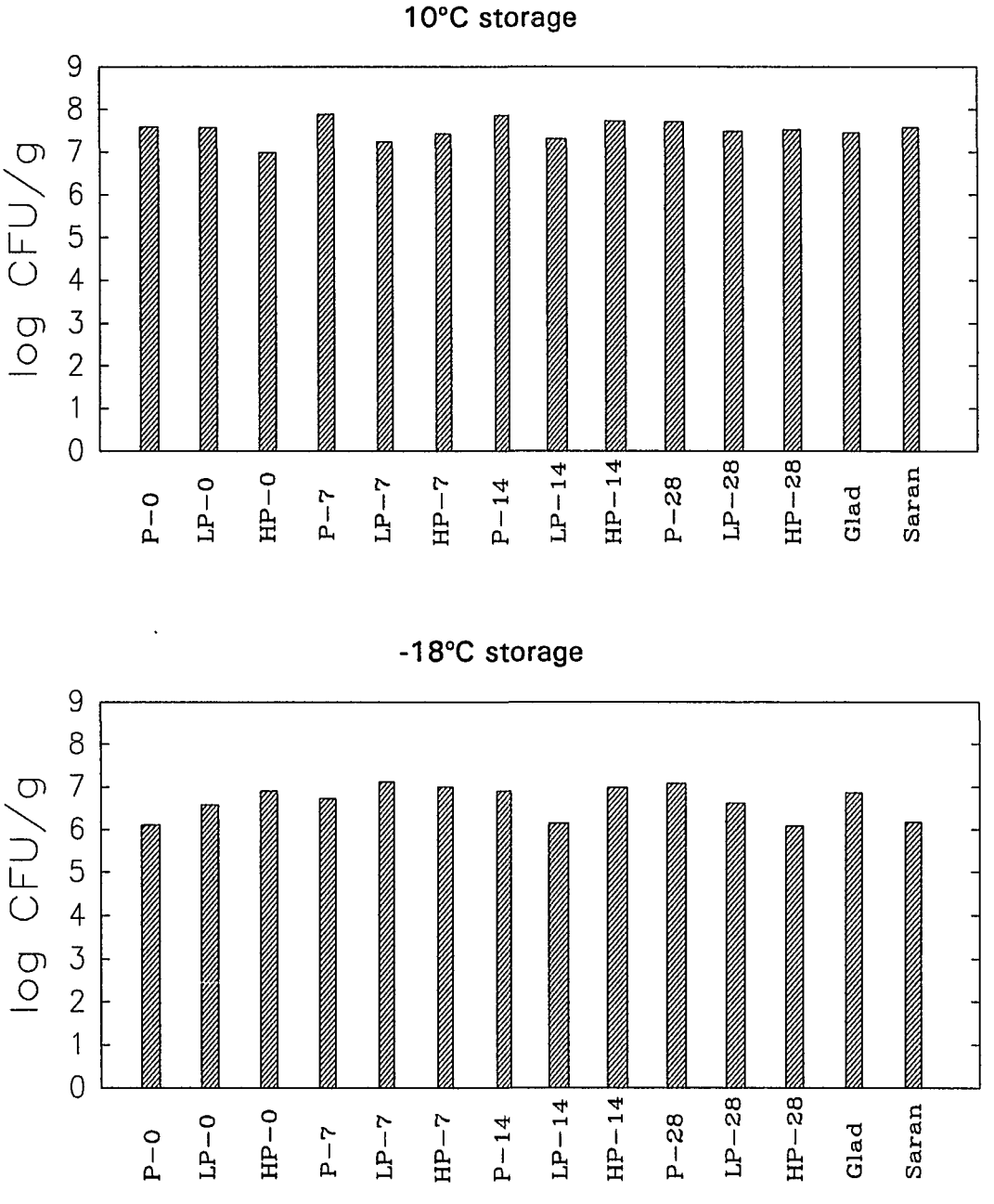

Figure 3. Standard plate counts of ground beef packaged with the starch-polyethylene films stored at 10°C for 48 h (upper) and -18°C for 4 weeks (lower) (each value represents an average of two replicates)

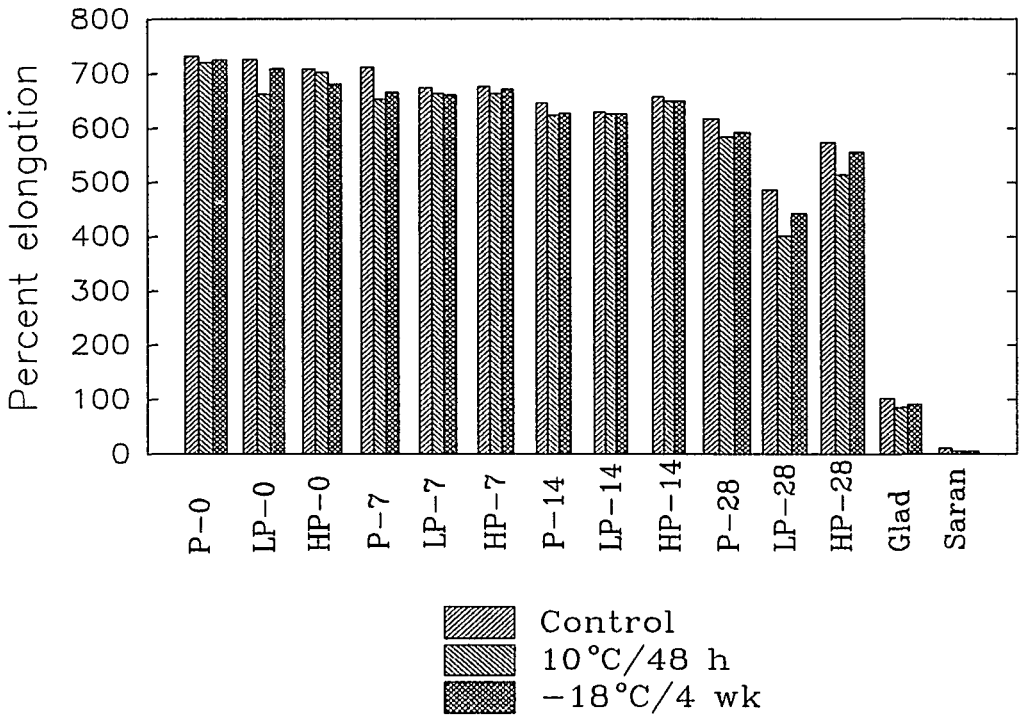

Figure 4. Percent elongation of the starch-polyethylene films packaged ground beef (each value represents an average of four replicates)

SUMMARY AND CONCLUSION

Degradable starch-polyethylene plastics containing pro-oxidant and/or high- or low-MW oxidized-polyethylene represented significantly increased rates of oxidative-thermal degradation and photodegradation. Oxidized-polyethylene addition did not impair film color and thickness and with pro-oxidant produced a synergistic effect on the oxidative-thermal degradation of polyethylene. Addition of 15% oxidized-polyethylene, pro-oxidant and up to 14% starch to polyethylene films could be expected to increase the rate of degradation of such plastic in natural environments.

The results from the pure-culture assay were inconclusive due to the cell mass accumulation on the surface of the films, which inhibited the oxidative-chemical degradation of the polyethylene. The extracellular-enzyme assay illustrated biodegradation for all the 14 and 28% starch-polyethylene films. Addition of oxidized-polyethylene reduced percent elongation of the starch-polyethylene in the enzyme assay. These results suggests that the starch-polyethylene films could degrade in a biologically active compost environment.

These degradable starch-polyethylene films generally exhibited good chemical resistent properties against oil and alkali but not against strong acids. Water vapor transmission of the films increased with increasing starch concentrations in the films, whereas oxygen permeability was not affected by

the addition of oxidized-polyethylene nor starch. However, oil oxidation was stimulated with films containing pro-oxidant and high-MW oxidized-polyethylene. Starch addition did not reduce the heat sealing strength nor did it accelerate microbial growth in ground beef. Mechanical property of all the films except for HP-28 used for packaging ground-beef was not significantly decreased after refrigerated and frozen storage. Therefore, oxidized-polyethylene films with 7 or 14% starch illustrated good potential as food packaging materials.

These results suggest that the novel degradable starch-polyethylene plastics containing oxidized-polyethylene and pro-oxidant have good thermal-oxidative degradability and photodegradability, and some biodegradability, and a specific degradable starch-polyethylene film is acceptable as a primary food container depending on the food product.

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ACKNOWLEDGEMENTS

I would like to express sincere gratitude to my major professor, Dr. Anthony L. Pometto III, for his constant support, encouragement, advice and professional leadership throughout this research.

I would like to extend thanks to my other committee members, Dr. Earl G. Hammond, Dr. Zivko Nikolov, Dr. Kenneth Prusa, and Dr. Joel Coats for their knowledge and comments to aid in the successful completion of this research.

I wish to extend my thanks to Dr. Alfred Fratzke for his help in FT-IR analysis. I wish to thank to Ken Johnson and Steve Niebuhr for their technical assistance and cooperation.

I want to express thanks to my graduate colleagues, Ali, Byungtae and Mahipal for their cooperation.

I would like to extend my special love and thanks to my family for their daily prayers, constant love, and tremendous encouragement. I want to express my thanks to my sister, Hyochung, who has studied with me at Iowa State University. She has always helped and encouraged me during this period. I cannot come up with any eloquent words to thank my mother and father for all that they have done with love for me. The only recompense I can offer is to dedicate this work to them.

Finally, thanks to God for giving me the strength and determination to complete this work.