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Thermal- and Bio-degradation of Starch-Polyethylene Films Containing High Molecular Weight Oxidized-Polyethylene

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Abstract

Starch-polyethylene films containing high molecular weight(MW) oxidized-polyethylene and prooxidant were prepared, and thermal- and bio-degradability of the films were determined. Increased levels of starch resulted in a corresponding reduction in mechanical strength of the films. However, the addition of high MW oxidized-polyethylene did not significantly reduce the percent elongation of the films. The films containing high MW oxidized-polyethylene and prooxidant were degraded faster than those containing no additives during the heat treatment. The films lost their measurable mechanical properties when their weight-average MW($\overline{M_w}$) fell below 50,000. Biodegradability of the films was determined by a pure culture assay with either *Streptomyces badius* 252, *S. setonii* 75Vi2 or *S. viridosporus* T7A, and by an extracellular enzyme assay using *S. setonii* 75Vi2. The results from pure culture assay indicated that biomass accumulation on the film surface inhibited chemical and biological degradation of the films. The extracellular enzyme assay demonstrated decrease of percent elongation and increase of carbonyl index of the films. Therefore, extracellular enzyme assay could be used as a good method to evaluate biodegradability of the films.

Key words: degradable plastics, biodegradation, thermal degradation, extracellular enzyme assay

INTRODUCTION

Conventional synthetic polymers are considered to be resistant to microbial attack because their high 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 or stops with increasing chain lengths(1). Polyethylene chains often consist of more than 1,000 ethylene units and in addition are branched, which increases their resistance to microbial attack. Polyethylene above a MW of several thousands crystallizes in folded chain in which chain ends are unlikely to be found near the surface and hence accessible to oxidation.

Polyethylene degradation has been explained in several studies. Corbin(2) studied biodegradation of polyethylene 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(4) 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(5) 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 and Karlsson(6) proposed that three stages were involved in polyethylene degradation under aerated cultivation over 10 years. In the first stage, the polymer changes rapidly until some kind of equilibrium with the environment is achieved. The second stage is characterized by a parabolic decline in oxygen uptake and carbon dioxide evolution and slow changes of mechanical properties and MW. In the final stage, rapid deterioration of structure, loss of all mechanical properties, and the

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nearly complete mineralization can be observed. Polyethylene degradation in landfill is estimated to be 100 to 200 years(7).

Degradable plastics are materials which degrade faster than conventional plastics when exposed to various environmental conditions(8). 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. Polyethylene can be rendered more degradable by blending in various additives that accelerate chemical and biological degradation(9-12). Plastic containing starch as a filler is one kind of degradable plastic(13-16). Modified starch, gelatinized starch, and oxidized-polyethylene have been used as fillers to improve the biodegradability of plastics(17-21). Chemical degradation accelerates biological degradation of the polyethylene(12,22) as well as starch degradation(23).

Several methods have been used to measure the biodegradability of plastics. In various soil studies, production of $^{14}CO_2$ from ^{14}C-[labeled] polyethylene and changes in polymer properties such as tensile strength, molar mass, and weight loss have been used(3,4,24,25). Soil burial tests traditionally have been used to determine degradation because of their similarity to landfill disposal(26-28). Composting studies are considered good indices of biodegradation due to their activity and reproducibility (11,29). However, all field studies require 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. In this study, cast films containing corn starch, a prooxidant, high MW oxidized-polyethylene, and polyethylene were prepared, and thermal- and bio-degradability of the films were evaluated.

MATERIALS AND METHODS

Film preparation

For the preparation of starch-polyethylene films, linear low density polyethylene(Dow Chemical Co., Midland, MI, USA), native corn starch(American Maize-Products Co., Hammond, IN, USA), high MW oxidized-polyethylene(Aldrich Chemical Co., Milwaukee, WI, USA), and POLYCLEAN II(Archer Daniel Midland Co., Decatur, IL, USA) were used. POLYCLEAN II as a prooxidant contained native corn starch(40%), vegetable oil, and manganese stearate(280~330 ppm Mn) in polyethylene pellets. Native corn starch was dried in a vacuum oven at 100°C until moisture content was less than 0.3%. Moisture content was determined by a Karl Fisher titration (30). Different combinations of cast films were prepared (Table 1) by mixing the components in a twin-screw extruder(Model 15-02-000 extruder, C.W. Brabender, South Hackensack, New Jersey, USA). The barrel temperatures were sequentially 185, 195, 200, and 195°C. The die temperature was 190°C and the screw speed was 20 rpm. The rods from the twin-screw extruder were air-cooled and pelletized. The pellets were cast into films using a single-screw extruder(C.W. Brabender, South Hackensack, New Jersey, USA). The barrel sequential temperatures were 175, 185, 190, and 195°C and a die temperature was 200°C, and a screw speed was 15 rpm. The films were rolled with a water-cooled Univex take-off system, and then stored in polyethylene bags at 4°C.

Thermal degradation assay

The films were cut into strips(2.5×10.2 cm) in machine direction and were placed into a forced air oven at 70°C with both sides of strips exposed to air. The strips were taken out after 2, 4, 6, 8, 10, 12, 16 or 20 days and evaluated for mechanical properties, MW distribution,

Table 1. Amount of the various compounds per kilogram in starch-polyethylene films

Film designation	Starch content (%)	Native corn starch (g)	POLY-CLEAN II (g)	High MW oxidized-polyethylene (g)	Polyethylene (g)
PE-0	0				1000
PE-7	7		180		820
PE-14	14	70	180		750
PE-28	28	210	180		610
HPE-0	0			150	850
HPE-7	7		180	150	670
HPE-14	14	70	180	150	600
HPE-28	28	210	180	150	460

POLYCLEAN II contained 280 to 330 ppm Mn and 40% corn starch plus vegetable oil

and carbonyl index.

Microorganisms

The lignocellulose-degrading *Streptomyces viridosporus* T7A(ATCC 39115), *Streptomyces badius* 252(ATCC 39117), and *Streptomyces setonii* 75Vi2(ATCC 39116) were used for the pure culture assay, and *Streptomyces setonii* 75Vi2 was used for the extracellular enzyme assay. *S. badius* 252 and *S. viridosporus* T7A degrade starch whereas *S. setonii* 75Vi2 does not. Microorganisms were maintained on agar slants at 4°C.

Film disinfection

The films were cut into strips(2.5×10cm) in the machine direction and chemically disinfected as follows: Strips were soaked into 70% ethanol for 3 hr with stirring and transferred to 300ml of sterile 0.6%(w/v) yeast extract(Difco Laboratories, Detroit, MI, USA) plus 8ml of antibiotic solution(penicillin/streptomycin/neomycin solution, Sigma chemical Co., St. Louis, MO, USA), and then incubated for 15 hr at 37°C. After incubation, the strips were soaked into 1L of Universal disinfection solution containing 20ml of bleach and 8ml of filter-sterilized Tween 80 dissolved in sterile distilled water. The strips were transferred to 1L of sterile water and stirred for 1 hr. The strips were washed successively in 95% and 70% ethanol, placed into sterile petri dishes, and dried for 15 hr at 45°C.

Pure culture assay

A modified disinfection method from Pometto et al.(31) was used. A chemically disinfected strip was aseptically added to 100ml of sterile culture medium containing 0.6% (w/v) yeast extract medium plus mineral salts solution (12), inoculated with culture spores, and incubated with shaking at 125 rpm at 37°C for 4 weeks. Zero-control (uninoculated-unincubated films) and uninoculated-control (uninoculated-incubated films) were also prepared. After incubation, strips were harvested by soaking in 70% ethanol for 30 min and drying at 45°C for 15 hr. Mechanical properties, MW distribution, and carbonyl index of the strips were evaluated for determination of biodegradability.

Extracellular enzyme assay

A fifty liter culture of *S. setonii* 75Vi2 was prepared in 0.6%(w/v) yeast extract in a Braun U-50 fermentor (Allentown, PA, USA) and incubated at 37°C until a pH > 8.0 was achieved. The reactor was harvested into a 50L polypropylene carboy and stored overnight at 4°C to allow the bacteria to settle to the bottom. Cells were removed by filtration through glass wool and centrifugation at 8,000 rpm for 30 min. The supernatant was concentrated to 4L by using a hollow-fiber filtration unit(Amicon Corp., Danvers, MA, USA) 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. Twenty milliliter of antibiotic solution,(penicillin/streptomycin/neomycin solution, Sigma chemical Co., St. Louis, USA) was added to 1L of the filter-sterilized(active enzyme) and heat-sterilized(inactive enzyme) concentrated supernatant. The disinfected film strips were added aseptically to flasks containing 1L of either active- or inactive-enzyme culture, and incubated with shaking at 125 rpm and 37°C for 3 weeks. Films were harvested by soaking in 70% ethanol for 30 min and drying at 45°C for 15 hr and mechanical properties and carbonyl index of the strips were measured.

Measurement of mechanical properties

Tensile strength, percent elongation, and strain energy of the cast films were measured using an Instron Model 4502 Universal Tester(Instron Corporation, Canton, MA). The strips were equilibrated to 50% relative humidity for at least 40 hr prior to testing(32). The thickness of each strip was measured with a hand-held caliper. Crosshead speed was 500mm/min and the starting gap between the jaws was 50mm. Tensile strength and percent elongation were calculated by using series IX Automated Materials Testing System software(Instron Corp., version 4.09).

Determination of polyethylene MW distribution

Forty five milligram of plastic sample was added to a bottle containing 30ml of 1, 2, 4-trichlorobenzene with Santanox(antioxidant)(Monsanto, Akron, OH, USA). The bottle was heated in an oven at 150°C for 4 hr. Eight milliliter of dissolved sample was transferred to a Waters filter vial(Waters/Millipore Co., Milford, MA, USA). The polyethylene MW distribution was determined using a Waters Model 150C(Waters/Millipore Co.) high- temperature gel-permeation chromatography(HT-GPC) and calibrated with ten standards with MW range of 2,700 to 1,870,000.

Three Water's columns were used in series, and each column had a functional MW range of 2,700 to 610,000 daltons. The mobile phase was 1,2,4-trichlorobenzene (Burdick & Jackson/Bacter Inc., GC/GPC grade, Markeson, MI, USA) at 1 ml/min, and sample injection volume was 200μl. MW calibration was achieved with a set of nine different polystyrene MW standards with peak MWs ranging from 2,700 to 2,700,000. Temperatures of columns, injector and refractive index detector were at 140°C, and solvent pump at 50°C. $\overline{M_w}$ was determined by using Maxima 820 computer software(Waters/ Millipore Co.).

FT-IR spectroscopy

FT-IR analysis was performed using a Bruker Instruments(Model IR 113V, Billerica, MA, USA) controlled by Bruker IFS version 12/87 software. The area of carbonyl region(1700~1731 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)(33). Values for which p was <0.05 were considered significantly different.

RESULTS AND DISCUSSION

Mechanical properties of films

Mechanical properties of the prepared starch-polyethylene films are shown in Table 2. Increased levels of starch resulted in a corresponding reduction in mechanical strength. Tensile strength represents the force per unit of area required to tear the film(34). Significant reduction in tensile strength resulted from the addition of starch and high MW oxidized-polyethylene to polyethylene. Tensile strength decreased averaged 13%, 28%, 46% for the films containing 7%, 14%, and 28% starch, respectively, when compared with the films containing no starch. Percent elongation represents the film's ability to stretch(34). Starch addition to the polyethylene films reduced the percent elongation. The films containing 7%, 14%, and 28% starch showed lower percent elongations of 3%, 10%, and 20% than those containing no starch. The addition of high MW oxidized-polyethylene, however, did not significantly change the percent elongation. Percent elongation decreased only

Table 2. The initial mechanical properties of the experimental films[1)]

Film designation	Tensile strength (kg/mm^2)	Percent elongation (%)	Strain energy (kg · mm)
PE-0	3.22±0.27	764±40	1263±115
PE-7	2.73±0.22	747±33	1270±106
PE-14	2.07±0.07	683±13	834± 34
PE-28	1.81±0.07	633±11	741± 7
HPE-0	2.38±0.24	753±36	1026±108
HPE-7	2.14±0.01	718±10	878± 22
HPE-14	1.93±0.10	677± 8	765± 22
HPE-28	1.21±0.09	582±15	531± 48

[1)]Each value is a mean for 4 replicates

1.4%, 3.9%, 0.9%, and 8.0% by the addition of high MW oxidized-polyethylene in the films with 0%, 7%, 14%, and 28% starch, respectively. Strain energy represents the work required to take the film to its breaking point(34). Strain energy values were reduced by the addition of high MW oxidized-polyethylene and starch to polyethylene. Nevertheless, tensile strength, percent elongation, and strain energy for HPE-14 film were not significantly reduced when compared with PE-14 film(p>0.05).

Thermal degradation

The addition of high MW oxidized-polyethylene, starch, and prooxidant accelerated the thermal degradation rates, which were determined by Instron, HT-GPC, and FT-IR. Decrease in percent elongation during the heat treatment was accelerated by the addition of prooxidant, high MW oxidized-polyethylene, and starch(Fig. 1). The films containing both prooxidant and high MW oxidized-polyethylene became very brittle after 2 to 4 days of heat treatment and degraded more rapidly than those without prooxidant and high MW oxidized-polyethylene. Films containing no prooxidant and starch(PE-0, HPE-0) did not almost degrade during the heat treatment(Fig. 1).

Changes in MW distribution for the films which were analyzed by HT-GPC during the heat treatment are shown in Fig. 2. The reduction of $\overline{M_w}$ was paralleled the loss of mechanical strength of the films. The films containing high MW oxidized-polyethylene, prooxidant, and starch were degraded faster than those containing no additives. The films lost their measurable mechanical properties when their $\overline{M_w}$ fell below 50,000. These results consists with those of Holmstrom and Sorvik(35) who found that further changes in the mechanical proper-

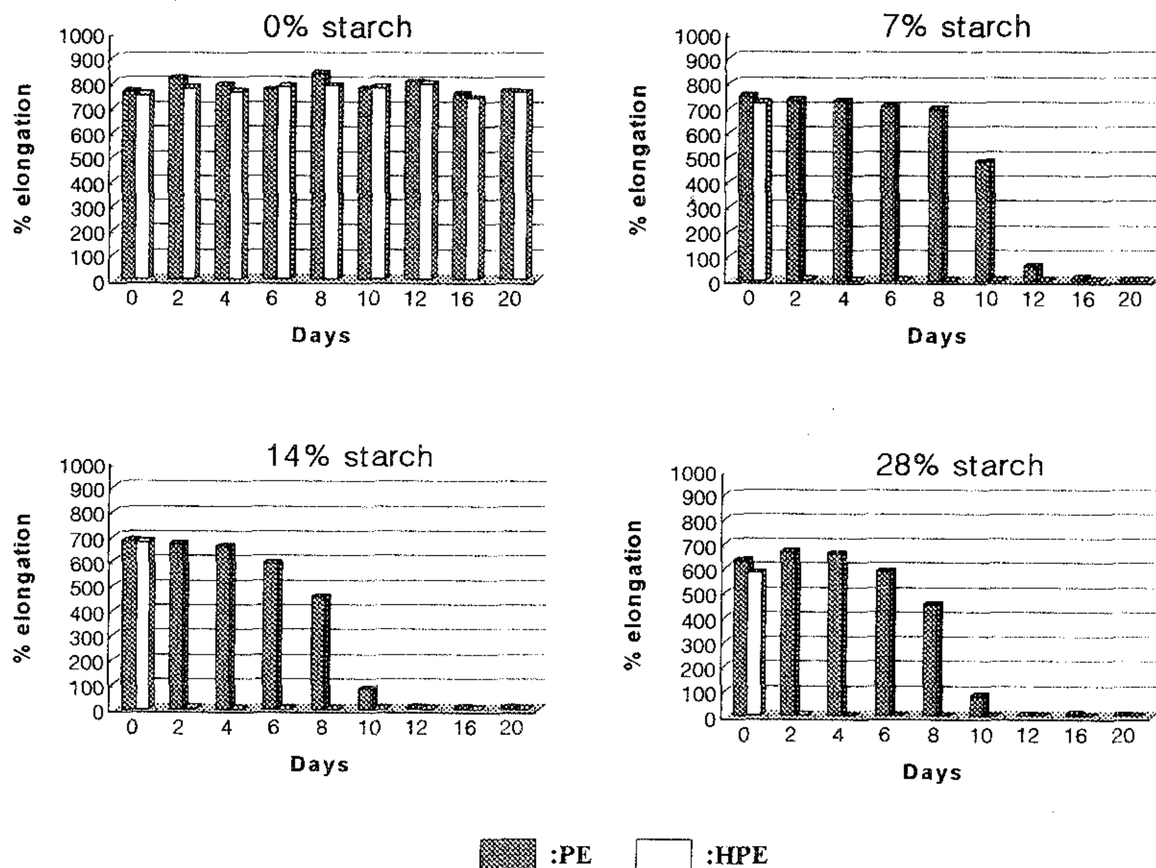

Fig. 1. Change of percent elongation of the films by heat treatment at 70°C for 20 days.
Each data point represents an average of four replicates.

ties and MW distributions were not observed after achieving a $\overline{M_w}$<50,000 by long-term exposure at temperatures below 150°C.

Carbonyl indices of the films were affected in the heat treatment by the presence of high MW oxidized-polyethylene(Table 3). Benham and Pullukat(36) detected ketone and carboxyl groups from the oxidation of polyethylene and Albertsson et al.(3,5) determined the biodegradability of polyethylene using the carbonyl index. The wavelength range used for the carbonyl index in our study included carboxylic acid, ester, aldehyde and ketone absorption bands. Chemical degradation mechanisms of plastics are not well understood, but prooxidant is considered as an initiator in oxidation of plastics(37). It forms alkoxy radicals which seem to yield aldehydes and ketones through chain scission(9). These reactive groups are prone to further free radical formation and subsequent oxidation. The result obtained from this study also demonstrated that prooxidant played an important role in thermal oxidation by showing higher carbonyl index in the films containing POLYCLEAN II than that in the films without POLYCLEAN II. The addition of starch also increased the carbonyl index. High MW oxidized-polyethylene did not great increase carbonyl index except HPE-14 when the films containing the same level of starch were compared.

Table 3. Carbonyl index change of the films by the heat treatment or by the extracellular enzyme treatment

Film designation	Carbonyl index[1)]	
	Heat treatment	Enzyme treatment
PE-0	0	0.001
PE-7	1.21	0
PE-14	1.89	0
PE-28	2.17	0
HPE-0	0.01	0.013
HPE-7	0.93	0.003
HPE-14	3.77	0.002
HPE-28	2.17	0.001

[1)]Each value is a mean for two replicates

The presence of high MW oxidized-polyethylene and

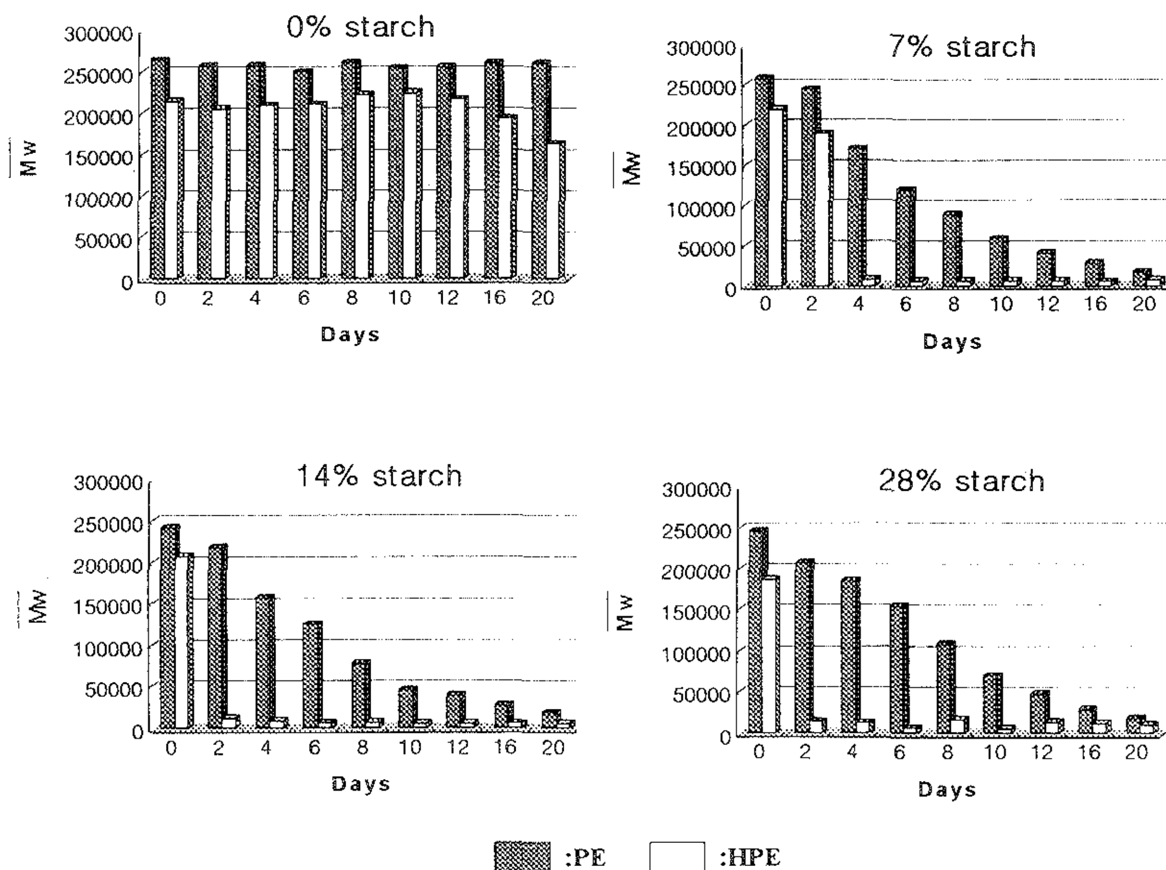

Fig. 2. Change of $\overline{M_w}$ of the films by heat treatment at 70°C for 20 days.
Each data point represents an average of two replicates.

prooxidant produced a synergistic increase in the thermal degradation of the polyethylene during the oven treatment. The degradation rate for films containing high MW oxidized-polyethylene and prooxidant was faster than the sum of the degradation rates for the film containing high MW oxidized-polyethylene and only prooxidant.

Pure culture assay

Two kinds of assays, pure culture assay and extracellular enzyme assay, were used for the determination of biodegradability of the films. The changes in percent elongation and MW distribution in comparison between the zero-control and uninoculated-control films were measures of chemical oxidative degradation. These changes were due to the conditions such as incubation temperature, transition metals in the medium and films, pH, dissolved oxygen, and mechanical shaking. Percent elongations were generally lower in the uninoculated-control than zero-control(Fig. 3). Changes in $\overline{M_w}$ of the polyethylene gave no constant pattern in contrast to the significant thermal degradation demonstrated in heat treatments to these films(Fig. 4). This result was attributed to the relatively mild temperature and short incubation period. For many HT-GPC chromatograms, a second unknown peak was observed at 33 to 37 min, which might be belong to oligomer produced from polymer degradation(Fig. 5). This peak did not affect the $\overline{M_w}$ obtained because only

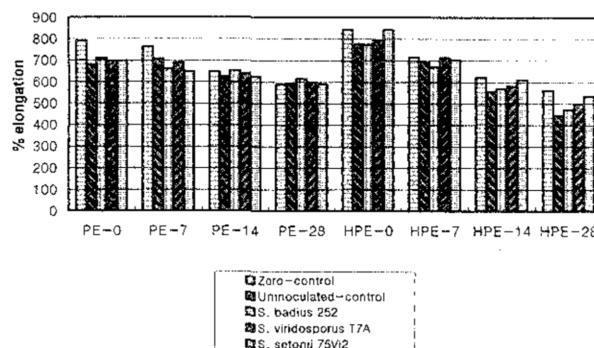

Fig. 3. Change of percent elongation for films by pure culture of ligninolytic *Streptomyces*.
Each data point represents an average of four replicates.

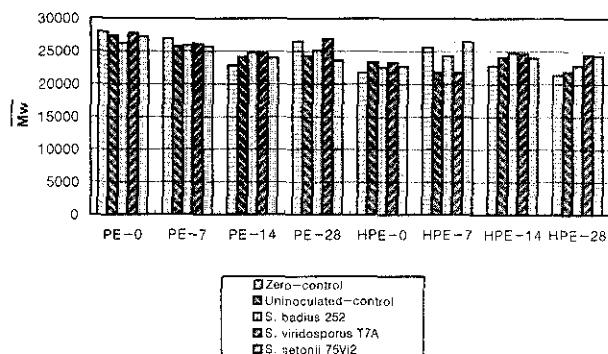

Fig. 4. Change of $\overline{M_w}$ for films by pure culture of ligninolytic *Streptomyces*.
Each data point represents an average of two replicates.

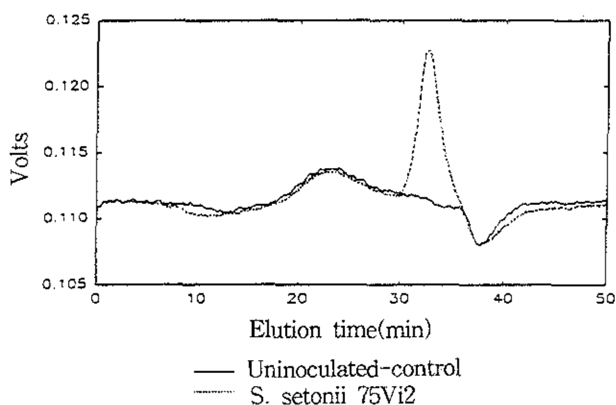

Fig. 5. HT-GPC chromatograms of HPE-14 in pure culture assay.

the data with elution time less than 30 min was used for $\overline{M_w}$ analysis.

Changes between microorganism-treated films and the uninoculated-control films are measures of biological degradation. Changes in mechanical properties and $\overline{M_w}$ in the various films did not coincide(Fig. 3, Fig. 4). Reductions in $\overline{M_w}$, which represent high MW polyethylene degradation, were observed for film PE-7(*S. badius*, *S. viridosporous*, and *S. setonii*), PE-28(*S. setonii*), and HPE-7(*S. badius*). Peak shift to the right of the HT-GPC chromatogram was observed in many films treated with *S. setonii* 75Vi2 and in some films treated with *S. viridosporus* T7A(Fig. 5). This shift to the right in the chromatogram indicates a decrease of overall $\overline{M_w}$ caused by polyethylene breakdown.

In some instances pure-culture treated samples were less degraded than controls and cell mass accumulation on the film was observed during the incubation. Thus, reduced oxidative chemical degradation could be the result of cell mass accumulation or biofilm formation on

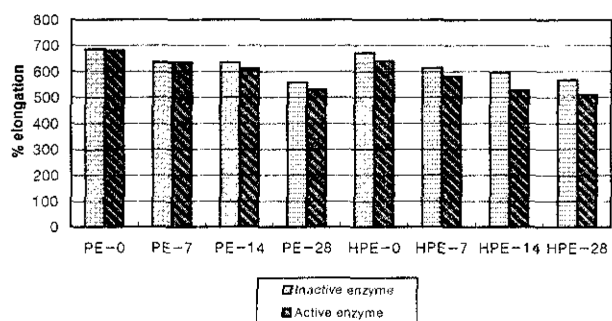

Fig. 6. Change of percent elongation for films treated by extracellular enzyme of *Streptomyces setonii* 75Vi2.
Each data point represents an average of four replicates.

the film, which lowered the oxygen tension at the film surface. This reduction in oxygen tension on the film surface could also retard biodegradation by low microbial activity. Such inhibition was observed for each of the film types for at least one bacterial culture, and HPE-28 degradation was inhibited by all the cultures. Thus, it is suggested that cell mass accumulation on plastic films is not a very good index for biodegradation evaluation.

Extracellular enzyme assay

Extracellular enzyme assay eliminates any possible influence from cell mass accumulation on the films. The changes of percent elongation and FT-IR ratio in the films treated with inactive- or active-enzyme are shown in Fig. 6 and Table 3, respectively. Synthetic plastics are hardly attacked by enzymes because of the hydrophobic property. HPE films illustrated percent elongation reduction by the active-enzyme treatment. This suggests that the carboxyl or ketone functional groups in high MW oxidized-polyethylene helped enzymatic access to the 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 in the film composition, the polyethylene concentration correspondingly decreased(Table 1). This reduction in total polyethylene for the 14 and 28% starch films could explain the detectable changes in mechanical properties for these films after treatment with active-enzyme. Alcohols are considered as intermediates in the oxidation of hydrocarbons before the formation of ketone and aldehydes(8). Aldehydes and ketones are formed by oxidation of alcohol and changes in carbonyl groups have been used as a sign of polyethylene oxidation(36,38).

HPE films showed increases in carbonyl index by the active enzyme treatment(Table 1). Therefore, catalytic effect of high MW oxidized-polyethylene in polyethylene biodegradation was also represented by FT-IR analysis. These results suggest that extracellular enzyme assay can be used as a good method to evaluate biodegradability of the films.

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