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Evaluation of degradability of hydroxypropylated potato starch/polyethylene blend films

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Abstract

Potato starch was modified by hydroxypropylation, and films were prepared from blends of polyethylene (PE) with hydroxypropylated starch (HPS) with different degrees of substitution. Thermal degradability of the films was evaluated by heat treatment at 70 °C for 12 weeks. The carbonyl index of HPS/PE films increased whereas that of native starch (NS)/PE films did not change during heat treatment. Additionally, tensile strength and percent elongation of HPS/PE films decreased during heat treatment with increasing degree of starch hydroxypropylation. Biodegradability was determined after incubation of the films with *Pseudomonas aeruginosa* ATCC 13388 at 35 °C for 4 weeks. The HPS/PE film inoculated with *P. aeruginosa* demonstrated a further increase in the carbonyl index and a decrease of mechanical strength when compared to the corresponding uninoculated control. The surface of the HPS/PE film incubated with *P. aeruginosa* was destroyed after incubation, as revealed by SEM.

Keywords: Hydroxypropylation; Starch; Polyethylene; Thermal degradability; Biodegradability

1. Introduction

Plastics have been widely used because of their light weight, inertness, transparency, and low cost. Plastic products can cause serious environmental pollution because they are not biodegradable. Landfills are the dominant disposal sites for waste plastics. The waste management problem generated by plastics in landfills has prompted the development of degradable plastics. Degradable plastics that respond to chemical, photo and/or biological attack have been developed.

One kind of biodegradable plastic is a polymer containing a biodegradable filler. Starch is an appropriate material as a degradable filler because it is cheap and can improve degradability (Gage, 1990; Jane, Lim, & Paetau, 1993). However, the addition of starch to plastic usually weakens the mechanical strength of films. Therefore, it is necessary to develop a method to improve the mechanical properties of starch-filled plastics. One possible method is to modify starch chemically. Griffin (1977a,b) proposed a process for making a film with improved mechanical strength and biodegradability from a polyolefin, fatty acid, fatty acid ester, and starches modified by a silicone treatment. Westhoff, Otey, Mehltretter, and Russell (1974) used a mixture of poly(vinylalcohol) (PVA) and modified starch to develop water-soluble packaging plastics. Kim and Lee (2002) studied the characteristics of crosslinked potato starch-filled, linear, low-density polyethylene (LLDPE) films. Lee, Kim, and Kim (1999) investigated the mechanical properties of films consisting of blends of oxidized starch and LLDPE. Evangelista, Nikolov, Wei, Jane, and Gelina (1991) found that corn starch with octenylsuccinate groups exhibited better mechanical properties than native corn starch when incorporated into LLDPE films at levels between 5 and 25%, but that biodegradation was retarded by octenylsuccinylation.

Starch can be modified by esterification, etherification, and oxidation (Loomis, Hopkins, & George, 1993). When starch is hydroxypropylated, internal hydrogen bonding is weakened. Hydroxypropylated starch gives improved shelf life, freeze/thaw stability, cold storage stability, cold water swelling, and a reduced gelatinization temperature, as well as retarded retrogradation. Therefore, hydroxypropylated starch has a wide spectrum of applications in the food industry (Tuschhoff, 1987).

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Biodegradation is the breakdown of materials by the action of living organisms. Bacteria and fungi are important for plastic degradation (Imam & Gould, 1990; Potts, 1978). Plastics may be degraded biophysically by microorganisms where cell growth causes mechanical damage. Furthermore, direct enzymatic action is possible, in which enzymes produced by microorganisms attack components of the plastic. The biodegradable filler, starch, provides a nutrient source for microorganisms. Environmental conditions such as moisture, temperature, light, nutrients, pH, metals, salts, metabolites, and cofactors greatly influence the onset and rate of degradation (Mayer & Kaplan, 1993).

Tests for biodegradability of polymers can be classified broadly into field tests and laboratory tests. Biodegradation can be evaluated by measuring changes in the physical properties of the plastics, by studying chemical changes in the plastic films, or by assessing biological activity (Maddever & Chapman, 1989). Production of $^{14}CO_2$ from polyethylene labeled with ^{14}C (Albertsson, 1978; Albertsson, Banhidi, & Beyer-Ericsson, 1978), changes of polymer properties such as tensile strength and weight loss (Aminabhavi & Balundgi, 1990; Pometto, Johnson, & Kim, 1993), and increase of bacterial mass (Aminabhavi & Balundgi, 1990; Potts, 1978) have been used to measure the biodegradability of polymers. However, because many of these methods require a long period to determine the biodegradability, fast, sensitive, uniform and reproducible methods are needed.

In this study, potato starch was modified by hydroxypropylation and films from blends of hydroxypropylated starch (HPS) with polyethylene (PE) were prepared containing 5% of HPS. Thermal- and bio-degradability of these films were measured by using a quick and accurate method and compared to those of film containing native starch (NS).

2. Materials and methods

2.1. Preparation of hydroxypropylated potato starch

Potato starch was extracted by the alkali precipitation method (Lee, Pyun, Cho, Yu, & Lee, 1984) and hydroxypropylation of starch was conducted according to the procedure of Wootton and Manasathit (1983). Potato starch (100 g) was dispersed in distilled water (426 ml), and Na_2SO_4 (45 g) was slowly added to the dispersion at 40 °C. This solution was adjusted to pH 11.5 with 1 M NaOH. The desired quantity of propylene oxide (2.5, 5.0, 7.5, 10.0%/starch, w/w) was added to the solution, and the container with the solution was sealed with a glass lid. It was shaken for 40 h at 40 °C. The reaction was stopped by adding 1 M HCl until the solution reached pH 5, and then filtered through Toyo No. 2 filter paper. The prepared starch was washed and filtered three times with 1 l of distilled water. It was dried at 40 °C for 48 h, then passed through a 100-mesh sieve.

2.2. Determination of degree of substitution

The degree of substitution in HPS was determined by the procedure of Johnson (1969). It was measured spectrophotometrically after the HPS was reacted with ninhydrin until it became purple. The degree of substitution was calculated using a calibration curve prepared with a propylene glycol standard solution.

2.3. X-ray diffraction analysis

The X-ray diffraction pattern of starch was determined using an X-ray diffractometer (X'pert PW3710, Philips, Netherlands) with a reference of target: Cu Kα, voltage: 30 kV, current: 20 mA, diffraction angle $2\theta: 5-40°$, and scanning speed: 0.04° 2θ/s. The relative crystallinity of the starch was determined following Komiya, Nara, and Tsu's (1986) method.

2.4. Scanning electron microscopy (SEM)

Morphology of native and hydroxypropylated potato starch was examined using a SEM (Hitachi S-4200, Japan) at a magnification of 700 × .

2.5. HPS/PE film preparation

HPS/PE cast films (1 kg) were prepared using 900 g of linear low-density polyethylene (LLDPE), 50 g of prooxidant (IR1025, Novon International, INC., NY, USA), and 50 g of hydroxypropylated potato starches with different degrees of substitution. The potato starch was dried in a vacuum oven until the final moisture content was less than 0.3%. A masterbatch was prepared by compounding PE and starch (1:1 w/w) by using a kneader (Haake Pheomex 3000, Germany) operating at 150 °C and 50 rpm. The masterbatch was mixed with PE and prooxidant in a Haake Rheocord 90 equipped with a single-screw extruder (Rheomex 254, Germany) to give 5% (w/w) hydroxypropylated potato starch in the starch/PE films. The extruder barrel was thermocontrolled and the temperature of the four consecutive heating zones were 150, 145, 150, and 150 °C. The screw speed was 20 rpm. The extruded rods (diameter, 0.25 cm) were air-cooled and then pelletized into 0.5 cm chips. The chips were extruded into cast films using an extruder (Postex Haake Fisions, Germany) with barrel temperatures of 120, 140, 150, and 150 °C and a screw speed of 55 rpm. The films containing the native potato starch were prepared by the same process. Film thickness ranged from 0.11 to 0.12 mm.

2.6. Determination of thermal degradability of films

HPS/PE films were cut into strips (1 × 3 cm) in the machine direction. Strips of the films were placed in a 70 °C forced-air oven, with both sides exposed to air for 12 weeks.

The strips were taken out every week and thermal degradability of the films was determined using FT-IR spectroscopy and mechanical measurements using an Instron.

2.6.1. Measurement of carbonyl index

FT-IR spectroscopy (IFS 120 HR, Bruker, Germany) was employed to determine the changes of the carbonyl index of the films (Albertsson et al., 1978; Kim, Pometto, Johnson, & Fratzke, 1994; Pometto et al., 1993). The carbonyl index is the ratio of the carbonyl peak area (1705–1740 cm^{-1}) divided by the methylene peak area (1471–1485 cm^{-1}). The reason for division by methylene peak area is to eliminate the affect of film thickness. Each film was attached to a FT-IR plate and scanned from 600 to 4000 cm^{-1}.

2.6.2. Determination of mechanical properties

An Instron Universal Testing Machine (AGS-500A, Shimadzu, Japan) was used to measure the changes of the films' mechanical properties. Tensile strength and percent elongation were determined to evaluate the mechanical properties of the films. Film strips were equilibrated to 50% relative humidity for at least 40 h at 25 °C prior to testing. The Instron operation conditions were as follows: a load cell, 50 kg; load range, 5; and crosshead speed, 100 mm/min. The mechanical properties of each film were measured with ten replicates.

2.7. Determination of biodegradability of films

2.7.1. Chemical disinfection of film

HPS/PE films were cut into strips (1 × 3 cm) and soaked in a fresh disinfectant solution containing 8 ml of Tween 80, 20 ml of bleach, and 972 ml of sterile water. The solution was stirred for 2 h. Each film was taken out with sterile forceps and placed in a covered beaker containing 1 l sterile distilled water. It was stirred for 1 h. The films were subsequently transferred and washed sequentially with 95% (v/v) ethanol, 70% ethanol, and sterile distilled water.

2.7.2. Incubation of films with *Pseudomonas aeruginosa*

Disinfected film strips were aseptically added to a sterilized nutrient broth. Strips in the nutrient broth were incubated for 24 h at 35 °C in a shaking incubator at 100 rpm before inoculation to ensure asepsis. The nutrient broth was then inoculated with *Pseudomonas aeruginosa* (ATCC 13388) and the flasks were incubated in a shaking incubator at 100 rpm at 35 °C for 4 weeks. The control was prepared by the same procedure without inoculation with *P. aeruginosa*.

2.7.3. Determination of biodegradability

The incubated film strips were harvested and washed in sterile distilled water. They were transferred to a 70% ethanol solution and left for 30 min. The films were dried at 45 °C in an oven for 3 h. Five replicates were conducted for each kind of film. Biodegradability was evaluated by determining the carbonyl index and hydroxyl index using FT-IR spectroscopy and by determining the mechanical properties of the films using an Instron Universal Testing Machine. The test method was the same as that described previously. Additionally, the surface morphology of the films was examined by SEM after incubation.

2.8. Statistical analysis

The data was analyzed using the Statistical Analysis System (SAS institute, Inc., 1995). Significance was determined at the 5% level.

3. Results and discussion

3.1. Determination of degree of substitution

The degree of substitution in hydroxypropylated starch is shown in Table 1. This result demonstrates that the potato

Table 1
Hydroxypropyl group contents and degree of substitution of hydroxypropylated potato starches

Type of starch	Propylene oxide concentration (%)	Content of hydroxypropyl groups (%)	Degree of substitution
NS	0	ND[a]	ND[a]
2.5 HPS	2.5	1.8	0.05
5.0 HPS	5.0	3.3	0.10
7.5 HPS	7.5	6.0	0.18
10.0 HPS	10.0	12.5	0.40

[a] ND: not determined.

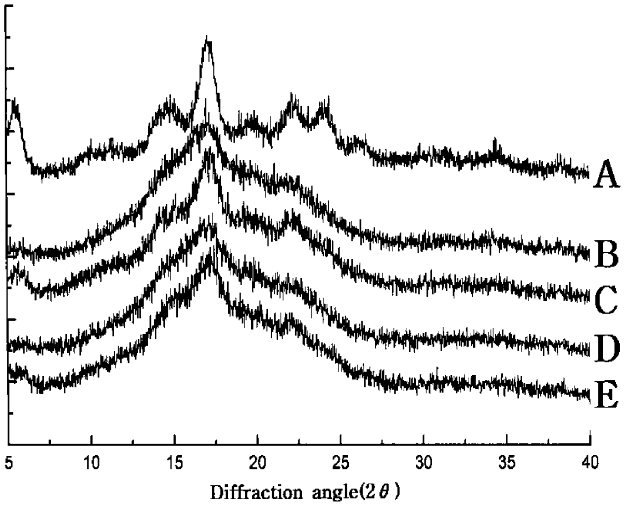

Fig. 1. X-ray diffraction patterns of hydroxypropylated potato starches. (A) NS; (B) 2.5 HPS; (C) 5.0 HPS; (D) 7.5 HPS; (E) 10.0 HPS.

Table 2
Relative crystallinity of hydroxypropylated potato starches

Variety	Type of starch				
	NS	2.5 HPS	5.0 HPS	7.5 HPS	10.0 HPS
Crystallinity (%) (Ac[a]/(Ac + Aa[b])	41	37	34	33	33

[a] Ac: crystalline area.
[b] Aa: amorphous area.

starch was successfully hydroxypropylated. The hydroxypropyl group content of the starch was proportional to the propylene oxide concentration ($r^2 = 0.93$). Comparing this result with hydroxypropylation in maize starch (Yook, Pek, & Park, 1991), the degree of substitution in potato starch is higher than that in maize starch when the same propylene oxide concentration is used.

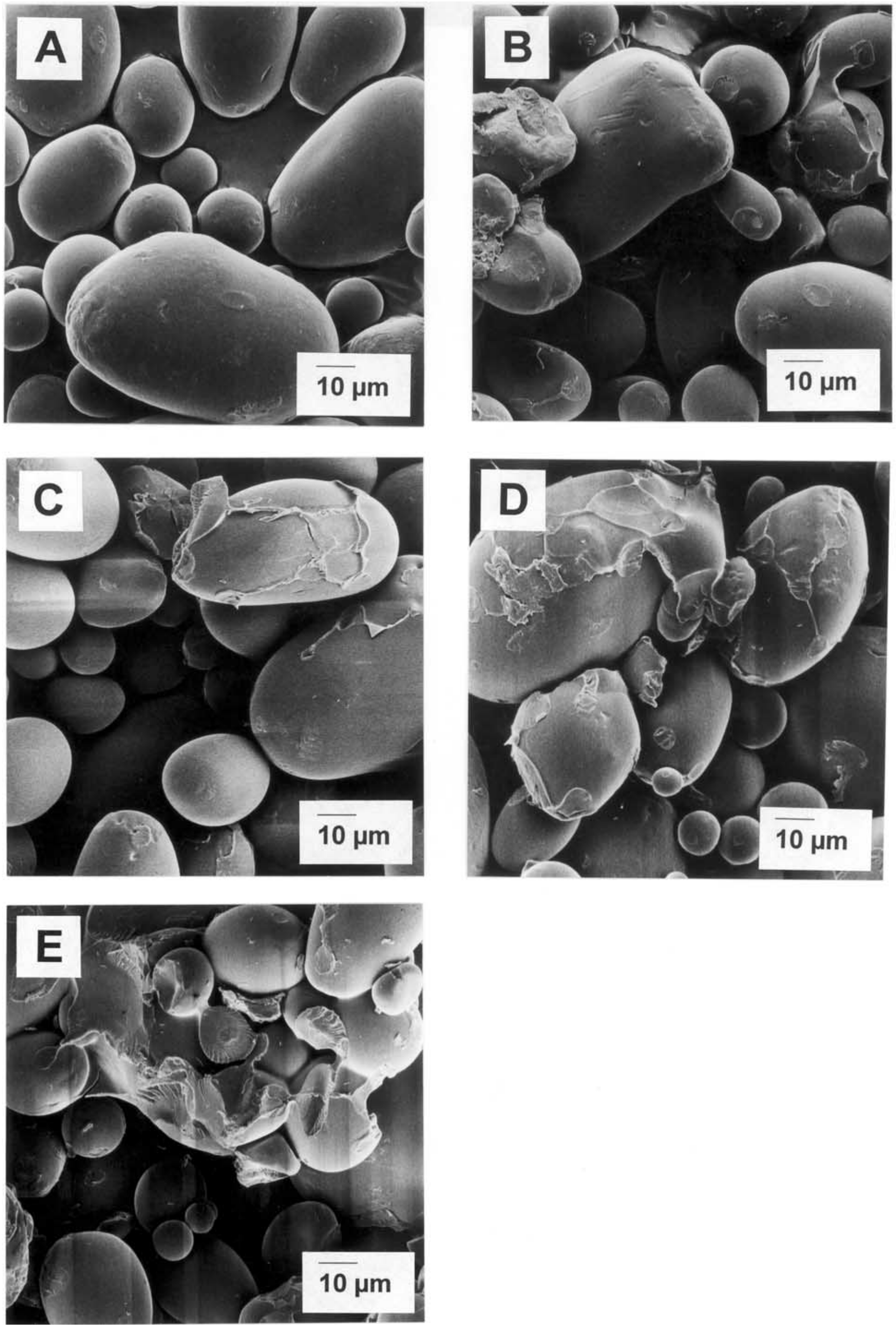

Fig. 2. Scanning electron micrographs (× 700) of hydroxypropylated potato starches. (A) NS; (B) 2.5 HPS; (C) 5.0 HPS; (D) 7.5 HPS; (E) 10.0 HPS.

3.2. X-ray diffraction analysis

The crystallinity of potato starch was reduced by hydroxypropylation (Fig. 1). The crystallinity of hydroxypropylated starch decreased as the substitution degree increased (Table 2). This result implies that a high degree of hydroxypropylation might affect not only the amorphous region, but also the crystalline regions of the starch.

3.3. Starch morphology

The granular morphology of hydroxypropylated and native potato starch is presented in Fig. 2. SEM showed that the starch surface became gradually rougher with the increase of the degree of substitution. It was also observed that some portion of starch granule was disrupted by the severe chemical modification for the 10.0 HPS sample.

3.4. Thermal degradability of HPS/PE film

3.4.1. Changes of FT-IR spectrum

The HPS/PE films contained a prooxidant to accelerate chemical degradation of the films. The prooxidant consists of a transition metal and unsaturated compounds to generate free radicals. The carbonyl peak was greatly increased by heat treatment and the peak height was increased with the increase of the heat treatment period (Fig. 3). The HPS/PE film showed an induction period when there is little change in the carbonyl index, and after that period the carbonyl index increased rapidly during thermal degradation of

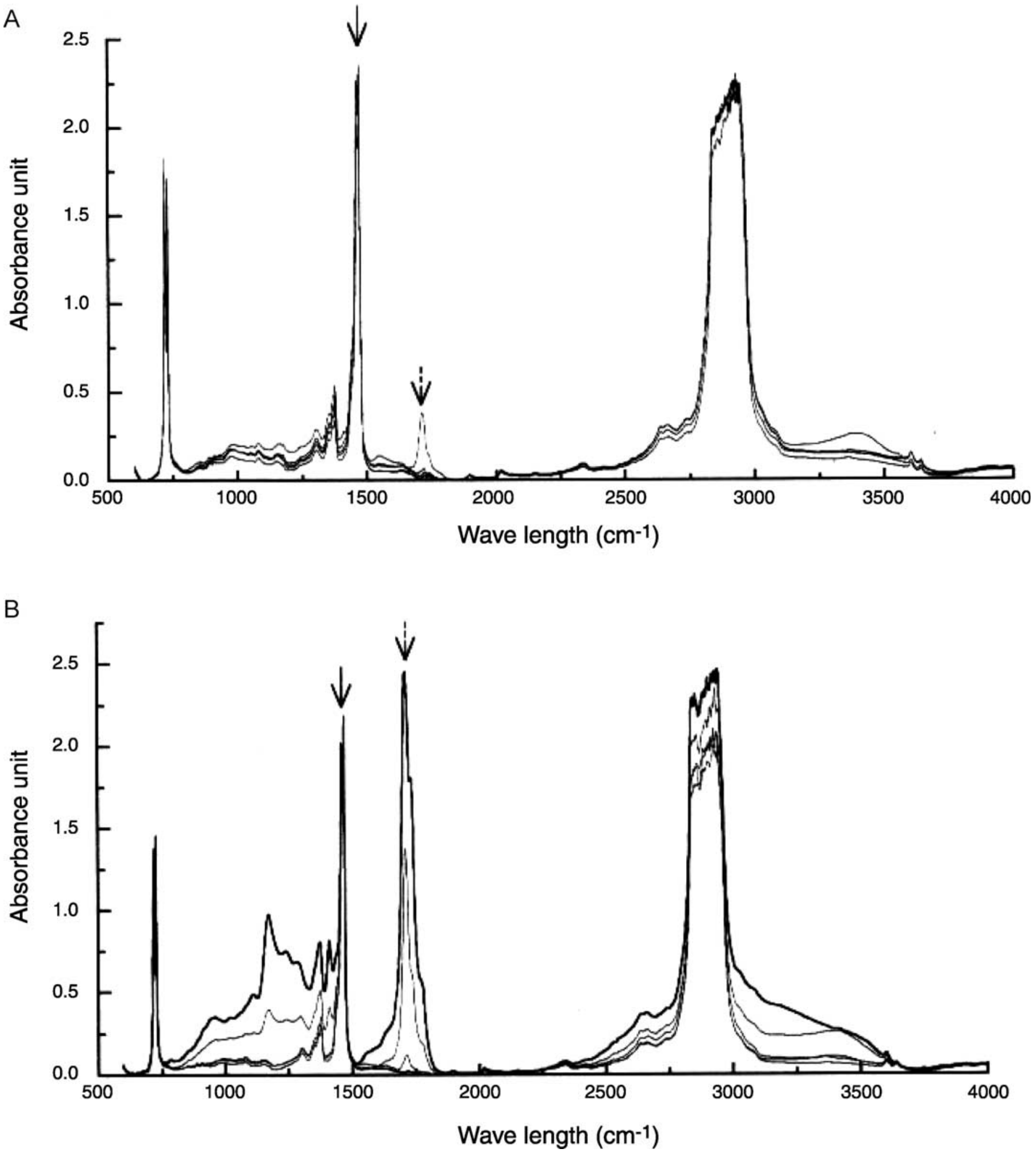

Fig. 3. FT-IR spectra of starch–polyethylene films by heat treatment at 70 °C for 12 weeks. (A) Native/PE film; (B) 10.0 HPS/PE film. For each set of spectra the top-to-bottom sequence is 12, 8, 7, 1 and 0 week of heat treatment. ↓ points to the methylene peak (1471–1485 cm^{-1}) and ⇣ points to the carbonyl peak (1705–1740 cm^{-1}), respectively.

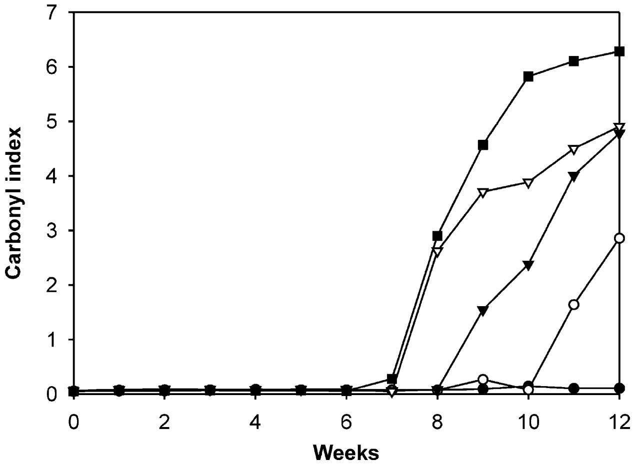

Fig. 4. Changes in the carbonyl index of hydroxypropylated potato starch–polyethylene films on heat treatment at 70 °C for 12 weeks.●, NS/PE; ○, 2.5 HPS/PE; ▼, 5.0 HPS/PE; ▽, 7.5 HPS/PE; ■, 10.0 HPS/PE.

the films (Fig. 4). This pattern is very similar to the chain reaction by free radicals in autooxidation. Ketone, aldehyde, and carboxyl groups can be formed during film oxidation (Evangelista et al., 1991). Therefore, the level of film oxidation can be evaluated by measuring the extent of these functional groups. The carbonyl index representing the change of carbonyl groups has been used to determine the extent of PE oxidation (Albertsson, Andersson, & Karlsson, 1987; Benham & Pullukat, 1976).

The carbonyl index of the NS/PE film showed little change during the 12 weeks of thermal treatment (Fig. 4). However, the carbonyl indices of 10.0 and 7.5 HPS/PE film suddenly increased after 7 weeks, and those of 5.0 film and 2.5 HPS/PE film increased after 8 and 10 weeks, respectively.

Hydroxypropyl groups are more susceptible to oxidation, which could produce more carbonyl compounds. The carbonyl index of HPS/PE films was higher according to the increase of the degree of hydroxypropylation of starch. This means that the more starch is hydroxypropylated, the faster chemical degradation of the film occurs. NS/PE film was thought to be little degraded because the carbonyl index did not increase during the heat treatment period.

3.4.2. Mechanical property changes of HPS/PE films

Tensile strength and percent elongation of 7.5 and 10.0 HPS/PE film significantly decreased after 7 weeks of heat treatment, while those of NS/PE film decreased after 11 weeks (Fig. 5). Moreover, 7.5 and 10.0 HPS/PE films became too brittle to determine their mechanical properties after 9 weeks. The 2.5 and 5.0 HPS/PE films showed a slower reduction of tensile strength than 7.5 and 10.0 HPS/PE films. The tensile strength of 2.5 and 5.0 HPS/PE films decreased after 9 weeks of heat treatment. These results indicate that HPS/PE films chemically degraded faster than NS/PE films, and the films containing more hydroxypropylated starch degraded even faster. Changes in tensile strength and percent elongation of the films were similar. In addition, a decrease of the mechanical strength and increase in the carbonyl index suddenly occurred at 6–7 weeks of heat treatment. Therefore, it is suggested that chemical oxidation weakens the mechanical strength of the films.

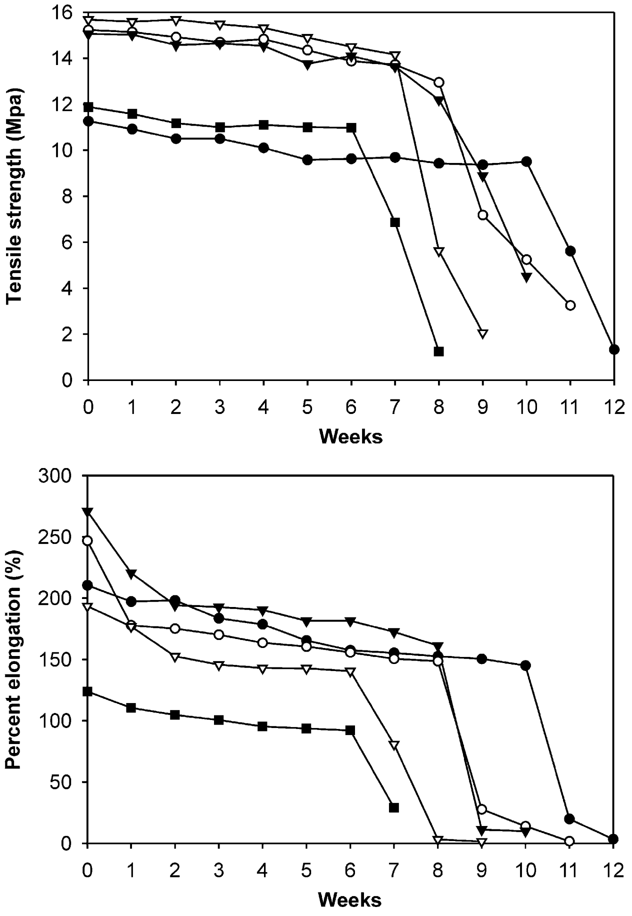

Fig. 5. Changes of tensile strength and percent elongation of hydroxypropylated potato starch–polyethylene films by heat treatment at 70 °C for 12 weeks.●, NS/PE; ○, 2.5 HPS/PE; ▼, 5.0 HPS/PE; ▽, 7.5 HPS/PE; ■, 10.0 HPS/PE.

3.5. Biodegradability of PE/HPS film

3.5.1. Changes in FT-IR spectrum

The carbonyl index of HPS/PE films treated with *Pseudomonas aeruginosa* ATCC 13388 was measured and compared with the corresponding control films that were inoculated without *P. aeruginosa*. *P. aeruginosa* ATCC 13388 is used in the assay to determine resistance of plastics to bacteria in the ASTM method (1990). The carbonyl indices of NS/PE film were not significantly different between the inoculated film and the uninoculated control film (Fig. 6). However, in the 2.5 and 5.0 HPS/PE films, the carbonyl indices of inoculated films were higher than those of the corresponding control film although there were no significant differences between

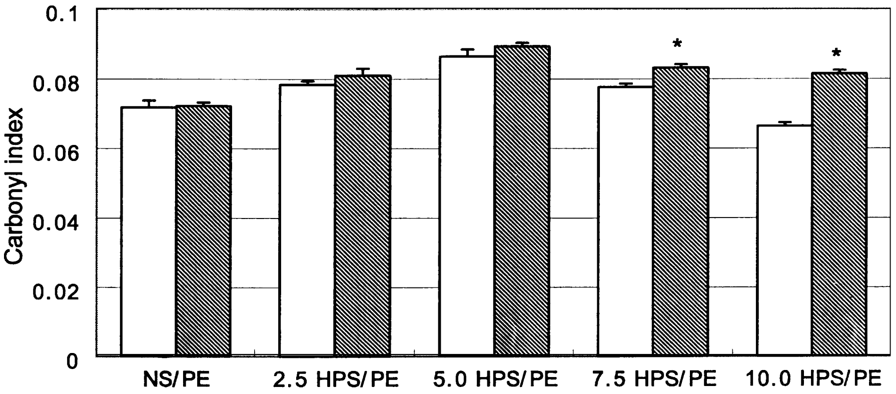

Fig. 6. Changes of carbonyl index of hydroxypropylated potato starch–polyethylene films cultured with *Pseudomonas aeruginosa* for 4 weeks. □, control; ▨, incubation with *Pseudomonas aeruginosa* ATCC 13388. The symbol (*) means that the inoculated film is significantly different from the control film at $p < 0.05$.

them. Additionally, the carbonyl indices of 7.5 and 10.0 HPS/PE films showed a significant increase in the films treated with *P. aeruginosa* when compared to the corresponding uninoculated control film after incubation ($p < 0.05$). These results suggest that films containing HPS undergo faster biodegradation than films with NS. Carbonyl groups in the HPS/PE films could take part in the further oxidative degradation and this oxidative gradation could synergistically increase the biodegradation of films.

3.5.2. Changes of mechanical properties

Changes in the tensile strength of the films after incubation for 4 weeks are shown in Fig. 7. After incubation, there was no significant change in tensile strengths and percent elongations between the NS/PE films treated with *P. aeruginosa* and the control films incubated without *P. aeruginosa*. However, tensile strength and percent elongation of all HPS/PE films inoculated with *P. aeruginosa* decreased compared with the corresponding uninoculated control films. In particular, the 10.0 HPS/PE

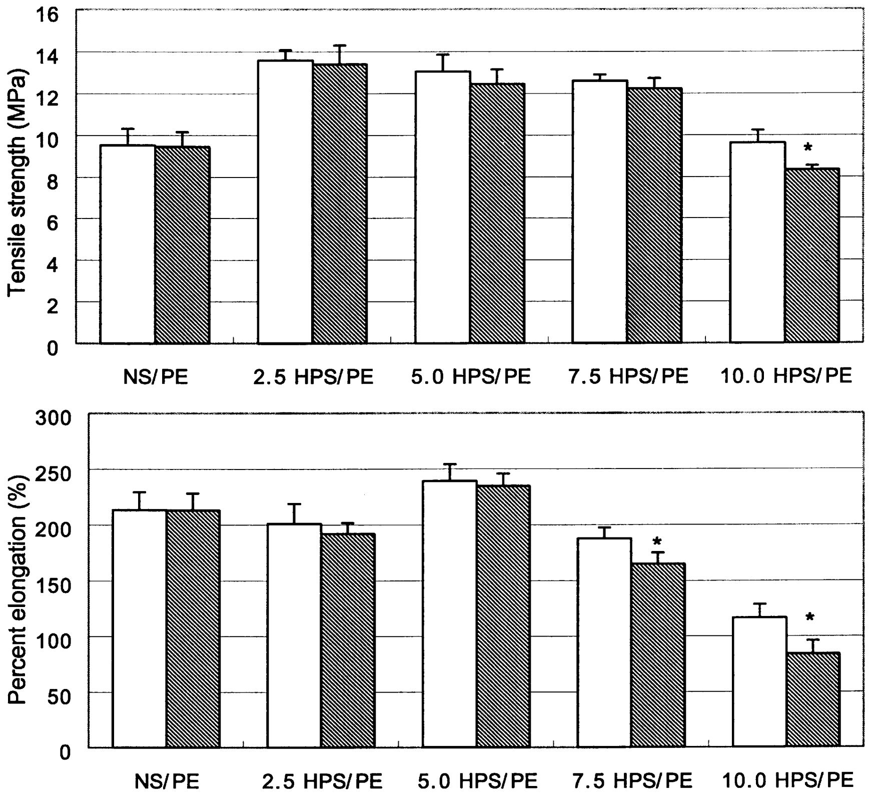

Fig. 7. Changes in the mechanical properties of hydroxypropylated potato starch–polyethylene films cultured with *Pseudomonas aeruginosa* for 4 weeks. □, control; ▨, incubation with *Pseudomonas aeruginosa* ATCC 13388. The symbol (*) means that the inoculated film is significantly different from the control film at $p < 0.05$.

film treated with *P. aeruginosa* demonstrated a significant decrease in mechanical strength when compared to the corresponding uninoculated control film after incubation ($p < 0.05$). This result is consistent with the increase of the carbonyl index after incubation.

Starch modification can help or inhibit biodegradation of plastics depending on the modification kind. Films prepared with oxidized potato starch showed accelerated biodegradation (Kim & Kim, 2001), but films containing corn starch with octenylsuccinate groups retarded biodegradation (Evangelista et al., 1991). The ability of microorganisms is critical for their survival in the environment because of intense competition for limited resources (Imam & Gould 1990). The hydrophilic groups of films are susceptible to microbial access. During the incubation of the HPS/PE films with *P. aeruginosa*, some carbonyl groups could be generated by chemical oxidation, which might make the films more susceptible to microbial attack.

3.6. Morphology of film

Film morphology was examined using a SEM to confirm the effects of microorganism inoculation on the surface of the HPS/PE film. The morphology is presented in Fig. 8. The NS/PE film incubated without inoculation (A) showed the original starch granule shape and the smooth film surface. The 7.5 HPS/PE film incubated without inoculation (B) also revealed an almost unchanged film surface. However, the 7.5 HPS/PE film inoculated with *P. aeruginosa* (D) showed surface destruction. At a higher magnification (2000 ×), the 7.5 HPS/PE film incubated with inoculation (F) showed that the film surface around starch was severely disrupted and starch granule was also destroyed when compared to the NS/PE film incubated with inoculation (E). Therefore, it was suggested that hydroxypropylated starch might be highly biodegradable, resulting in a reduction of film continuity, which could give rise to

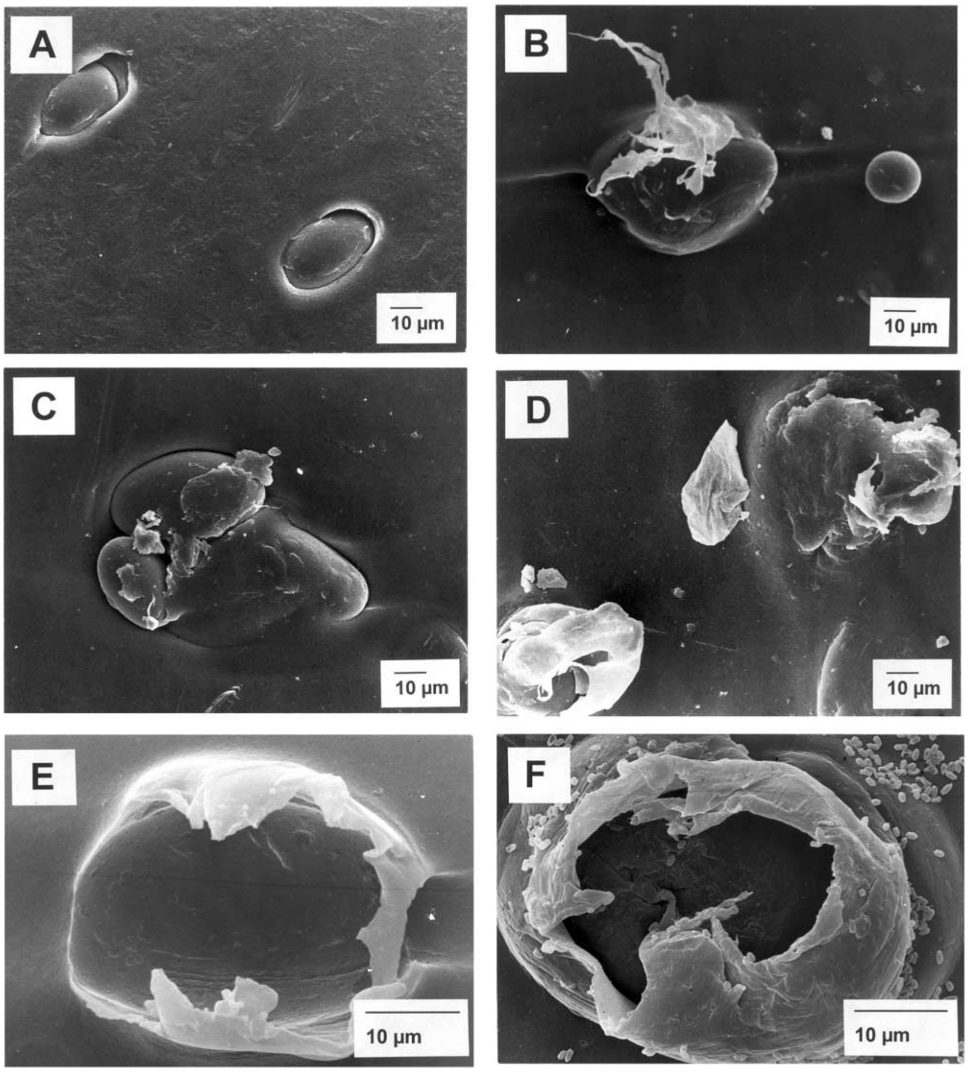

Fig. 8. Scanning electron micrograph of hydroxypropylated potato starch–polyethylene films cultured with *Pseudomonas aeruginosa* for 4 weeks. (A) NS/PE film incubated without inoculation (× 700); (B) 7.5 HPS/PE film incubated without inoculation (× 700); (C) NS/PE film inoculated with inoculation (× 700); (D) 7.5 HPS/PE film with inoculation (× 700); (E) NS/PE film inoculated with inoculation (× 2000); (F) 7.5 HPS/PE film with inoculation (× 2000).

a collapse of the film structure and a decrease in the mechanical properties of film.

4. Conclusions

Thermal degradability and biodegradability of films prepared from blends of PE with hydroxypropylated potato starch were evaluated by measuring the changes of the carbonyl index and mechanical properties of films. The carbonyl index of HPS/PE films increased but mechanical strength decreased in line with the increase in the degree of substitution in the starch during heat treatment. This implies that the higher the hydroxypropylation of starch, the faster chemical degradation of the HPS/PE. The HPS/PE film inoculated with *P. aeruginosa* demonstrated a further increase in the carbonyl index and a decrease in mechanical strength when compared to the corresponding uninoculated control. However, NS/PE film showed that there was little change between inoculated film and uninoculated film in the carboxyl index and mechanical strength. It suggests that biodegradability of the films can be accelerated by the addition of hydroxypropylated starch.

Acknowledgements

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